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**SYNTHESIS AND CHARACTERIZATION OF SOME
NANOSIZED ORTHOBORATES AND BIMETALLIC METAL
OXIDES**

DOCTOR OF PHILOSOPHY, CHEMISTRY

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF SOME NANOSIZED ORTHOBORATES AND BIMETALLIC METAL OXIDES

PHD THESIS

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BOLU ABANT İZZET BAYSAL UNIVERSITY

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In the first part of this thesis, the synthesis and structural characterization of magnesium orthoborate ($\text{Mg}_3\text{B}_2\text{O}_6$) with the kotoite crystal structure were investigated. Initially, the effects of various starting materials and different boron source ratios on the formation of a pure kotoite phase were examined. To obtain products with high phase purity and desirable structural properties, optimal synthesis parameters were systematically determined. Subsequently, doping with selected rare earth elements (RE^{3+}) was carried out to evaluate the effects of dopant type and concentration on the physicochemical properties of the synthesized orthoborate materials. The influence of dopant type and concentration was analyzed by assessing changes in crystallite size, surface area, and density, providing insights into the structure–property relationships of doped magnesium orthoborates at the nanoscale.

In the second part of the thesis, spinel-type mixed metal oxide nanoparticles with the general formula MMn_2O_4 (where $\text{M} = \text{Mg}, \text{Co}, \text{Ni}$) were synthesized using the solution combustion method. Tartaric acid, glycine, and urea were utilized as fuels to investigate the role of fuel type in governing the structural and chemical characteristics of the resulting spinel phases. The synthesized materials were characterized using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). In addition, thermal treatments at various calcination temperatures were applied to assess their influence on crystallinity, phase development, and structural stability.

Overall, this work provides a comprehensive understanding of how compositional and processing parameters affect the synthesis, phase formation, and structural properties of borate-based and spinel-type oxide nanomaterials, with potential implications for advanced functional material design.

KEYWORDS: Magnesium orthoborate, Kotoite, Rare earth doping, Spinel-type oxides, Solution combustion synthesis

ÖZET

BAZI NANOBOYUTLU ORTOBORATLAR VE İKİLİ METAL OKSİTLERİN SENTEZİ VE KARAKTERİZASYONU

DOKTORA TEZİ

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Bu tez çalışmasının birinci bölümünde, kotoit kristal yapısına sahip magnezyum ortoboratın ($Mg_3B_2O_6$) sentezi ve yapısal karakterizasyonu incelenmiştir. İlk olarak, farklı başlangıç maddeleri ve değişen bor kaynağı oranlarının saf kotoit fazının oluşumu üzerindeki etkileri araştırılmıştır. Yüksek faz saflığına ve istenen yapısal özelliklere sahip ürünlerin elde edilmesi amacıyla optimum sentez parametreleri sistematik olarak belirlenmiştir. Ardından, seçilen nadir toprak elementleri (RE^{3+}) ile katkılama yapılarak, katkı türü ve konsantrasyonunun sentezlenen ortoborat malzemelerin fizikokimyasal özelliklerine etkisi değerlendirilmiştir. Katkı türü ve konsantrasyonunun kristalit boyutu, yüzey alanı ve yoğunluk gibi parametrelerde meydana getirdiği değişimler analiz edilerek, katkının nanometre ölçeğindeki magnezyum ortoboratların yapı-özellik ilişkilerine etkisi ortaya konmuştur.

Tezin ikinci bölümünde ise, genel formülü MMn_2O_4 ($M = Mg, Co, Ni$) olan spinel tipi karışık metal oksit nanoparçacıkları çözeltide yanma yöntemi kullanılarak sentezlenmiştir. Yakıt türünün spinel faz oluşumu üzerindeki etkisini incelemek amacıyla tartarik asit, glisin ve üre gibi farklı yakıtlar kullanılmıştır. Elde edilen ürünler X-ışını difraksiyonu (XRD) ve Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) teknikleri ile karakterize edilmiştir. Ayrıca, farklı kalsinasyon sıcaklıklarında uygulanan ısı işlemleri ile kristallilik, faz oluşumu ve yapısal kararlılık üzerindeki etkiler detaylı olarak değerlendirilmiştir.

Bu çalışma genel olarak, borat temelli ve spinel tipi oksit nanomalzemelerin sentezi, faz oluşumu ve yapısal özellikleri üzerine bileşimsel ve işlem parametrelerinin etkilerini kapsamlı bir şekilde ortaya koymakta ve ileri işlevsel malzeme tasarımı için bilimsel bir temel sunmaktadır.

ANAHTAR KELİMELER: Magnezyum ortoborat, Kotoit, Nadir toprak elementi katkılama, Spinel tipi oksitler, Çözeltide yanma yöntemi,

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1.INTRODUCTION

1.1 Magnesium Orthoborates

Magnesium orthoborate, $\text{Mg}_3\text{B}_2\text{O}_6$ ($3\text{MgO} \cdot \text{B}_2\text{O}_3$), is a member of the magnesium borates family, which are found in the kotoite phase and have applications including use as anti-corrosive materials and as catalysts in the conversion of hydrocarbons.

In recent years, there has been a notable increase in interest surrounding the synthesis of magnesium borates, largely due to their frequent utilization in a range of technological applications. These include thermoluminescence and the incorporation of these materials as a luminescent component within the screens of cathode ray tubes (Ma et al., 2003; Qasrawi et al., 2005; Wang et al., 2007; Elssfah et al., 2007; Tao & Li, 2008; Dosler et al., 2010; Li et al., 2010; Zhu et al., 2011; Li et al., 2012; Chen et al., 2012).

The mineral ($\text{Mg}_3\text{B}_2\text{O}_6$) also known as kotoite, is typically found in borate deposits with a high magnesium content. Its discovery was first documented by Watanabe in 1939 (Frost & Xi, 2012).

Kotoite ($\text{Mg}_3\text{B}_2\text{O}_6$) has a space group of Pnmn and an orthorhombic crystal lattice system with cell parameters $a = 5.398(2)$, $b = 8.416(2)$, and $c = 4.497(2)$ Å. The microwave dielectric properties of the mineral kotoite ($\text{Mg}_3\text{B}_2\text{O}_6$), which has a particle size of 500 to 1000 μm in single phase, were examined, and it was found that the Qxf values were higher than 200 000 GHz (Dosler, Kržmanc, & Suvorov, 2010; Dosler, Kržmanc, Jančar, & Suvorov, 2010). This demonstrates that the electrical properties of kotoite are quite strong, which further highlights the importance of this material in technological applications.

As evidenced by our research in the literature, the synthesis of kotoite -type magnesium borate can be achieved through several methods, including the high-temperature solid-state synthesis method (Dosler, Kržmanc, & Suvorov, 2010; Zhou, Sun, Hu, Fu, & Dou, 2012), solvothermal (Xu, Li, Zhang, Zhang, Liu, & Zhao, 2008), and others. The synthesis of pure kotoite-type magnesium borate, $\text{Mg}_3\text{B}_2\text{O}_6$, is challenging due to the co-formation of suanite ($\text{Mg}_2\text{B}_2\text{O}_5$) and kotoite

($\text{Mg}_3\text{B}_2\text{O}_6$) compounds, which can occur during the synthesis process. Various methods have been employed to synthesize this compound, including the microwave synthesis method (Güler, Kurtuluş, Ay, Çelik, & Doğan, 2009), precipitation reaction (Chen, Gu, & Ni, 2012), and solid state (Morkan et al.).

The existing literature on the subject indicates that suanite is formed as a secondary phase. A group of researchers synthesizing single-crystal nanobelt magnesium borate ($\text{Mg}_3\text{B}_2\text{O}_6$) observed the formation of the suanite phase ($\text{Mg}_3\text{B}_2\text{O}_5$) as a byproduct under Ar/ H_2O gas conditions at 1100°C for 90 minutes (Zhang, Li, & Zhang, 2006).

Furthermore, scientific studies have demonstrated that in the absence of the suanite phase ($\text{Mg}_2\text{B}_2\text{O}_5$), the unreacted MgO phase is observed in the environment. The reason for this phenomenon has been attributed to the loss of boron oxide at elevated temperatures.

Subsequently, a group of researchers conducted synthesis studies for $\text{Mg}_3\text{B}_2\text{O}_6$ using an 11 wt.% excess of a boron source. The researchers reported that at 900°C , the formation of MgO was prevented in the XRD patterns of the resulting $\text{Mg}_3\text{B}_2\text{O}_6$ compound, although the $\text{Mg}_2\text{B}_2\text{O}_5$ phase was still present. Subsequent studies involving $\text{Mg}_3\text{B}_2\text{O}_6$ reported the synthesis of high-purity magnesium borate with a 3D flower-like structure via the precipitation method. However, the XRD patterns indicated poor crystallinity, which made it challenging to determine the presence of the $\text{Mg}_2\text{B}_2\text{O}_5$ or MgO phases.

In a subsequent study, magnesium diborate ($\text{Mg}_3\text{B}_2\text{O}_6$) was synthesized using a high-temperature solid-state synthesis method, whereby the material was heated to 1300°C for a period of two hours. Despite the use of an 11 wt.% excess boron source, the powder XRD data indicated the presence of MgO as an impurity phase (Zhou, Sun, Hu, Fu, & Dou, 2012).

In conclusion, a variety of scientific studies have utilized diverse methodologies and techniques to synthesize magnesium borate in kotoite form. However, the majority of these studies have not been successful in achieving a single-phase kotoite magnesium borate. Accordingly, the initial objective of this study is to investigate the impact of precursor types, including magnesium oxide,

magnesium carbonate, magnesium sulfate, and magnesium nitrate, as well as the quantity of the boron source, on the synthesis of magnesium borate in kotoite form. The objective is to ascertain the most effective method for synthesizing single-phase kotoite magnesium borate.

Furthermore, studies published in the literature since 1974 have investigated the enhancement of the structural properties of metal borates through the introduction of various metal dopants. For example, the luminescence spectrum changes of the $\text{Ba}_2\text{Cd}(\text{BO}_3)_2$ compound doped with Eu^{2+} were investigated, revealing a luminescence peak at 606 nm with a Stokes shift of $11,000\text{ cm}^{-1}$ (Akella & Keszler, 1995).

The luminescence properties of the $\text{Sr}_2\text{Mg}(\text{BO}_3)_2$ compound doped with Eu^{3+} and Eu^{2+} ions were determined under UV excitation (Diaz & Keszler, 1996, 1997). Additionally, the photoluminescence properties of $\text{BaZr}(\text{BO}_3)_2$ and $\text{SrAl}_2\text{B}_2\text{O}_7$ phosphors prepared via the classical solid-state method with Eu^{3+} doping were investigated. Both compounds exhibited strong emission at 615 nm, attributed to the $5\text{D}_0 \rightarrow 7\text{F}_2$ transition of Eu^{3+} ions, making them suitable for use in plasma display panels (Tian, Yu, Pyun, Park, & Mho, 2004).

Lithium tetraborate ($\text{Li}_4\text{B}_2\text{O}_7$) was synthesized using the Czochralski technique and activated with Cu and Eu dopants to achieve luminescent properties. Luminescence studies on Eu-doped lithium tetraborate revealed that the compound exhibits a blue emission peak at 370 nm in single-crystal form, while in a glassy structure, a red emission peak at 615 nm was observed (Ignatovych et al., 2004).

In subsequent years, thermoluminescence properties of $\text{Sr}_2\text{Mg}(\text{BO}_3)_2$ compounds doped with Tm^{3+} , Tb^{3+} , and Dy^{3+} ions were investigated using the high-temperature solid-state synthesis method. The $\text{Sr}_2\text{Mg}(\text{BO}_3)_2:0.04\text{Dy}$ compound exhibited emission bands at 480, 579, 662, and 755 nm (Liu et al., 2006). Additionally, $\text{Ca}_3(\text{BO}_3)_2$ doped with Ce^{3+} ions in concentrations of 0.00005 and 0.0001 was synthesized via solid-state reactions. Luminescence properties were examined only for low-concentration phosphors, as higher concentrations resulted in undesirable phases. Two emission peaks at 392 and 420 nm were reported (Berezovskaya, Efryushina, Rodnyi, Voloshinovskii, & Dotsenko, 2006).

The luminescence properties of another metal borate, $\text{BaZr(BO}_3)_2\text{:Eu}$, were investigated using Vacuum UV and UV energies and it was reported that they gave quite different emission bands at different excitation energies (VUV, UV) (Gou, Wang, & Li, 2007).

$\text{Ba}_{2(1-x)}\text{Ce}_x\text{Na}_x\text{Ca(BO}_3)_2$ and $\text{Ba}_2\text{Ca}_{1-2x}\text{Ce}_x\text{Na}_x\text{(BO}_3)_2$ phosphors were obtained by high-temperature solid-state synthesis method, Na^+ ion was used as a co-activator here, and the excitation and emission wavelengths of the Ce^{3+} ion from two different lattice directions (Ba^{2+} and Ca^{2+} directions) were determined by determining their optimum concentrations (Lin, Liang, Han, Zhong, & Su, 2007). In another study of the same working group, it was revealed that the luminescence properties of the $\text{Ba}_2\text{Ca(BO}_3)_2$ compound activated by the Ce^{3+} ion changed with the addition of Na^+ and K^+ ions as co-activators (Lin et al., 2009).

In the luminescence studies of lithium magnesium borate compounds prepared by adding different rare earth metals such as Tb, Gd, Dy, Pr, Mn, Ce, and Eu by solid state diffusion technique, it was determined that terbium (Tb) was the most stable thermoluminescent peak among these rare earth metals at 240°C and this peak was observed at 550 nm (green emission peak) (Anishia, Jose, Annalakshmi, & Ramasamy, 2011).

The luminescence properties of $\text{Sr}_2\text{Mg(BO}_3)_2\text{:Ce}^{3+}$ and $\text{Sr}_2\text{Mg(BO}_3)_2\text{:Pr}^{3+}$ phosphors, which were synthesized by solid state method using Ce^{3+} and Pr^{3+} dopes, were determined and it was explained that they have five excitation bands (Liang, Lin, Zhang, Dorenbos, & Su, 2011). In another study, Tb^{3+} doped $\text{Sr}_2\text{Mg(BO}_3)_2$ phosphorus was synthesized by solid state reaction, and a study on the vacuum UV luminescence property of the compound was revealed (Lin, Liang, Su, & Zhang, 2011).

The $\text{Ba}_2\text{Mg(BO}_3)_2\text{:Eu}^{3+}$ phosphor was synthesized using the classical solid-state method. The reaction was prepared according to the formula $\text{Ba}_{2(1-x)}\text{MgEu}_x\text{Na}_x\text{(BO}_3)_2$ ($x = 0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13, 0.15$) and processed by heating at 600°C for 30 minutes, followed by 900°C for 6 hours. Examination of the Vacuum UV–VIS luminescence properties revealed that the charge transfer energy bands of $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ were around 231 nm. The dominant

emission bands were identified at 172 nm due to the $^5D_0 \rightarrow ^7F_1$ transitions, and another emission band at 395 nm was associated with the $^5D_0 \rightarrow ^7F_2$ transitions (Lin, Liang, Zhang, & Su, 2011).

The $Ba_2Mg(BO_3)_2:Eu^{2+}$ phosphor was synthesized using the combustion method. Starting materials included $Ba(NO_3)_2$, $Mg(NO_3)_2 \cdot 6H_2O$, Eu_2O_3 , H_3BO_3 , and NH_2CONH_2 as the fuel. These materials were dissolved in water, and the combustion reaction was carried out at 600°C. To complete the thermal transformation, the product was further heated at 800°C for 5 hours. The synthesized phosphor exhibited intense yellow emission bands in the range of 250–400 nm (Yao, Xue, & Yan, 2011).

The $Ba_2Mg(BO_3)_2:Eu^{2+}$ phosphor was synthesized using the conventional solid-state method, involving heating at 600°C for 30 minutes followed by 950°C for 6 hours. Under near-ultraviolet excitation, this phosphor was found to emit intense yellow light. Its broad emission band ranging from 250 nm to 400 nm makes it a suitable candidate for LED applications (Zhang, Fei, Shi, & Gong, 2011). Phosphors $Sr_2Mg(BO_3)_2:Ce^{3+},Li^+$ and $Sr_2Mg(BO_3)_2:Ce^{3+},Li^+,Mn^{2+}$ were synthesized via the conventional solid-state method by heating at 900°C for 12 hours. These phosphors exhibited blue and red luminescence emission bands, as reported in the study (Zhang & Seo, 2011).

Phosphors synthesized through various methods have demonstrated distinct photoluminescence properties:

1. **$Sr_3Y_2(BO_3)_4:Eu^{3+}$** synthesized via the sol-gel Pechini method exhibited red emission, making it suitable for use in plasma panels and luminescent tubes (Shyichuk & Lis, 2011).
2. **$Eu^{3+}:Mg_3B_2O_6$** , prepared using the hydrothermal method, showed strong red emission due to the $5D_0 \rightarrow 7F_J$ ($J = 1, 2, 3$) transitions of Eu^{3+} ions (Pang et al., 2011).
3. Comparative studies of Ce^{3+} -doped $X_2Z(BO_3)_2$ ($X = Ba, Ca$; $Z = Ca, Mg$) phosphors synthesized via the solid-state method revealed that **$Ba_2Ca(BO_3)_2:Ce^{3+}$** and **$Sr_2Mg(BO_3)_2:Ce^{3+}$** exhibited similar spectroscopic

properties, while $\text{Ba}_2\text{Mg}(\text{BO}_3)_2\text{:Ce}^{3+}$ showed distinct characteristics. Furthermore, the luminescence properties of $\text{X}_2\text{Z}(\text{BO}_3)_2$ phosphors were found to vary with the concentration of Ce^{3+} ions (Lin, Liang, Zhang, & Tao, 2012).

1.2 Bimetallic Metal Oxides

With the advancements in science, technology continues to progress rapidly, and it is the scientific community that benefits the most from this development. The improvement of instruments used in scientific research, the use of more durable and purer materials in synthesis, and the emergence of new devices capable of analyzing morphological structures have all contributed to the continuous advancement of the scientific field. As a result of these developments, even minor modifications in synthesis methods can now be easily evaluated for their impact on the final product, allowing for the production of purer and more advanced materials compared to the past. In recent years, the scientific community has increasingly focused not on discovering entirely new materials, but rather on enhancing existing ones through novel synthesis methods to achieve greater durability and improved properties. It has been observed that even changing only the synthesis method can lead to significant morphological changes in the material, and studies in the literature have shown that these morphological characteristics can influence the overall chemical properties of the material.

In recent years, spinel-structured compounds have attracted significant attention due to their superior electrical and magnetic properties, leading to their widespread use as cathode materials in various advanced technological applications such as fuel cells, ceramics, sensors, lithium-ion batteries, and solar cells and ceramics, magnetism, optics and catalysis because of their excellent thermal and chemical stability (Dastjerdi, Shokrollahi, & Mirshekari, 2023; Patra, Naik, Bhatt, & Kaushik, 2019; Sukhorukov, Telegin, Naumov, & Surzhikov, 2023; Gajraj & Mariappan, 2022).

With the rapid advancement of technology, the importance of spinel-structured materials has grown accordingly (Malavasi, Tealdi, Amboage, Mozzati, & Flor, 2005; Zhao et al., 2015). Because of their flexibility and the ability to adjust

properties through compositional modifications of Spinel-type compounds, MM_2X_4 (M: Metal, X:Chalcogen) make them especially significant.

Among transition metal oxides, spinel-type oxides stand out for their unique structural and electronic characteristics. The spinel crystal framework accommodates multiple oxidation states, a feature that is advantageous for catalytic applications (Pawar et al., 2025).

Among the many types of spinels, manganese-based spinel materials are the most preferred in technological applications due to their low cost, high natural abundance, low toxicity, ability to exhibit multiple valence states, and the significant Jahn-Teller effect (Molenda et al., 2005; Park et al., 2006; Kwang et al., 2007; Datta et al., 2014; Ma et al., 2014; Chowdhury et al., 2014).

However, in the literature, these materials are typically synthesized using conventional methods such as high-temperature solid-state synthesis (Azzoni et al., 2001; Malavasi et al., 2002, 2004, 2005), hydrothermal synthesis (Zhao et al., 2015), sol-gel (Hosseini et al., 2011), precipitation, and solvothermal methods (Zhai et al., 2013).

These traditional approaches tend to limit the electrical properties of the materials, as such properties are directly influenced by structural characteristics like particle size, surface area, and crystal structure. These structural features also play a crucial role in determining the electrical conductivity of the material.

Rechargeable magnesium-ion batteries (MIBs) represent a promising alternative to lithium-ion battery (LIB) technology for meeting future large-scale mobile and stationary energy storage demands. In addition to the high stability and natural abundance of magnesium metal, MIBs offer several potential advantages, including greater atmospheric stability and a higher melting point than lithium, making them more safer (Yoo et al., 2013). Spinel metal oxides (MMn_2O_4) have catalysis properties because of their unique structural and chemical properties and this lead to them suitable for both thermal and photocatalytic pathways (Pawar et al., 2025).

In the reviewed literature, the properties of compounds and their synthesis methods and conditions have been extensively studied; however, limited studies have been found regarding the synthesis of spinel-structured manganite compounds using the solution combustion method. Solution combustion synthesis is considered a highly valuable technique, as it allows for the rapid preparation of materials and results in compounds with high surface area, high purity, and a homogeneous structure (Ma et al., 2006; Wen et al., 2012; Shafiaan et al., 2013). Applying this technique to the compounds planned for synthesis is expected to offer both time and energy efficiency, providing significant economic benefits for our country. Moreover, it is anticipated that this method will have a positive impact on the electrical and magnetic properties of the spinel-structured manganite compounds.

1.2.1 Studies on Spinel-Structured Magnesium Manganite (MgMn_2O_4)

MgMn_2O_4 spinel can be synthesized by sol-gel method, hydrothermal method and solid-state reaction (Zainol et al., 2019; Ariyoshi & Masuda, 2020; Harudin et al., 2020). Mn-based spinel oxides MMn_2O_4 ($\text{M} = \text{Zn}, \text{Co}, \text{Fe} \dots$) have attracted significant attention because of their environmental friendliness, low toxicity and high theoretical specific capacity and shows potential application in the field of anode material for Li-ion batteries (Ji et al., 2020).

Azzoni et al. (2001) synthesized $\text{Mg}_{1-x}\text{Mn}_{2-x}\text{O}_4$ ($0 < x < 1$) solid solutions using the conventional solid-state method at 1000°C to investigate the effect of the Mg/Mn ratio on magnetic properties. They observed that an increase in manganese ion content led to stronger magnetic interactions.

Malavasi et al. (2002) prepared $\text{Mg}_{1-x}\text{Mn}_{2-x}\text{O}_4$ ($0 < x < 1$) compounds by heating the materials at 1200°C for six days using the classical solid-state method, forming them into pellets. They studied the effects of the Mg/Mn ratio on the structural and electrical properties and reported that the increase in manganese ion concentration resulted in enhanced positive charge carriers, thereby improving the electrical properties.

Malavasi et al. (2004) synthesized MgMn_2O_4 using the solid-state method and fabricated thin films via the RF magnetron sputtering technique. The structural

and morphological characterizations were carried out using X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM). The study noted minimal degradation in thin films at 500 °C but emphasized that structural distortions might occur in spinel structures at higher temperatures due to the formation of inverse spinel phases during thin-film deposition.

Malavasi et al. (2005) investigated the structural behavior of MgMn_2O_4 spinel oxide synthesized via the solid-state method under high pressure using X-ray diffraction. Under a pressure of 30 GPa, the spinel structure transformed into an orthorhombic phase similar to the CaMn_2O_4 structure.

Ling and Mizuno (2013) explored the thermodynamics and kinetics of the structural transition of MgMn_2O_4 from spinel to post-spinel. They demonstrated that the thermodynamic stability of the post-spinel phase is governed by the electronic configuration of transition metals. Additionally, they found that MgMn_2O_4 , when used as a cathode material in lithium-ion batteries, exhibited an energy density approximately 1.3 times higher than that of LiMn_2O_4 .

Zhao et al. (2015) synthesized MgMn_2O_4 via the hydrothermal method and investigated the effects of cobalt doping on the structural properties of the compound. They also evaluated its electrochemical performance for potential use as an anode material in lithium-ion batteries. Their findings indicated that cobalt doping significantly influenced the electrochemical behavior of the material. Among the synthesized compounds— MgMn_2O_4 , $\text{MgMn}_{1.5}\text{Co}_{0.5}\text{O}_4$, and MgMnCoO_4 —they reported that **$\text{MgMn}_{1.5}\text{Co}_{0.5}\text{O}_4$** exhibited the highest electrochemical performance and concluded that this composition is well-suited for use as a high-performance electrode material in lithium-ion batteries.

Zainol et al. (2019) synthesized and characterized Ti-doped MgMn_2O_4 as a cathode material for magnesium-ion batteries by self-propagating combustion method and citric acid as a reducing agent. The precursors of MgMn_2O_4 and $\text{MgMn}_{(2-x)}\text{Ti}_x\text{O}_4$, ($x = 0.1$) were annealed at 700 °C for 24 h and characterized by using Simultaneous Thermal Analysis (STA), X-ray diffraction (XRD), and Field Emission Scanning Electron Microscopy (FESEM). Tetragonal spinel-structure MgMn_2O_4 with space group of $I4_1/amd$ can be clearly identified. The diffraction

peaks of $\text{MgMn}_{1.9}\text{Ti}_{0.1}\text{O}_4$ is broader than that of MgMn_2O_4 , which can be attributed to the poor crystallinity and smaller particle size.

Wang et al. (2022) synthesized porous structure MgMn_2O_4 by a reverse co-precipitation method at annealing temperature of 700–900 °C and by solid-state reaction method for comparison. Annealing temperature on phase, morphology and particle size and effect of different methods were examined. As the annealing temperature increases, the inversion parameter of MgMn_2O_4 decreases, indicating that the material tends to form normal spinel structure at high temperature. The porous MgMn_2O_4 microspheres exhibit excellent electrochemical performance as anode materials for lithium batteries, delivering a higher cycling capacity than samples prepared via the solid-state reaction method.

Wang et al. (2022) in their study nanoparticle MgMn_2O_4 was synthesized by sol gel technique using citric acid / sucrose as chelators and ethanol / water as solvent. The electrochemical and microstructural features were examined in relation to the changing synthesis conditions. Regarding the X-ray photoelectron spectroscopy (XPS) results, all samples were of mixed spinel structure Mg and Mn ions occupied both tetrahedral and octahedral sites. As electrochemical performance, the sample prepared by using citric acid/ethanol has the highest charge-discharge capacity.

Wang et al. (2024) synthesized MgMn_2O_4 graded porous microspheres using a new template-assisted method and investigated their electrochemical properties. The study demonstrated that achieving a controlled pore size distribution and tailored morphology enhanced ion diffusion capability and electrode performance. The study shows that pore engineering can provide significant improvements in capacity and cycling stability for MgMn_2O_4 -based energy storage systems. The full-cell test result indicates MgMn_2O_4 material has potential application as anode for Li-ion batteries.

1.2.2 Studies on Spinel-Structured Cobalt Manganite (CoMn_2O_4)

Cobalt manganese oxide can be synthesized using various methods such as solid-state, sol–gel, and hydrothermal methods. The synthesis method of the spinel

oxide, CoMn_2O_4 can change the structural and chemical properties of the material. (Sowmiya & Vijayalakshmi, 2024). Cobalt manganite is generally an inverse spinel oxide and because of this feature, spinel oxide synthesized using non-conventional routes followed by analysis of its magnetic properties. (Habjanič et al., 2014, Popović et al., 2017) Nithya et al. (2025) also stated that CoMn_2O_4 spinel oxide exhibits a wide band gap depend on synthesis methods and characterization techniques.

Zhang et al. (2006) investigated the particle size and magnetic properties of spinel CoMn_2O_4 synthesized via a facile method. Using X-ray photoelectron spectroscopy, they found that the particle size increased from 5.3 nm to 12 nm. Magnetically, the compound exhibited ferrimagnetic behavior at low temperatures and paramagnetic behavior at room temperature, indicating temperature-dependent magnetic properties

Hosseini et al. (2011) synthesized spinel CoMn_2O_4 using sol-gel combustion and precipitation methods by heating at 700 °C for 6 hours. They compared the effects of these methods on the physical and chemical properties of the compound and concluded that the sol-gel combustion method is preferable due to the higher presence of the normal spinel phase compared to the precipitation method.

Hu et al. (2012) reported that the synthesis technique used for CoMn_2O_4 via a facile method significantly influenced the morphology of the compound, enhancing both its capacity and stability as a lithium-ion battery anode. After structural modifications, they found that under a current density of $100 \text{ mA} \cdot \text{g}^{-1}$, the compound delivered a capacity of $894 \text{ mAh} \cdot \text{g}^{-1}$ after 65 cycles.

Zhou et al. (2012) synthesized spinel CoMn_2O_4 via the precipitation method and evaluated its electrochemical performance as an anode material for lithium-ion batteries. They reported a specific capacity of $830 \text{ mAh} \cdot \text{g}^{-1}$ at $200 \text{ mA} \cdot \text{g}^{-1}$, which remained at $624 \text{ mAh} \cdot \text{g}^{-1}$ after 50 cycles, indicating excellent electrochemical performance.

Koo et al. (2013) synthesized CoMn_2O_4 at various temperatures ranging from 700 °C to 920 °C and fabricated thin films using pulsed laser deposition. They investigated the structural and magnetic properties and found that temperature affected both properties, with increasing temperature promoting a transition from normal to inverse spinel structure.

Zhai et al. (2013) studied the electrical properties of CoMn_2O_4 synthesized via the solvothermal method. They reported that changes in synthesis method led to significant improvements in electrical conductivity and durability compared to other hybrid materials.

Koo et al. (2014) synthesized CoMn_2O_4 at temperatures between 720 °C and 820 °C and studied the effects of temperature on particle size and morphology. While particle growth was observed with increasing temperature, a morphological transformation to a nanorod structure was also reported.

Yang et al. (2014) synthesized CoMn_2O_4 in nanofiber form using the electrospinning method. Electrochemical analysis showed that the compound had a specific capacity of $526 \text{ mAh} \cdot \text{g}^{-1}$ after 50 cycles at a current density of $400 \text{ mA} \cdot \text{g}^{-1}$, demonstrating its potential as a promising anode material for lithium-ion batteries.

Zhao et al. (2014) examined the performance of AMn_2O_4 ($\text{A}=\text{Zn}$, $\text{Zn}_{0.5}\text{Co}_{0.5}$, Co) compounds synthesized by precipitation for use as anodes in lithium-ion batteries. They reported a suitability ranking of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Mn}_2\text{O}_4 < \text{CoMn}_2\text{O}_4 < \text{ZnMn}_2\text{O}_4$ based on electrochemical performance.

Kutty et al. (2018) investigated the structural and magnetic properties of CoMn_2O_4 synthesized via a sol–gel auto-combustion method with the glycine as fuel. Synthesized product has been calcinated at 700 °C for 10 h. Submicron-sized cobalt manganite particles with well-defined lattice fringes are defined by electron microscopy, while low-temperature magnetic investigations revealed that the prepared CMO as a ferrimagnetic spinel due to the presence of uncompensated electronic states.

Sowmiya and Vijayalakshmi (2024) explored the optimal synthesis method for CoMn_2O_4 nanostructures to improve supercapacitor performance.

Hydrothermal, sol–gel, and solid-state synthesis methods are used to define the optimal synthesis method effect its supercapacitor applications for cobalt manganese oxide. X-ray diffraction analysis revealed that the solid-state method produced the most stable and uniformly structured CMO among these three synthesis method.

Pawar et al. (2025) demonstrated that cerium doping improves the efficiency of CoMn_2O_4 catalysts for selective oxidation reactions by lowering activation energy. Structure-activity relation and impact of Cr on catalyst and kinetic properties were examined in detail. The study identified the presence of Mn^{4+} , Mn^{3+} , and Ce^{3+} active sites are the key crucial point for the observed catalytic activity. Furthermore, the study offers a comparative analysis of the mechanistic and performance aspects of thermal and photocatalytic oxidation.

1.2.3 Studies on Spinel-Structured Nickel Manganite (NiMn_2O_4)

Spinel-type nickel manganite (NiMn_2O_4 - AB_2O_4), a transition metal oxide with the cubic spinel structure known for its negative temperature coefficient, It is also important for the flexible incorporation of various ions, where A and B represent divalent and trivalent cations, respectively. NiMn_2O_4 contains both tetrahedral and octahedral sites. NiMn_2O_4 compounds have also been extensively investigated due to their promising magnetic, electrical, and electrochemical properties, making them suitable for applications in thermistors, lithium-ion batteries, and thin-film devices because of having high electrical conductivity, good electrochemical performances, abundance in nature, low cost, low toxicity, and environmental friendliness (Galeb et al., 2024). Numerous synthesis techniques such as co-precipitation (Ashcroft et al., 2006), sol–gel (Zhang et al., 2013), hydrothermal (Britto et al., 2022), combustion synthesis (Vijaya Sankar et al., 2015), solvothermal (Kaviyarasu et al., 2014), and spray pyrolysis (Li et al., 2017) have been employed in the literature to tailor the structural and functional characteristics of these materials. Nickel manganite (NiMn_2O_4) shows a partially inverse cubic structure.

Schmidt et al. (2001) synthesized pure NiMn_2O_4 via thermal treatment at 800 °C for 50 hours and fabricated thin films using electron beam evaporation. They

investigated the temperature-dependent resistivity of the films and found the experimental conduction exponent n to be 0.28 (compared to the theoretical 0.25), attributing the deviation to changes in the valence states of manganese ions.

Schmidt et al. (2002) synthesized NiMn_2O_4 via the precipitation method and produced thick films using two techniques: one with organic binders and the other with glass powders. The films fabricated with glass powders exhibited higher resistance and better surface quality.

Csete de Gyorgyfalva and Reaney (2003) explored the thermal decomposition behavior of NiMn_2O_4 synthesized via solid-state reaction. Structural deterioration of the spinel phase was observed at a critical temperature of 907°C , resulting in the formation of a rock salt NiO phase. At higher temperatures, Mn-rich spinel phases were identified.

Pena et al. (2005) examined the magnetic properties of undoped and metal-doped (Ga, Zn, Ni, Cr) NiMn_2O_4 . The paramagnetic-to-ferromagnetic transition temperature of undoped NiMn_2O_4 was 110 K, and this temperature decreased with increasing dopant concentration.

Schmidt et al. (2005) performed thermal conversion of $\text{Ni}(\text{MnO}_4)_2 \cdot x\text{H}_2\text{O}$ at 900°C to obtain NiMn_2O_4 and studied its kinetics and structural properties. The activation energy of the pure spinel phase was calculated as 108 ± 4 kJ/mol.

In another study by Schmidt et al. (2005), thin films of 700 nm thickness were produced via magnetron sputtering using pellets sintered at 800°C for 40 hours. Morphological analysis revealed that the grain size increased from 20 nm to 50 nm with increasing synthesis temperature (800 – 1200°C).

Ashcroft et al. (2006) compared two precipitation routes for NiMn_2O_4 synthesis. The method incorporating sodium hydroxide yielded purer and more stable spinel phases with smaller particle sizes than the oxide precursor route.

Sawant et al. (2007) synthesized NiMn_2O_4 using hydrazine-based precursors and reported the formation of nanoparticles.

Savić et al. (2008) investigated the effect of sintering temperatures (900, 1050, and 1200 °C) on the resistance and activation energy of NiMn₂O₄. Resistance decreased from 121.5 kΩ to 7.5 kΩ, while activation energy increased from 0.283 eV to 0.302 eV with temperature.

Jadhav and Puri (2009) synthesized Cu-doped NiMn₂O₄ compounds using the oxalate precursor method. The copper-doped samples exhibited enhanced microwave conductivity and absorption, with a maximum absorption at $x = 0.4$. Particle size also increased with Cu content.

Díez et al. (2010) studied the magnetic and dielectric properties of NiMn₂O₄ synthesized by heating Ni(MnO₄)₂·xH₂O at 900 °C for 24 hours. The magnetic moment was determined to be 6.27 μB.

Nelson-Cheeseman et al. (2010) modified the magnetic ground state of NiMn₂O₄ thin films. While the bulk compound exhibits a paramagnetic-to-ferromagnetic transition below 110 K, modified films retained ferromagnetic behavior down to 60 K due to reduced Mn⁴⁺ occupancy at octahedral sites.

Zhang et al. (2011) synthesized NiMn₂O₄ via sol-gel method and studied specific resistivity values at different temperatures. Resistivity values were found to be 6 Ω·cm² at 600 °C and 17 Ω·cm² at 800 °C.

Sagua et al. (2012) prepared NiMn₂O₄ using precipitation in a hydroxide medium and reported that 60% of Mn and 40% of Ni ions occupied octahedral sites in the spinel structure.

Watanabe et al. (2012) synthesized (Ni_{1-x}M_x)Mn₂O₄ (M = Zn, Mg; $x = 0, 0.1, 0.2$) compounds and measured their electrical resistance. Zn doping had negligible effect, whereas Mg doping led to increased electrical resistance.

Ryu et al. (2013) fabricated thin films of Co- and Fe-doped NiMn₂O₄ via aerosol deposition. The thermistor B constant increased from 4000 K (undoped) to 5000 K with 5% Co doping, and to 5600 K upon further Fe addition.

Zhang et al. (2013) used the sol-gel method to synthesize NiMn_2O_4 and characterized its morphology. The material exhibited a specific surface area of $201 \text{ m}^2/\text{g}$, particle sizes of 8–10 nm, and a specific capacitance of 169 F/g .

In a separate study, Zhang et al. (2013) investigated the optical properties of NiMn_2O_4 thin films with different thicknesses (300–1700 nm) using spectroscopic ellipsometry. The film thickness did not significantly affect the optical properties.

Gao et al. (2014) synthesized NiMn_2O_4 using the solid-state method and studied the effects of sintering temperature on its structural and electrochemical behavior. At 1100°C , a secondary NiO phase formed. The electrical resistance at room temperature was $2924 \Omega \cdot \text{cm}$ and the thermistor B constant was 3429 K .

Tadic et al. (2014) synthesized NiMn_2O_4 via the polymeric complex method at 1200°C and investigated its magnetic behavior. Three magnetic transitions were observed at $T_1:35$, $T_2:101$, and $T_3:120$. Upon applying a magnetic field, the first two transitions shifted significantly while the third remained unchanged.

Galeb et al. (2024) examined solution combustion-derived AMn_2O_4 ($\text{A} = \text{Ni, Cu, Co, Zn}$) nanoparticles to evaluate their suitability as supercapacitor electrode materials. In the synthesis of AMn_2O_4 ($\text{A} = \text{Ni, Cu, Co, Zn}$) nanoparticles, glycine-assisted solution combustion (SC) method was performed since this method provides low ignition temperature, rapid reaction time, avoidance of time consuming, affordability and simple experimental set up.

Dojčinović et al. (2025) investigated structural, magnetic, and electrochemical properties of NiMn_2O_4 nano-cotton particles and nanofibers for energy storage applications with the using sol-gel combustion synthesis with the glycine as fuel. Study shows that difference calcination temperature and difference in the precursors and procedure has significant affect on the crystal size as well as in lattice parameter, inversion degree and oxygen positional parameter.

1.3 Aim and Scope of the Study

1.3.1 Rare-Earth Metal Doped Magnesium Orthoborates

The initial section of this thesis is dedicated to the synthesis and comprehensive structural characterization of magnesium orthoborate ($\text{Mg}_3\text{B}_2\text{O}_6$) in its kotoite crystalline phase. The investigation begins by examining the influence of varying precursor materials and boron source ratios on the successful formation of a phase-pure kotoite compound. Through a series of systematic experiments, optimal synthesis parameters were established to obtain materials exhibiting superior phase purity and tailored structural properties.

Building upon insights from the existing literature, the second aim of the study is to elucidate the structural modifications induced by doping magnesium orthoborate with rare earth metals within the pure kotoite matrix. The effects of these dopants on the unit cell parameters were rigorously analyzed using X-ray diffraction data processed with the Jana2006 software suite (Petricek, Dusek, & Palatinus, 2011). Subsequently, key physical characteristics including crystallite size, surface area, and density were calculated from the diffraction data using the Debye-Scherrer equation.

In summary, this segment of the research encompasses several critical stages: first, the optimization of starting materials and boron source quantities to synthesize phase-pure $\text{Mg}_3\text{B}_2\text{O}_6$; second, determination of the ideal rare earth dopant concentrations followed by the doping process and comprehensive characterization of the resulting materials; third, evaluation of thermal stability through thermogravimetric and differential thermal analyses; and finally, detailed structural analysis coupled with calculations of crystallite size, density, and surface area, all conducted through advanced software and analytical techniques.

1.3.2 Bimetallic oxides

In the second part of this study, the fabrication of Mn-based spinel type of nanomaterials given with the formula, AMn_2O_4 (A: Mg, Co and Ni) via Solution Combustion, SCS method will be done. The synthesis of these type of spinel oxides is rarely done and not adequately reported. Hence, the aim is to prepare AMn_2O_4 (A: Mg, Co and Ni) via SCS technique using different organic fuels and heating

temperature. To identify and characterize the bond variation and structural properties of the products, FT-IR spectroscopy and X-Ray diffraction techniques are employed, respectively.



2. MATERIALS and METHOD

2.1 Chemicals

The following chemicals were used in the synthesis of the products:

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Magnesium nitrate hexahydrate

$\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$: Manganese(II) nitrate tetrahydrate

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Cobalt(II) nitrate hexahydrate

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Nickel(II) nitrate hexahydrate

$\text{C}_4\text{H}_6\text{O}_6$, L(+)-Tartaric acid: Merck (pure 99.0%)

$\text{CH}_4\text{N}_2\text{O}$, Urea: Merck (pure 99.5%)

$\text{C}_2\text{H}_5\text{NO}_2$, Glycine: Merck (pure $\geq 99.7\%$)

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Lanthanum(III) nitrate hexahydrate

$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ — Neodymium(III) nitrate hexahydrate

$\text{Pb}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$; Merck (pure %99.00)

$\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ — Sigma-Aldrich (pure %99.00)

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00)

$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; SigmaAldrich (pure %99.00),

$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00),

$\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00),

$\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00),

$\text{Dy}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00)

$\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00)

$\text{Lu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00)

$\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$; Sigma-Aldrich (pure %99.00)

KBr: Spectroscopic grade and it was used for making IR pellets. It was dried at 150°C before using.

2.2 Furnaces

All the reactions have been carried out in air with the aid of Nuve MF 1400, Nuve 1200 and Protherm 1600 furnaces. Heating ranges were 450-900°C.

2.3 Instruments

2.3.1 X-Ray Powder Diffractometer

X-ray powder diffraction patterns (**XRD**) were recorded on Rigaku miniflex, BD127412, and CuK α (30-40 kV, 10-20 mA, $\lambda=1.54056$ Å) radiation in 2θ range from 6.00° to 70.00° . Indexing of the XRD pattern was checked by the OriginPro 2015 program. The least square refinement procedure of the unit cell parameters was done by Jana2006. The least square refinement procedure of the unit cell parameters was done by Jana2006 (Petricek, 2011). The crystallite sizes of products were estimated based on the XRD patterns using the Debye-Scherrer's equation (Patterson, 1939; Chandrappa and Venkatesha, 2012; Phadatare et al., 2013)

$$t = \frac{K\lambda}{\beta \cos\theta}$$

(t is the crystal size (nm), K is the structure factor, and is usually taken as 0.9, wavelength $\lambda=1.5406$ (CuK α), β (radian) and θ is the bragg angle)

The densities of the resulting compounds are calculated using the following formula. (d : density, M : molecular weight, N : Avogadro's number and a,b,c : unit cell parameters)

$$d = \frac{8M}{Nabc}$$

Within the specific surface area, it is determined using the following formula.

$$S = \frac{6}{dt} \quad (D: \text{Density}, T: \text{Crystallite Size})$$

Lattice Constant Calculations:

In a tetragonal crystal structure, the lattice constants are denoted by a (for the length of the unit cell edge along the two equivalent axes) and c (for the length of the unit cell along the third axis, which is perpendicular to the a - b plane). The a and c constants are essential for determining the geometry of the unit cell and can be calculated using X-ray diffraction (XRD) data, particularly from the angles of diffraction peaks.

For a tetragonal crystal system, the relationship between the d-spacing (interplanar spacing) and the lattice constants is given by Bragg's Law and the generalized equation for a tetragonal lattice:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Where:

- **d** is the interplanar spacing (calculated from the angle of diffraction, 2θ).
- **a** and **c** are the lattice constants along the **a** and **c** axes.
- **h, k, l** are the Miller indices for a given diffraction peak.

To calculate **a** and **c**, you would typically use multiple diffraction peaks with known **h, k, l** values and their corresponding **2θ** values. From the **2θ** values, you can compute **d** using Bragg's law:

$$n\lambda = 2d \sin(\theta)$$

Where:

- **λ** is the wavelength of the X-ray used.
- **θ** is the Bragg angle (half of the **2θ** value from the XRD spectrum).

Once you have the **d** values for multiple reflections (different **h, k, l**), you can solve the above equation for **a** and **c**.

2.3.2 Fourier Transform Infrared Spectrophotometer (FTIR)

Shimadzu Fourier Transform Infrared (FTIR) Spectrophotometer was used to obtain the spectra of the products in the region of the 4000-400 cm⁻¹. Spectra of solid samples were taken from KBr pellets using 0.0010:0.150 (wt/wt) product to KBr ratio.

2.3.3 Thermal Analysis

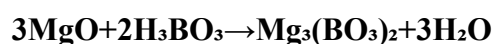
TG/DTA 6300, SII EXSTAR 6000 Differential Thermal Analyzer instrument was used to investigate the thermal properties of products. The powder samples of products was placed in a platinum crucible and heated from 20 oC to 1400°C with a heating rate of 10°C/min.

2.4 Synthesis Methods

2.4.1 Synthesis of Magnesium Borate

In the first stage of this study, it was planned to synthesize kotoite -type magnesium orthoborate in pure form by high temperature solid state method. For this, various sources of magnesium such as MgO, MgCO₃, MgSO₄ and MgNO₃ and H₃BO₃ were used as a source of boron. The substances were weighed separately in stoichiometric ratios, mixed homogeneously in an agate mortar and crushed. The mixtures obtained were synthesized by heating in a high temperature furnace at 450 °C for 4 hours, at 600 °C for 3 hours, and at 900 °C for 48 hours. At the end of each heating, the substances were cooled to room temperature, mixed homogeneously and crushed. Characterization of the resulting products was performed using X-ray powder diffraction and infrared spectroscopy.

Magnesium oxide (MgO) can be reacted with boric acid (H₃BO₃) to form magnesium borate.



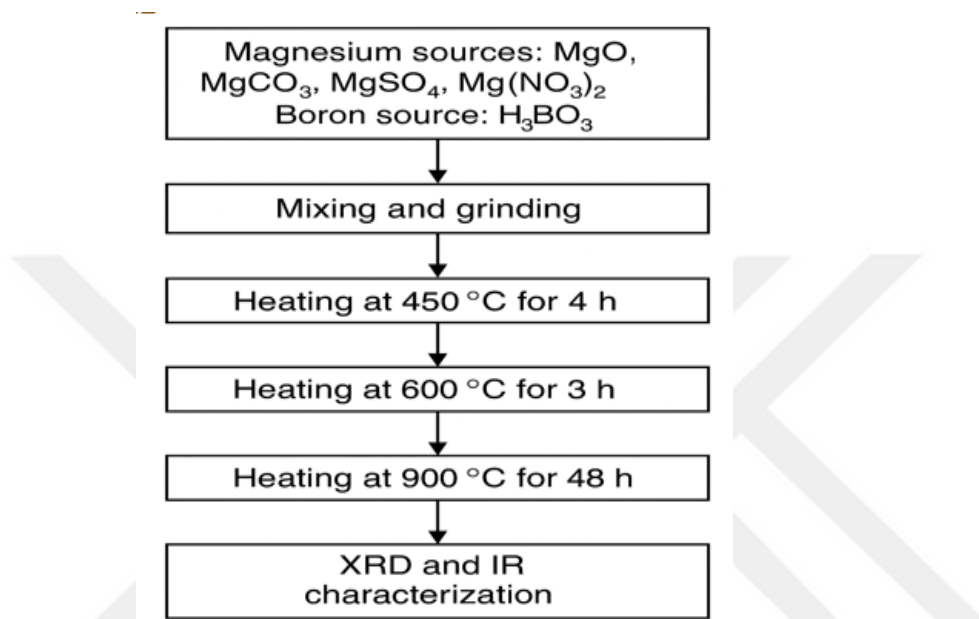
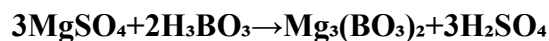
Magnesium carbonate (MgCO₃) can be used as the magnesium source, and it reacts with boric acid to form magnesium borate. The carbonate is decomposed in the reaction.



Magnesium nitrate (Mg(NO₃)₂) can also react with boric acid, with the nitrate providing magnesium and the formation of magnesium borate.



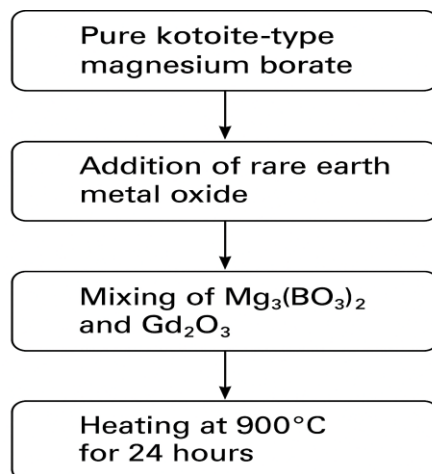
To synthesize kotoite-type magnesium borate using magnesium sulfate (MgSO_4) as the magnesium source and boric acid (H_3BO_3) as the boron source via the high-temperature solid-state method.



Scheme1 : Process for obtaining pure $\text{Mg}_3\text{B}_2\text{O}_6$ compound

2.4.2 Determination of the Optimum Concentration Amount of the Rare Earth metal

Rare earth metals were doped to the synthesized pure kotoite-type magnesium borate compound in the form of oxides. Since the periodic table is located in the middle of the order of rare elements, gadolinium rare earth metal was used to determine the optimum value. The concentrations given in Table 1 were also weighed separately as $\text{Mg}_3(\text{BO}_3)_2$ ve Gd_2O_3 substances and mixed homogeneously in an agate mortar. The resulting mixture was heated at 900°C for 24 hours and gadolinium doped magnesium borate compound was obtained.



Scheme 2: Process of obtaining Gd₂O₃ doped Mg₃B₂O₆ compound

Where:

- Mg₃(BO₃)₂ is magnesium borate.
- Gd₂O₃ is gadolinium oxide, which provides Gd³⁺ ions.
- The reaction leads to Gd-doped magnesium borate with the formula Mg_{3-x}Gd_x(BO₃)₂, where x is the dopant concentration.

The reaction is based on the idea that Gd can replace magnesium in the Mg₃(BO₃)₂ lattice.

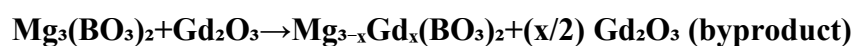


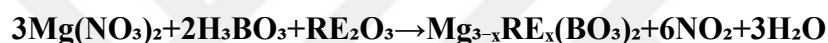
Table 2.1. Gadolinium ion concentrations in Mg₃(BO₃)₂

Products	Gd ₂ O ₃ (% wt.)
A	0.00
B	0.10
C	0.50
D	1.00
E	5.00
F	10.0
G	15.0
H	20.0

2.4.3 Addition of Rare Earth Metals at Determined Optimum Concentration

It is clearly seen that the kotoite-type magnesium borate is obtained by doping gadolinium oxide at a rate of 0.10 by weight per cent in a single phase and all of the diffraction lines belong only to the compound kotoite, $\text{Mg}_3\text{B}_2\text{O}_6$, (ICDD no: 75–1807). For this reason, the optimum additive value was determined as 0.10 and oxides of lanthanum (La), neodymium (Nd), cerium (Ce), erbium (Er), praseodymium (Pr), samarium (Sm), europium (Eu), terbium (Tb), dysprosium (Dy), holmium (Ho), ytterbium (Yb) and lutetium (Lu) rare earth metals were doped to magnesium borate in accordance with the procedure used in the doping of gadolinium rare earth metal.

The general reaction can be represented as follows:



Magnesium Nitrate ($\text{Mg}(\text{NO}_3)_2$): Used as the source of magnesium.

Boric Acid (H_3BO_3): A 5% excess of boric acid is used to ensure complete formation of the borate structure.

Rare Earth Oxides (RE_2O_3): The rare earth oxide (such as La_2O_3 , Nd_2O_3 , etc.) is used to provide the rare earth metal ions (RE^{3+}) for doping.

2.4.4 Synthesis of MMn_2O_4 (M: Mg, Co and Ni) using Tartaric Acid, Glycine and Urea fuels

The solution combustion synthesis (SCS) method is a novel and highly efficient technique that enables the rapid formation of complex compounds. In this process, a stoichiometric mixture of metal precursors in nitrate form (oxidants) and an appropriate fuel (reductant), such as hydrazine, urea, or glycine, is dissolved in water. Upon gradual evaporation and gel formation, the mixture undergoes spontaneous ignition, leading to the formation of the desired product in a single-step combustion reaction. One of the primary advantages of this method is the ability to control the structural parameters of the synthesized materials by adjusting the fuel-to-oxidant ratio and overall composition. Additionally, this technique

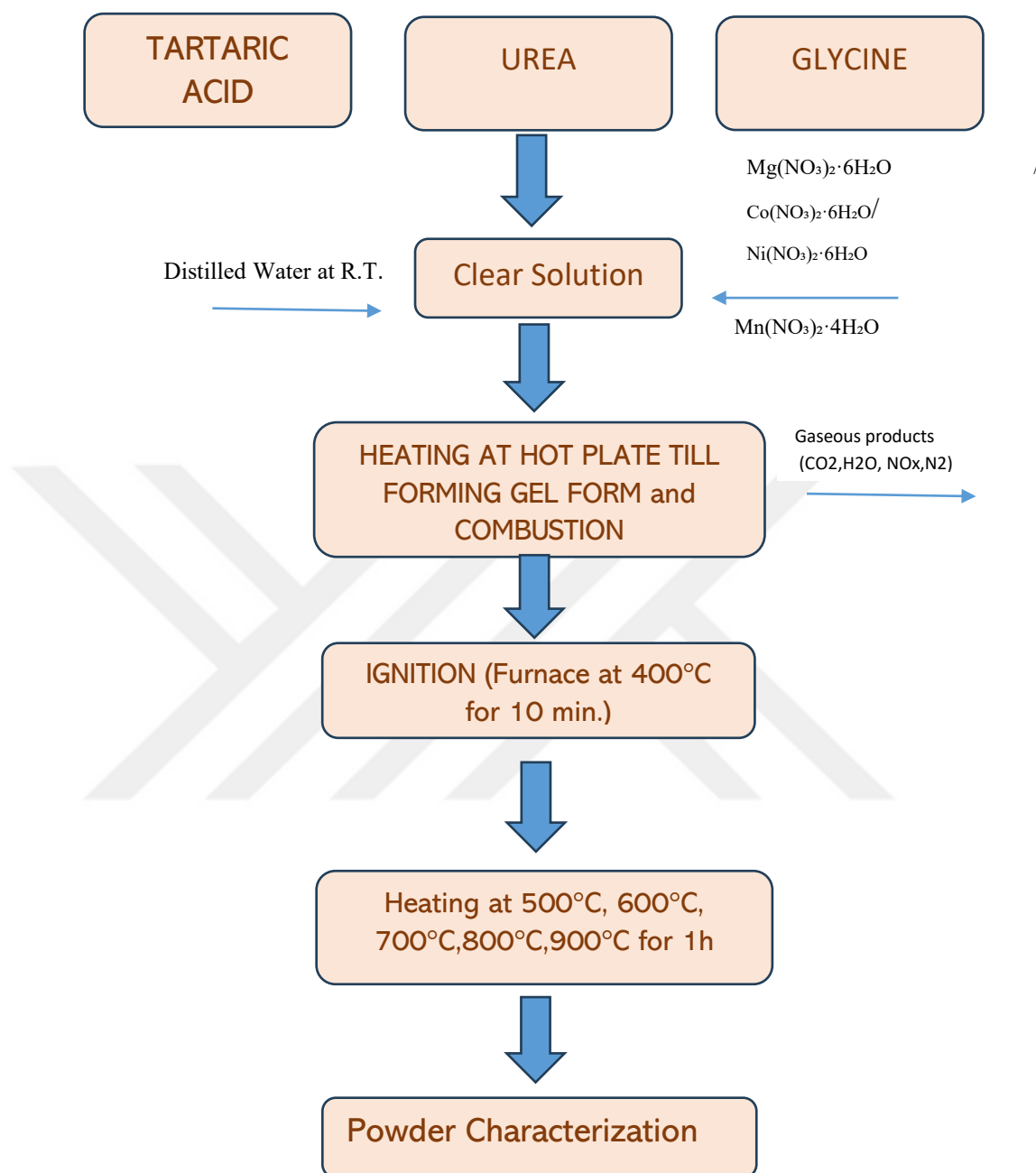
allows for the synthesis of highly pure, homogeneous materials with high surface area at relatively low temperatures and in very short reaction times.

In this study, the metal nitrates $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was used as oxidizing agents, while three different fuels—urea, glycine, and tartaric acid—serve as the reducing agents. As summarized in Scheme 3, the starting materials were added according to its stoichiometry and dissolved in deionized water and the solution was heated to evaporate the water until a gel-like mixture was formed. The solution was stirred and evaporated at $\sim 360^\circ\text{C}$ till gel-form. After the solution reached a gel form, combustion was observed. Subsequently, to complete the combustion process, transferred into a preheated furnace at 400°C , 10 min to complete the combustion process. The resulting ash-like powders was ground uniformly and divided to 6 samples for characterization. These were as synthesis, 500°C , 600°C , 700°C , 800°C , 900°C . The heated samples were taken directly from the synthesized material and calcined at the 500°C , 600°C , 700°C , 800°C , 900°C temperatures for 1 hour to analyse the temperature effect.

In this work, solution combustion method was chosen as synthesis method because it is a simple and cost effective method. It also has the advantages of fast heating rates with short reaction times, combustion in low temperature in order to produce very fine powders.

Finally, the structural characterization of the synthesized nanoparticle products will be carried out using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR).

FUELS



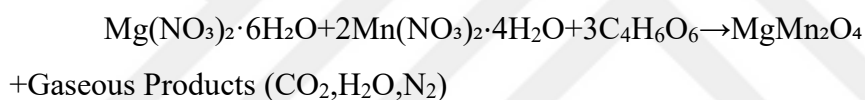
Scheme 3: General working procedure for MMn_2O_4 (M: Mg, Co and Ni) and fuels (TA, Urea and Glycine) via SCS method

2.4.5 Synthesis of MgMn_2O_4 using Tartaric Acid, Glycine and Urea fuels

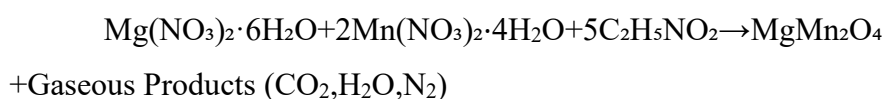
Nanocrystalline MgMn_2O_4 powders were synthesized using an inorganic oxidizer–fuel-based solution combustion approach. Magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), manganese(II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), and tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), glycine ($\text{C}_2\text{H}_5\text{NO}_2$) and urea ($\text{CH}_4\text{N}_2\text{O}$) were used as the starting materials. All reagents were of analytical grade and used without further purification. A stoichiometric mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and tartaric acid, glycine and urea were prepared based on the total oxidizing and reducing valences.

The overall redox reaction for the formation of MgMn_2O_4 using magnesium nitrate, manganese nitrate and;

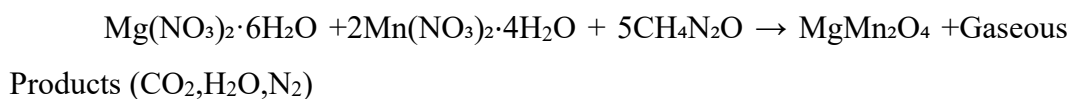
Tartaric Acid as a fuel is predicted as follow;



Glycine as a fuel is predicted as follow;



Urea as a fuel is predicted as follow;



Gaseous products include primarily H_2O , CO_2 , N_2 , and NO_x , resulting from the oxidation of glycine and decomposition of nitrates

The precursor mixture ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and selected fuel (tartaric acid, glycine and urea) were dissolved using a minimal volume of distilled water until achieving a homogenous and uniform solution. This solution was placed

in a porcelain evaporating dish and subjected to heating at approximately **370 °C** on a hot plate to facilitate solvent removal and induce gel formation.

When tartaric acid is used as fuel; light brown gel was formed and after 10 minutes left in hot plate, the sample turned to dark brown. Then, product was transferred into a preheated muffle furnace at 400 °C for 10 min, where intense and rapid combustion occurred due to the elevated temperature.

When Glycine is used as fuel; as the temperature increased, a vigorous flame-assisted combustion reaction was observed with sudden ignition and rapid release of gases. The reaction mixture exhibited foaming behavior, and gas bubbles formed along the edges of the porcelain evaporating dish. At this stage, the product took on a viscous and sticky gel-like consistency, indicating the onset of gelation and combustion. Subsequently, obtained product was transferred into a preheated muffle furnace at 400 °C for 10 min, where intense and rapid combustion occurred due to the elevated temperature. This thermal treatment caused the immediate collapse of the foamed structure and the complete disappearance of gas bubbles. The sample was maintained in the furnace for 10 minutes, MgMn_2O_4 was obtained as black color as shown below.

Similar process was also followed for urea fuel.



Picture 1: MgMn_2O_4 product by using tartaric acid (a), glycine (b), urea (c) fuel

To improve the crystallinity and phase purity of the synthesized MgMn_2O_4 powder, obtained as the product was divided into 6 samples and introduced to **500 °C, 600 °C, 700 °C, and 800 °C, 900 °C** each for 1 hour. These heat treatments

were carried out to facilitate the removal of residual organic content, promote complete phase formation, and improve structural ordering within the spinel lattice.

In each heating temperature, the samples were allowed to cool to room temperature and subsequently ground into fine powders for characterization. The resulting materials were analyzed using X-ray diffraction (XRD) to determine their crystalline phases and assess the degree of phase purity. In addition, Fourier-transform infrared spectroscopy (FTIR) was performed to examine the decomposition of organic functional groups, confirm the elimination of residual carbonaceous species and observe the metal to oxygen bond..

2.4.6 Synthesis of CoMn₂O₄ using Tartaric Acid, Glycine and Urea fuels

CoMn₂O₄ nanocrystalline powders were synthesized using an inorganic salt precursor, Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), manganese(II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O), and an organic fuel tartaric acid (C₄H₆O₆), glycine (C₂H₅NO₂) and urea (CH₄N₂O) via a solution combustion method. The stoichiometric amounts of Co(NO₃)₂·6H₂O, Mn(NO₃)₂·4H₂O, and organic fuels (TA, glycine, urea) were calculated based on the total oxidizing and reducing valence to maintain redox balance and solution combustion reaction.

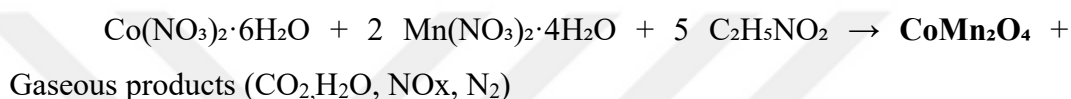
The reactants were dissolved in a minimal amount of distilled water in a porcelain evaporating dish to obtain a homogeneous solution. The solution was then heated on a hot plate at approximately 370 °C to facilitate solvent evaporation and gelation occurred gradually.

The initially homogeneous solution exhibited a deep burgundy coloration. Upon gelation, the presence of glycine as a fuel triggered a highly exothermic combustion reaction, characterized by vigorous flame propagation and substantial material loss. The gel was promptly transferred into a muffle furnace preheated to 400 °C. During this transfer, a spontaneous and violent combustion event was observed, indicative of the highly reactive nature of fuel-rich combustion systems, and consistent with previously reported behaviors in similar synthesis conditions..

To ensure the removal of residual organic species and byproducts resulting from incomplete combustion, the material was maintained in the furnace for an additional 10 minutes. This brief high-temperature treatment facilitated the decomposition of remaining carbonaceous residues and promoted the onset of crystallization of the CoMn_2O_4 spinel phase.

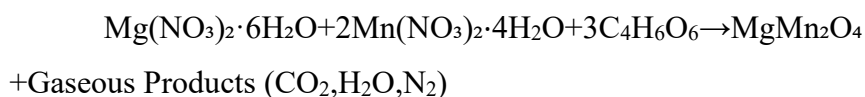
The synthesis of CoMn_2O_4 was carried out using the same procedure, with tartaric acid and urea serving as the fuel. The predicted overall combustion reaction is expressed as:

Glycine as a fuel the reaction is predicted as follow;

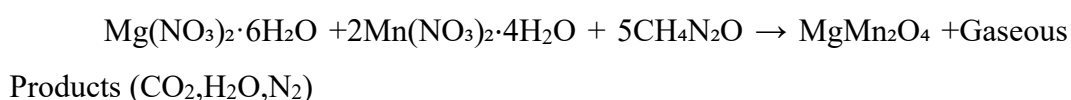


Picture 2: Solution combustion synthesis of CoMn_2O_4 with Glycine fuel

Tartaric Acid as a fuel the expected reaction is given as follow;



Urea as a fuel the predictex reaction can be written as follow;



In order to enhance the crystallinity and phase purity of the synthesized CoMn_2O_4 powders, obtained product was divided to 6 samples and introduced to **500 °C, 600 °C, 700 °C, and 800 °C, 900 °C** each for 1 hour. These thermal treatments were performed to ensure the elimination of residual organic species and improve structural ordering within the spinel framework.

After each heat treatment, the samples were allowed to cool to room temperature and were subsequently ground into fine powders for further characterization. The phase composition and degree of crystallinity of the calcined materials were analyzed by X-ray diffraction (XRD). In parallel, Fourier-transform infrared spectroscopy (FTIR) was employed to analyze the thermal decomposition of organic moieties, verify the effective removal of residual carbon-containing species, and identify the characteristic vibrational modes corresponding to metal–oxygen bonds within the spinel oxide structure.

2.4.7 Synthesis of NiMn_2O_4 using Tartaric Acid, Glycine and Urea fuels

Nanocrystalline NiMn_2O_4 powders were synthesized using a solution combustion method. Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and manganese(II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) served as the metal sources and oxidizing agents, while tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$), glycine ($\text{C}_2\text{H}_5\text{NO}_2$) and urea ($\text{CH}_4\text{N}_2\text{O}$) was used as the fuel.

A similar synthesis protocol, thermal treatment, and characterization procedures were also applied to NiMn_2O_4 . Phase identification and structural analysis were conducted using X-ray diffraction (XRD), while Fourier-transform infrared spectroscopy (FTIR) was employed to verify the decomposition of organic functional groups and the successful formation of the targeted spinel oxide phase.



Picture 3: NiMn_2O_4 product by using tartaric acid (a), glycine (b), urea (c)

3. RESULTS

3.1. XRD Characterization of Magnesium Orthoborates

3.1.1 Adjustment of the Type of Starting Materials and the Amount of Boron Source

Kotoite type magnesium borate was synthesized using four different sources of magnesium such as MgO, MgCO₃, MgSO₄ and MgNO₃ and H₃BO₃ as a source of boron with the high temperature solid state method. The mixtures obtained were synthesized by heating in a high temperature furnace at 450 °C for 4 hours, at 600 °C for 3 hours, and at 900 °C for 48 hours. Characterization of the resulting products was performed using X-ray powder diffraction and infrared spectroscopy.

In the XRD designs Figure 3.1 obtained as a result of the study, it was observed that the compounds of kotoite, Mg₃B₂O₆, (ICDD no: 75–1807), and suanite, Mg₂B₂O₅, (ICDD no: 83–0625) were formed together in two phases for MgO and MgCO₃ starting materials. When MgSO₄ is used as a source of magnesium, it has been observed that the MgO (ICDD no: 65-0476) phase is formed together with the compound of the kotoite, Mg₃B₂O₆ (ICDD no: 75-1807). When the magnesium source was changed to MgNO₃, a small amount of MgO (ICDD no: 65-0476) phase was observed. Thereupon, the amount of boric acid was increased by 5% and in the XRD pattern given in Figure 3.1-e, it is clearly seen that the kotoite-type magnesium borate was obtained in a single phase and all of the diffraction peaks belonged only to the compound of the kotoite, Mg₃B₂O₆, (ICDD no: 75–1807).

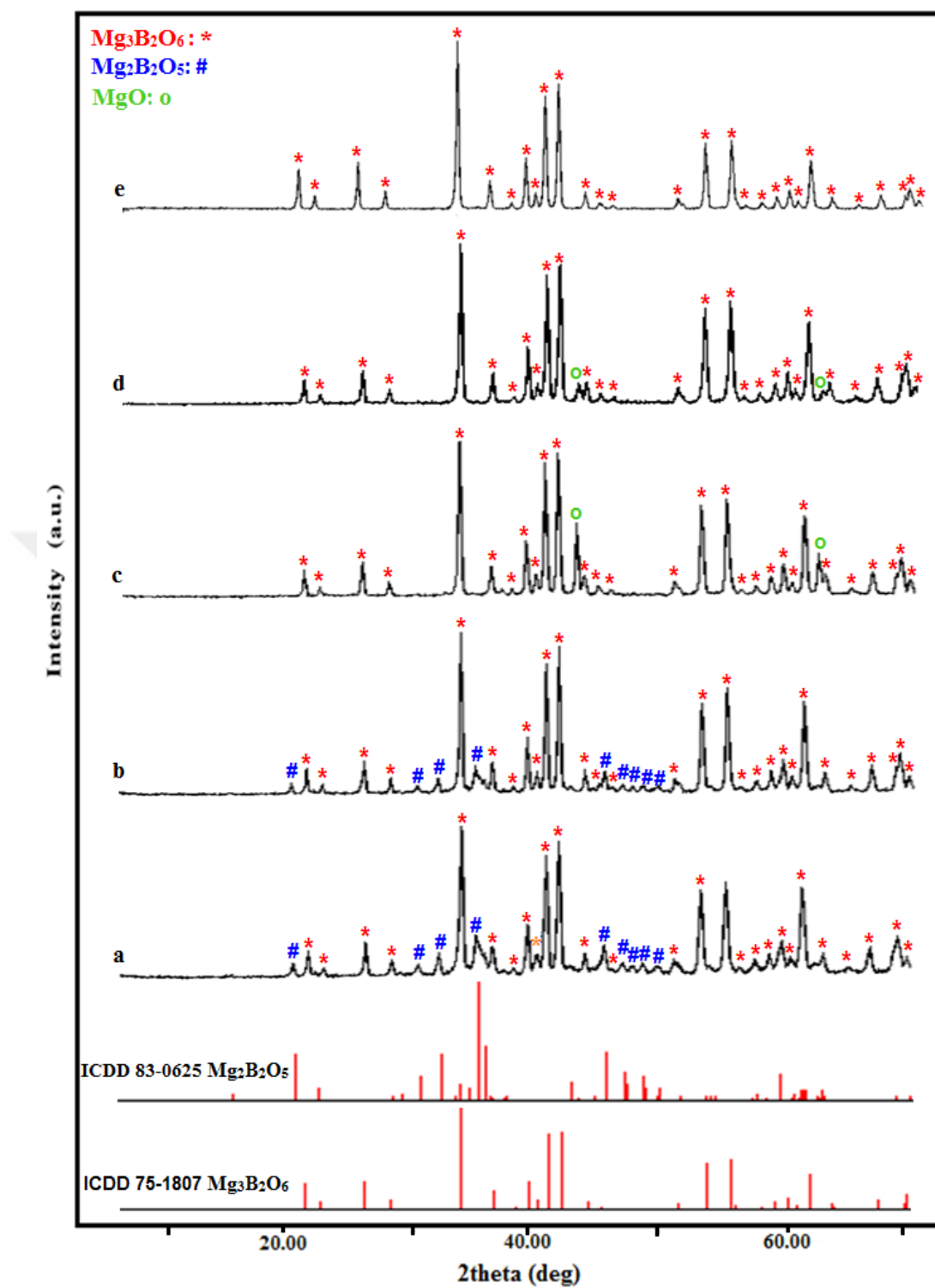


Figure 3.1. X-ray powder diffraction patterns of the products obtained using MgO (a), MgCO_3 (b), MgSO_4 (c), $\text{Mg}(\text{NO}_3)_2$ (d) and $\text{NO}_3)_2$ (5% excess boric acid) (e) as starting material

3.1.2 Determination of the Amount of Rare Earth Metal to be Doped

Characterization of the resulting products was performed using X-ray powder diffraction and infrared spectroscopy methods. XRD patterns of borate products obtained by doping gadolinium are given in Figure 3.2. In the XRD patterns of all products, it was observed that while kotoite, $\text{Mg}_3\text{B}_2\text{O}_6$, (ICDD no: 75-1807) was observed as the main phase, diffraction lines belonging to gadolinium borate, GdBO_3 , (ICDD no: 18-0483) were formed while the amount of gadolinium was increased, and the intensity of these lines gradually increased in direct proportion to the amount of gadolinium.



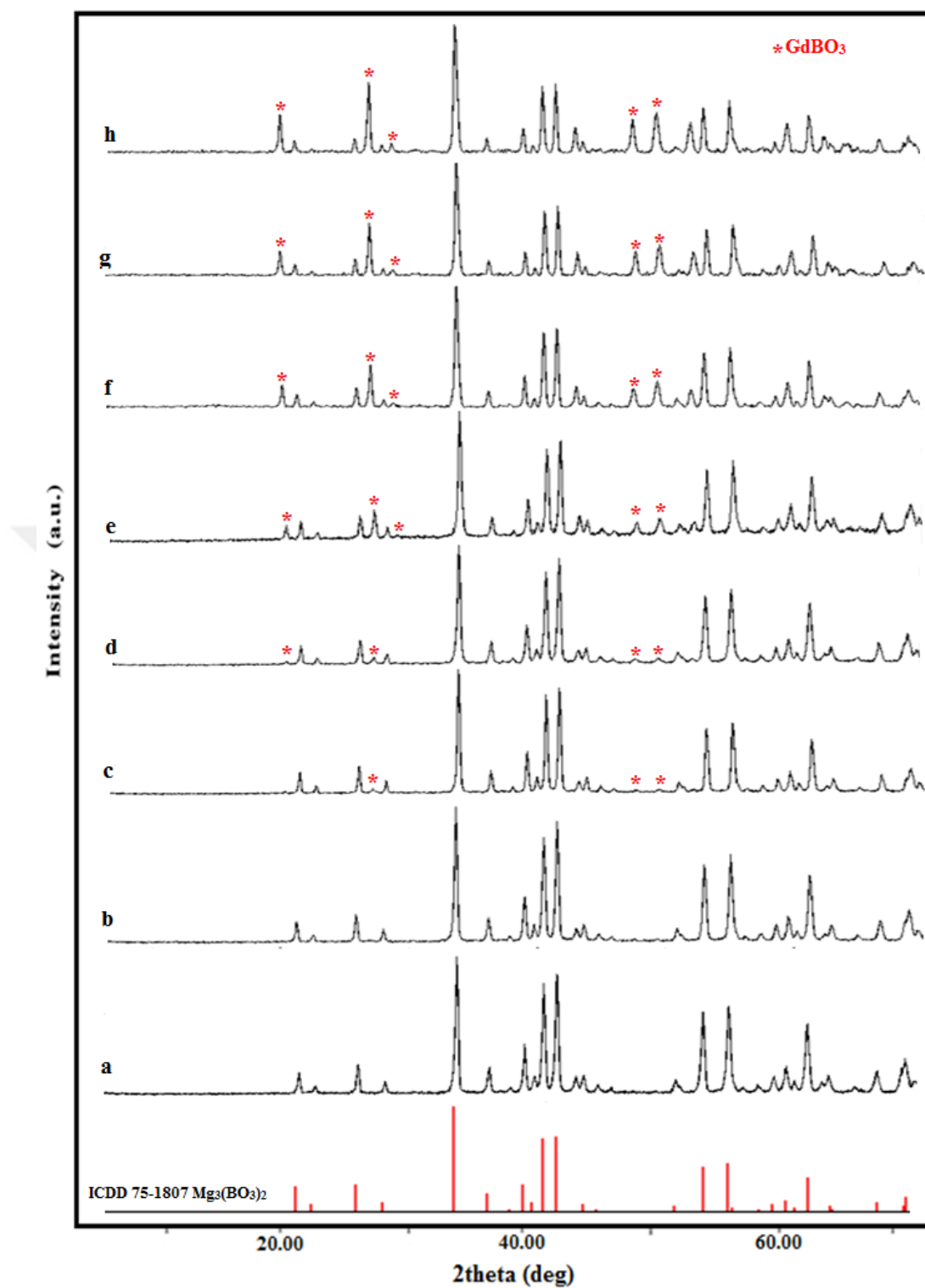


Figure 3.2 X-ray diffraction patterns of $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.00 (a), 0.10 (b), 0.50 (c), 1.00 (d), 5.00 (e), 10.0 (f), 15.0 (g), and 20.0 (h) wt% Gd_2O_3

3.1.3 Addition of Rare Earth Metals at Determined Optimum Concentration

In the XRD pattern given in Figure 3.2-b, which is obtained by doping gadolinium oxide at a rate of 0.10 by weight per cent, it is clearly seen that the kotoite-type magnesium borate is obtained in a single phase and all of the diffraction lines belong only to the compound kotoite, $\text{Mg}_3\text{B}_2\text{O}_6$, (ICDD no: 75–1807). For this reason, the optimum additive value was determined as 0.10 and oxides of lanthanum (La), neodymium (Nd), cerium (Ce), erbium (Er), praseodymium (Pr), samarium (Sm), europium (Eu), terbium (Tb), dysprosium (Dy), holmium (Ho), ytterbium (Yb) and lutetium (Lu) rare earth metals were doped to magnesium borate in accordance with the procedure used in the doping of gadolinium rare earth metal. XRD patterns of the obtained products are given in Figures 3.3, 3.4 and 3.5.

When the XRD patterns of the obtained products are examined, it is clearly seen that the kotoite -type doped magnesium borate is obtained in a single phase and all of the diffraction peaks belong only to the compound of the kotoite, $\text{Mg}_3\text{B}_2\text{O}_6$, (ICDD no: 75–1807). Therefore, it is possible to say that the contributions made do not change the kotoite structure and the kotoite structure is preserved intact.

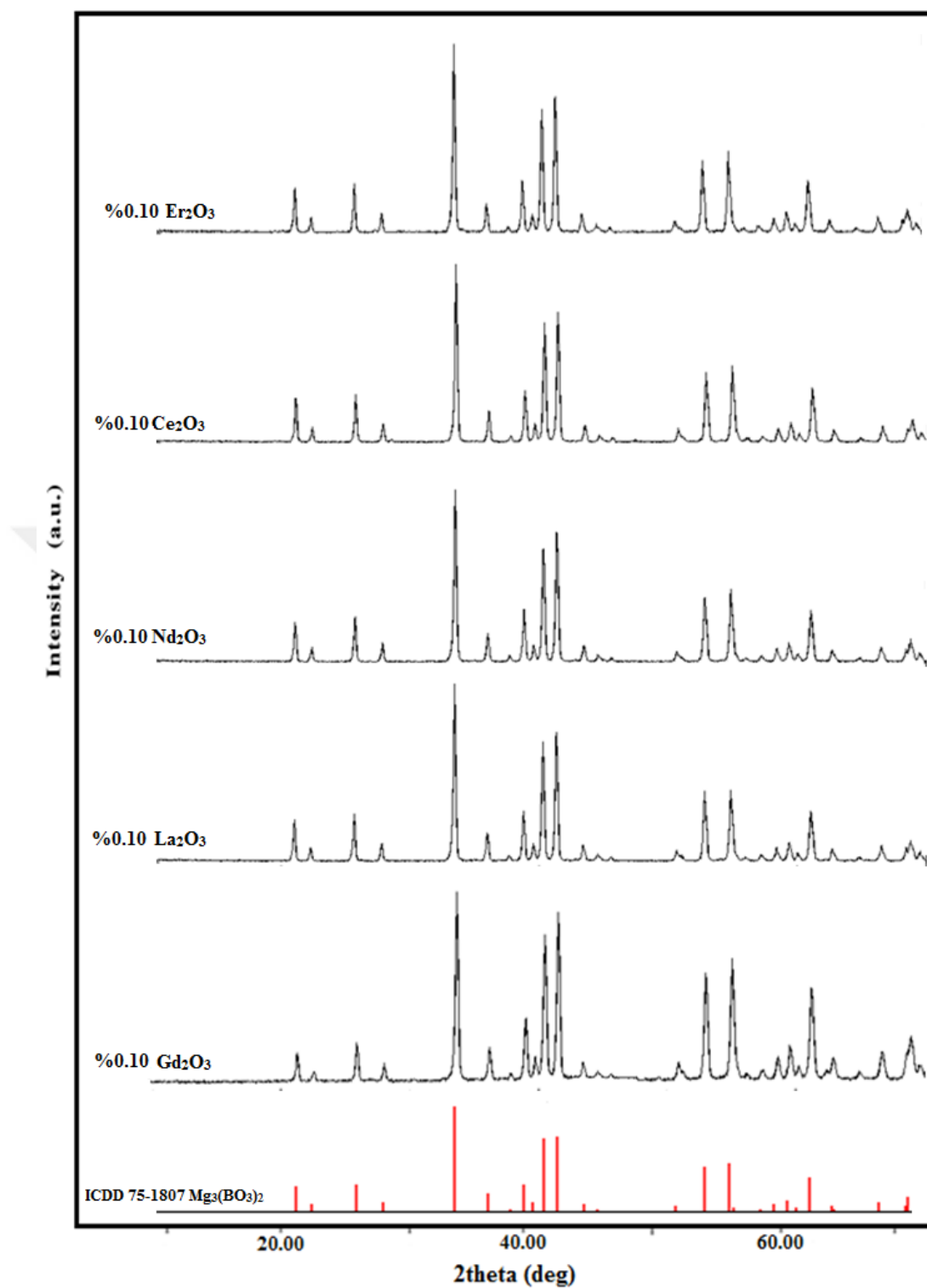


Figure 3.3 X-ray diffraction patterns of $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.10 wt% Gd_2O_3 , 0.10 wt% La_2O_3 , 0.10 wt% Nd_2O_3 , 0.10 wt% Ce_2O_3 , and 0.10 wt% Er_2O_3

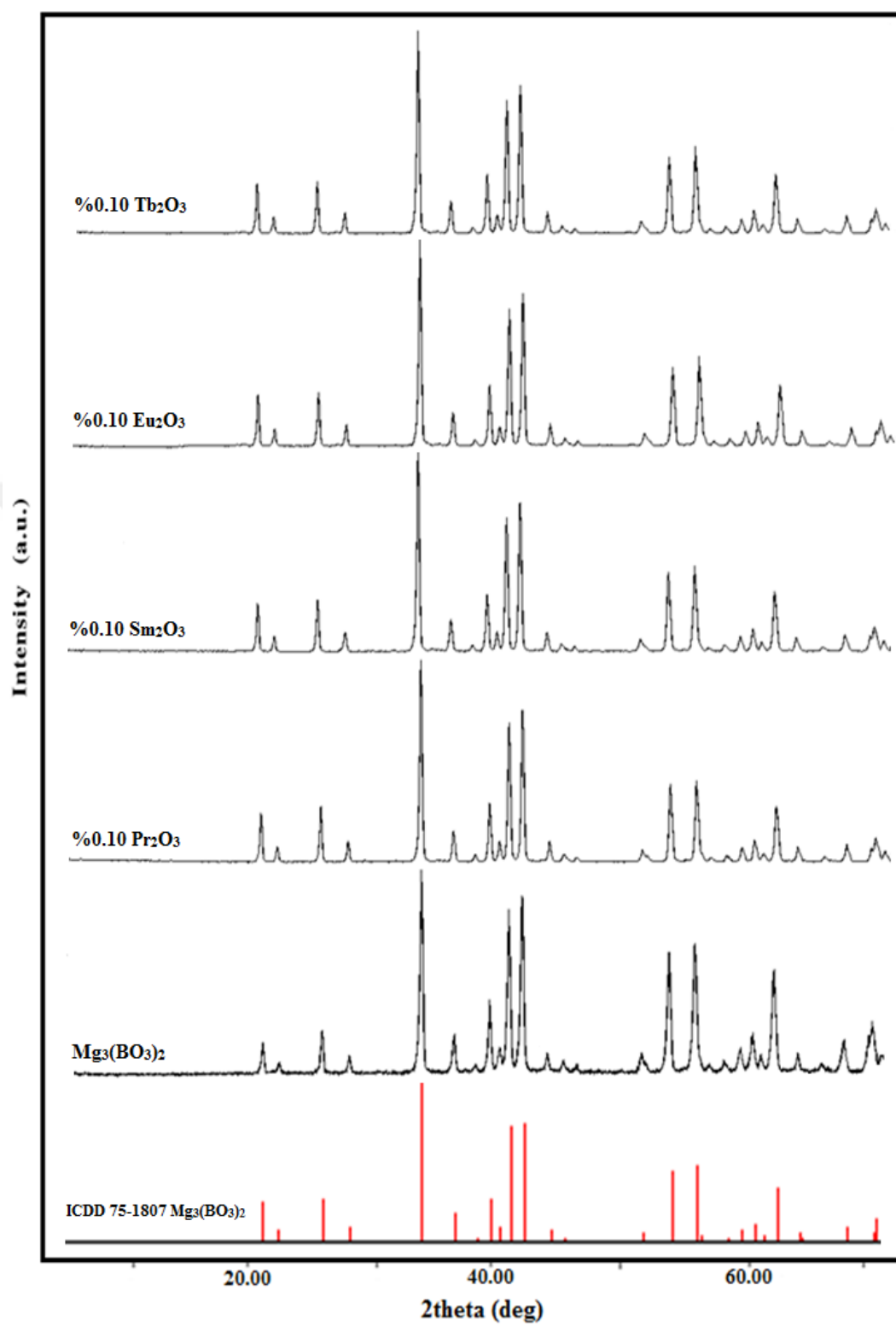


Figure 3.4 X-ray diffraction patterns of pure Mg₃(BO₃)₂ and doped Mg₃(BO₃)₂ compounds obtained by adding 0.10 wt% Pr₂O₃, 0.10 wt% Sm₂O₃, 0.10 wt% Eu₂O₃, and 0.10 wt% Tb₂O₃

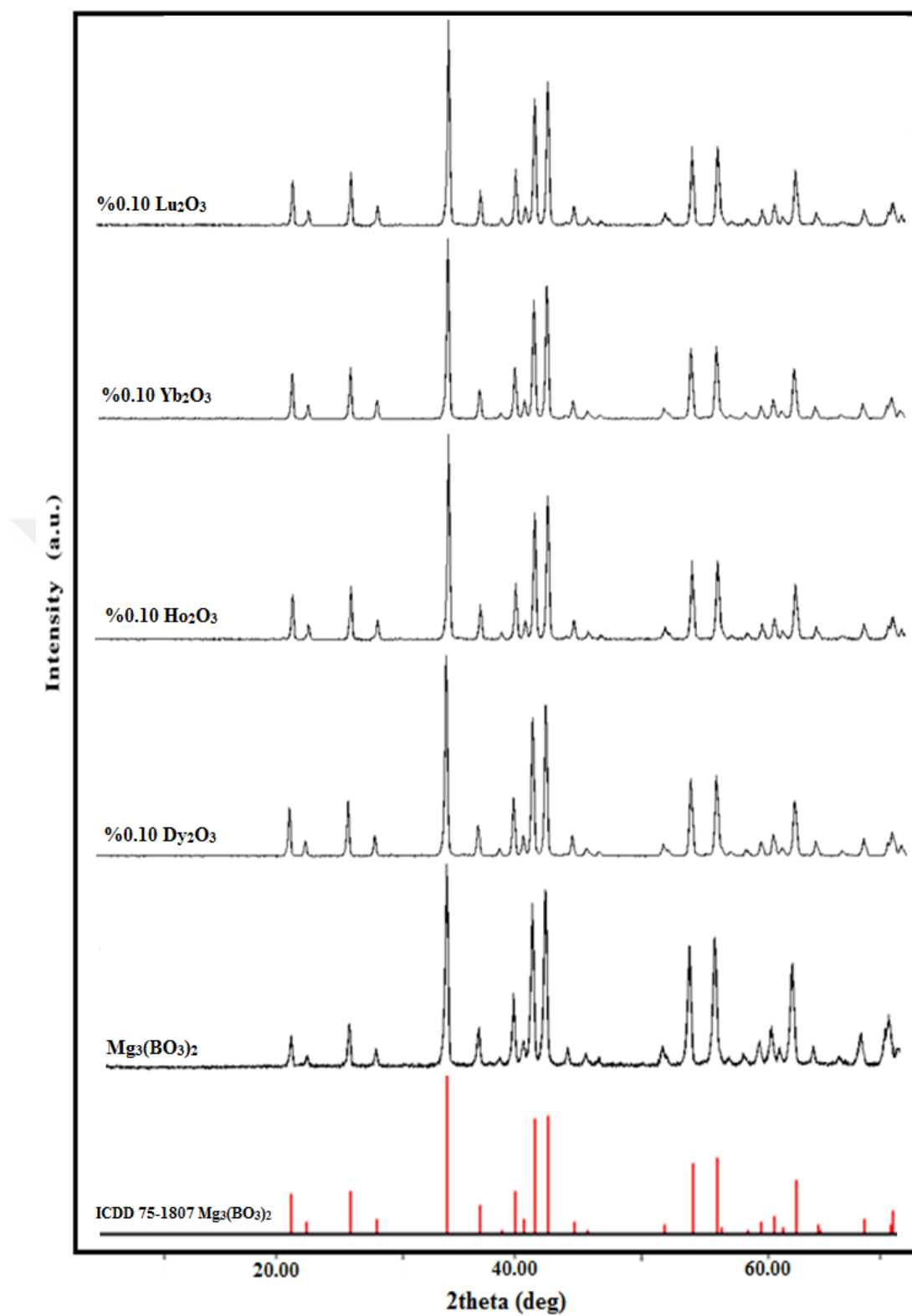


Figure 3.5 X-ray diffraction patterns of pure $\text{Mg}_3(\text{BO}_3)_2$ and doped $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by adding 0.10 wt% Dy_2O_3 , 0.10 wt% Ho_2O_3 , 0.10 wt% Yb_2O_3 , and 0.10 wt% Lu_2O_3

3.2 IR Characterization of Magnesium Orthoborates

3.2.1 Adjustment of the Amount of Boron Source

The infrared studies conducted parallel to the XRD analysis of the obtained products are given in Figure 3.6. When examining the infrared spectra, in parallel with the XRD patterns, when MgO and MgCO₃ starting materials were used, vibration bands of suanite (Mg₂B₂O₅) were observed alongside the vibration bands of kotoite (Mg₃B₂O₆). However, in the product synthesized using MgSO₄, it is observed that there are no vibration bands belonging to suanite (Mg₂B₂O₅), only kotoite vibration bands are present.

In the infrared spectra of borates, vibration bands concentrate in the range of 2000-500 cm⁻¹, and the vibration modes of borates are in three regions. The first region is between 1200-1600 cm⁻¹, where vibration bands originating from asymmetric stretching of the B-O bond in the BO₃ unit are found. The second region is in the range of 800-1200 cm⁻¹, where vibration bands result from the stretching of B-O bonds in the tetrahedral BO₄ unit. The last region is around 700 cm⁻¹, where vibration bands originate from B-O-B bonds in the crystal (Zhang, Li, & Zhang, 2006; Akella & Keszler, 1995; Güler, Kurtuluş, Ay, Çelik, & Doğan, 2009). The B₂O₅ group found in suanite is formed by the common bonding of two non-identical BO₃ units to one oxygen. Therefore, we can interpret the vibration bands in the infrared spectrum of Mg₂B₂O₅ according to these non-identical interconnected BO₃ units, and these vibration frequencies are located around 1500, 1450, 1020 cm⁻¹ (Dosler, Kržmanc, Jančar, & Suvorov, 2010). According to this information, the frequencies of infrared vibration bands are given in Table 3.1.

Table 3.1 Frequencies of infrared vibration bands of products obtained using MgO, MgCO₃, MgSO₄, Mg(NO₃)₂ and Mg(NO₃)₂ (5% excess boric acid) as starting materials.

	Vibration frequency	MgO	MgCO ₃	MgSO ₄	Mg(NO ₃) ₂	Mg(NO ₃) ₂ (5% excess boric acid)
Mg₃B₂O₆	$\nu_2(\text{BO}_3)$	661, 610	664, 611	664, 611	661, 611	655, 611
Mg₃B₂O₆	$\nu_1(\text{BO}_3)$	736	746	724	731	731
Mg₃B₂O₆	$\nu_3(\text{BO}_3)$	1293, 1203	1290, 1205	1278, 1196	1289, 1212	1278, 1193
Mg₂B₂O₅	$\nu_3(\text{BO}_3)$	1448, 1497, 1028	1502, 1455, 1028	----	----	----
H₂O	$\nu(\text{OH})$	3421	3419	3453	3412	3430

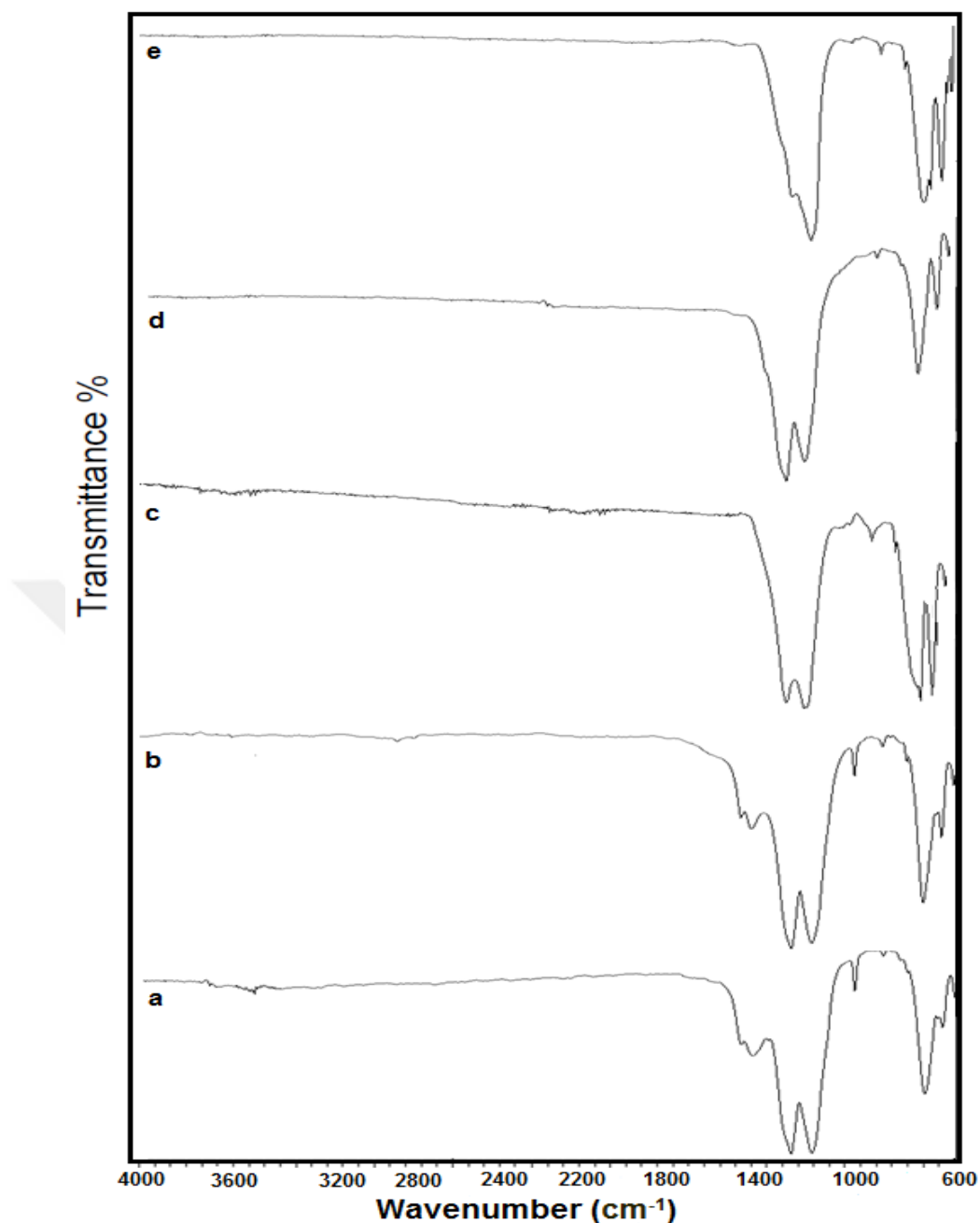


Figure 3.6 Infrared spectra of the products obtained using MgO (a), MgCO₃ (b), MgSO₄ (c), Mg(NO₃)₂ (d), and Mg(NO₃)₂ with 5% excess boric acid (e) as starting materials

3.2.2 Determination of the Amount of Rare Earth Metal to be Added

When the infrared spectra Figure 3.7 of the obtained products are examined, it is seen that the vibration bands of the kotoite, Mg₃B₂O compound are located in

parallel with the XRD patterns, and it is observed that the vibration bands of GdBO_3 begin to form in the compounds where the additive amount of gadolinium metal is high and increase in parallel with the amount of metal.

Magnesium borates of the kotoite type are very difficult to purify. Magnesium pyroborate, commonly known by the name of suanite to a greater or lesser extent, is obtained in combination with the compound $\text{Mg}_2\text{B}_2\text{O}_5$. The B_2O_5 group in Suanit is formed by the joint bonding of two non-identical BO_3 units to one oxygen. Therefore, we can interpret the vibration bands in the infrared spectrum of $\text{Mg}_2\text{B}_2\text{O}_5$ with respect to this non-identical interconnected unit of BO_3 , and the frequencies of these vibration bands are around 1500, 1450, 1020 cm^{-1} (Zhang, Li, & Zhang, 2006). When the infrared spectra of the products obtained in this study are examined, it is seen that there are no peaks of the suanite. On the other hand, it can be clearly seen in Figure 7 that the intensity of the vibration band (Akella & Keszler, 1995) of GdBO_3 around $\sim 860 \text{ cm}^{-1}$ increases with the increase in the amount of Gd_2O_3 admixture. The optimum value of the additive amount determined on the basis of this information (0.10 % wg.) is also supported by the infrared results in parallel with the XRD patterns. The frequencies of the infrared vibration bands are given in Table 3.2.

Table 3.2 Frequencies of infrared vibration bands of products obtained by Gd_2O_3 doping

	Frequency	a	b	c	d	e	f	g	h
$\text{Mg}_3\text{B}_2\text{O}_6$	$\nu_2(\text{BO}_3)$	659, 609	657, 611	657, 613	659, 611	657, 611	657, 611	657, 611	657, 613
$\text{Mg}_3\text{B}_2\text{O}_6$	$\nu_1(\text{BO}_3)$	734	734	734	736	734	734	732	734
$\text{Mg}_3\text{B}_2\text{O}_6$	$\nu_3(\text{BO}_3)$	1286, 1209	1286, 1209	1286, 1207	1288, 1211	1288, 1209	1288, 1211	1286, 1211	1286, 1213
GdBO_3	$\nu_3(\text{BO}_3)$	-----	-----	-----	-----	862	862	862	860
H_2O	$\nu(\text{OH})$	3440	3441	3450	3470	3462	3444	3431	3481

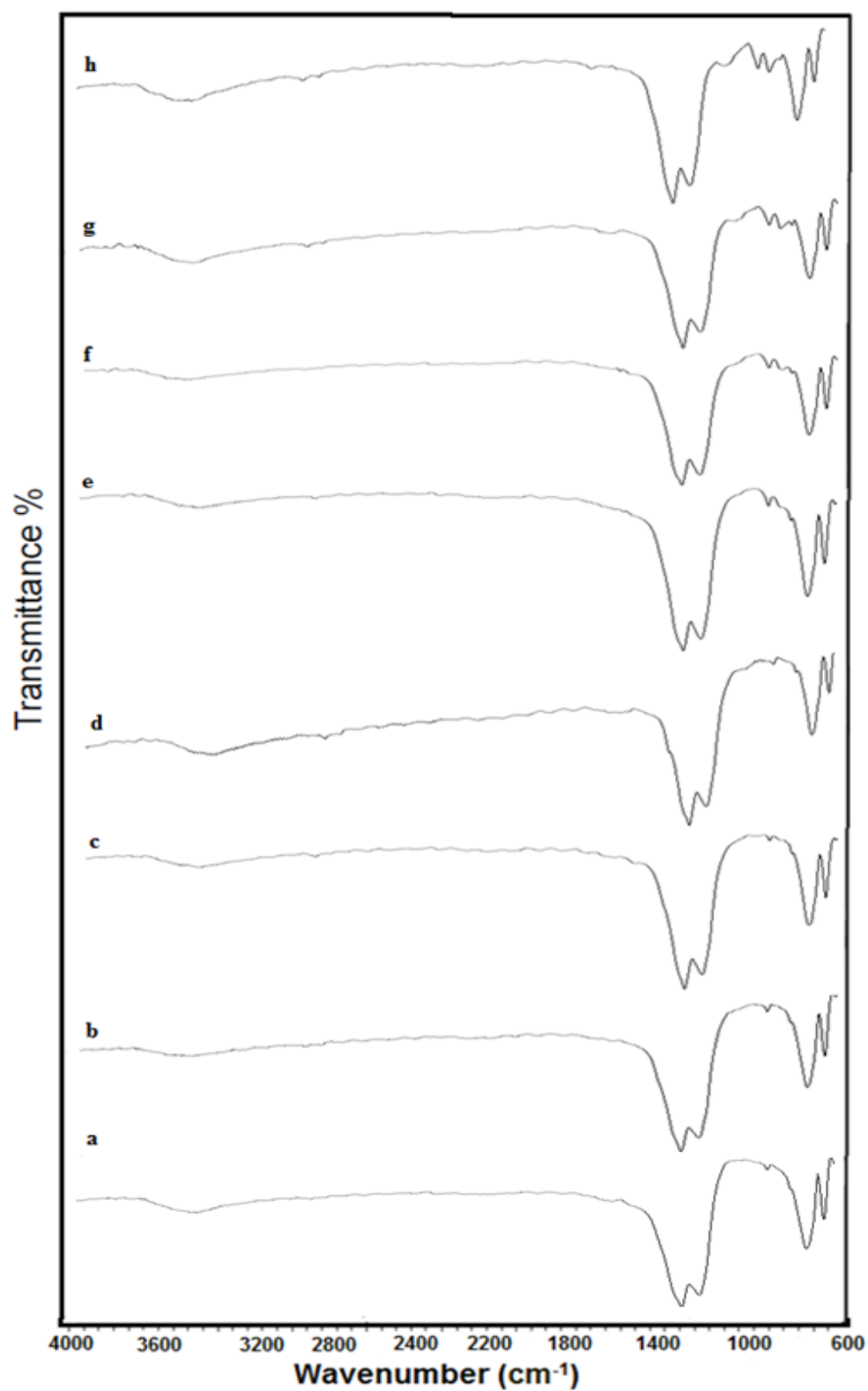


Figure 3.7 Infrared spectra of Mg₃(BO₃)₂ compounds obtained by doping with 0.00 (a), 0.10 (b), 0.50 (c), 1.00 (d), 5.00 (e), 10.0 (f), 15.0 (g), and 20.0 (h) wt% Gd₂O₃

3.2.3 Addition of Rare Earth Metals at Determined Optimum Concentration

The infrared spectra of the obtained products are given in Figures 3.8, 3.9 and 3.10. In the determined optimum value (0.10 wt.%), it is seen that the vibration bands of cathode, $\text{Mg}_3\text{B}_2\text{O}_6$, are parallel to the XRD patterns in the infrared spectra of the $\text{Mg}_3(\text{BO}_3)_2$ compounds doped with .) La_2O_3 , Nd_2O_3 , Ce_2O_3 , Er_2O_3 , Pr_2O_3 , Sm_2O_3 , Eu_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Yb_2O_3 and Lu_2O_3 . The frequencies of the infrared vibration bands are given in Table 3.3 ; Frequencies of infrared vibration bands of products obtained by doping Ln_2O_3 (Ln: Gd, La, Nd, Ce, Er, Pr, Sm, Eu, Tb, Dy, Ho, Yb and Lu)

Table 3.3 Frequencies of infrared vibration bands of products obtained by doping Ln_2O_3 (Ln: Gd, La, Nd, Ce, Er, Pr, Sm, Eu, Tb, Dy, Ho, Yb and Lu)

	$\text{Mg}_3\text{B}_2\text{O}_6$	$\text{Mg}_3\text{B}_2\text{O}_6$	$\text{Mg}_3\text{B}_2\text{O}_6$	$\text{Mg}_3\text{B}_2\text{O}_5$	H_2O
	$\nu_2(\text{BO}_3)$	$\nu_1(\text{BO}_3)$	$\nu_3(\text{BO}_3)$	$\nu_3(\text{BO}_3)$	$\nu(\text{OH})$
0.10% wt. Gd_2O_3	657, 611	734	1286, 1209	--	3441
0.10% wt. La_2O_3	655, 608	730	1285, 1210	--	3419
0.10% wt. Nd_2O_3	658, 609	732	1288, 1212	--	3441
0.10% wt. Ce_2O_3	659, 611	734	1287, 1211	--	3437
0.10% wt. Er_2O_3	655, 608	734	1289, 1212	--	3441
0.10% wt. Pr_2O_3	661, 611	736	1290, 1213	--	3412
0.10% wt. Sm_2O_3	661, 613	736	1290, 1213	--	3431
0.10% wt. Eu_2O_3	661,615	736	1290, 1213	--	3419
0.10% wt. Tb_2O_3	659, 614	736	1292, 1215	--	3441
0.10% wt. Dy_2O_3	659, 613	736	1292,1211	--	3437
0.10% wt. Ho_2O_3	659, 613	736	1292, 1211	--	3441
0.10% wt. Yb_2O_3	659, 613	736	1292, 1215	--	3452
0.10% wt. Lu_2O_3	659,617	736	1292, 1215	--	3437

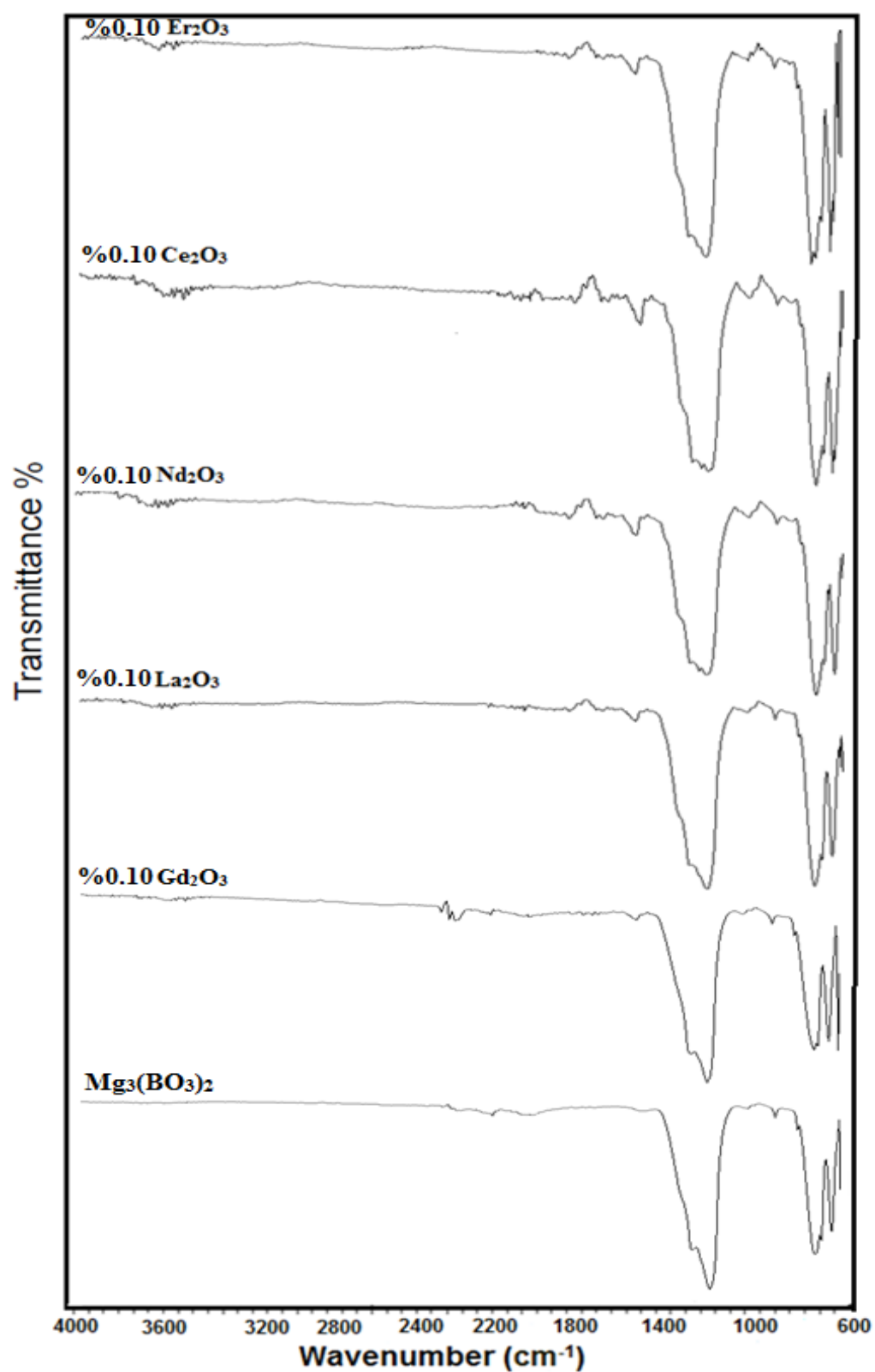


Figure 3.8 Infrared spectra of pure $\text{Mg}_3(\text{BO}_3)_2$ and $\text{Mg}_3(\text{BO}_3)_2$ compounds doped with 0.10 wt% Gd_2O_3 , 0.10 wt% La_2O_3 , 0.10 wt% Nd_2O_3 , 0.10 wt% Ce_2O_3 , and 0.10 wt% Er_2O_3

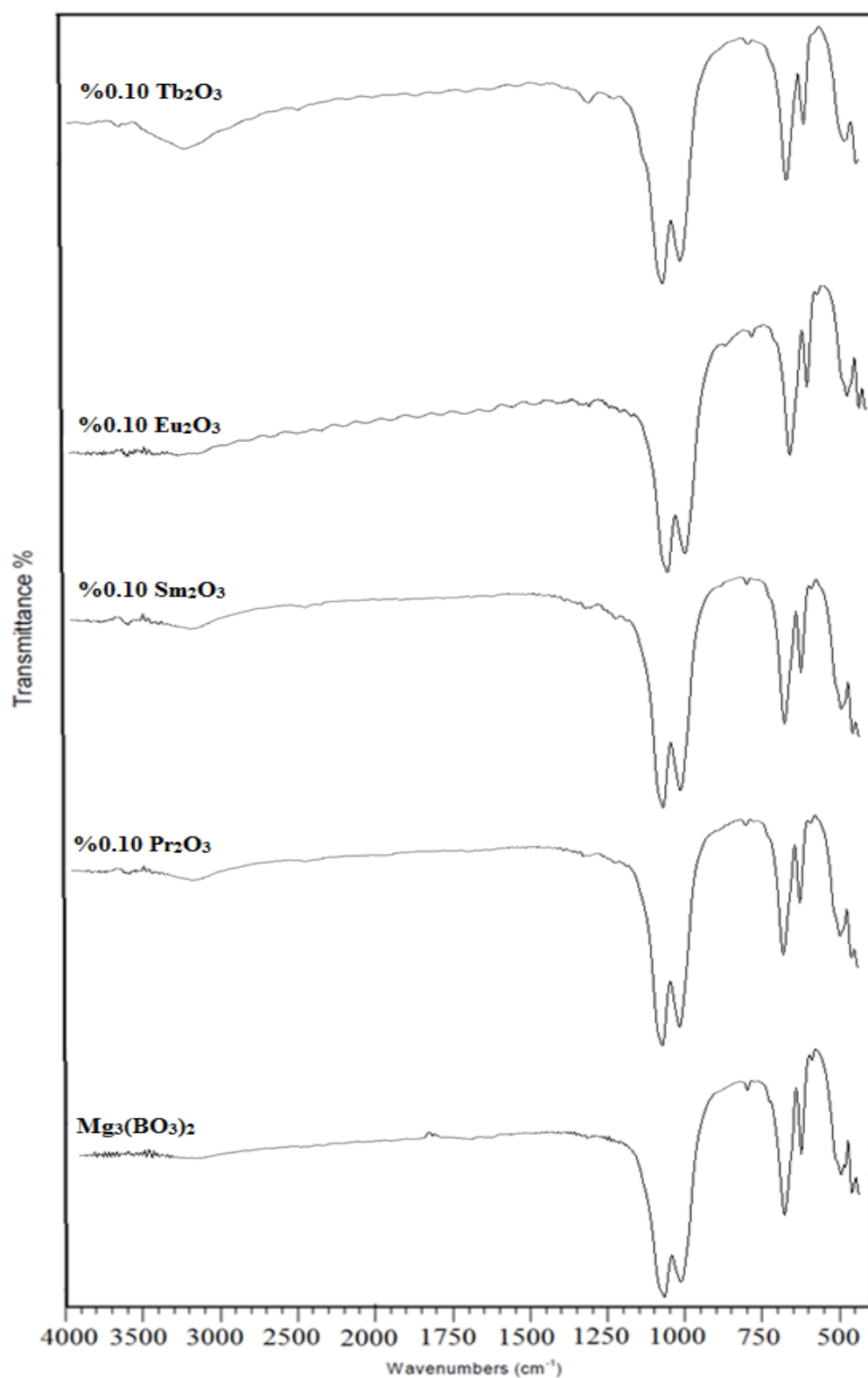


Figure 3.9 Infrared spectra of pure $\text{Mg}_3(\text{BO}_3)_2$ and $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.10 wt% Pr_2O_3 , 0.10 wt% Sm_2O_3 , 0.10 wt% Eu_2O_3 , and 0.10 wt% Tb_2O_3 .

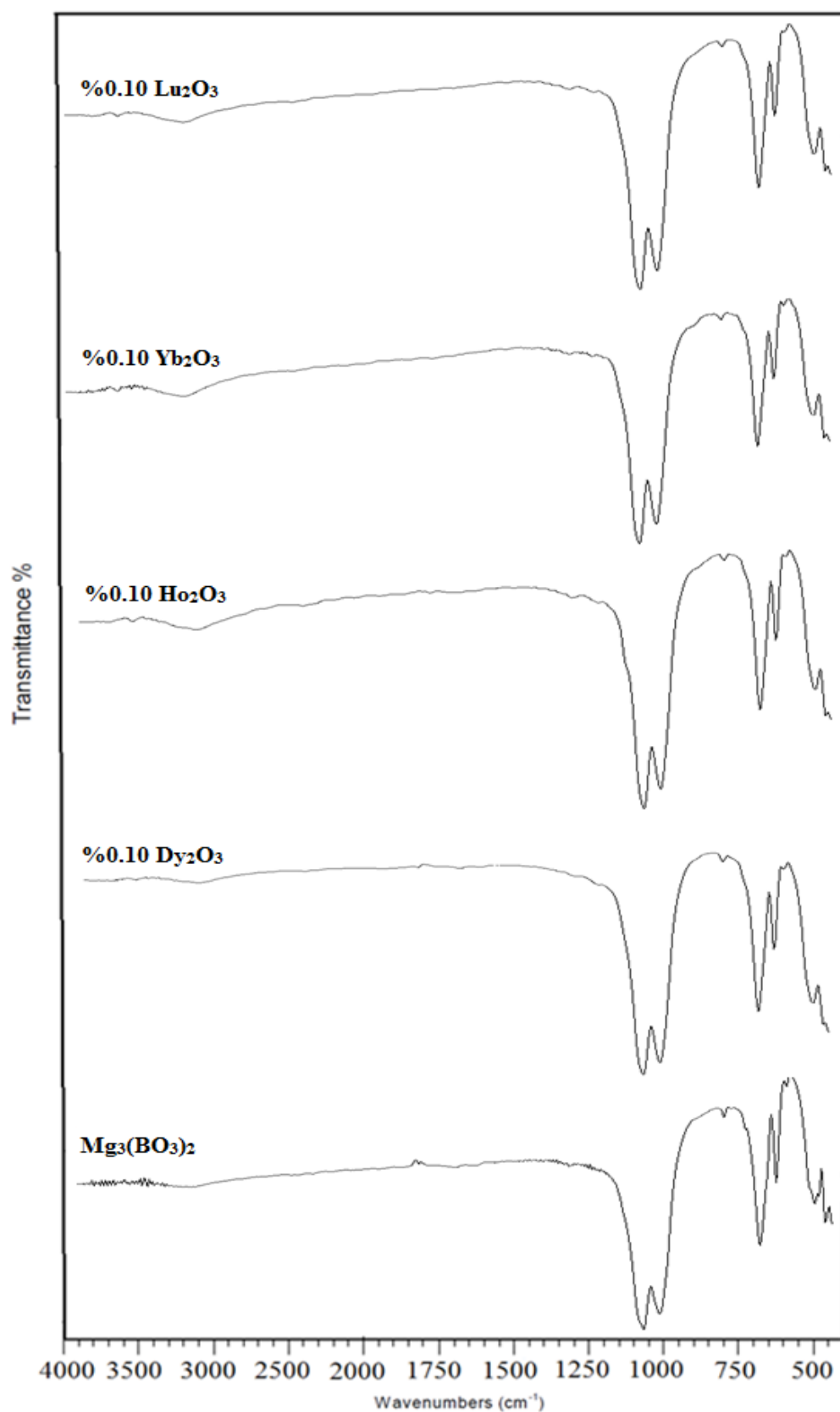


Figure 3.10 Infrared spectra of pure $\text{Mg}_3(\text{BO}_3)_2$ and $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.10 wt% Dy_2O_3 , 0.10 wt% Ho_2O_3 , 0.10 wt% Yb_2O_3 , and 0.10 wt% Lu_2O_3

3.3 Thermogravimetric-differential thermal analysis (TG/DTA)

Data

3.3.1 Investigation of Thermal Data of Products Obtained by Changing the Amount of Gd_2O_3 Added to the Material

In this study, the thermal behavior of all products obtained was examined by Thermogravimetric-differential thermal analysis (TG/DTA) method. Figure 3.11 shows the thermogravimetric-differential thermal analysis (TG/DTA) data of $Mg_3(BO_3)_2$ compounds obtained by adding Gd_2O_3 at the ratios of 0.10, 0.50, 1.00, 5.00, 10.0, 15.0, 20.0 by weight and pure.

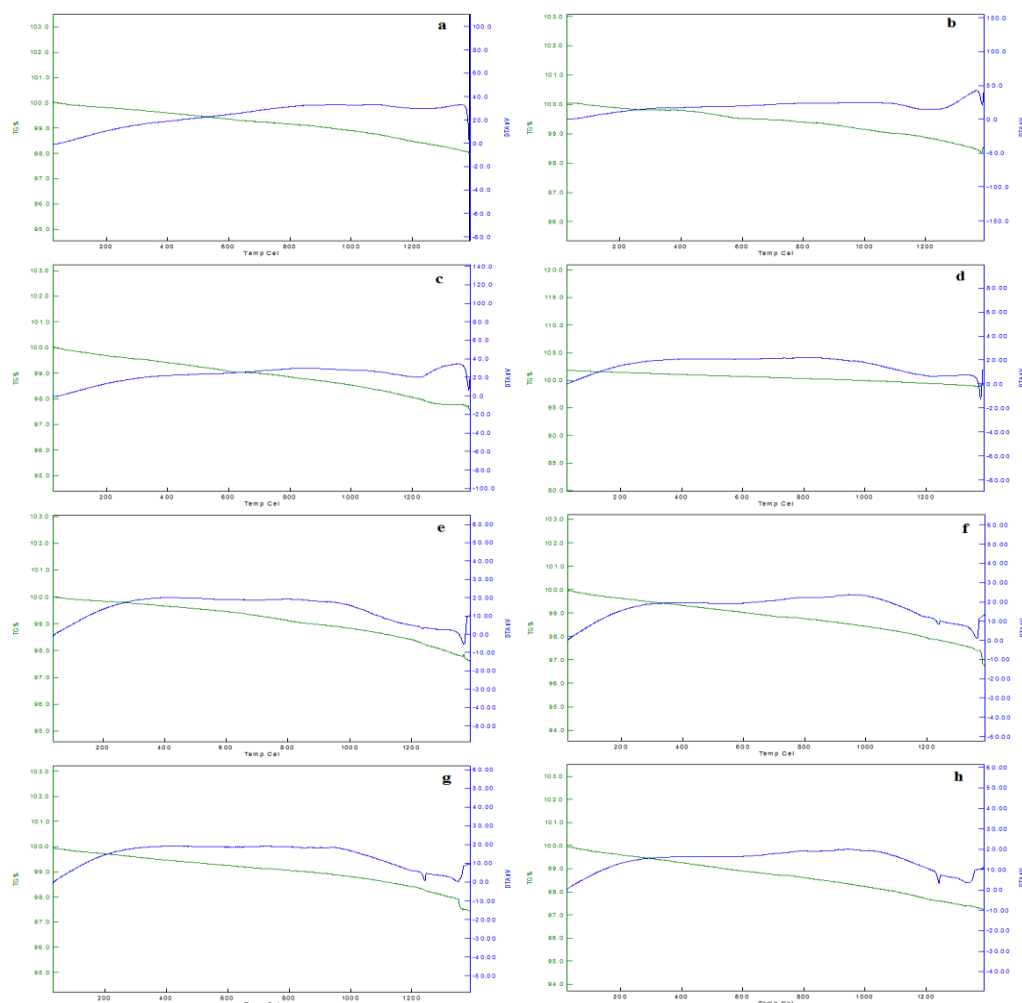


Figure 3. 11 Thermogravimetric analysis (TG) / differential thermal analysis (DTA) data of $Mg_3(BO_3)_2$ compounds obtained by doping with 0.00 (a), 0.10 (b), 0.50 (c), 1.00 (d), 5.00 (e), 10.0 (f), 15.0 (g), and 20.0 (h) wt% Gd_2O_3

When these thermograms are examined, it is observed that the melting point of pure $Mg_3(BO_3)_2$ is around 1400 °C, as the Gd_2O_3 contribution increases, the melting point decreases as expected, and when 0.10 percent Gd_2O_3 is added by

weight, the melting point of pure $\text{Mg}_3(\text{BO}_3)_2$ remains the same. As the amount of additive increases, a second melting point of GdBO_3 is observed at 1220°C .

3.3.2 Investigation of Thermal Data of Products Obtained by Doping Different Rare Earth Metals

In Figures 3.12, 3.13 and 3.14, the results of Thermogravimetric-differential thermal analysis (TG/DTA) of $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by adding 0.10 percent by weight La_2O_3 , Nd_2O_3 , Ce_2O_3 , Er_2O_3 , Pr_2O_3 , Sm_2O_3 , Eu_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Yb_2O_3 and Lu_2O_3 are given. When these thermograms are examined, it is seen that the melting point of pure $\text{Mg}_3(\text{BO}_3)_2$ is 0.10 % to $\text{Mg}_3(\text{BO}_3)_2$. When different rare earth metals were added, there was no change in thermal data. It is thought that this is caused by the very small amount of rare earth metals contributed.

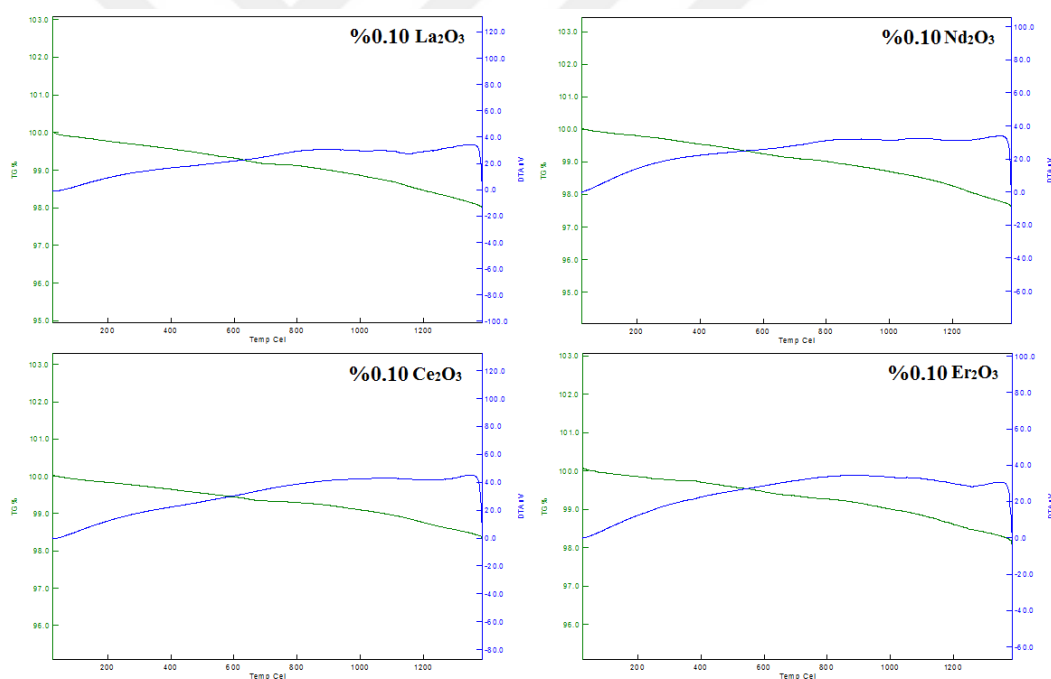


Figure 3.12 Thermogravimetric–differential heat analysis (TG/DTA) data of $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.10 wt% La_2O_3 , 0.10 wt% Nd_2O_3 , 0.10 wt% Ce_2O_3 , and 0.10 wt% Er_2O_3

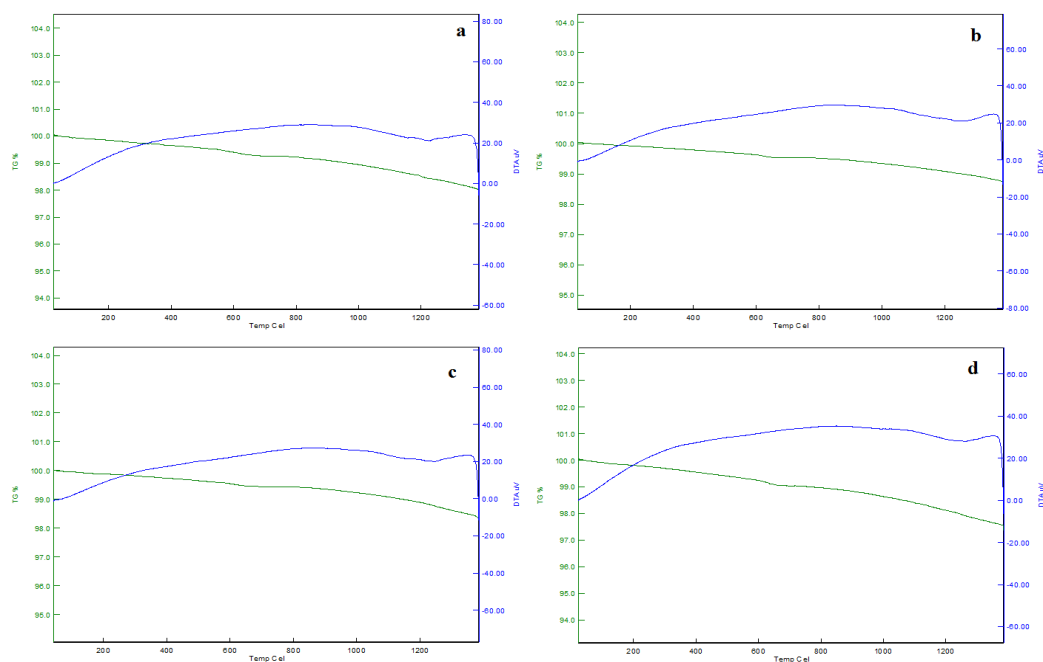


Figure 3.13 Thermogravimetric–differential heat analysis (TG/DTA) results of $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.10 wt% Pr_2O_3 (a), 0.10 wt% Sm_2O_3 (b), 0.10 wt% Eu_2O_3 (c), and 0.10 wt% Tb_2O_3 (d)

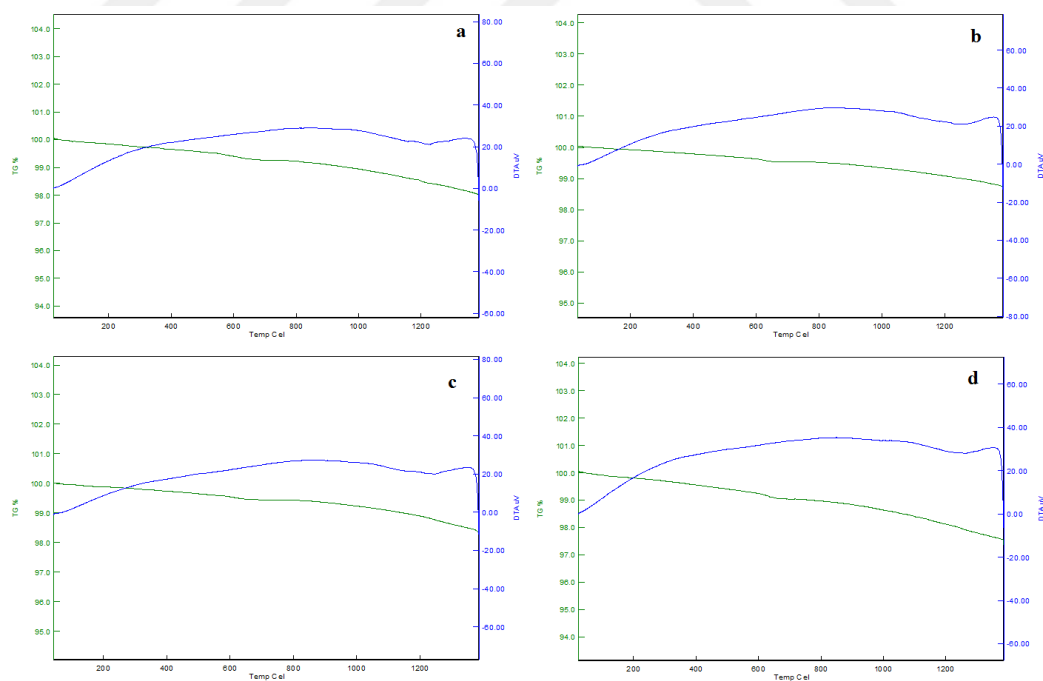


Figure 3.14 Thermogravimetric–differential heat analysis (TG/DTA) results of $\text{Mg}_3(\text{BO}_3)_2$ compounds obtained by doping with 0.10 wt% Dy_2O_3 (a), 0.10 wt% Ho_2O_3 (b), 0.10 wt% Yb_2O_3 (c), and 0.10 wt% Lu_2O_3 (d)

3.4 Jana2006 Analysis of Synthesized Materials and Calculation of Crystal Size, Density and Surface Area Using Debye-Scherrer Equation

3.4.1 Jana2006 Analysis of Determination of Starting Materials and Detailed Structural Parameters of $\text{Mg}_3(\text{BO}_3)_2$ Compound Obtained in Pure Form

As the GOF obtained as a result of the Jana2006 analysis, the fit factor value approaches one, it is understood that the harmony with the pure structure is good. When the GOF values of the compounds obtained from MgO, MgCO_3 , MgSO_4 , MgNO_3 and $\text{Mg}(\text{NO}_3)_2$ (5% more boric acid) were examined, it was seen that they were 2.49, 2.62, 1.89, 1.45 and 1.33, respectively. It is understood from this that the analysis result most compatible with the pure kotoite structure is obtained as a result of the XRD of the starting substance $\text{Mg}(\text{NO}_3)_2$ (5% more boric acid). The analysis designs obtained as a result of the Jana2006 analysis are given in Figure 3.15 and the detailed Jana2006 analysis results are given in Table 3.4.

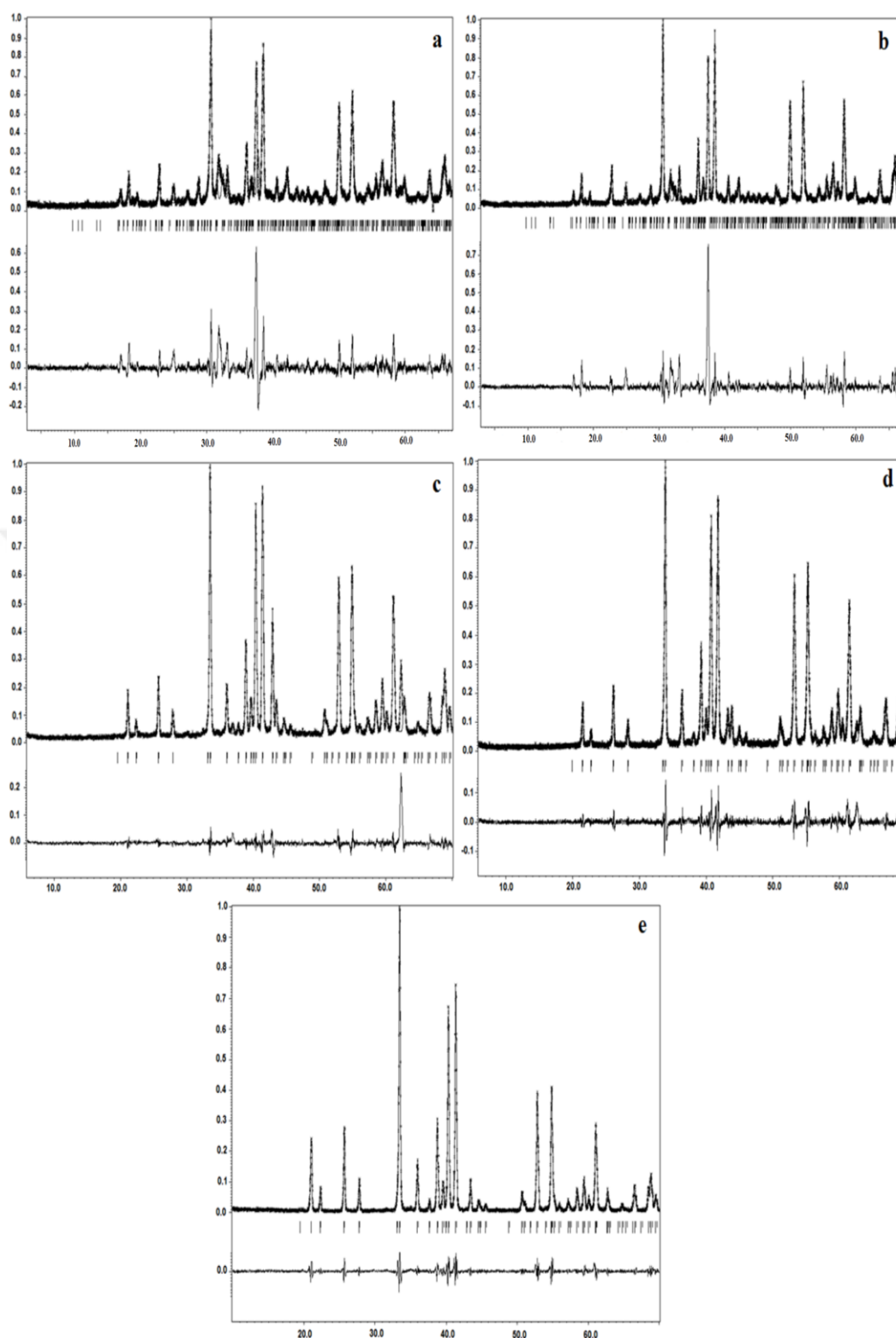


Figure 3.15 Jana2006 analysis designs for MgO (a), MgCO₃ (b), MgSO₄ (c), Mg(NO₃)₂ (d) ve Mg(NO₃)₂ (5% excess boric acid) (e) materials

Table 3.4 Jana2006 Detailed Analysis Results for $\text{Mg}_3(\text{BO}_3)_2$ Obtained Using Different Starting Materials

<i>Samples</i>	<i>MgO</i>	<i>MgCO₃</i>	<i>MgSO₄</i>	<i>Mg(NO₃)₂</i>	<i>Mg(NO₃)₂ (%5 excess boric acid)</i>
<i>Diffractionmeter</i>	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku
<i>Radiation type</i>	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α
<i>Monochromator</i>	Graphite	Graphite	Graphite	Graphite	Graphite
<i>Wavelength (Å)</i>	1.5405	1.5405	1.5405	1.5405	1.5405
<i>Refined profile range (°2θ)</i>	10.00-70.00	10.00-70.00	10.00-70.00	10.00-70.00	10.00-70.00
<i>Step size (°2θ)</i>	0.02	0.02	0.02	0.02	0.02
<i>GOF</i>	2.49	2.62	1.89	1.45	1.33
<i>R_P</i>	19.54	20.46	8.88	12.14	11.57
<i>R_{WP}</i>	28.44	29.96	15.31	16.48	16.58
<i>V</i>	205.0	205.0	205.0	206.0	204.6

GOF, R_P, R_{WP}: agreement factors, *V*: volume

The crystalite size was calculated using the Debye-Scherrer equation for the pure $\text{Mg}_3(\text{BO}_3)_2$ compound obtained and it was found that the crystalite size was 40.50 nm, the density was 12.35 g/cm³ and the surface area was 11.95 m²/g. In the literature, it is emphasized that the particle size is in the range of 0.5 to 1 nm. When these data reported in the literature are compared with the results obtained in this study, it is seen that the product we obtained has a particle size 4 times larger. This is an important factor for the electrical properties of the compound. Detailed analysis results are given in Table 3.5.

Table 3.5 Detailed structural parameters of $\text{Mg}_3(\text{BO}_3)_2$ compound obtained in pure form

<i>Material</i>	Powder crystal
<i>Formul</i>	$\text{Mg}_3\text{B}_2\text{O}_6$
<i>Simetri</i>	orthorhombic
<i>Space group</i>	Pnnm
<i>a (Å)</i>	5.399(9)
<i>b (Å)</i>	8.424(6)
<i>c (Å)</i>	4.506(5)
<i>α (° degree)</i>	90.000
<i>β (° degree)</i>	90.000
<i>δ (° degree)</i>	90.000
<i>d (g/cm³)</i>	12.35
<i>t (nm)</i>	40.50
<i>S (m²/g)</i>	11.95

3.4.2 Jana2006 Analysis for Determination of the Amount of Rare Earth Metal to be Contributed and Calculation of Crystal Size, Density, Surface Area Using the Debye-Scherrer Equation

0.10, 0.50, 1.00, 5.00, 10.0, 15.0, 20.0 % wt for determination of the optimum concentration. When the Jana2006 patterns given in Figure 3.16 obtained as a result of the Jana2006 analysis of $\text{Mg}_3(\text{BO}_3)_2$ Compounds obtained by Gd_2O_3 Doped were examined, the most compatible data was 0.10 % net. It is seen that it belongs to the compound obtained by doping Gd_2O_3 . 0.10, 0.50, 1.00, 5.00, 10.0, 15.0, 20.0 % w. When the GOF values of $\text{Mg}_3(\text{BO}_3)_2$ Compounds obtained by adding Gd_2O_3 were examined, it was calculated using the JANA2006 program that they were 1.24, 2.63, 2.78, 2.80, 3.05, 3.56 and 3.92, respectively. The most compatible compound is 0.10 % wt. While it is seen that there is Gd_2O_3 , it is understood that as the amount of Gd_2O_3 increases, the harmony is lost and the borate

phase begins to deteriorate. Detailed Jana2006 analysis results are given in Table 3.6.

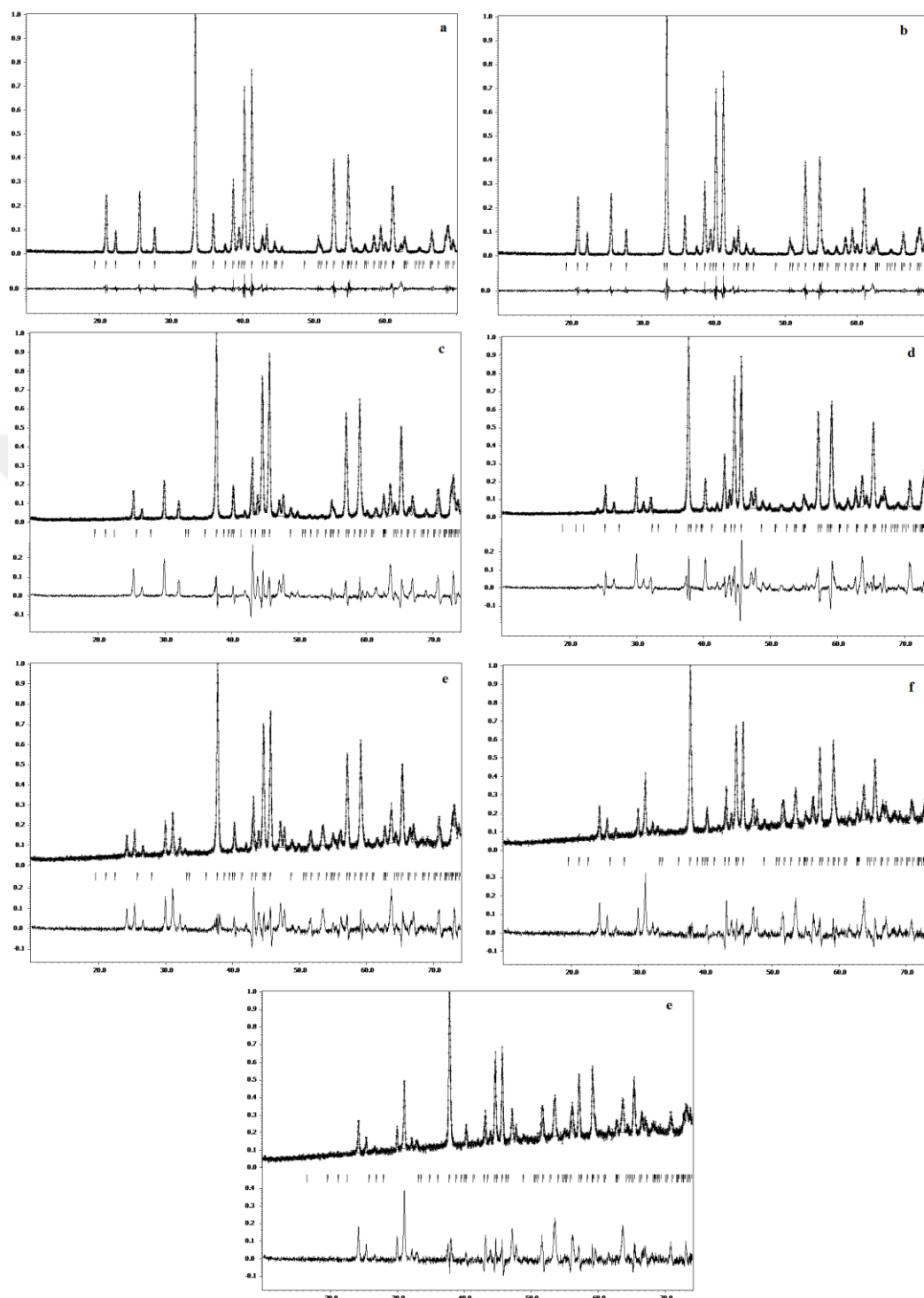


Figure 3.16 Jana2006 analysis patterns of the products obtained by doping with different amounts of Gd_2O_3 : 0.10 wt% (a), 0.50 wt% (b), 1.00 wt% (c), 5.00 wt% (d), 10.0 wt% (e), 15.0 wt% (f), and 20.0 wt% (g)

Table 3.6: Jana2006 detailed analysis results of products obtained by adding Gd₂O₃ at different rates

Products	0.10 % wt. Gd₂O₃	0.50 %wt Gd₂O₃	1.00 % wt. Gd₂O₃	5.00 % wt Gd₂O₃	10.0 % wt Gd₂O₃	15.0 % wt Gd₂O₃	20.0 % wt. Gd₂O₃
Diffractionmeter	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku
Radiation type	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α	Cu K α
Monochromator	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
Wavelength (Å)	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405
Refined profile range(°2θ)	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00
Step size (°2θ)	0.02	0.02	0.02	0.02	0.02	0.02	0.02
GOF	1.24	2.63	2.78	2.80	3.05	3.56	3.92
R_P	9.64	11.00	12.15	12.81	15.41	21.10	22.20
R_{WP}	15.49	16.36	17.80	18.56	21.70	27.85	31.46
V	203.7	204.5	207.6	207.7	208.1	208.2	208.3

GOF, R_P, R_{WP}: agreement factors, **V:** volume

In order to examine the effects of the amount of Gd₂O₃ added on the crystal size, density, and surface area of the substance, the crystal size was calculated using the Debye-Scherrer equation, and then the density and surface area were calculated. The findings revealed that as the quantity of Gd₂O₃ augmented, the crystal size diminished from 39.69 nm to 34.01 nm, the density augmented from 12.35 g/cm³ to 16.78 g/cm³, and the surface area diminished from 12.24 m²/g to 10.51 m²/g. The results of the calculations are presented in detail in Table 3.7.

Table 3.7 Detailed structural parameters of the products obtained by doping Gd₂O₃ at different ratios

Products	0.10 % wt. % Gd₂O₃	0.50 wt. % Gd₂O₃	1.00 wt. % Gd₂O₃	5.00 wt. % Gd₂O₃	10.0 wt. % Gd₂O₃	15.0 wt. % Gd₂O₃	20.0 wt. % Gd₂O₃
Material	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal
Symmetry	orthorhombic	orthorhombic	orthorhombic	Orthorhombic	orthorhombic	orthorhombic	Orthorhombic
Space group	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm
a (Å)	5.427(9)	5.397(8)	5.471(6)	5.424(9)	5.434(3)	5.432(1)	5.434(7)
b (Å)	8.461(4)	8.414(9)	8.309(7)	8.462(0)	8.468(3)	8.465(4)	8.464(2)
c (Å)	4.522(1)	4.502(0)	4.479(6)	4.521(7)	4.526(2)	4.525(2)	4.526(0)
α(°degree)	90.000	90.000	90.000	90.000	90.000	90.000	90.000
β(°degree)	90.000	90.000	90.000	90.000	90.000	90.000	90.000
δ(°degree)	90.000	90.000	90.000	90.000	90.000	90.000	90.000
d (g/cm³)	12.35	12.49	12.66	13.35	14.46	15.63	16.78
t (nm)	39.69	38.65	34.13	34.12	34.09	34.06	34.01
S (m²/g)	12.24	12.42	13.88	13.17	12.17	11.27	10.51

3.4.3 Doping of rare earth metals at the determined optimum concentration and Jana2006 analysis of the obtained materials and calculation of crystal size, density, surface areas using the Debye-Scherrer Equation

Jana2006 patterns of La₂O₃, Nd₂O₃, Ce₂O₃, Er₂O₃, Pr₂O₃, Sm₂O₃, Eu₂O₃, Tb₂O₃, Dy₂O₃, Ho₂O₃, Yb₂O₃ and Lu₂O₃ rare earth metals doped at the determined optimum concentration are given in Figures 3.17 and Figure 3.18. According to Jana 2006 data, the XRD patterns of the doped compounds obtained overlap with the kotoite structure. When GOF data are considered, values close to 1 are obtained, which shows that the compliance with the kotoite structure is very good. When the

crystal size, density and surface area were calculated using the Debye-Scherrer equation, similar results were obtained for all rare earth metals. Crystal size was found to be 39.68 nm, density 12.40 g/cm³ and surface area 12.20 m²/g. Compared to the pure Mg₃B₂O₆ compound, an increase in density and surface area was observed, while the crystal size was found to decrease.

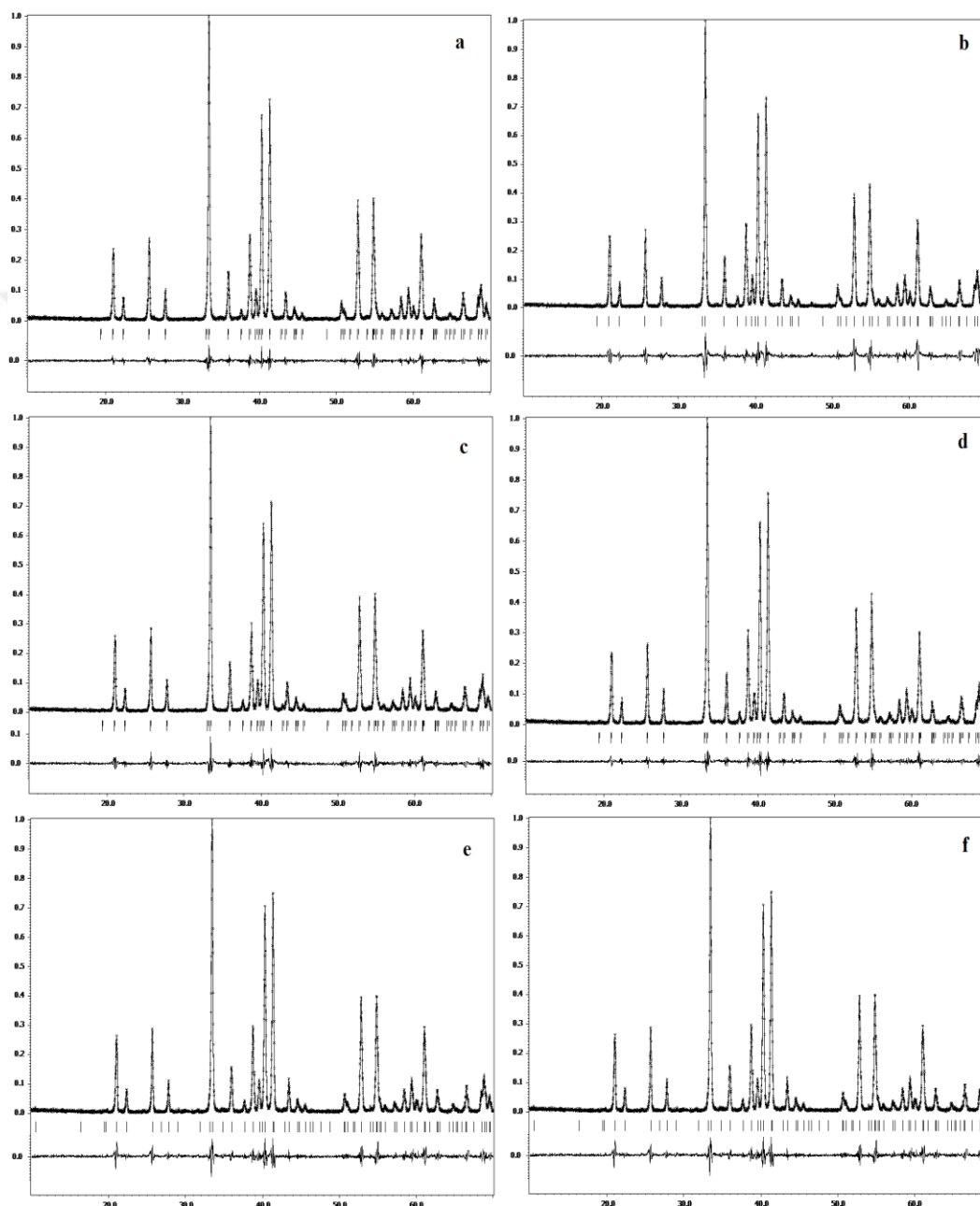


Figure 3.17 Ln₂O₃; Ln: La (a), Ce (b), Pr (c), Nd (d), Sm (e) and Eu (f), Jana2006 analysis patterns of doped products

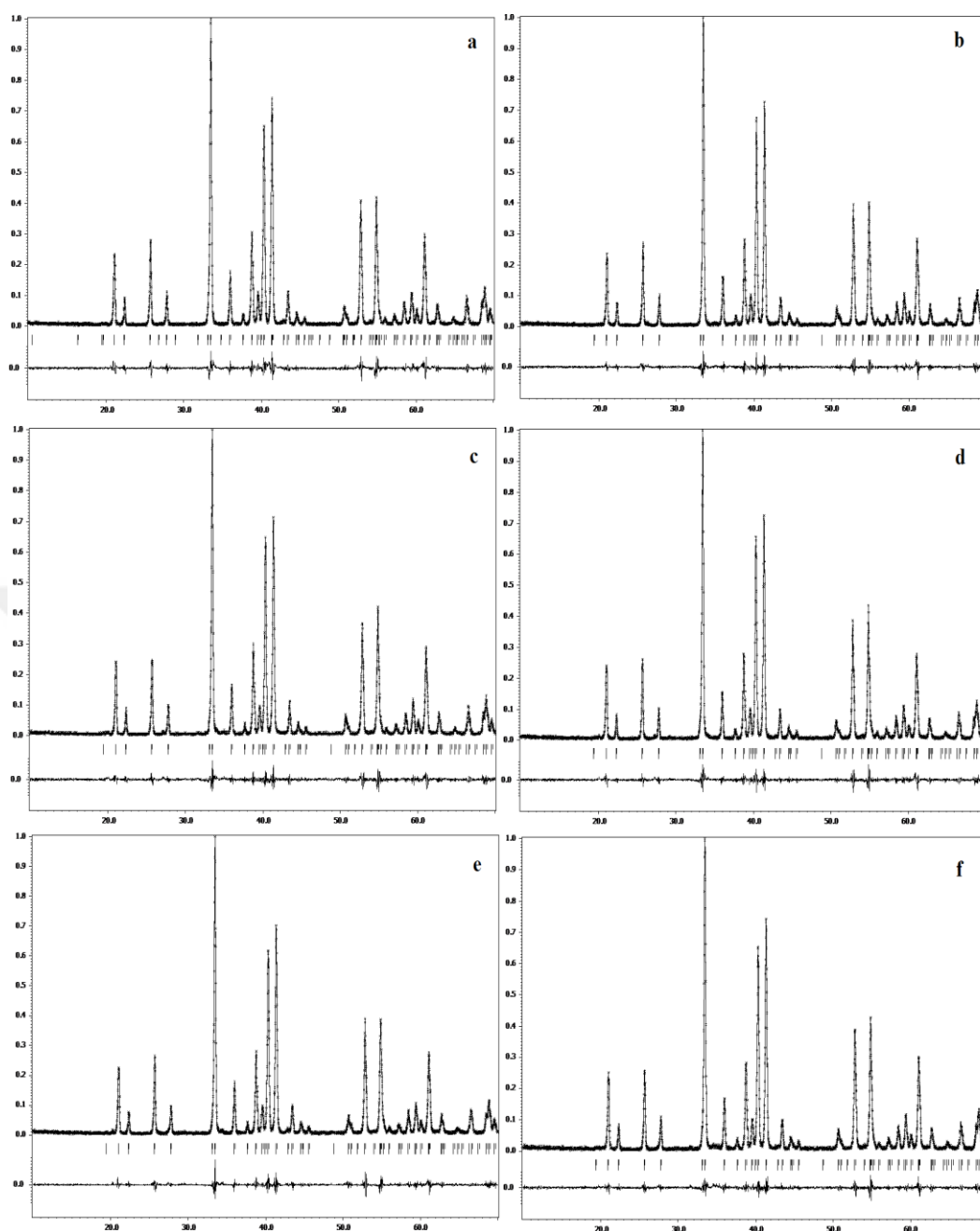


Figure 3.18 Ln_2O_3 ; Ln: Tb (a), Dy (b), Ho (c), Er (d), Yb (e) and Lu (f), Jana2006 analysis designs of products obtained by additive

Table 3.8 Jana2006 detailed analysis results of products obtained by adding Ln₂O₃ (Ln: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Lu)

<i>Products</i>	<i>0.10 % wt. La₂O₃</i>	<i>0.10 % wt. Ce₂O₃</i>	<i>0.10 % wt. Pr₂O₃</i>	<i>0.10 % wt. Nd₂O₃</i>	<i>0.10 % wt. Sm₂O₃</i>	<i>0.10 % wt. Eu₂O₃</i>	<i>0.10 % wt. Gd₂O₃</i>	<i>0.10 % wt. Tb₂O₃</i>	<i>0.10 % wt. Dy₂O₃</i>	<i>0.10 % wt. Ho₂O₃</i>	<i>0.10 % wt. Er₂O₃</i>	<i>0.10 % wt. Yb₂O₃</i>	<i>0.10 % wt. Lu₂O₃</i>
<i>Diffraktometre</i>	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku	Rigaku
<i>Radiation type</i>	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα
<i>Monochromator</i>	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite	Graphite
<i>Wavelength (Å)</i>	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405	1.5405
<i>Refined profile range(°2θ)</i>	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00	10.00- 70.00
<i>Step size (°2θ)</i>	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
<i>GOF</i>	1.14	1.53	1.30	1.13	1.32	1.32	1.24	1.32	1.15	1.22	1.19	1.15	1.17
<i>R_P</i>	8.91	12.79	10.23	8.92	11.38	9.99	9.64	9.99	9.04	9.33	9.34	9.04	8.75
<i>R_{WP}</i>	14.26	19.23	16.29	14.14	16.68	16.43	15.49	16.43	14.35	15.07	14.79	14.35	14.62
<i>V</i>	204.4	203.6	204.3	204.5	205.0	204.8	203.7	205.0	204.7	204.6	204.6	204.6	204.4

GOF, R_P, R_{WP}: agreement factors, V: volume

Table 3.9 Detailed structural parameters of the products obtained by doping with Ln₂O₃ (Ln: Gd, La, Nd, Ce, Er, Pr, Sm, Eu, Tb, Dy, Ho, Yb, and Lu)

<i>Products</i>	<i>0.10 % wt.La₂O₃</i>	<i>0.10 % wt. Ce₂O₃</i>	<i>0.10 % wt. Pr₂O₃</i>	<i>0.10 % wt. Nd₂O₃</i>	<i>0.10 % wt. Sm₂O₃</i>	<i>0.10 % wt. Eu₂O₃</i>	<i>0.10 % wt. Gd₂O₃</i>	<i>0.10 % wt. Tb₂O₃</i>	<i>0.10 % wt. Dy₂O₃</i>	<i>0.10 % wt. Ho₂O₃</i>	<i>0.10 % wt. Er₂O₃</i>	<i>0.10 % wt. Yb₂O₃</i>	<i>0.10 % wt. Lu₂O₃</i>
<i>Product</i>	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal	Powder crystal
<i>Symmetry</i>	Orthorho mbic	Orthorho mbic	orthorho mbic	orthorho mbic	orthorho mbic	orthorho mbic	orthorh ombic	Orthorho mbic	Orthorho mbic	orthorho mbic	orthorho mbic	orthorho mbic	Orthorh ombic
<i>Space Gr</i>	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm	Pnnm
<i>a (Å)</i>	5.397(5)	5.389(9)	5.396(0)	5.398(0)	5.399(9)	5.399(9)	5.427(9)	5.399(9)	5.399(9)	5.398(9)	5.398(8)	5.398(6)	5.397(8)
<i>b (Å)</i>	8.413(4)	8.403(6)	8.412(0)	8.414(4)	8.424(6)	8.414(8)	8.461(4)	8.424(6)	8.414(8)	8.414(8)	8.415(2)	8.415(4)	8.413(9)
<i>c (Å)</i>	4.502(0)	4.495(2)	4.500(8)	4.501(9)	4.506(5)	4.506(5)	4.522(1)	4.506(5)	4.502(7)	4.502(5)	4.502(7)	4.502(7)	4.501(2)
<i>α (° degree)</i>	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000
<i>β (° degree)</i>	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000

Table 3.9 (continued) Detailed structural parameters of the products obtained by doping with Ln₂O₃ (Ln: Gd, La, Nd, Ce, Er, Pr, Sm, Eu, Tb, Dy, Ho, Yb, and Lu)

<i>δ</i> (° degree)	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000	90.000
<i>d</i> (g/cm ³)	12.40	12.45	12.41	12.40	12.37	12.38	12.35	12.37	12.39	12.40	12.40	12.40	12.40
<i>t</i> (nm)	39.70	39.70	39.70	39.70	39.69	39.69	39.69	39.69	39.69	39.69	39.69	39.68	39.68
<i>S</i> (m ² /g)	12.18	12.18	12.18	12.19	12.22	12.21	12.24	12.22	12.20	12.19	12.19	12.19	12.19

3.5 XRD Characterization of Spinel-Structured AMn_2O_4 (A = Mg, Ni, Co) Compounds

3.5.1 XRD Patterns of MgMn_2O_4 Synthesized Using Tartaric Acid, Glycine and Urea at Different Calcination Temperatures

Tetragonal spinel-structured MgMn_2O_4 was synthesized with different fuels such as tartaric acid, glycine and urea by the solution combustion method. The products can be clearly identified in the XRD characterization. Obtained product by SCS was calcinated at 500 °C, 600 °C, 700 °C, 800°C, 900 °C for 1h.

Figure 3.19, Figure 3.20 and 3.21 shows the XRD diffraction patterns of MgMn_2O_4 which was synthesized with tartaric acid, glycine and urea, accordingly. All the fingerprint peaks, namely (101), (200), (103), (211), (202), (220), (312), (303), (224), and (400) appeared in the XRD patterns as shown in Figure 3.19, Figure 3.20 and 3.21 (ICDD PDF#23–0392) crystal planes of tetragonal spinel MgMn_2O_4 phase for all fuels at calcination temperature 500 °C, 600 °C, 700 °C, 800°C, 900 °C. XRD analysis revealed that in the synthesis of MgMn_2O_4 using tartaric acid (TA) as the fuel, the crystal structure was formed even without the application of heat treatment. For all there fuels, when the calcination temperature increased, an enhancement in crystallinity was observed.

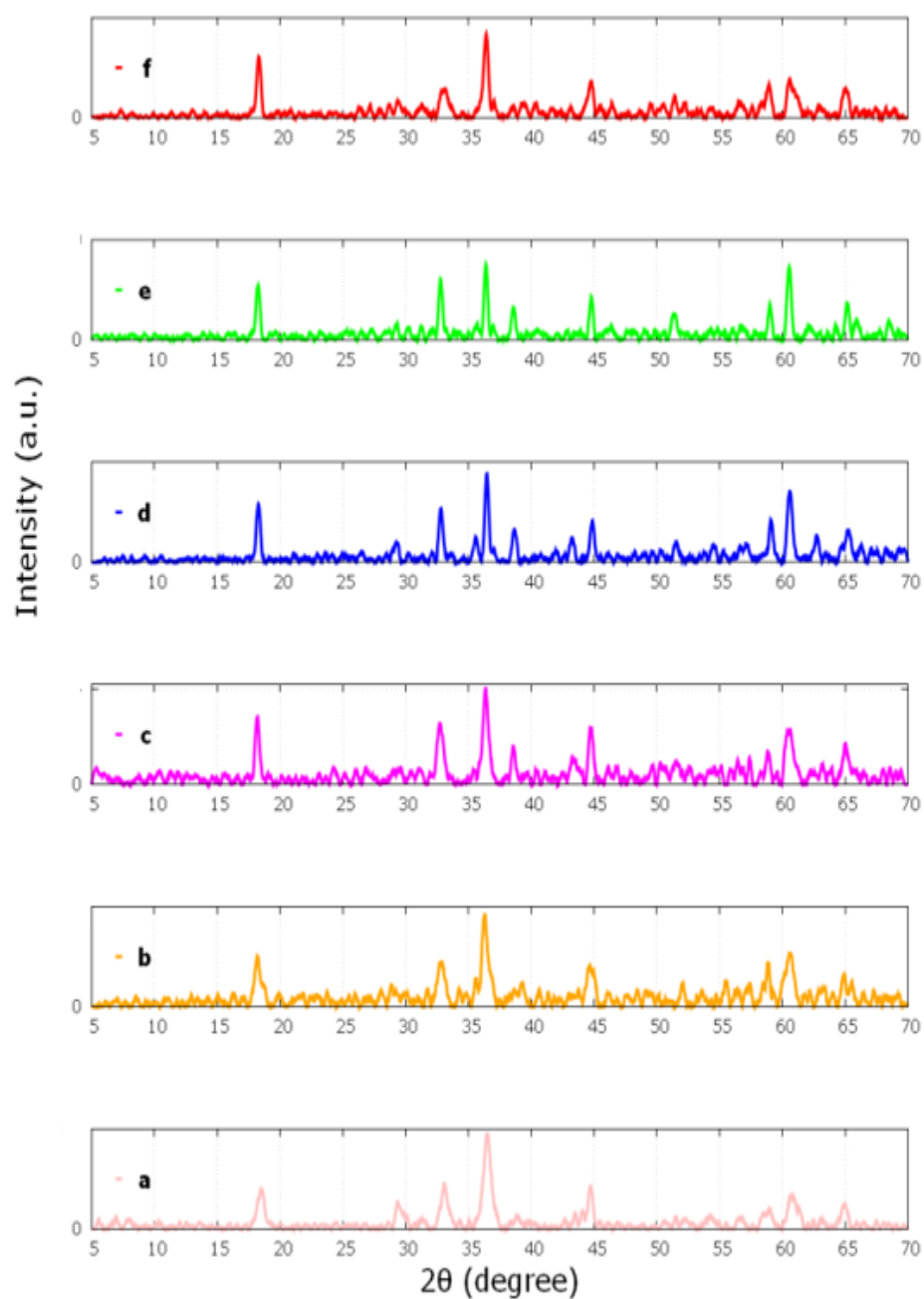


Figure 3.19 X-ray diffraction (XRD) patterns of MgMn_2O_4 synthesized using tartaric acid: (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

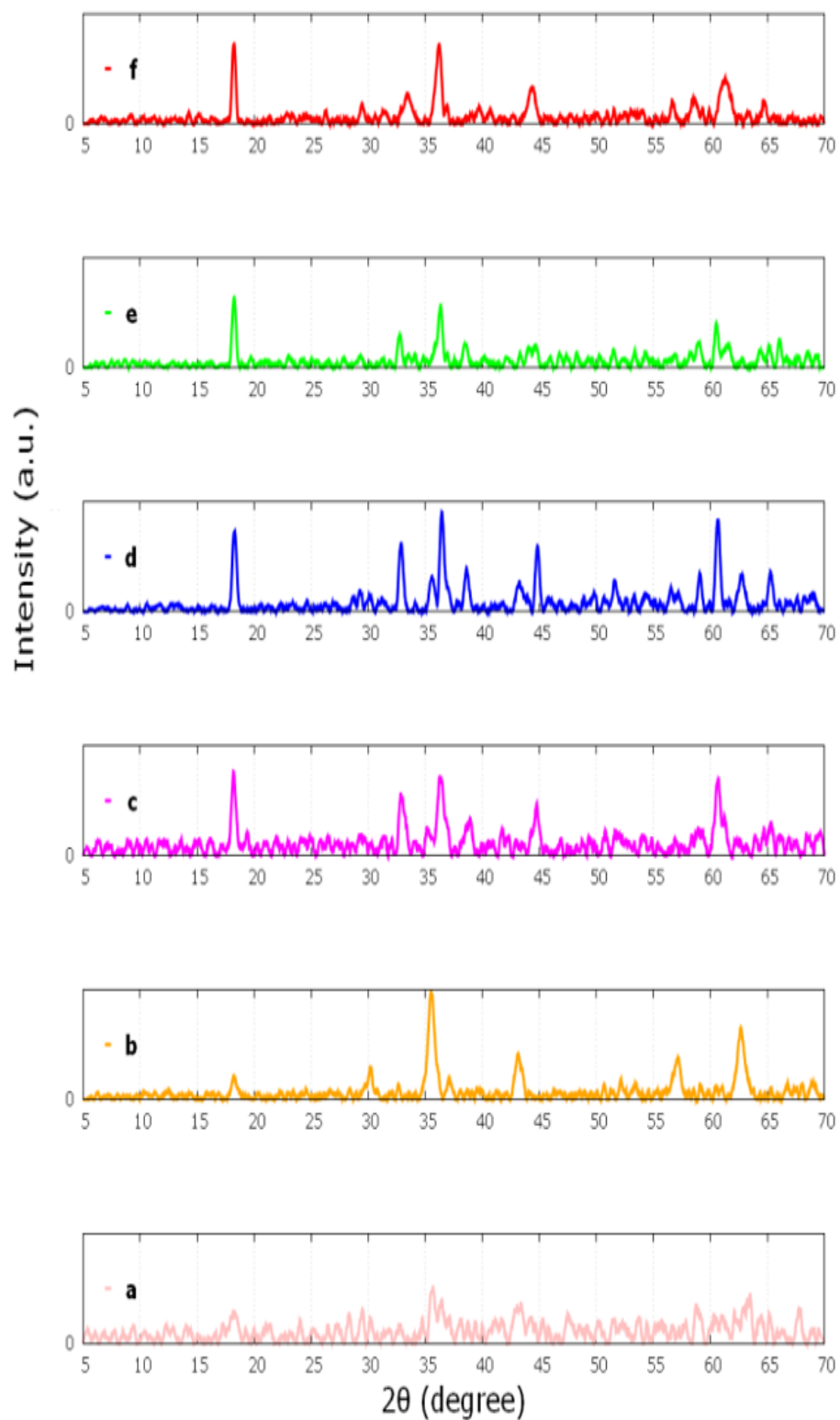


Figure 3.20 X-ray diffraction (XRD) patterns of MgMn_2O_4 synthesized using glycine: (a) as-synthesized, (b) calcined at 500°C , (c) 600°C , (d) 700°C , (e) 800°C , and (f) 900°C

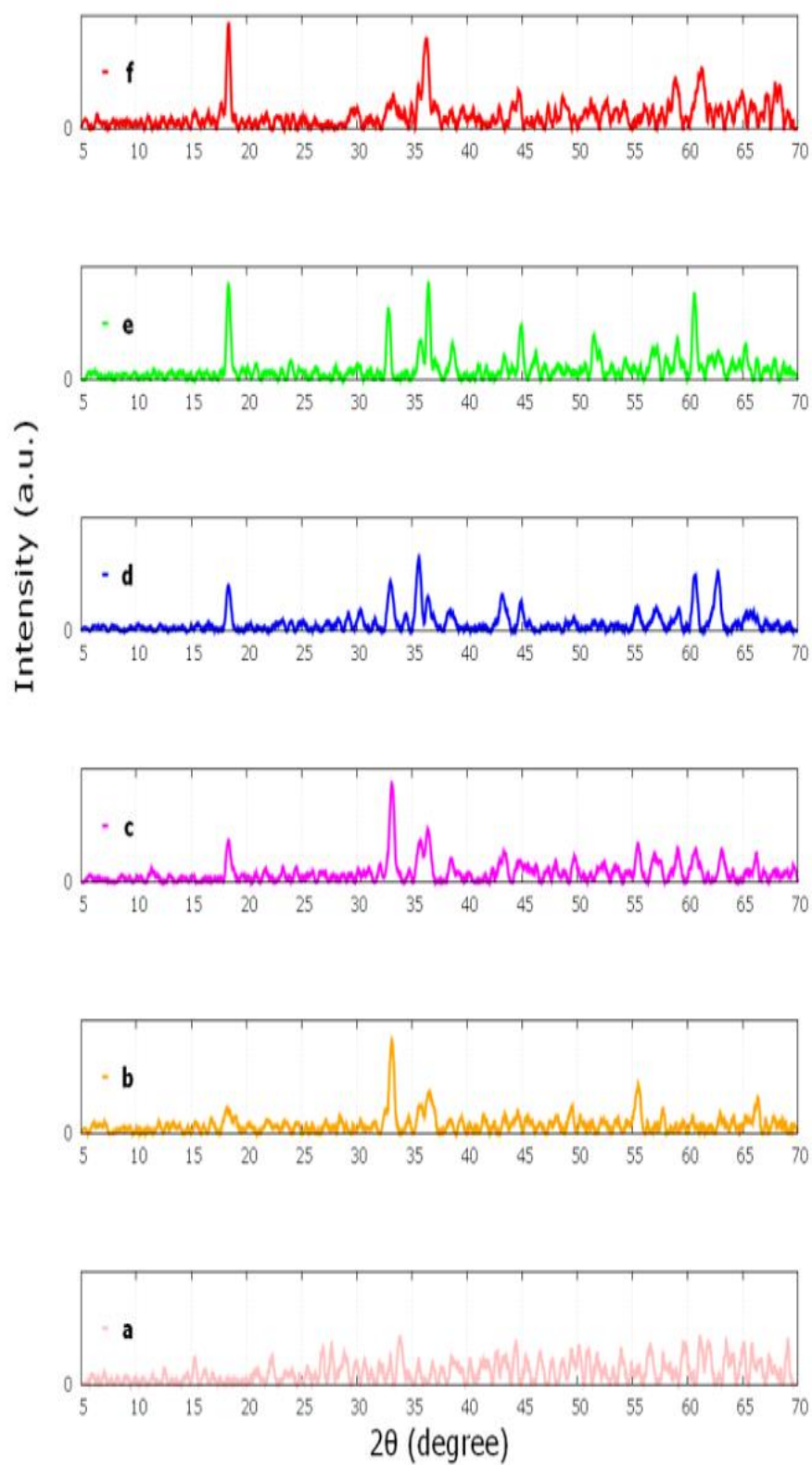


Figure 3.21 X-ray diffraction (XRD) patterns of MgMn_2O_4 synthesized using urea: (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

3.5.1.1 Cell Parameters of MgMn_2O_4 Synthesized Using TA, Glycine and Urea

The lattice parameters (a and c) of MgMn_2O_4 synthesized using tartaric acid (TA), glycine, and urea as fuels were calculated from the XRD data by indexing the characteristic tetragonal spinel reflections. The calculated values are consistent with the standard ICDD data for tetragonal MgMn_2O_4 , confirming successful phase formation in all samples. Slight variations in the lattice constants were observed depending on the fuel type, which can be attributed to differences in combustion temperature, reaction kinetics, and the extent of gas evolution during the synthesis process. Vigorous combustion (as with glycine and urea) can promote rapid crystallization and introduce microstructural strain or oxygen vacancies, leading to small changes in a and c values. In contrast, the slower combustion of tartaric acid tends to produce parameters closer to the equilibrium spinel lattice. The c/a ratios for all samples were in the range of ~ 1.57 – 1.60 , consistent with the expected Jahn–Teller distortion caused by Mn^{3+} ions in octahedral sites. These minor differences in cell parameters may have implications for the physical properties of the material.

In the use of TA, the XRD patterns of samples are shown in Table 3.10, all the diffraction peaks, located at $2\theta = 18.320, 29.370, 33.200, 36.420, 39.240, 44.800, 51.440, 58.940, 60.560, 65.020$ were corresponding to the (101), (112), (103), (211), (004), (220), (105), (321), (224), and (400) crystal planes of MMnO spinel phase (ICDD PDF#23–0392).

Table 3.10 Cell Parameters of MgMn_2O_4 Synthesized Using Tartaric Acid Fuel, calcinated at 900°C

No.	Peak Position, 2θ	Interplanar Spacing, d (Å)	Miller Indices (hkl)
1	18.320	4.838	101
2	29.370	3.041	112
3	33.200	2.696	103
4	36.420	2.465	211
5	39.240	2.294	004
6	44.800	2.021	220
7	51.440	1.775	105
8	58.940	1.567	321
9	60.560	1.527	224
10	65.020	1.433	400

When the 2θ is 44.800° , the interplanar spacing (d) is $2.021 \text{ \AA}$, and the Miller indices (hkl) are (220), the lattice constant a was calculated as $5.716 \text{ \AA}$, and the lattice constant c was calculated as $9.176 \text{ \AA}$, c/a : **1.60**

When Glycine is used as a fuel, the XRD patterns of samples are shown in Table 3.11, all the diffraction peaks, located at $2\theta = 18.200, 29.940, 33.240, 36.200, 39.680, 44.280, 52.640, 58.820, 61.120$ and 65.040 were corresponding to the (101), (112), (103), (211), (004), (220), (105), (321), (224), and (400) crystal planes of MMO spinel phase (ICDD PDF#23–0392).

Table 3.11 Cell Parameters of MgMn_2O_4 Synthesized Using Glycine Fuel, calcinated at 900°C

No.	Peak Position, 2θ	Interplanar Spacing, $d \text{ (\AA)}$	Miller Indices (hkl)
1	18.200	4.870	101
2	29.940	2.981	112
3	33.240	2.693	103
4	36.200	2.479	211
5	39.680	2.269	004
6	44.280	2.043	220
7	52.640	1.737	105
8	58.820	1.568	321
9	61.120	1.515	224
10	65.040	1.432	400

When the 2θ is 44.280° , the interplanar spacing (d) is $2.043 \text{ \AA}$, and the Miller indices (hkl) are (220), the lattice constant a was calculated as $5.778 \text{ \AA}$, and the lattice constant c was calculated as a $9.076 \text{ \AA}$ with the 2θ :39.680 and Miller indices (hkl) are (004) and .

When Urea is used as fuel, the XRD data of samples are shown in Table 3.12 sample, all the diffraction peaks, located at $2\theta = 18.380, 30.080, 33.300, 36.160, 39.680, 44.680, 52.680, 58.920, 61.360$ and 64.960 were corresponding to the (101), (112), (103), (211), (004), (220), (105), (321), (224), and (400) crystal planes of MMO spinel phase (ICDD PDF#23–0392).

Table 3.12 Cell Parameters of MgMn_2O_4 Synthesized Using Urea Fuel, calcinated at 900 °C

No.	Peak Position, 2θ	Interplanar Spacing, d (Å)	Miller Indices (hkl)
1	18.380	4.823	101
2	30.080	2.968	112
3	33.300	2.688	103
4	36.160	2.482	211
5	39.680	2.269	004
6	44.680	2.026	220
7	52.680	1.736	105
8	58.920	1.566	321
9	61.360	1.509	224
10	64.960	1.434	400

When the 2θ is 44.680°, the interplanar spacing (d) is 2.026 Å, and the Miller indices (hkl) are (220), the lattice constant a was calculated as **5.730 Å**, and the lattice constant c was calculated as with the **9.076 Å** with the 2θ : 39.680 and Miller indices (hkl) are (004).

The crystalline size of tetragonal spinel MgMn_2O_4 was calculated using the Debye-Scherrer equation for the three fuels; TA, glycine and urea. Results shows that all MgMn_2O_4 synthesized with the different fuel are in nanosized and crystallinity is generally increase with the temperature.

Table 3.13 Crystallite Size of MgMn_2O_4 Synthesized Using TA, Glycine and Urea Fuel, calcinated at 900 °C

Temperature (°C)	Crystallite Size of MgMn_2O_4		
	Tartaric Acid	Glycine	Urea
500°C	19.35 nm	11.79 nm	23.64 nm
600°C	19.1 nm	38.8 nm	19.84 nm
700°C	27.7 nm	22.00 nm	22.23 nm
800°C	31.3 nm	25.75 nm	30.6 nm
900°C	21.35 nm	26.9 nm	39.53 nm

3.5.2 XRD Patterns of CoMn_2O_4 Synthesized Using Tartaric Acid, Glycine and Urea at Different Calcination Temperatures

Tetragonal spinel-structured CoMn_2O_4 was synthesized with different fuels such as tartaric acid, glycine and urea by the solution combustion method. can be clearly identified in the XRD characterization. Obtained product was calcinated at 500 °C, 600 °C, 700 °C, 800°C, 900 °C for 1h.

Tetragonal spinel-structure CoMn_2O_4 can be clearly identified in the XRD characterization. All the fingerprint peaks, namely (1 0 1), (1 1 2), (2 0 0), (1 0 3), (2 1 1), (0 0 4), (2 2 0), (2 0 4), (3 1 2), (3 2 1), (2 2 4) and (1 1 6) crystal planes of spinel phase CoMn_2O_4 (**JCPDS 77-0471**) appeared in the XRD patterns as shown in Figure 3.24, Figure 3.25, Figure 3.26. When TA is used as fuel, the as-synthesized sample shows clear spinel peaks even without heat treatment, indicating partial crystallization during combustion. The as-synthesized pattern exhibits weaker peaks compared to TA, implying a higher proportion of amorphous content after combustion. Crystallinity improves significantly after calcination at 500–600 °C, with peak intensities stabilizing at higher temperatures. The as-synthesized material shows broad, low-intensity peaks, sharp peaks appear only after calcination above 600 °C, with the highest intensity observed at 900 °C. The XRD results indicate that while all three fuels produce tetragonal CoMn_2O_4 upon calcination, tartaric acid enables partial crystallization during synthesis, glycine achieves high crystallinity at moderate temperatures through rapid combustion, and urea requires higher temperatures to develop well-ordered spinel structures due to its denser combustion ash and slower cation homogenization.

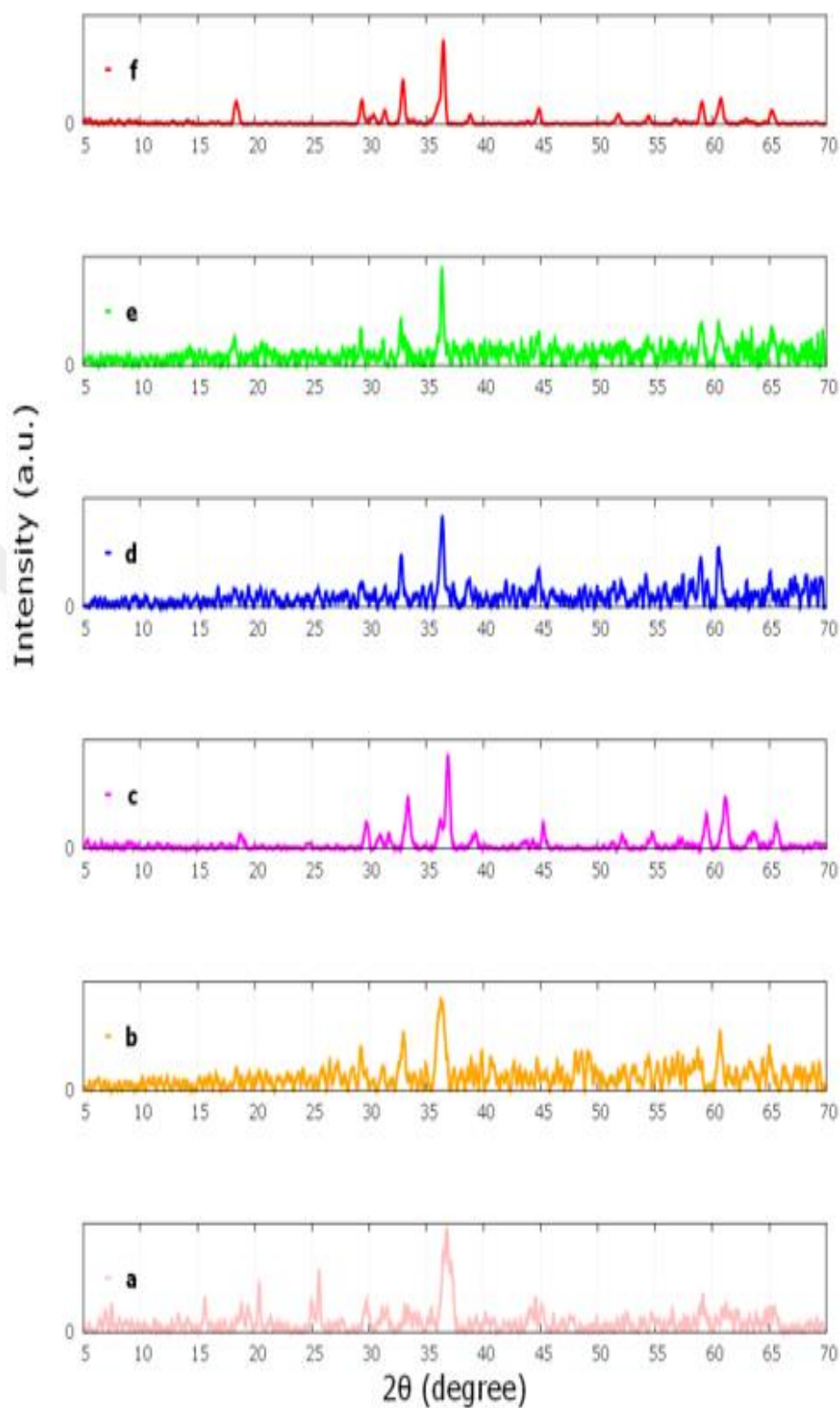


Figure 3.22 X-ray diffraction (XRD) patterns of CoMn_2O_4 synthesized using tartaric acid: (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

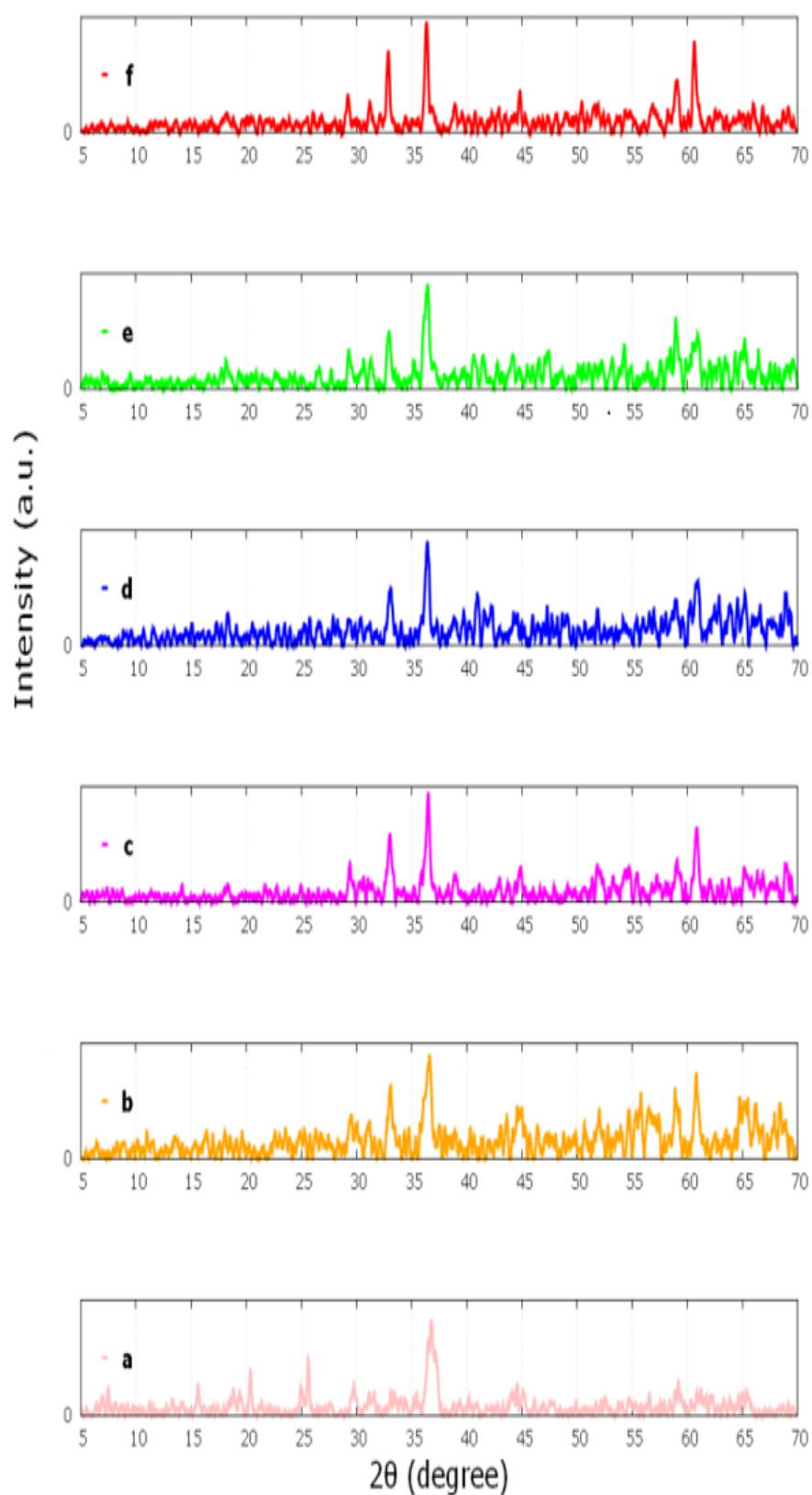


Figure 3.23 X-ray diffraction (XRD) patterns of CoMn_2O_4 synthesized using glycine: (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

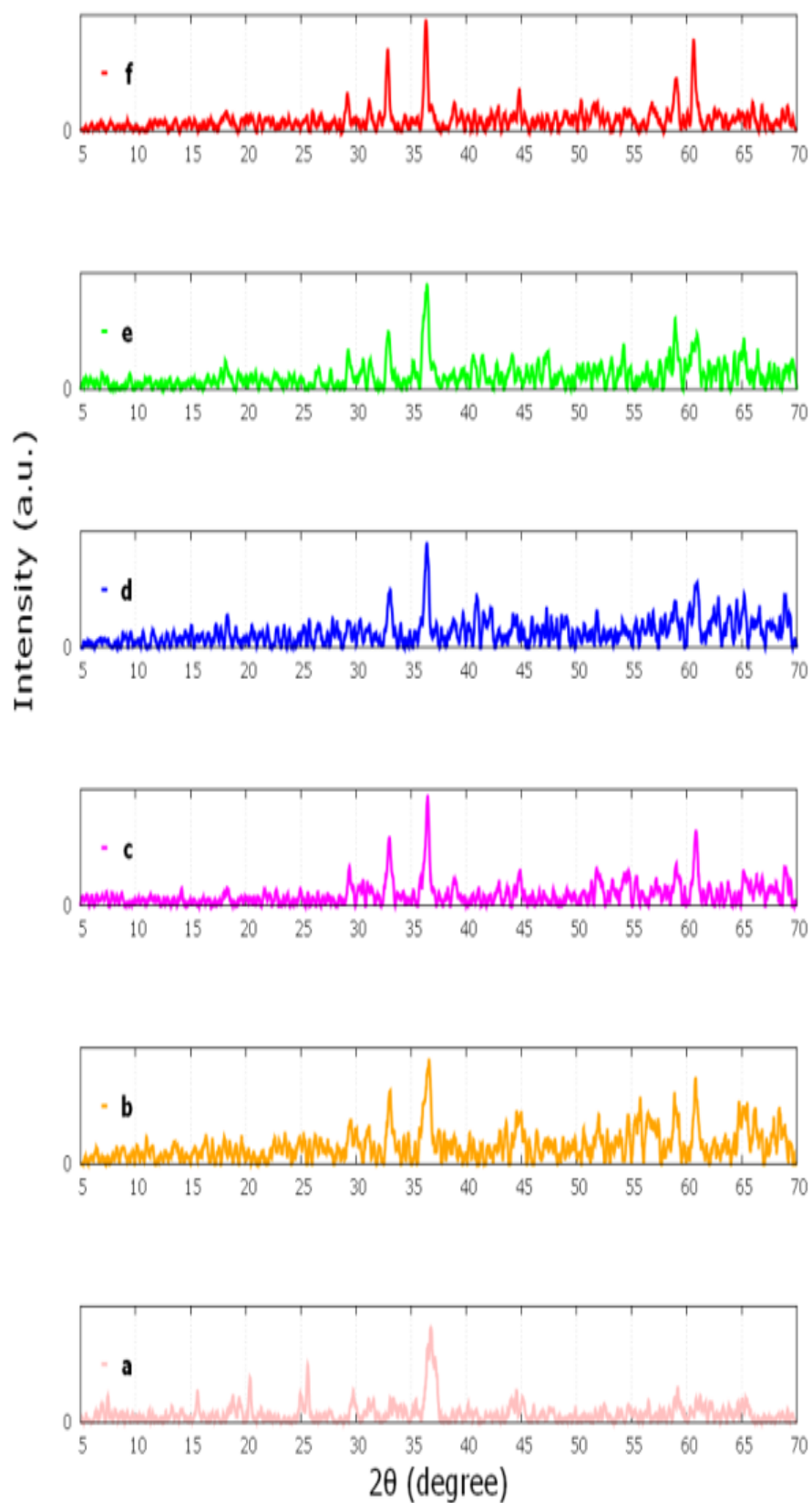


Figure 3.24 X-ray diffraction (XRD) patterns of CoMn_2O_4 synthesized using urea: (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

3.5.2.1 Cell Parameters of CoMn₂O₄ Synthesized Using TA, Glycine and Urea

The lattice parameters (*a* and *c*) of CoMn₂O₄ synthesized using tartaric acid (TA), glycine, and urea as fuels were calculated from the XRD data by indexing the characteristic tetragonal spinel reflections. For all three fuels, the obtained values are in good agreement with (JCPDS 77-0471) data, confirming the formation of the tetragonal spinel phase. Minor variations in the lattice constants were observed depending on the type of fuel used, which can be attributed to differences in combustion temperature, gas evolution, and the resulting defect density during synthesis.

Table 3.14 Cell Parameters of CoMn₂O₄ Synthesized Using Tartaric Acid Fuel, calcinated at 900 °C

No.	Peak Position, 2 θ	Interplanar Spacing, <i>d</i> (Å)	Miller (hkl) Indices
1	18.660	4.751	101
2	29.800	2.99	112
3	31.760	2.815	200
4	33.620	2.663	103
5	36.860	2.436	211
6	37.120	2.420	004
7	45.320	1.999	220
8	52.120	1.753	204
9	54.700	1.677	312
10	59.500	1.552	321
11	61.140	1.151	224
12	65.540	1.423	116

When the 2 θ is 31.760°, the interplanar spacing (*d*) is 2.815 Å, and the Miller indices (hkl) are (200), the lattice constant ***a*** was calculated as **5.630 Å**, and the lattice constant ***c*** was calculated as with the **9.680 Å** with the 2 θ : 37.120 and Miller indices (hkl) are (004).

Glycine is used in the synthesis of CoMn₂O₄ with the solution combustion technique. The XRD patterns of samples are shown in Table 3.15, all the diffraction peaks, located at 2 θ = 18.400, 29.320, 31.360, 32.940, 36.480, 38.900 ,44.860, 51.820, 54.480, 59.140, 60.80 and 65.180 were corresponding to the correspond to lattice planes (1 0 1), (1 1 2), (2 0 0), (1 0 3), (2 1 1), (0 0 4), (2 2 0), (2 0 4), (3 1

2), (3 2 1), (2 2 4) and (1 1 6) crystal planes of spinel phase of CoMn_2O_4 (JCPDS 77-0471).

Table 3.15 Cell Parameters of CoMn_2O_4 Synthesized Using Glycine Fuel, calcinated at 900 °C

No.	Peak Position, 2θ	Interplanar Spacing, d (Å)	Miller (hkl) Indices
1	18.400	4.818	101
2	29.320	3.043	112
3	31.360	2.850	200
4	32.940	2.716	103
5	36.480	2.460	211
6	38.900	2.313	004
7	44.860	2.019	220
8	51.820	1.763	204
9	54.480	1.683	312
10	59.140	1.561	321
11	60.80	1.523	224
12	65.180	1.430	116

When the 2θ is 31.360° , the interplanar spacing (d) is 2.850 Å, and the Miller indices (hkl) are (200), the lattice constant **a** was calculated as **5.705 Å**, and the lattice constant **c** was calculated as **9.25 Å** with the 2θ : 38.900 and Miller indices (hkl) are (004).

Urea is used as a fuel, the XRD patterns of samples are shown in Table 3.16 sample, all the diffraction peaks, located at $2\theta=18.300$, 29.780, 32.780, 33.140, 36.460, 37.760, 45.00, 52.520, 54.180, 60.280 61.020 and 65.200 were corresponding to the correspond to lattice planes (1 0 1), (1 1 2), (2 0 0), (1 0 3), (2 1 1), (0 0 4), (2 2 0), (2 0 4), (3 1 2), (3 2 1), (2 2 4) and (1 1 6) crystal planes of spinel phase CoMn_2O_4 CoMn_2O_4 (JCPDS 77-0471).

Table 3.16 Cell Parameters of CoMn_2O_4 Synthesized Using Urea Fuel, calcinated at 900 °C

No.	Peak Position	Interplaner Spacing	Miller Indices
	2θ	d (Å)	(hkl)
1	18.300	4.843	101
2	29.780	2.997	112
3	32.780	2.730	200
4	33.140	2.700	103
5	36.460	2.462	211
6	37.760	2.380	004
7	45.00	2.012	220
8	52.520	1.740	204
9	54.180	1.691	312
10	60.280	1.534	321
11	61.020	1.517	224
12	65.200	1.429	116

When the 2θ is 32.780° , the interplanar spacing (d) is 2.730 Å, and the Miller indices (hkl) are (200), the lattice constant **a** was calculated as **5.460 Å**, and the lattice constant **c** was calculated as **9.522 Å** with the 2θ : 37.760 , d : 2.380 and Miller indices (hkl) are (004).

The crystallite size of CoMn_2O_4 samples synthesized using different fuels was estimated from the XRD peak broadening by applying the Debye–Scherrer equation, providing insight into the effect of calcination temperature and fuel type on the microstructural development. At low temperature (500 °C), glycine produces the largest crystallites, tartaric acid the smallest, and urea intermediate sizes. This reflects differences in combustion intensity and gas evolution—glycine burns vigorously, producing high local temperatures that can promote sintering even before calcination. The crystallite size of CoMn_2O_4 increased with calcination temperature for all fuels, with tartaric acid showing the most regular growth trend, glycine producing the largest initial crystallites due to vigorous combustion, and urea yielding more variable sizes likely influenced by microstrain and porosity effects in the combustion-derived ash.

Table 3.17 Crystallite Size of CoMn_2O_4 Synthesized Using TA, Glycine and Urea Fuel, calcinated at 900 °C

Temperature (°C)	Crystallite Size of CoMn_2O_4		
	Tartaric Acid	Glycine	Urea
500°C	12.74 nm	36.4 nm	17.42 nm
600°C	12.08 nm	26. 46 nm	28.48 nm
700°C	23.80 nm	26. 29 nm	26.73 nm
800°C	31.5 nm	30.72 nm	18.46 nm
900°C	29. 4 nm	29.42 nm	23.9 nm

3.5.3. XRD Patterns of NiMn_2O_4 Synthesized Using Tartaric Acid, Glycine and Urea at Different Calcination Temperatures

The XRD diffraction patterns Figure 3.25, Figure 3.26, Figure 3.27 manifested a marked resemblance to the cubic structural attributes of NiMn_2O_4 (JCPDS card no: 71-0852), unequivocally ascribed to the Fd-3m space group. In all three series, the diffraction patterns are dominated by the spinel reflections . When TA and urea are used as a fuel, even the as-synthesized powder shows clear spinel peaks and partial crystallization during combustion. Peak intensities and sharpness increase steadily from 500 to 900 °C. The as-synthesized sample is more amorphous; pear are more sharpen with temperature with the glycine fuel. Compared with the other two products, NiMn_2O_4 exhibits higher crystallinity and sharper diffraction peaks than MgMn_2O_4 and CoMn_2O_4 across all fuels.

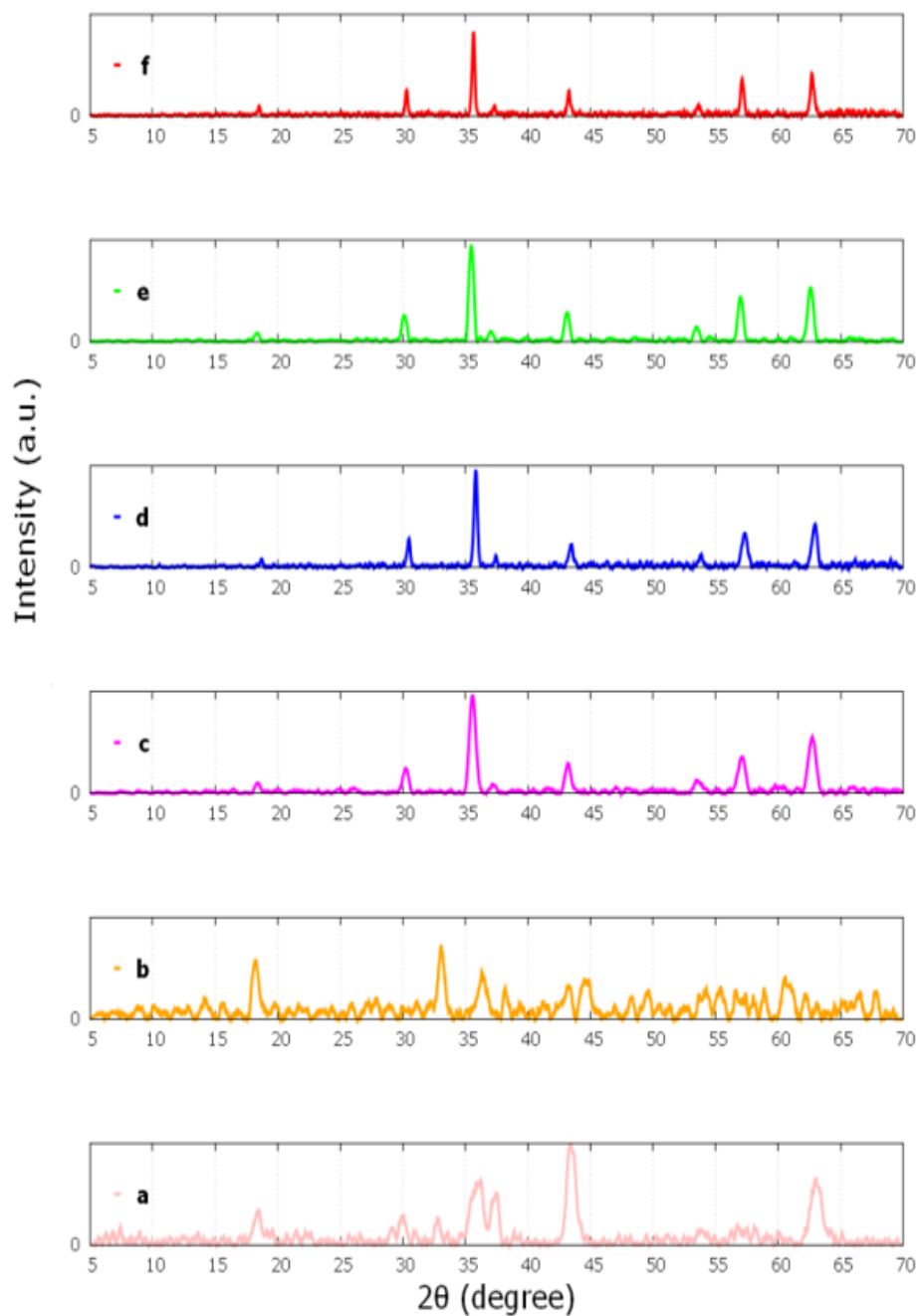


Figure 3.25 X-ray diffraction (XRD) patterns of NiMn_2O_4 synthesized using tartaric acid (TA): (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

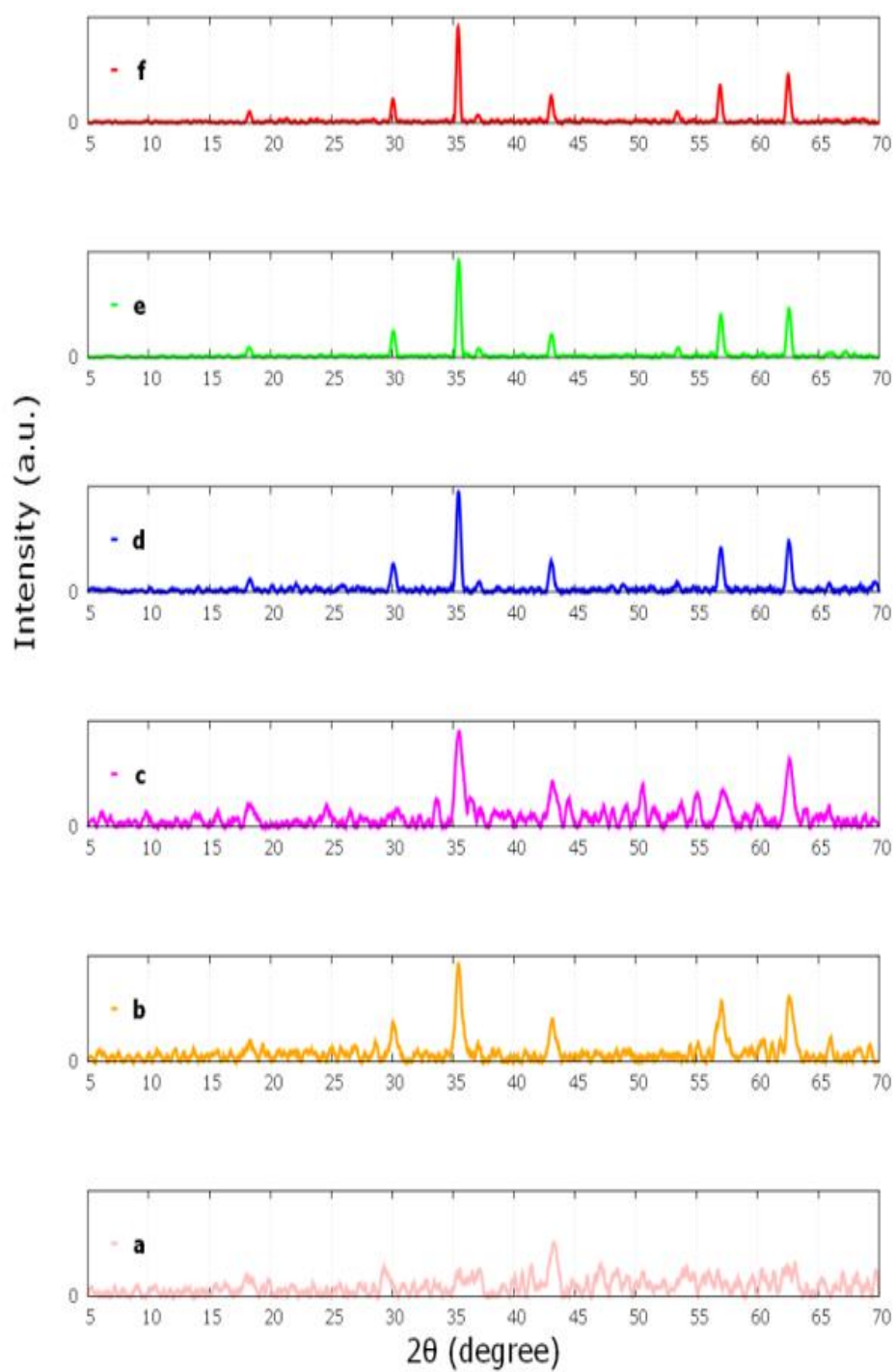


Figure 3.26 X-ray diffraction (XRD) patterns of NiMn_2O_4 synthesized using glycine (Gly): (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

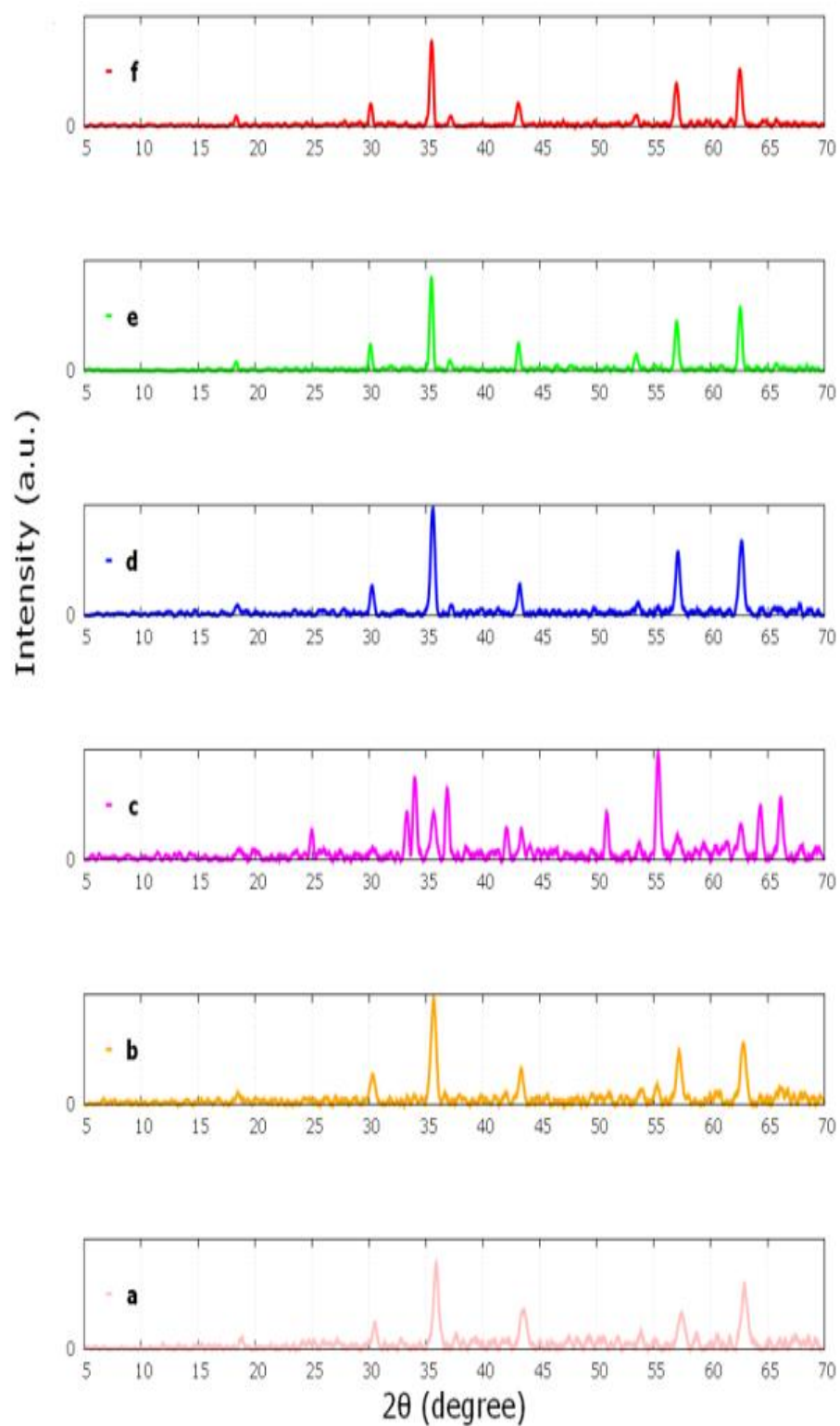


Figure 3.27 X-ray diffraction (XRD) patterns of NiMn_2O_4 synthesized using urea: (a) as-synthesized, (b) calcined at 500 °C, (c) 600 °C, (d) 700 °C, (e) 800 °C, and (f) 900 °C

3.5.3.1. Crystallite Size of NiMn₂O₄ Synthesized Using TA, Glycine and Urea Fuels

Crystallite size calculation is performed using the Scherrer equation. Calculation details are mentioned in the method section and

Table 3.18 Crystallite Size of NiMn₂O₄ Synthesized Using TA, Glycine and Urea Fuel, calcinated at 500°C , 600°C , 700°C , 800°C , 900 °C

Fuel Type	Temperature (°C)	Crystalite Size (nm)
Tartaric Acid	500°C	22.16 nm
Tartaric Acid	600°C	15.3 nm
Tartaric Acid	700°C	30.97 nm
Tartaric Acid	800°C	15.5 nm
Tartaric Acid	900°C	37.47 nm
Glycine	500°C	18.97 nm
Glycine	600°C	21.85 nm
Glycine	700°C	16.0 nm
Glycine	800°C	19.0 nm
Glycine	900°C	28.5 nm
Urea	500°C	27.01 nm
Urea	600°C	21.84 nm
Urea	700°C	20. 95 nm
Urea	800°C	28.0 nm
Urea	900°C	24.78 nm

3.6 Characterization of Infrared Spectra

3.6.1 FTIR Spectra of MgMn_2O_4 Synthesized Using Tartaric Acid, Glycine and Urea at Different Calcination Temperatures

Figure 3.28, Figure 3.29 and Figure 3.30 shows nanosized MgMn_2O_4 product using tartaric Acid, glycine and urea at different calcination temperatures. When the all three fuels, the as-synthesized sample shows a broad O–H stretching band ($\sim 3400\text{ cm}^{-1}$) and an H–O–H bending band ($\sim 1620\text{ cm}^{-1}$) and tartaric acid fuel-derived features in the $1700\text{--}1400\text{ cm}^{-1}$ region. Bands near $600\text{--}650\text{ cm}^{-1}$ and $500\text{--}550\text{ cm}^{-1}$, assignable to metal–oxygen stretching in the spinel lattice. As the calcination temperature is increased, the water- and fuel-related bands significantly disappear and are essentially absent and the spinel M–O bands sharpen from $\geq 500\text{ }^\circ\text{C}$.

When the tartaric acid is used as fuel, In the Figure 3.30 shows that the $\sim 1500\text{ cm}^{-1}$ peak at $800\text{ }^\circ\text{C}$ is likely due to surface carbonate (CO_3^{2-}) vibrations caused by CO_2 adsorption from air onto the MgMn_2O_4 surface during cooling after calcination. Many studies on spinel ferrites and manganites report carbonate bands in the $1400\text{--}1500\text{ cm}^{-1}$ range after high-temperature calcination due to atmospheric CO_2 adsorption. (Wang et al., 2013; Smith & Johnson, 2015; Chen et al., 2018)

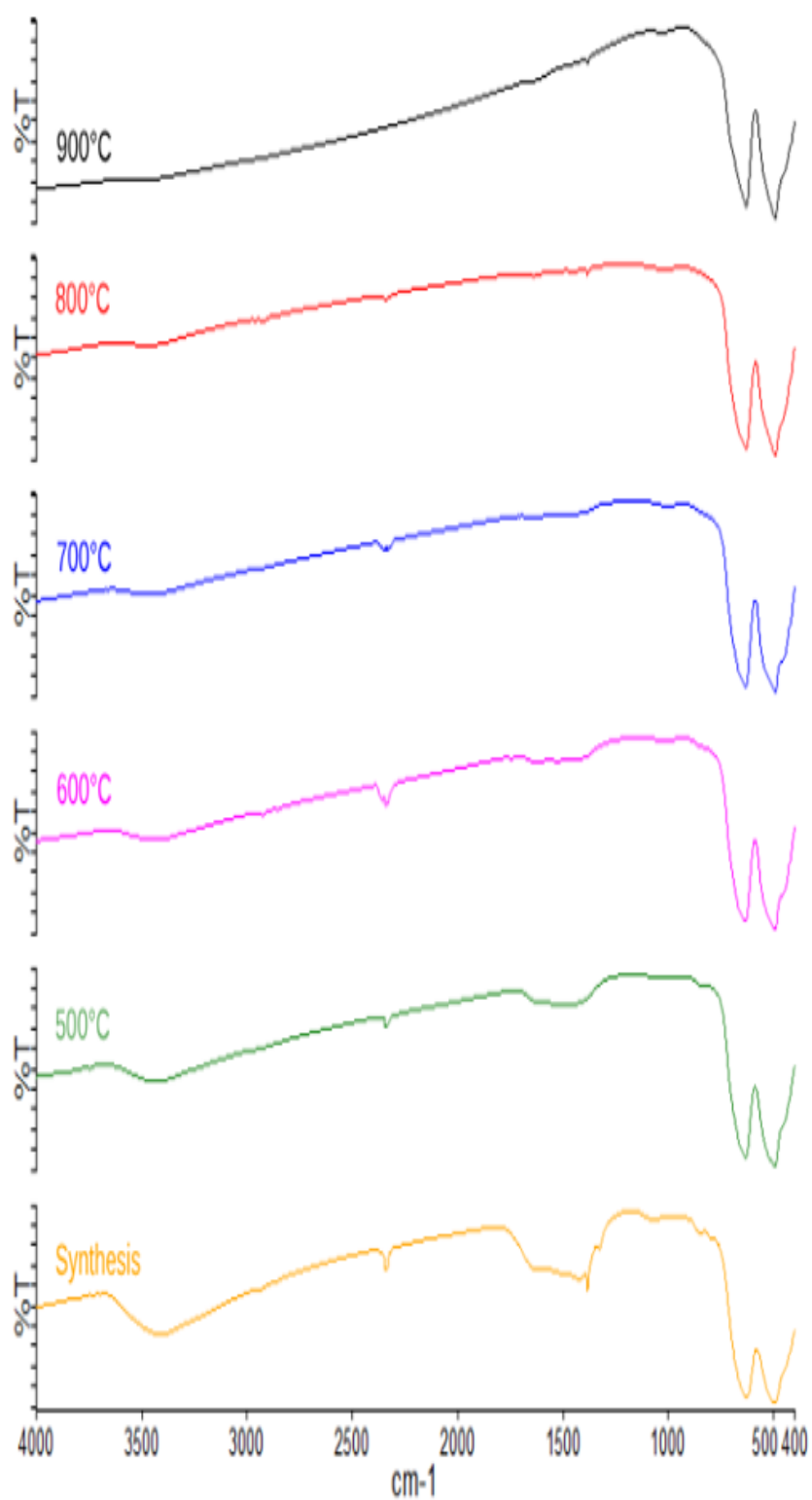


Figure 3.28: Infrared (IR) spectra of MgMn_2O_4 synthesized using tartaric acid (TA) and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

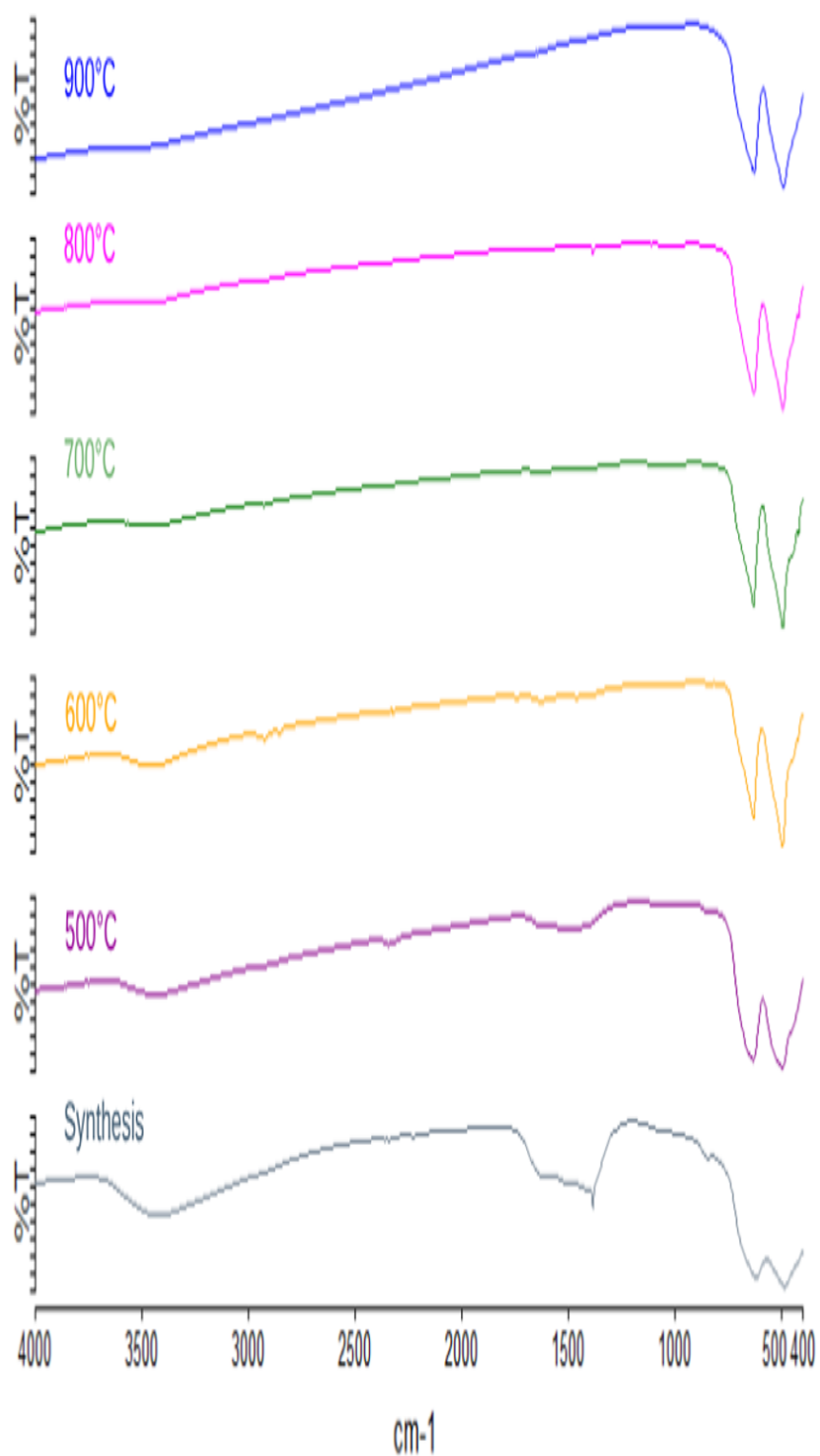


Figure 3.29 Infrared (IR) spectra of MgMn_2O_4 synthesized using Glycine and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

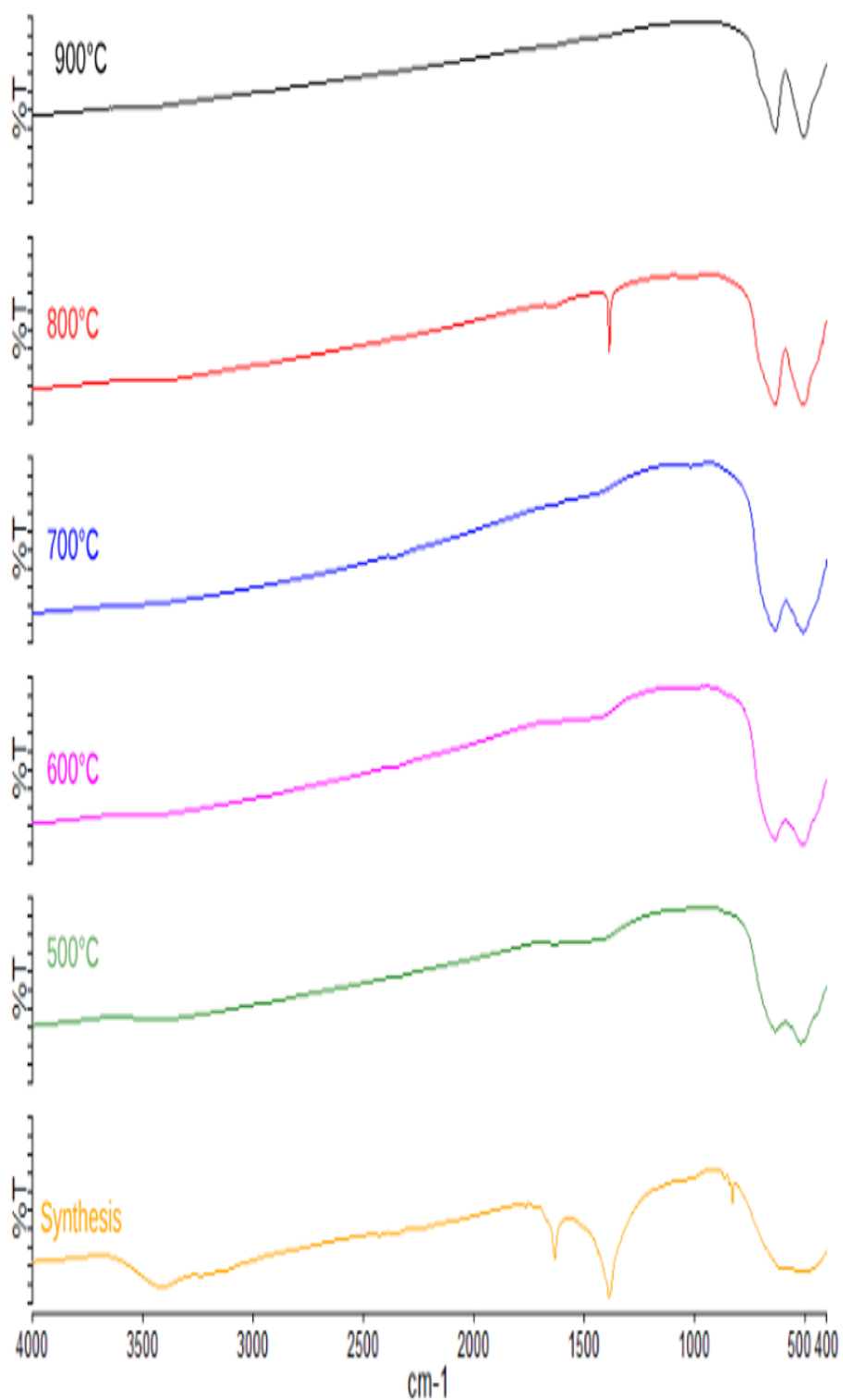


Figure 3.30 Infrared (IR) spectra of MgMn_2O_4 synthesized using Urea and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

3.6.2 FTIR Spectra of CoMn₂O₄ Synthesized Using Tartaric Acid, Glycine and Urea at Different Calcination Temperatures

In the FTIR spectra of CoMn₂O₄ as-synthesized sample using tartaric acid Figure 3.31, glycine Figure 3.32 and urea; Figure 3.33 adsorbed water and surface hydroxyls are shown $\sim 3400\text{ cm}^{-1}$, near $\sim 1600\text{ cm}^{-1}$. Organic glycine fuel precursor bands are seen between $\sim 1700\text{--}1000\text{ cm}^{-1}$ (amide/Carboxylate C=O, C–N/C–O and C–H related modes). As the calcination temperature rises, these bands progressively decrease in intensity and largely disappear at $\geq 500\text{ }^{\circ}\text{C}$. Characteristic of spinel oxides: M–O stretching modes in the $\sim 600\text{--}700\text{ cm}^{-1}$ region and metal–oxygen lattice modes below 500 cm^{-1} , which sharpen at $800\text{--}900\text{ }^{\circ}\text{C}$. (Chanda & Ghosh, 2012; Kamble & Patil, 2014; Rathod & Jadhav, 2015).

Table 3.19 Assignment of Infrared bands for CoMn₂O₄ synthesized using tartaric acid (TA) and calcined at various temperatures.

Wavenumber (cm ⁻¹)	Assignment	Remarks
$\sim 3400\text{--}3450$	O–H stretching	Adsorbed water or surface hydroxyl groups; intensity decreases with increasing calcination temperature.
~ 1600	H–O–H bending	Deformation mode of adsorbed water.
$\sim 1350\text{--}1450$	C–O stretching (carboxylate groups)	Originating from tartaric acid residues; bands disappear above $700\text{ }^{\circ}\text{C}$.
$\sim 1050\text{--}1100$	C–O–C stretching	Organic remnants from precursor; removed upon high-temperature calcination.
$\sim 600\text{--}700$	M–O stretching (Mn–O, Co–O) in spinel lattice	Characteristic vibrations of spinel CoMn ₂ O ₄ ; peaks become sharper at $\geq 700\text{ }^{\circ}\text{C}$.
<500	Metal–oxygen lattice vibrations	Fingerprint region of spinel oxides.

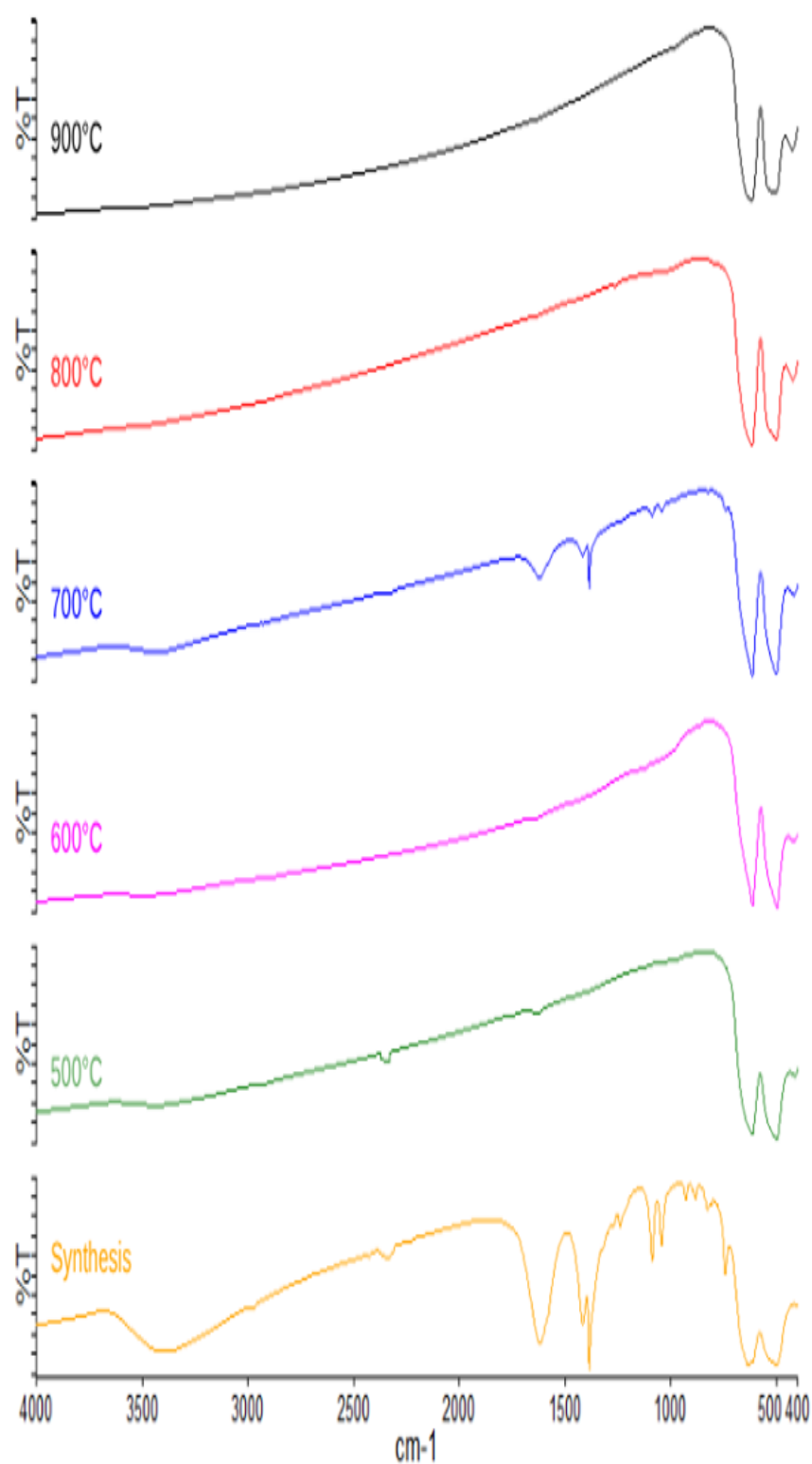


Figure 3.31 Infrared (IR) spectra of CoMn_2O_4 synthesized using tartaric acid (TA) and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

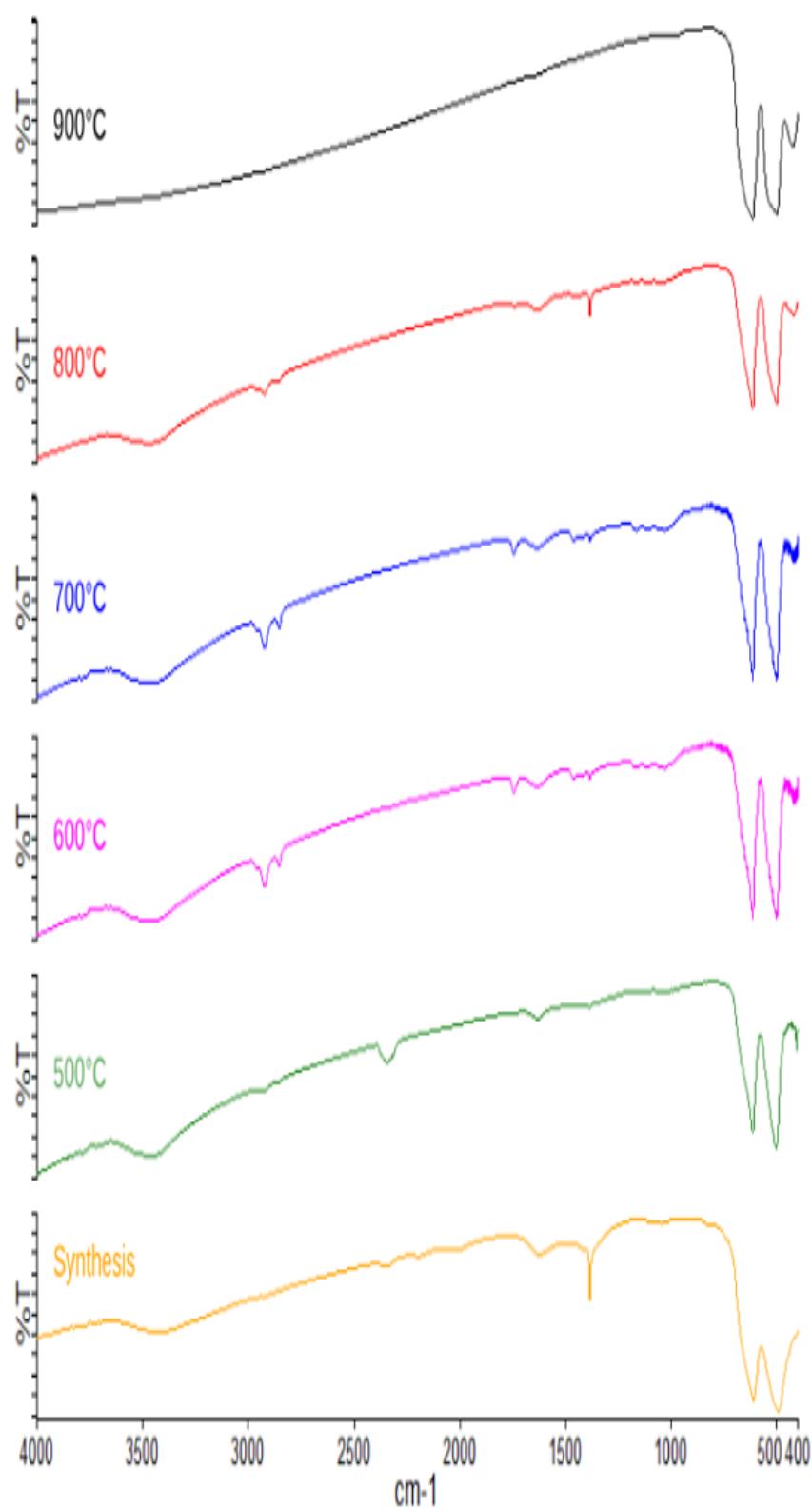


Figure 3.32 Infrared (IR) spectra of CoMn_2O_4 synthesized using Glycine and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

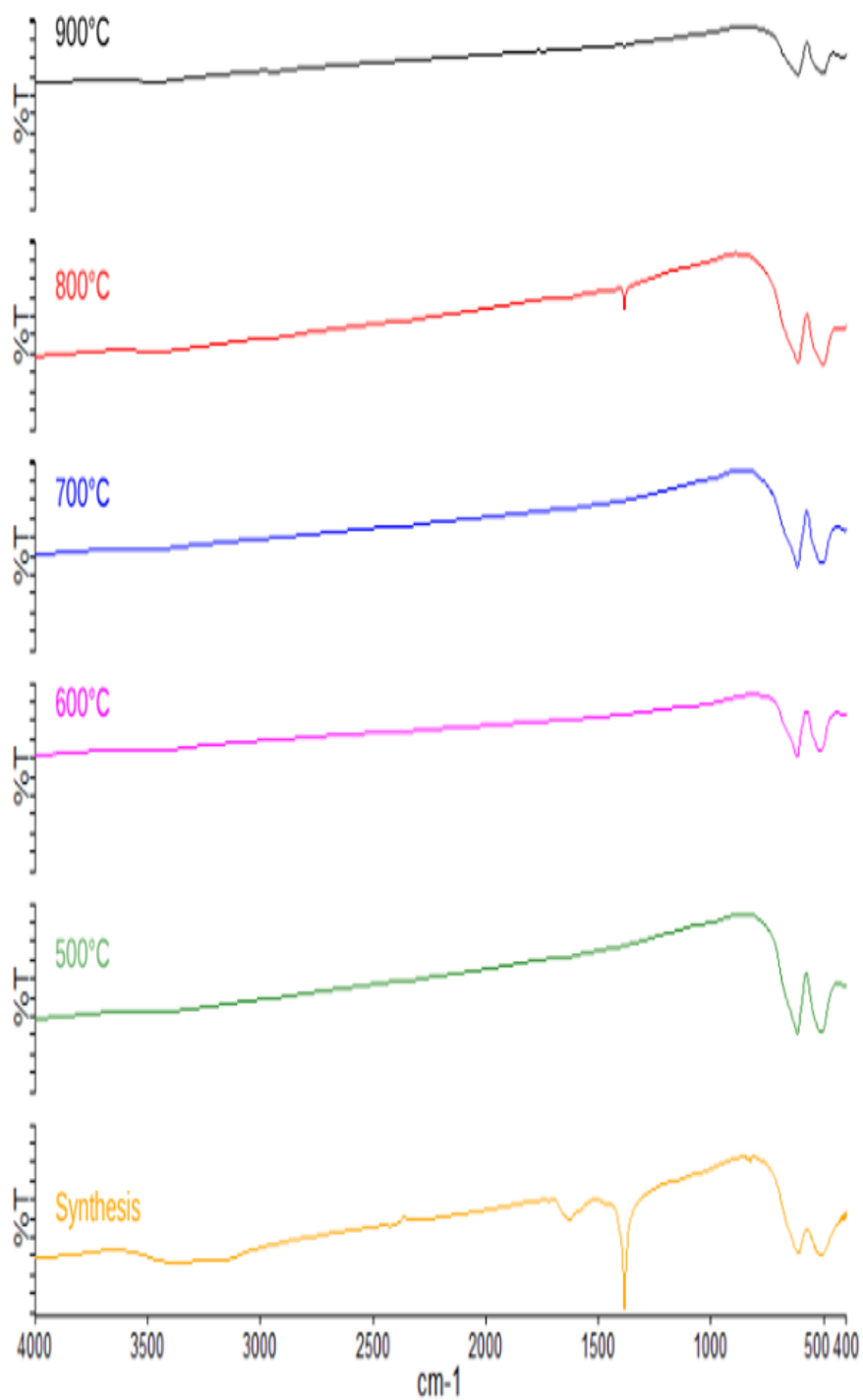


Figure 3.33 Infrared (IR) spectra of CoMn₂O₄ synthesized using Urea and calcined at various temperatures: as-synthesized, 500 °C, 600 ° C, 700 ° C, 800 ° C, and 900 ° C

3.6.3 FTIR Spectra of NiMn₂O₄ Synthesized Using Tartaric Acid, Glycine and Urea at Different Calcination Temperatures

Figure 3.34, Figure 3.35 and Figure 3.36 shows that FTIR spectra of NiMn₂O₄ synthesized using tartaric acid, glycine and urea at different calcination temperatures. The as-synthesized NiMn₂O₄ powder shows broad O–H stretching near $\sim 3400\text{ cm}^{-1}$ and an H–O–H bending band at $\sim 1620\text{ cm}^{-1}$ and weak–moderate band region in the $1700\text{--}1400\text{ cm}^{-1}$ attributable to carboxylate/C=O and C–H⁻¹. These organic-related bands significantly disappear after $\geq 500\text{ }^{\circ}\text{C}$. M–O stretching vibrations ($\sim 600\text{--}700\text{ cm}^{-1}$) and metal–oxygen lattice modes ($<500\text{ cm}^{-1}$), which become more intense at $\geq 500\text{ }^{\circ}\text{C}$. All the organic residuals and water disappear after $\geq 500\text{ }^{\circ}\text{C}$.

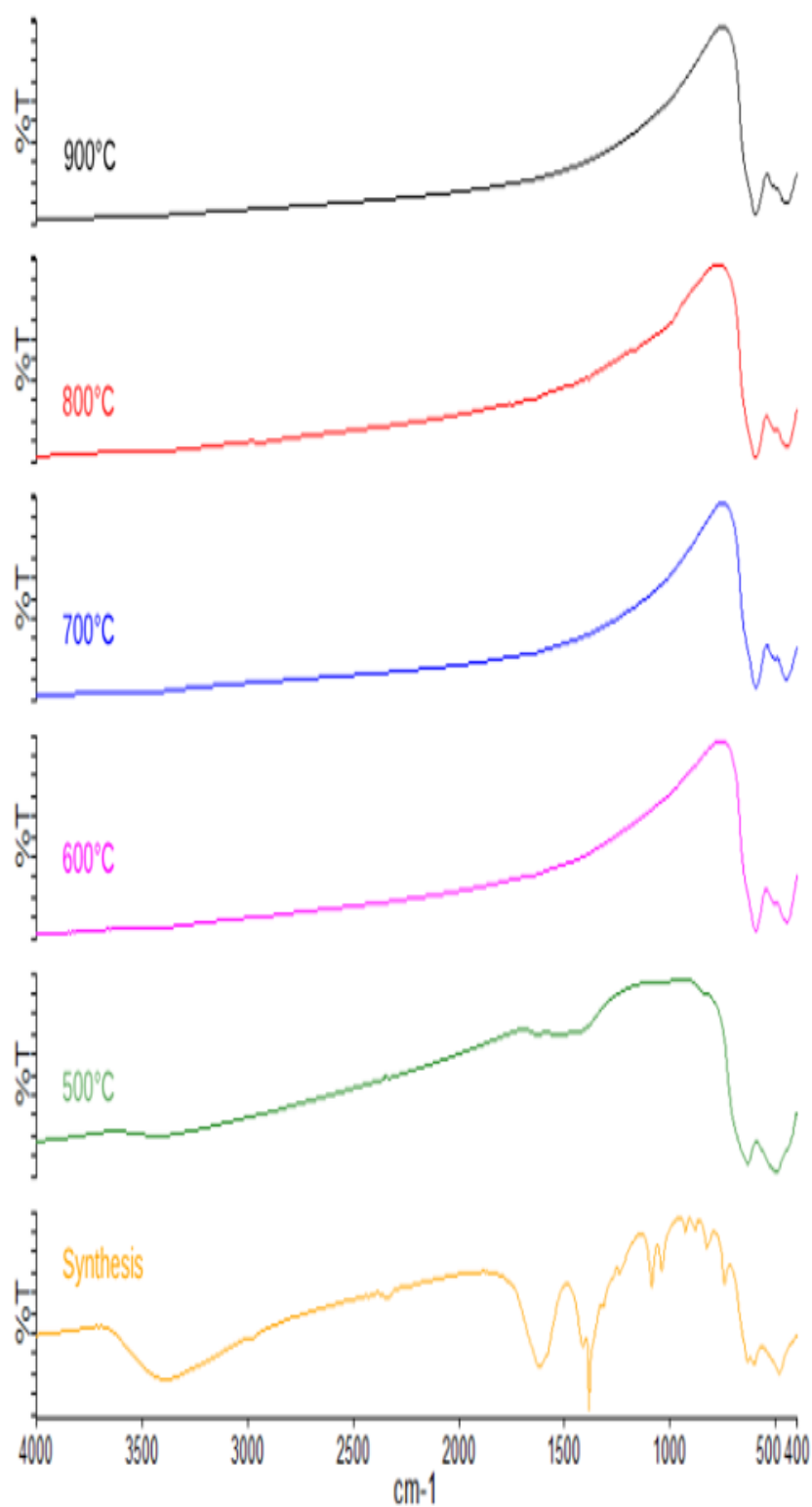


Figure 3.34 Infrared (IR) spectra of NiMn_2O_4 synthesized using tartaric acid (TA) and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

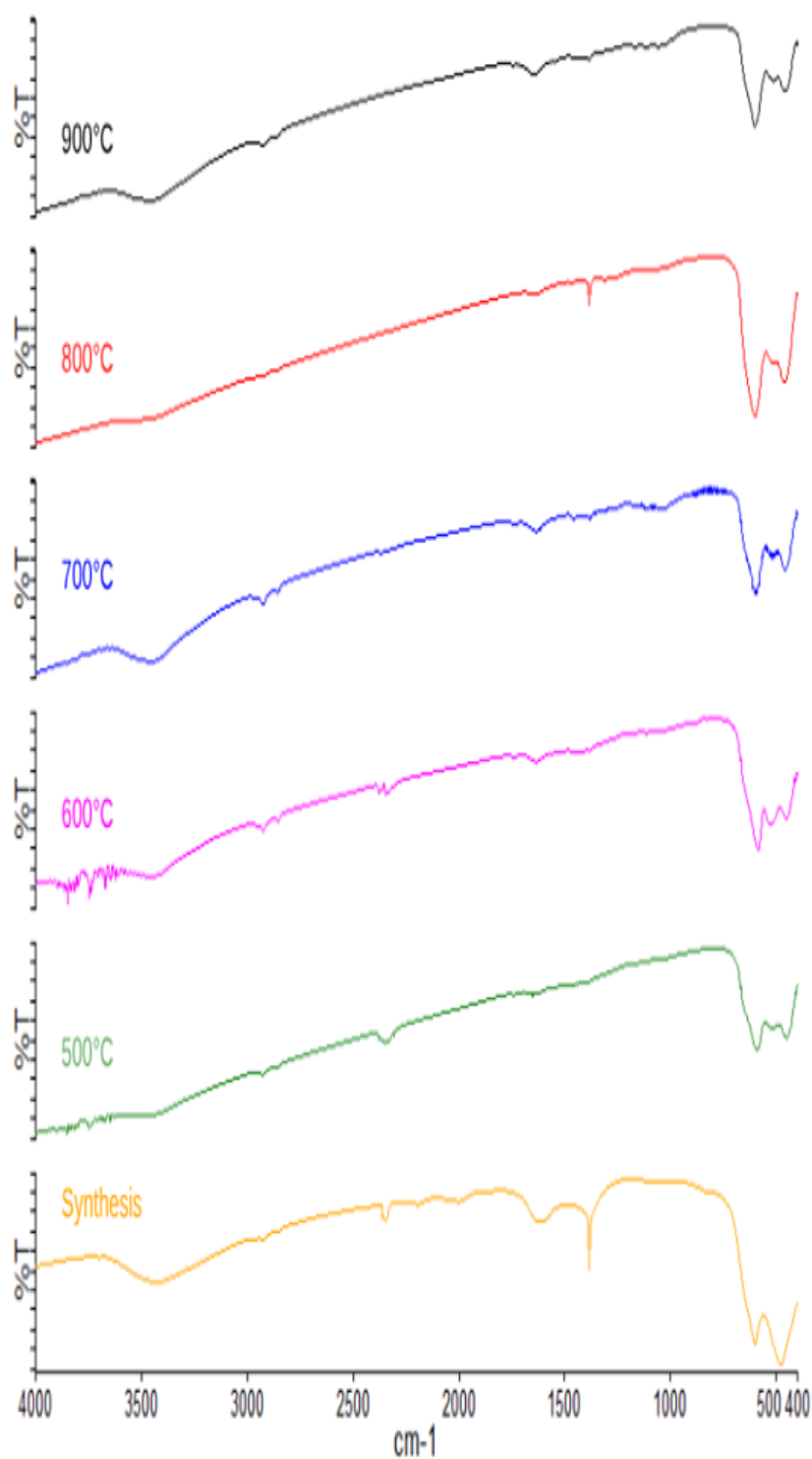


Figure 3.35 Infrared (IR) spectra of NiMn_2O_4 synthesized using Glycine and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

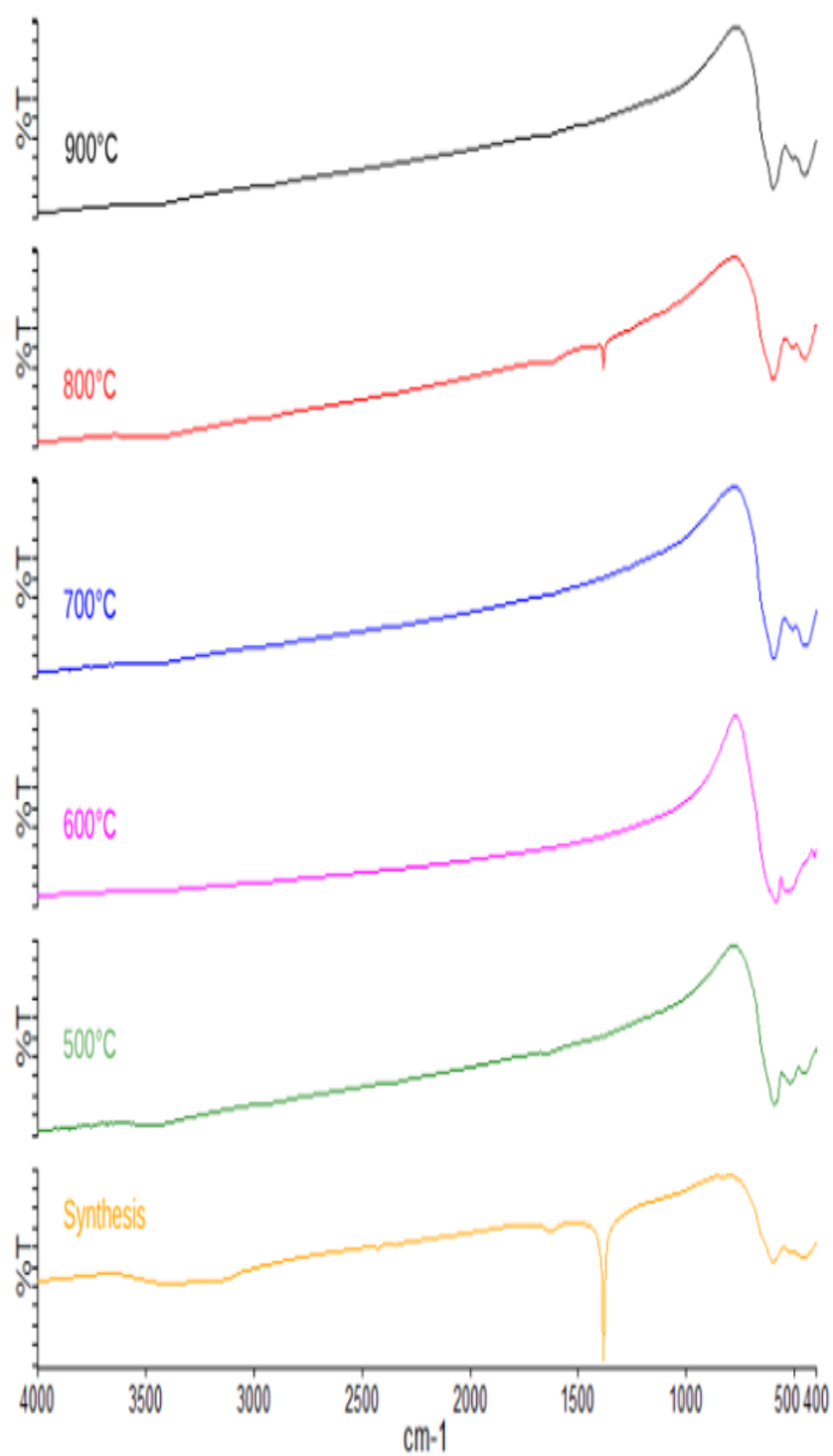


Figure 3.36 Infrared (IR) spectra of NiMn_2O_4 synthesized using Urea and calcined at various temperatures: as-synthesized, 500 °C, 600 °C, 700 °C, 800 °C, and 900 °C

4. DISCUSSION

In the first part of this thesis, the magnesium orthoborate compound in the form of kotoite was obtained in pure form by determining the appropriate method and suitable starting materials that can be obtained in a single phase. Subsequently, various rare earth metals were introduced to the obtained material at suitable concentrations, and the resulting structural alterations were identified through X-ray diffraction analysis using the Jana2006 program. Thereafter, the crystal dimensions, densities, and surface areas of the metal-doped borate materials were calculated using the Debye-Scherrer equation.

The findings of this study are presented below:

-MgO, MgCO₃, MgSO₄ and MgNO₃ starting materials were used to synthesize Mg₃(BO₃)₂ material. Mg₃(BO₃)₂ material was successfully obtained by high temperature solid state method using Mg(NO₃)₂ and 5% excess boric acid in single phase by heating at 900°C for 48 hours.

- The XRD pattern of the material obtained using Mg(NO₃)₂ and 5% excess boric acid shows that the kotoite structure is preserved intact and the diffraction peaks belong only to the kotoite compound, Mg₃B₂O₆, (ICDD no: 75-1807).

- When the infrared spectra of the obtained material are examined, it is seen that there are vibration bands belonging to kotoite, (Mg₃B₂O₆) in parallel with the XRD patterns.

- Thermogravimetric-differential thermal analysis (TG/DTA) method was used to comparatively examine the changes in thermal properties. However, since the amount of doped rare earth metals was quite small, it was determined that they did not cause any thermal change.

- Jana2006 analyses were performed for Mg₃(BO₃)₂ obtained using different starting materials and GOF values were found to be 2.49, 2.62, 1.89, 1.45 and 1.33 for materials synthesized using MgO, MgCO₃, MgSO₄ and Mg(NO₃)₂ (with 5% excess boric acid) starting materials, respectively. As a result, it was determined by

comparing the GOF values that the material obtained using $\text{Mg}(\text{NO}_3)_2$ (with 5% excess boric acid) is the most compatible with the pure kotoite structure.

- The density (d), crystallite size (t) and surface area (s) for the obtained pure $\text{Mg}_3(\text{BO}_3)_2$ compound were calculated using the Debye-Scherrer equation and it was found that the obtained pure compound has a density of 12.35 g/cm^3 , crystallite size of 40.50 nm and surface area of $11.95 \text{ m}^2/\text{g}$.

- The obtained magnesium borate compound in the form of kotoite was doped with Gd_2O_3 at various ratios to determine the optimum concentration. The reason why Gd_2O_3 compound was preferred is that it is located in the middle of the periodic table among rare earth metals and it is thought that it can give a general idea for all rare earth metals and Jana2006 analyzes were performed for the materials obtained by adding 0.10, 0.50, 1.00, 5.00, 10.0, 15.0, 20.0 % net. and it was found that the most compatible data with both XRD data and Jana2006 analysis belongs to 0.1 % net. compound. Since diffraction lines belonging to GdBO_3 started to be seen in XRD data at higher concentrations, the optimum concentration value for doping was determined as 0.1 wt. %.

- When the density (d), crystal size (t) and surface area (s) for the materials obtained by doping Gd_2O_3 at various ratios were calculated using the Debye-Scherrer equation, it was observed that the density increased from 12.35 g/cm^3 to 16.78 g/cm^3 with the amount of Gd_2O_3 in the material, while the crystal size (t) and surface area (s) decreased from 39.69 nm to 34.0 nm and from $12.24 \text{ m}^2/\text{g}$ to $10.51 \text{ m}^2/\text{g}$, respectively.

- In the XRD patterns of the materials obtained by doping La_2O_3 , Nd_2O_3 , Ce_2O_3 , Er_2O_3 , Pr_2O_3 , Sm_2O_3 , Eu_2O_3 , Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Yb_2O_3 and Lu_2O_3 rare earth metals into $\text{Mg}_3(\text{BO}_3)_2$ at the optimum value determined, It was determined that the kotoite structure was preserved intact and single phase materials were obtained in which the diffraction peaks belonged only to the kotoite, $\text{Mg}_3\text{B}_2\text{O}_6$, (ICDD no: 75-1807) compound was obtained.

- Jana2006 analyses were performed on the obtained $\text{Mg}_3(\text{BO}_3)_2$ materials doped with various rare earth metals and GOF values for La_2O_3 , Nd_2O_3 , Ce_2O_3 ,

Er₂O₃, Pr₂O₃, Sm₂O₃, Eu₂O₃, Tb₂O₃, Dy₂O₃, Ho₂O₃, Yb₂O₃ and Lu₂O₃ rare earth metals were 1.14, 1.53, 1.30, 1.13, 1.32, 1.32, 1.32, 1.24, 1.32, 1.15, 1.22, 1.15, 1.22, 1.19, 1.15 and 1.17, respectively. These results show that the materials we obtained are compatible with the kotoite structure.

- 0.1% wt. When the density (d), crystal size (t) and surface area (s) for the materials obtained by doping La₂O₃, Nd₂O₃, Ce₂O₃, Er₂O₃, Pr₂O₃, Sm₂O₃, Eu₂O₃, Tb₂O₃, Dy₂O₃, Ho₂O₃, Yb₂O₃ and Lu₂O₃ were calculated using the Debye-Scherrer equation, it was found that the density (d), crystal size (t) and surface area (s) were generally the same.

In the second part of this thesis, the spinel metal oxides (MMn₂O₄ M: Mg, Co and Ni) as nano particle products were synthesized solution combustion method using various fuels such as tartaric acid, glycine and urea and calcinated at 500 °C, 600 °C, 700 °C, 800 °C and 900 °C. Solution combustion method was selected because it is a simple, cost effective method. It also has the advantages of fast heating rates with short reaction times, combustion at low temperature in order to produce very fine powders. Also, tartaric acid using as a fuel, it is a novel approach in the synthesis of spinel metal oxides (MMn₂O₄ M: Mg, Co and Ni) with SCS method. The calcined products were obtained from the initially synthesized material, and each was heated separately; no sequential heating process was applied. Variation in fuel type and calcination temperature directly addresses the research question on their effects on material properties. A comprehensive characterization of the materials revealed their structural characteristics, with X-ray diffraction confirming that nanosized particulate compounds were obtained. Crystallite size was calculated with the Debye-Scherrer equation and lattice parameters were calculated for the tetragonal MgMn₂O₄, CoMn₂O₄ and cubic structural NiMn₂O₄.

Crystallite size is calculated with the Debye-Scherrer equation. Nanoparticle size between 19-40 nm was obtained for Tetragonal spinel-structured MgMn₂O₄. Lattice parameters were calculated as a: 5.716 Å, c: 9.176 Å with tartaric acid, a: 5.778 Å, c: 9.076 Å with glycine and a: 5.730 Å, c: 9.076 Å with urea fuel at calcinated at 900 °C. Fuel-dependent lattice parameters indicate varying tetragonal distortion and slight volume changes, consistent with differences in Mn

oxidation state, oxygen vacancy concentration, and cation inversion induced by combustion chemistry. The trend (tartaric giving the largest c/a) implies either higher Mn^{3+} fraction or greater residual strain than glycine; glycine shows the lowest distortion, consistent with higher temperature / improved ordering. When the fuel and temperature effect considered, crystallite size generally increased with calcination temperature, consistent with thermally driven grain growth. The fuel type significantly influenced the growth: urea produced the largest crystallites at 900 °C, 39.5 nm, whereas tartaric acid yielded smaller sizes 21.4 nm, likely due to differences in combustion temperature, gas evolution and chelation-driven nucleation density. The FTIR analysis showed full consistency with the XRD results, confirming the formation of the intended $MgMn_2O_4$ spinel phase. With increasing calcination temperature, all absorption bands related to organic residues and physically/chemically bound water progressively disappeared, indicating complete removal of precursor-related species.

Tetragonal spinel-structure $CoMn_2O_4$ can be clearly identified in the XRD characterization. Lattice parameters were calculated as a : 5.630 Å, c : 9.680 Å with using tartaric acid, a : 5.705 Å, c : 9.25 Å with the using glycine and a : 5.460 Å, c : 9.522 Å with using urea fuel at calcinated at 900 °C. At 900 °C the lattice parameters show a clear fuel dependence: urea yields the smallest cell volume but the highest tetragonal distortion ($c/a \approx 1.744$), glycine produces the lowest distortion ($c/a \approx 1.621$), and tartaric acid gives the largest unit-cell volume, consistent with fuel-driven differences in Mn valence, oxygen stoichiometry, cation inversion, and residual strain. Crystallite size varied significantly with both fuel type and calcination temperature. In general, higher calcination temperatures promoted grain growth, but the effect was strongly dependent on the combustion fuel. Glycine resulted in unusually large crystallites even at 500 °C, consistent with its high combustion temperature, whereas tartaric acid showed a gradual increase with temperature, peaking at 800 °C. Urea-fuelled samples displayed the highest sizes at intermediate temperatures (600–700 °C) but decreased at higher temperatures, likely due to increased microstrain or structural changes. These variations highlight the strong influence of fuel chemistry on nucleation and growth during solution combustion synthesis. Different fuels release different volumes of gases (CO_2 , H_2O , NH_3), affecting nucleation density and growth rates. Glycine

usually gives the highest adiabatic temperature, explaining the large size at low calcination temperature. Also, the FTIR analysis showed full consistency with the XRD results, confirming the formation of the intended CoMn_2O_4 spinel phase.

The XRD patterns exhibited by the NMO powders manifested a marked resemblance to the cubic structural attributes of NiMn_2O_4 (JCPDS card no: 71-0852), unequivocally ascribed to the Fd-3m space group. The presence of band positioned at 463 cm^{-1} signified the characteristic vibration mode linked to Ni-O-Mn. The FTIR data obtained for the NMO materials, combined with XRD studies, indicated the presence of well-formed spinel-NMO without any impurities. The crystallite size of NMO was further calculated with the help of Scherrer's formula $t = 0.9\lambda/\beta\cos\Theta$ by taking most intense peak. Crystallite size variation with temperature showed fuel-dependent behavior. Glycine-fuelled samples displayed a generally increasing size trend with calcination temperature, reflecting steady thermal growth. Urea produced relatively stable sizes across the 500–700 °C range, with a maximum at 800 °C before a slight decrease at 900 °C. Tartaric acid yielded pronounced non-monotonic changes, with the smallest sizes at 600 and 800 °C and the largest crystallites at 900 °C (37.47 nm). These differences are attributed to variations in combustion temperature, gas evolution, chelation effects, and their influence on nucleation density, growth rate, and residual strain in the spinel structure.

5. CONCLUSION

In this study, magnesium orthoborate in the form of kotoite ($\text{Mg}_3\text{B}_2\text{O}_6$) was successfully synthesized in pure single-phase form by determining the appropriate method and suitable starting materials. Comparative experiments using MgO , MgCO_3 , MgSO_4 , and $\text{Mg}(\text{NO}_3)_2$ as magnesium sources demonstrated that the most phase-pure kotoite structure was obtained via the high-temperature solid-state method using $\text{Mg}(\text{NO}_3)_2$ with 5% excess boric acid, calcined at 900 °C for 48 h. XRD and FTIR analyses confirmed the preservation of the kotoite structure, while TG/DTA analysis indicated that the small amounts of rare earth dopants did not significantly affect the thermal properties of the host compound. Structural refinement using the Jana2006 program yielded the lowest GOF value (1.33) for the $\text{Mg}(\text{NO}_3)_2$ -based synthesis, confirming its superior structural compatibility with the reference kotoite phase. The Debye–Scherrer analysis of the pure $\text{Mg}_3\text{B}_2\text{O}_6$ revealed a crystallite size of 40.50 nm, density of 12.35 g/cm³, and surface area of 11.95 m²/g. Doping studies began with Gd_2O_3 to determine the optimum rare earth substitution level. Structural and diffraction data indicated that 0.1 wt.% was the optimal concentration, as higher doping levels led to the appearance of secondary GdBO_3 phases. At the optimum Gd_2O_3 concentration, density increased while crystallite size and surface area decreased, suggesting lattice incorporation and possible defect generation. Extending the study to a broader range of rare earth dopants (La, Nd, Ce, Er, Pr, Sm, Eu, Tb, Dy, Ho, Yb, and Lu) at the 0.1 wt.% level confirmed that the kotoite structure remained intact in all cases, with no secondary phases detected by XRD. Jana2006 refinement results (GOF values ranging from 1.13 to 1.53) further verified the structural integrity and phase purity of the doped materials. The calculated densities, crystallite sizes, and surface areas for the doped samples were generally consistent across different rare earth elements, indicating similar structural accommodation mechanisms. Overall, this work demonstrates that phase-pure kotoite can be reproducibly synthesized from optimized starting materials and that rare earth doping at low levels preserves the structural integrity of the host lattice. The combination of XRD, FTIR, TG/DTA, and Jana2006 refinement provides a comprehensive understanding of the structural stability and microstructural evolution of rare earth–doped magnesium borates, offering a robust foundation for potential applications in optical, electronic, and ceramic materials.

In the second part of this work, tetragonal MgMn_2O_4 and CoMn_2O_4 , as well as cubic NiMn_2O_4 spinel nanoparticles, were successfully synthesized via the solution combustion method (SCS) using tartaric acid, glycine, and urea as fuels. The products were calcined at 500–900 °C and characterized to investigate the effects of calcination temperature and fuel type on particle size and crystallinity. Crystallite size was calculated with the Debye-Scherrer equation and lattice parameters were calculated for the tetragonal MgMn_2O_4 , CoMn_2O_4 and NiMn_2O_4 . and results shows that all synthesized products are nano sized. For each product synthesized with the three different fuels, an increase in crystallinity was observed even after short-term heating at low temperatures. In all fuels, crystallinity generally increased with increasing temperature. Furthermore, evaluation of the FTIR results revealed that all water and organic residues were removed after heating at 500 °C and showed full consistency with the XRD results, confirming the formation of the intended MgMn_2O_4 , CoMn_2O_4 and NiMn_2O_4 spinel phase.

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