

ABANT İZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES



SYNTHESIS AND CHARACTERIZATION OF UNDOPED AND
DOPED MAGNESIUM OXIDE NANOPARTICLES

MASTER OF SCIENCE

GÖZDE ŞAHİN

BOLU, JUNE 2017

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DEPARTMENT OF CHEMISTRY



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APPROVAL OF THE THESIS

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MAGNESIUM OXIDE NANOPARTICLES** submitted by **Gözde ŞAHİN** in
partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE**
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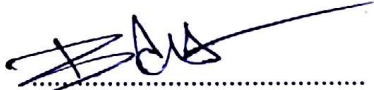
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Director of Graduate School of Natural and Applied Sciences

To my lovely family;

DECLARATION

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Gözde ŞAHİN

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF UNDOPED AND DOPED MAGNESIUM OXIDE NANOPARTICLES

MSC THESIS

GÖZDE ŞAHİN

ABANT İZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF
NATURAL AND APPLIED SCIENCES

DEPARTMENT OF CHEMISTRY

(SUPERVISOR: PROF. DR. AYŞE MORKAN)

BOLU, JUNE 2017

In this study, undoped and rare earth, RE, metal ion (RE:Pr^{+3} , Ho^{+3} , Tb^{+3}) doped magnesium oxide nanoparticles were synthesized by solution combustion synthesis method. The products obtained were well characterized by X-ray Diffraction (XRD), Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM), EDX (Energy Dispersive X-ray Analysis) techniques.

In the first part of this work, undoped magnesium oxide (MgO) was prepared using magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as an oxidizer and various fuels; tartaric acid, urea, citric acid, 1,6-Diaminohexane, hexamethylenetetramine, β -Alanine, glycine and carbohydrazide as reducers through the solution combustion method. It was found that tartaric acid, urea, citric acid, 1,6-diaminohexane, hexamethylenetetramine fuels were suitable while β -alanine, glycine and carbohydrazide fuels were not suitable in the synthesis of MgO nanoparticles because of causing very low amount of yield of the products. Hence the appropriate fuels were selected for the further processes in the synthesis of nano sized magnesium oxides.

In the second part of this thesis, 0.005, 0.01, 0.03 moles of RE metal ion (Pr^{+3} , Ho^{+3} , Tb^{+3}) doped MgO were synthesized using five different fuels; tartaric acid, hexamethylenetetramine, 1,6-Diaminohexane, citric acid, urea. In order to get rid of the organic compounds and to obtain a more crystalline material, the prepared products by combustion process at 400°C for 10 min. were heated at 400°C , 500°C respectively for one hour. Then, characterization was performed with IR, XRD, SEM, EDX for each concentration and temperature.

Continuation of this work, the effect of temperature, fuel, type of RE metal, concentration of RE metal on the properties of synthesized magnesium oxides such as crystallinity, crystallite size, purity and morphology were investigated.

KEYWORDS: : Solution Combustion Synthesis (SCS), MgO, RE metal doped MgO, XRD, SEM.

ÖZET

**KATKISIZ VE KATKILI MAGNEZYUM OKSİT
NANOPARÇACIKLARIN SENTEZİ VE KARAKTERİZASYONU
YÜKSEK LİSANS TEZİ
GÖZDE ŞAHİN
ABANT İZZET BAYSAL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ
KİMYA ANABİLİM DALI
(TEZ DANIŞMANI: PROF. DR. AYŞE MORKAN)
BOLU, HAZİRAN - 2017**

Bu çalışmada, katkısız ve nadir toprak metali iyonu, NTE, (NTE: Pr^{+3} , Ho^{+3} , Tb^{+3}) katkılı magnezyum oksit nanoparçacıkları, çözeltide yanma sentez yöntemi ile hazırlanmıştır. Elde edilen ürünlerin karakterizasyonu X-ışını Kırınımı (XRD), Kızılötesi Spektroskopisi (IR), Taramalı Elektron Mikroskopisi (SEM), Enerji Dağılımlı X-ışını Analizi (EDX) teknikleri ile yapılmıştır.

Bu çalışmanın ilk bölümünde, katkısız magnezyum oksit (MgO), magnezyum nitrat ($\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) kaynağı ve ayrı ayrı tartarik asit, üre, sitrik asit, 1,6-Diaminohekzan, heksametilentetramin, β -Alanin, glisin ve karbohidrazid yakıtları kullanılarak 400°C 'de çözeltide yanma sentez tekniği ile sentezlenmiştir. Bu yakıtlardan, tartarik asit, üre, sitrik asit, 1,6-Diaminoheksan, heksametilentetraminin, saf MgO sentezi için uygun olduğu ancak düşük verimli ürün edildiğinden β -Alanin, glisin ve karbohidrazid yakıtlarının ise uygun olmadığı saptanmış ve bu nedenle, sonraki aşamalarda bu son üç yakıt kullanılmamıştır.

Çalışmanın ikinci bölümünde, 0.005, 0.01, 0.03 mol oranlarında NTE (NTE: Pr^{+3} , Ho^{+3} , Tb^{+3}) katkılı magnezyum oksit nanoparçacıkları ayrı ayrı tartarik asit, 1,6-Diaminohekzan, heksametilentetramin, sitrik asit, üre yakıtları kullanılarak sentezlenmiştir. 400°C 'de 10 dakika yanma işlemi tamamlandıktan sonra organik bileşiklerden kurtulmak ve daha kristalin bir ürün elde etmek için, sentezlenen tüm ürünler bir saat boyunca sırasıyla 400°C , 500°C 'de ısıtılmış ve her konsantrasyon ve sıcaklık için elde edilen maddelerin karakterizasyonu gerçekleştirilmiştir.

Çalışmanın devamında sıcaklık, yakıt, katkılanan metalin çeşidi ve katkı metali konsantrasyonunun, sentezlenen magnezyum oksitin kristallik derecesine, kristalit büyüklüğüne, saflığına ve morfolojisine olan etkileri incelenmiştir.

ANAHTAR KELİMELEER: Çözelti Yanma Sentez Yöntemi, MgO , NTE katkılı MgO , XRD, SEM

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LIST OF ABBREVIATIONS AND SYMBOLS

SCS	: Solution Combustion Synthesis
CS	: Combustion Synthesis
SHS	: Self-propagating High-temperature Synthesis
XRD	: X-ray Diffraction Spectroscopy
FTIR	: Fourier-Transform Infrared Spectroscopy
SEM	: Scanning Electron Microscope
EDX	: Energy Dispersive X-ray Analysis
ICDD	: International Centre for Diffraction Data
R.T	: Room Temperature
TA	: Tartaric Acid
HMDA	: 1,6-Diaminohexane
HMTA	: Hexamethylenetetramine
CA	: Citric Acid
U	: Urea
Gly	: Glycine
CH	: Carbohydrazide
TL	: Thermoluminescence
OSL	: Optically Stimulated Luminescence
RE	: Rare Earth

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1. INTRODUCTION

1.1 Nanomaterials

Nanotechnology concern with design, fabrication and application of materials or structure in nanometer scale, one billionth of a meter or 10^{-9} meter. Nanotechnology has wide range of potential applications including medicine, biotechnology, water decontamination, agriculture, renewable and sustainable energy, physics, electrical engineering, mechanical engineering, materials science, and more. It also enables the production of stronger and lighter materials (P. Bueno et al., 2017; Chen and Yada, 2011; Emerich and Thanos, 2003; Hussein, 2016; Sahoo et al., 2007; Share et al., 2016).

Synthesis and operation of nanomaterials are the essential aspect of nanotechnology. Micrometer scale materials generally show the same properties with the bulk form, but nanometer scale materials show some remarkable specific properties distinctively different from the bulk form (Dowling, 2004). For example, while bulk gold does not exhibit catalytic properties, Au nanocrystal shows excellent low temperature catalyst feature (Cao, 2004). In energy storage systems, nanomaterials also have fast recharging capability, better durability, and high storage capacity than bulk material counterparts (Share et al., 2016).

There are several classes of inorganic nanoparticles such as nanometals, metal oxides, metal hydroxides, metal salts that show different feature in different fields. Among these inorganic classes, metal oxide nanoparticles have special interest. Nanosized magnesium oxides, manganese oxides, ferric oxides, aluminum oxides, cerium oxides, and titanium oxides are the examples of metal oxides. Metal oxides' high surface area, small particle size and shape, surface chemistry properties lead to have constituted various scientific interest (Topnani et al., 2010). They allow for numerous applications and uses in industry and consumer products such as environmental remediation, medical technology, energy, water treatment, personal care products etc. owing to their heightened electronic, chemical and physical

properties (Brys et al., 2016; Contreras et al., 2017; Emerich and Thanos, 2003). They also play an important role in the fabrication of nanoscale optoelectronic and electronic devices (Gandhi et al., 2011). Especially during the last decade efficient synthesis methods have been widely studied to obtain highly stable, shape-controlled, and monodisperse metal oxide nanomaterials (Hua et al., 2012).

1.2 Structure and Applications of MgO

Magnesium oxide is isomorphous compound with rock salt structure (face centered cubic-fcc) like NaCl (See Figure 1.1). The magnesium ions (Mg^{+2}) occupy the octahedral sites within the anion closed packed structure (Zhu et al., 2006).

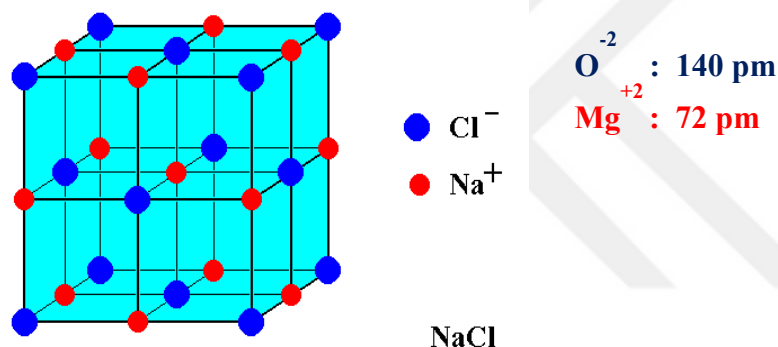


Figure 1. 1. NaCl structure. In MgO, Mg substitutes for Na, while O substitutes for Cl. The ionic radius of O will be larger than Mg

Magnesium oxide that have great ionicity and simple crystal structure seems to serve form outstanding building blocks for the construction of functional nanostructures, or to serve as a suitable model compound for the investigation of surface reactivity on oxides (P. B. Devaraja et al., 2014). The surface of MgO is enriched with low coordinated ions, acidic Mg^{2+} ions, basic oxygen anion, cationic magnesium vacancy and anionic oxygen vacancies. These surface defects and ions on the surface of MgO are the active sites for the chemical interaction with CO_2 , NO_2 , in the oxidation and decomposition of methanol, dehydrogenation of ethylbenzene, in the oxidation of CO, etc. (Choudhury and Choudhury, 2014). When the magnesium oxide particles are made smaller so as to include more defects, the new and useful features of MgO are further improved. Doping of rare earth or transition metals into the metals oxides also are very beneficial method to vary its

chemical and physical properties. Besides, rare earth or transition metal doped oxide generates lattice defects such as vacancies. These defects play a significant role in altering the physical and chemical features of the oxide to a specific extent (Cui et al., 2015; Lu et al., 2007).

The shape and size of MgO nanoparticles depend largely on their synthesis route and processing conditions. MgO nanostructures were synthesized with much different morphologies like nano particles (Park et al., 2006), nano tubes, nano wires, nano belts (Yan et al., 2008), nano sheets (Zhang et al., 2012), whiskers (with diameters of about 60–80 nm) (Shi et al., 2008), nano fibers (Shao et al., 2006), and other morphologies. When the size effect is determined in nanoparticles, reduction in the particle size in a crystalline system can result in remarkable modification of properties compared to those of bulk due to high surface-to-volume ratio. Due to its controllable speciality, it has attracted unusual interest for their primary features and technological applications. The high efficiency of the nanoparticle oxides is caused not only by their high surface area but also by the high concentration of low coordinated sites and structural defects on their surface.

Magnesium oxide has attracted great interest for its applications in the chemical and electronic industries. Its powder has been used in thermoluminescence (TL) dosimetry (Ziniker et al., 1973), pharmaceuticals (Shen et al., 2007), semiconductors, catalyst and catalyst support (Xu et al., 2001), waste remediation (Nagappa and Chandrappa, 2007) etc. MgO is known for a long time as thermoluminescent material (McKeever et al., 1995). In these kind of applications transition metal ions (notably Fe, Cr, Mn, Al, Ti, Ni, V) as dopant play a key role in the luminescence mechanism (Ahmed et al., 2016; Devaraja et al., 2015; Kato et al., 2016). Rare earth ions also have been playing an important role in modern lighting and display fields due to the abundant emission colors. Orante-Barrón et al. (2011) examined luminescence and thermoluminescence (TL), which is technique widely used in radiation dosimetry, computed radiography, properties of undoped and different doped lanthanides (Ln) and co-doped lithium(Li) MgO which is synthesized by SCS method. Also, Bos et al. (2006) studied on terbium-doped MgO (MgO:Tb^{3+}) to extend to number of suitable OSL materials for dosimetric applications. The Ln^{3+} ions which have luminescence properties have high luminescence quantum yield, narrow bandwidth, long-lived emission, large Stokes shifts, ligand-dependent

luminescence sensitization. Among the rare earth ions, Sm^{+3} emits strong orangish - red luminescence, Dy^{+3} white in the visible region, which are attractive in lighting color displays, plasma display panels (P. Devaraja et al., 2014; Kiran et al., 2017; C. Li and Lin, 2010). In addition to showing unique absorption and luminescence properties, nanocrystalline MgO exhibits ferromagnetism owing to the presence of oxygen or Mg vacancies. Kumar et al. (2012) have studied the influence of oxygen vacancies and hydride ions on the ferromagnetism in MgO nanocrystallites. Besides, Khamkongkao et al. (2017) studied to understand magnetic properties of MgO the transition from diamagnetism to ferromagnetism.

In catalysis application, magnesium oxide with high surface area and nanocrystalline structure exhibit good properties as both catalyst and catalyst support for some reactions such as dehydrohalogenation, dry reforming, oxidative dehydrogenation of butane, etc. To extend the application of MgO's as catalysts, it is essential to tailor their surface chemistry as well as morphologies, as the catalytic process occurs only over the surface. Small particulates MgO nanocrystals show unexpectedly high surface chemical reactivities that have allowed their successful use as high capacity destructive adsorbents for toxic chemicals, including chlorocarbons, organophosphorus compounds, and acid gases like SO_2 (Chesnokov et al., 2003; Mishakov et al., 2002; Xu et al., 2001).

MgO nanoparticles is also widely used for toxic waste remediation and antibacterial action due to its well-defined surface defect structure, which includes low-coordinated ions and vacancies and their abundant source of raw materials, high thermal stability, low biological toxicity and biodegradability (Di et al., 2012; Makhluf et al., 2005). It can absorb some ionic organic and waste gases because of the large number of defects present on the surface. Some studies show that doped MgO has more effective as inorganic antibacterial agents. Cai et al. (2017) studying revealed that Ag doped MgO can greatly enhance the antibacterial activity of MgO nanoparticles. Also, Cui et al. (2015) reported that the Cu-doped MgO exhibits better antibacterial activity than pure MgO due to the enhancement of defect concentration (oxygen vacancy) and copper content.

The another significant feature of MgO is that a wide band gap insulator with band gap of 7.8 eV. This feature make them functional both fundamental and

application studies for magnetic tunnel junction (MTJ) for semiconductor spintronics, as coating layer onto TiO₂ electrode to enhance the solar conversion efficiency, as additives in superconductor products, as refractory paints, as an antibacterial agent and as a substrate for the growth of thin film (Bhargava et al., 1998; Choudhury and Choudhury, 2014; Copp, 1995).

1.3 Synthesis Methods of Magnesium Oxide

The most conventional method of synthesis of MgO is the thermal decomposition of various magnesium salts or magnesium hydroxide which results in an inhomogeneous morphology and crystallite size with a low surface area (Ding et al., 2000). When it compares to other techniques, combustion technique has become more popular in the last decade. It is an important synthesis technique for oxide nanoparticles because of being very simple experimental set-up and providing molecular level of mixing, high degree of homogeneity, fast, ultra pure, large surface area, cost effective etc. Also, besides being able to be applied in the laboratory, SCS may be promising synthesis method for commercial needs (Premkumar et al., 2013; Umesh et al., 2012).

In industry, oxide powders are generally fabricated by high-temperature solid-state reactions, where the desired products are achieved simply by maintaining the solid mixture of reactants at a high temperature (Wen and Wu, 2014). However, in the synthesis of oxide nanostructure materials have been applied a lot of methods. Sol-gel (Kordas, 2000; Mbarki et al., 2015), hydrothermal synthesis (Wang et al., 2008), simple precipitation (Rezaei et al., 2011), flame metal combustion (Chae et al., 2017), chemical vapor deposition (Saitoh et al., 2002) are the some examples of producing highly quality nanosized powders. Most of these synthesis methods are not economically feasible for the large-scale production of nanoscale materials (A. R. Bueno et al., 2014). They usually include many complicated processes and consume much longer time. Moreover, they have not received much commercial attention due to lacking of reproducibility, reliability and cost effectiveness. Therefore, simple synthesis method was required to overcome these problems. Also, in prior review on combustion synthesis is published in 2002 revealed that conventional solid state self-

propagating high-temperature synthesis (SHS) being a gasless combustion process typically yield much coarser particles than solution combustion approach (Aruna and Mukasyan, 2008; Patil et al., 2002).

Rezaei et al. (2011) and Kumar and Kumar (2008) studies respectively show that the required temperature for the synthesis of MgO with simple precipitation method is from 600°C to 800 °C and 1000°C with sol-gel technique. Utamapanya et al. (1990) prepared ultrahigh surface area MgO powders with size of about 5 nm via a sol-gel technique. However, the need to synthesize and handle the costly and hazardous metal-organic precursors in the sol-gel procedure seems inconvenient and also not economically acceptable.

When all methods are considered, solution combustion synthesis (SCS) has been versatile, simple and rapid process that allows effective synthesis of wide range of nano-size materials with desired phase and morphology (Devaraja et al., 2015). These features make the method attractive for the production of technologically important materials when compared to the conventional synthesis method (Premkumar et al., 2013).

1.3.1 Solution Combustion Synthesis of MgO

Combustion Synthesis (CS) is oxidation-reduction reaction is used to produce useful materials like structural and functional advanced ceramics, alloys, catalysts and nanomaterials. This method was accidentally discovered in 1988 in Prof. Patil's lab in India (Ekambaram et al., 2005). Depending upon the nature of reactants: elements or compounds (solid, liquid or gas) and the exothermicity, CS is described as: self-propagating high temperature synthesis (SHS); low-temperature combustion synthesis (LCS), emulsion combustion, volume combustion (thermal explosion), gel-combustion, sol-gel combustion, solution combustion synthesis (SCS) etc. (Patil et al., 2002).

Owing to the having combination of combustion and a reactive solution, method is called as solution-combustion synthesis (SCS) method. Basically, SCS involves a self-sustained reaction in solutions of metal nitrates and different fuels.

The reaction occurs between fuel and oxygen-containing species. Final product is formed during decomposition of nitrates by providing conditions for rapid high-temperature interaction (Deshpande et al., 2004). Some notable features of SCS contribute to the unique properties of the synthesized products. Firstly, the initial reaction media existence in the liquid state (e.g. aqueous solution) allows mixing of the reactants on a molecular level, thus permitting precise and uniform formulation of the desired composition on the nanoscale. Secondly, the high reaction temperatures provide high product purity and crystallinity (Reddy et al., 2011). Lastly, the short process duration and formation of various gases like CO₂, N₂ during SCS inhibit particle size growth and ease synthesis of nanosized powders with a high specific surface area. All these properties make SCS attractive for the synthesis of nanomaterials for a variety of applications, including nanophosphors, catalysts, fuel cells, and biotechnology (Mukasyan and Dinka, 2007).

SCS method is based on the exothermic redox chemical reaction. It is carried out between a metal salt and a fuel resulting in nanocrystals with composition consistent with the initial reagents (Barron et al., 2016). Metal salts, including nitrates, sulfates and carbonates are used as oxidant and fuels as reducing reagents, such as urea, glycine, tartaric acid, starch, hexamine (F. T. Li et al., 2015). In this study, magnesium nitrate was used as oxidizing and TA, HMDA, HMTA, CA, U as reducing agent. Patil et al. (2002) study shows that some fuels are specific for a particular class of oxides e.g. urea for alumina and related oxides (Mimani, 2000), glycine for chromium and related oxides, carbohydrazide for zirconia and related oxides etc. After all, all fuels for SCS process have two basic functions. First one, they are the source of hydrogen and carbon, which on combustion form CO₂ and H₂O and release heat. Second one is forming complexes with the metal ions facilitating homogeneous mixing of the cations in solution.

SCS is also allow to yield nanosize oxide materials and obtain uniform doping of trace amounts of rare-earth impurity ions in a single step. (Bos et al., 2006) The studies in recent years show that the synthesis of nanophosphors is the most popular topic in SCS field. Also, SCS and investigating the role of dopants are the efficient way to synthesize TL / OSL material (Yukihara et al., 2013).

Urea and glycine are the most preferred fuels for the synthesis of phosphorus material. Because they are popular and attractive fuels for producing highly uniform, complex oxide ceramic powders with precisely controlled stoichiometry (Aruna and Mukasyan, 2008). Even though the glycine nitrate process (GNP) has been billed as ‘environmentally compatible (Chick et al., 1990), Pine et al. (2007) study has shown CO and NO_x as the products of incomplete combustion in GNP. Therefore, the potential for producing and emitting hazardous nitrogen oxides and CO must be considered for GNP technique in industrial scale.



Table 1.1. Studies of MgO

Doped Metal	Synthesis Method	References
CeO ₂	SCS	(Barron et al., 2016)
Li, Gd	SCS	(Oliveira, Doull, et al., 2013)
Cr ⁺³	SCS	(Devaraja et al., 2016)
Sm ⁺³	SCS	(Kiran et al., 2017b)
Mn ⁺²	Sol-gel method	(Ahmed et al., 2016)
Fe ⁺³	SCS	(Devaraja et al., 2015)
Dy ⁺³	SCS	(Devaraja, Avadhani, et al., 2014a)
Nd, Li	SCS	(Oliveira, Milliken, et al., 2013)
Eu ⁺³	SCS	(Devaraja, Avadhani, et al., 2014b)
Tb ⁺³	-	(Bos et al., 2006)
La with Co-doped Li	SCS	(Yukihara et al., 2013)
Ce, Tm, Eu, Tb and co-doped Li	SCS	(Orante-Barrón et al., 2011)
Undoped	Precipitation method	(Rezaei et al., 2011a)
Undoped	Facile Synthesis	(W. Wang et al., 2007)
Undoped	Hydrothermal Syn.	(Ding et al., 2000)
Undoped	Sol-gel Combustion	(A. R. Bueno et al., 2014)
Ta, W and Re	Nitrogen fixation	(Yadav et al., 2016)
Na, D, Ce, Eu, Gd, Dy and Yb	Carbon Arc Fusion Tech.	(Abraham et al., 1971)
Er + Li, Na and K	SCS	(Sivasankari et al., 2017)
Nb	Mechanochemical syn.	(Pukazhselvan et al., 2016)

2. AIM AND SCOPE OF THE STUDY

The aim of this study is to synthesize single phase, pure and qualified undoped and doped MgO nanoparticles by solution combustion synthesis method.

- MgO nanoparticles were prepared using tartaric acid, citric acid hexamethylenetetramine, 1,6-Diaminohexane, urea, carbohydrazide, glycine and β -Alanine fuels.
- The products obtained by the combustion process that completed at 400°C for 10 min. were furtherly heated at 400°C and 500°C, 1h respectively in order to increase the crystallinity.
- The characterization of undoped MgO was performed with IR, XRD, SEM and EDX for each temperature.
- MgO: RE (Pr^{+3} , Ho^{+3} , Tb^{+3}) nanoparticles were synthesized using five different fuels; tartaric acid, hexamethylenetetramine, 1,6-Diaminohexane, citric acid, urea.
- RE (Pr^{+3} , Ho^{+3} , Tb^{+3}) ion concentration was varied as 0.005, 0.01, 0.03 mol.
- RE doped MgO's were furtherly heated at 400°C and 500°C, 1h respectively after the combustion process was completed at 400°C for 10 min. and the characterization was performed with IR, XRD, SEM and EDX for each temperature.

As a summary, four different parameters; temperature, type of rare earth metal, concentration of doped metal ion and kind of fuel were examined about how they affect the crystallinity, crystallite size, morphology and purity of magnesium oxide nanoparticles.

3. MATERIALS AND METHODS

3.1 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: Merck (pure 99.0%)

$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Praseodymium (III) nitrate hexahydrate: Aldrich (pure 99.5)

$\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$: Holmium (III) nitrate pentahydrate: Aldrich (pure 99.5%)

$\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$: (III) nitrate hexahydrate: Aldrich (pure 99.5%)

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

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

$\text{C}_6\text{H}_{12}\text{N}_4$, Hexamethylenetetramine: Merck (pure 99.0%)

$\text{C}_6\text{H}_{16}\text{N}_2$, 1,6-Diaminohexane: Merck (pure 99.0%)

$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, Citric Acid Monohydrate: Merck (pure 99.5%)

$\text{C}_3\text{H}_7\text{NO}_2$, β -Alanine: Merck (pure 99.0%)

$\text{CH}_6\text{N}_4\text{O}$, Carbohydrazide: Merck (pure 98.0%)

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

KBr: Spectroscopic grade and it was used for making IR pellets.

It was dried at 180°C before using.

3.2 Instruments

3.2.1 X-Ray Powder Diffractometer

X-ray powder diffraction patterns (XRD) were recorded on Rigaku multiflex, BD127412, and CuK α (30-40 kV, 10-20 mA, $\lambda=1.54056$ Å) radiation. Indexing of the XRD pattern was checked by the Rigaku Programme.

3.2.2 Infrared Spectrophotometer

Shimadzu FT-IR-8400S 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 with KBr pellets using 0.0010:0.150 (wt/wt) product to KBr ratio.

3.2.3 Scanning Electron Microscope - Energy Dispersive X-ray

SEM-EDX photographs were taken using Jeol JSM 6390LV. The samples used for SEM were coated with carbon.

3.2.4 Furnaces

All the reactions have been carried out in air with the aid of Nuve MF 1400, Nuve 1200 and Protherm 1600 furnaces.

3.3 Experimental Procedure

3.3.1 Synthesis of Undoped MgO Using TA, HMDA, HMTA, CA and U Fuels

MgO nanocrystalline powders were obtained from an inorganic salt, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor and an organic fuel; TA, HMDA, HMTA, CA, U.

In the first step, stoichiometric amount of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and tartaric acid were mixed and dissolved in minimum amount of distilled water in porcelain evaporating dish. Homogenized solution was heated on hot plate at 370°C till the all gases evaporated. When the all gases were evaporated and gelation was started it was placed at the preheated (400°C) furnace for 10 min. Obtained solid substance was cooled down to room temperature and crushed down. Then, it was divided into two for the next heat treatment.

In the next step, substance was placed into the furnace at 400°C , 500°C respectively for 1 hour to remove organic compounds and observe the temperature effect. At the end of each heating period including 400°C , 10 minutes, the substance was crushed well and analyzed with FTIR and XRD.

MgO synthesis using HMDA, HMTA, CA, U fuels was carried out by the procedure described above.

3.3.2 Synthesis of Undoped MgO using β -Alanine, Carbohydrazide and Glycine Fuels

Stoichiometric amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and β -Alanine were mixed and dissolved in minimum amount of distilled water. Firstly, the reaction was carried out on the hot plate at 370°C in porcelain evaporating dish. A strong combustion was observed but sample was remained as gel in the middle of the evaporating dish. Therefore, the same reaction was repeated in the 400 mL glass beaker to get

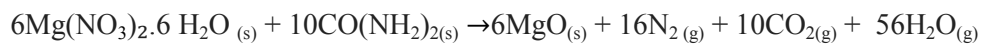
reasonable product. However, although three combustions were seen no significant amount of substance was obtained.

Stoichiometric amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and carbohydrazide were mixed and dissolved in minimum amount of distilled water in porcelain evaporating dish. Firstly, the reaction was carried out on the hot plate at 370°C but most of the substance remained as gel and fluffy or powder substance could not be obtained for analysis. Hence, the synthesis procedure was modified and first of all, the same mixture was heated on hot plate till all gases evaporated. Then, it was placed into the furnace that was set at 400°C for 5 min. However, at the end of this process most of the substance again was missing. Only IR analyses could be performed with the limited amount of substance.

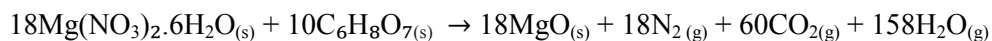
Stoichiometric amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and glycine were mixed and dissolved in minimum amount of distilled water in porcelain evaporating dish. When all the gases evaporated and gelation started, it calcined at the preheated (400°C) furnace for 5 min. The process was carried out twice but all substances again were missing.

The predicted reactions;

Urea Fuel:



Citric Acid Fuel:



Tartaric Acid Fuel:



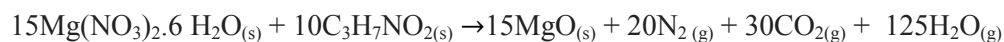
Hexamethylenetetramine:



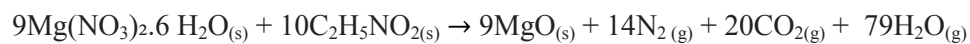
1,6-Diaminohexane:



β -Alanine:



Glycine:



Carbohydrazide:



3.3.3 Synthesis of Rare Earth (RE: Pr^{+3} , Ho^{+3} , Tb^{+3}) doped MgO Using TA, HMDA, HMTA, CA and U Fuels

Magnesium oxide (MgO) powders were synthesized with different amounts of Pr^{+3} , Ho^{+3} , Tb^{+3} ions by solution combustion process. Dopant concentrations were used as 0.005, 0.01, 0.03 mol.

The raw materials, magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) and praseodymium nitrate ($\text{Pr}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$), holmium nitrate ($\text{Ho}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$), terbium nitrate ($\text{Tb}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$) were the source of Mg and Pr, Ho, Tb respectively. Each RE metal nitrate was reacted with different fuels; TA, HMDA, HMTA, CA, U to prepare MgO:RE nanomaterials. Stoichiometric composition required for combustion process was calculated based on total oxidizing and reducing valances of oxidizer and fuel. The process was performed by dissolving above reagents together in a minimum amount of distilled water and the concentration of the rare earth metal ions were varied in the 0.005, 0.01, 0.03 mol. Using a magnetic stirrer, the materials were uniformly mixed in a porcelain evaporating dish and heated until gel formation was observed. Then, it was introduced into a preheated furnace maintained at 400°C . The entire combustion process for producing RE metal doped MgO substance took only 10 min.

Crushed sample was again placed into the preheated furnace 400°C , 500°C respectively for 1 hour to get rid of all organic compounds. At the end of each heating period including 400°C 10 min., the substances were analyzed with FTIR, XRD and SEM.

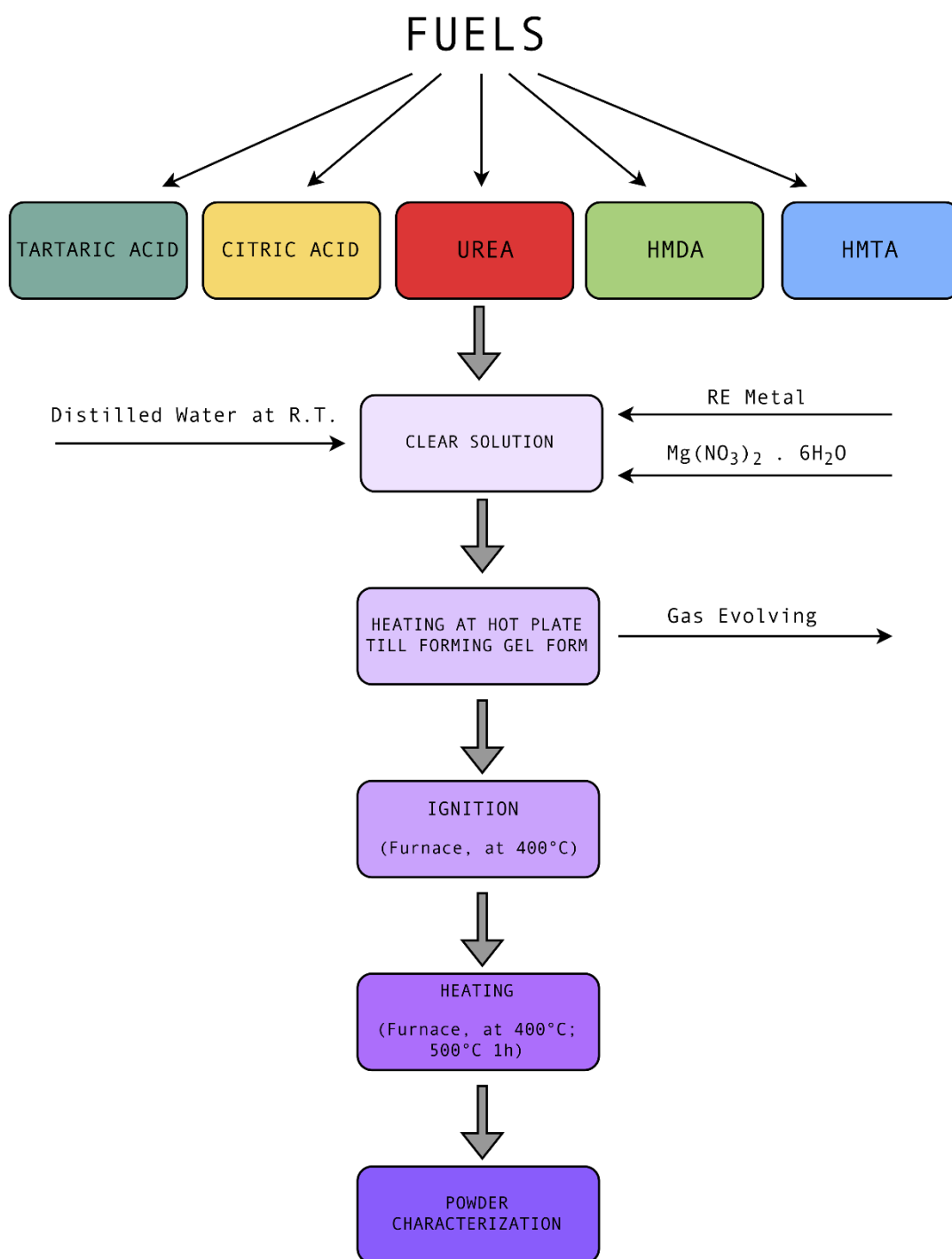


Figure 3.1. General working procedure for undoped and RE metal doped MgO preparation via SCS method

4. RESULTS AND DISCUSSIONS

4.1 Undoped MgO from TA, HMDA, HMTA, CA, U

Undoped magnesium oxide nanoparticles were synthesized via solution combustion method using TA, HMDA, HMTA, CA, U fuels respectively. Each fuel was used separately in the synthesis of magnesium oxide nanoparticles and fuel effect was examined on the structural variations. Besides, temperature effect was also investigated in this study. Each synthesized MgO with five different fuels was heated at 400°C for 1 hour and then 500°C for 1 hour. Finally, XRD and FTIR analysis were studied on each magnesium oxide prepared.

4.1.1 X-ray Powder Diffraction (XRD) Studies of Undoped MgO

Figure 4.1, 4.2 and 4.3 show powder X-ray diffraction patterns of magnesium oxide materials synthesized with different fuels and at different heating temperatures through SCS. As shown in the Table 4.1 below; the intensity order from the lowest to highest is TA, CA, HMDA, UREA, HMTA after the combustion process at 400°C 10 min.

Table 4.3. XRD pattern intensity changing with the temperature

FUELS	INTENSITY,cps (400°C, 10 min.)	INTENSITY,cps (400°C, 1h)	INTENSITY,cps (500°C, 1h)
TA	1250	1358	2008
HMDA	2800	4162	5204
HMTA	4754	6416	6416
CA	1770	2379	2954
U	2862	7400	7104

The MgO synthesized with TA has the lowest intensity at 400°C 10 min.; 1250 cps, 400°C for 1 h; 1358 cps and 500°C for 1 h; 2008 cps. The MgO prepared with HMTA has the highest intensity at 400°C for 10 min.; 4754 cps. Although HMTA has the highest intensity with good crystallinity at low temperature, XRD pattern shows that MgO still has HMTA fuel at 12.820 (2 θ); 1250 cps as shown in Figure 4.1. The X-ray diffraction lines of the products obtained with TA, CA were well matched with MgO ICDD card No. 75-0447 at 400°C for 10 min.

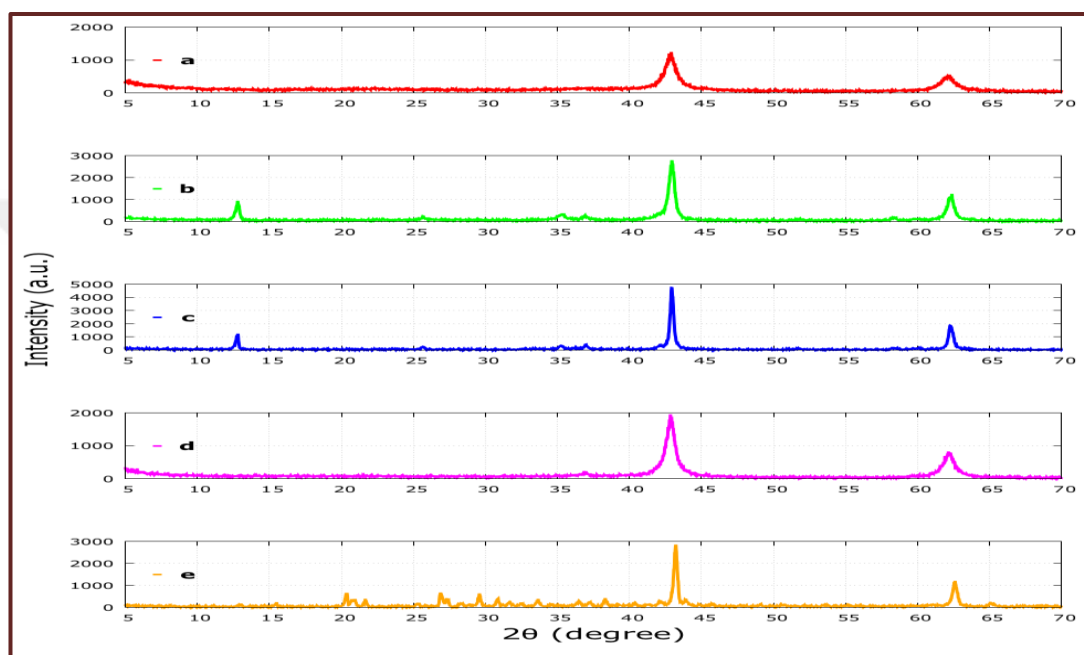


Figure 4. 1. XRD patterns of undoped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

It is clearly seen that all the impurities disappeared with heating at 400°C for 1 h. Fig. 4.2, presents the XRD patterns of the calcined products at 400°C for 1 h. In the examination of XRD patterns of MgO synthesized with urea reveals that the crystallinity increases dramatically when the magnesium oxide was heated at 400°C for 1 h after at 400°C 10 min. Thus, it has highest crystallinity among other fuels after heating process at 400°C; 7400 cps and 500°C; 7104 cps. When the other fuels are examined, it is clearly seen that all the intensity values increased with increasing temperature. After combustion process, heating at 400°C for 1 hour is enough temperature for all five fuels to obtain pure MgO.

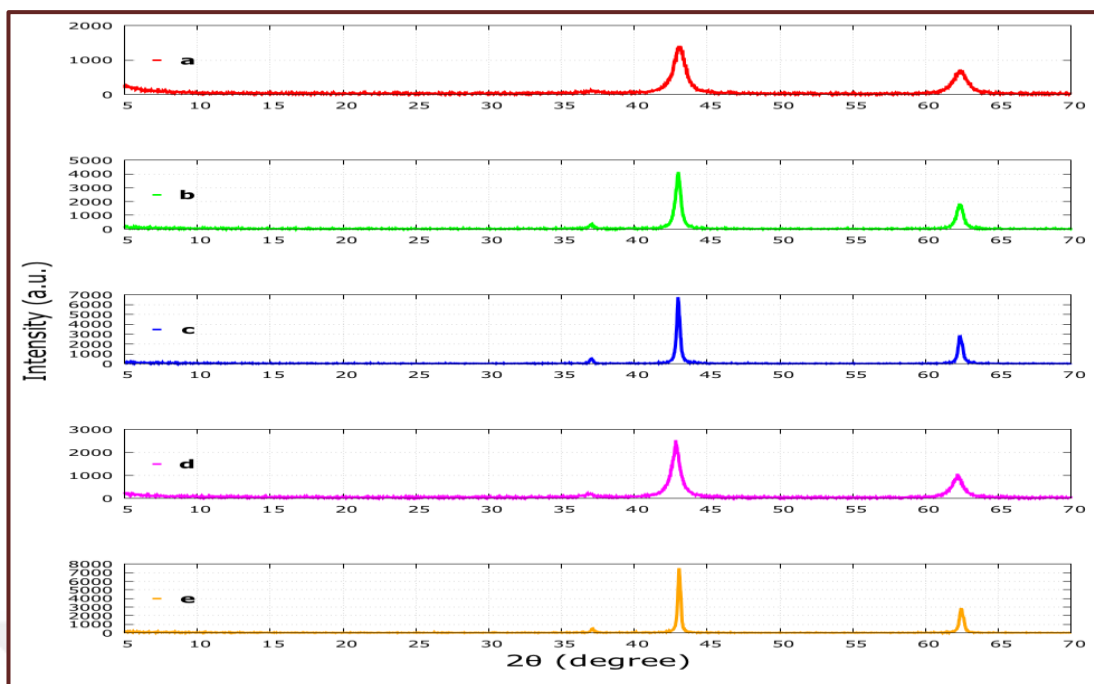


Figure 4. 2. XRD patterns of undoped MgO heated at 400°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

As a consequence, it was necessary to increase the calcination temperature to 500°C for all samples to investigate its influence on the combustion products of the five fuels. Fig.4.3. presents the XRD patterns of the calcined products at 500 °C. It is observed that the intensities of urea and HMTA at 400°C and 500°C change very slightly. In the synthesis of MgO that was used HMTA fuel the most gas evolution was observed. It is confirmed with the reactions are shown as above HMTA at which has the most moles of gases / moles of MgO. Also, Dhananjaya et al. (2012) study shows that the liberation of gaseous products during combustion reaction increased the surface area of the powder product by creating micro and nanoporous regions. Consequently, HMTA and U are the optimum fuels in our study because their products have high crystallinity at lower temperature (400°C). The X-ray diffraction lines of all the products obtained were well matched with MgO ICDD data card No. 75-0447 for each fuel at 400°C and 500°C for 1 h.

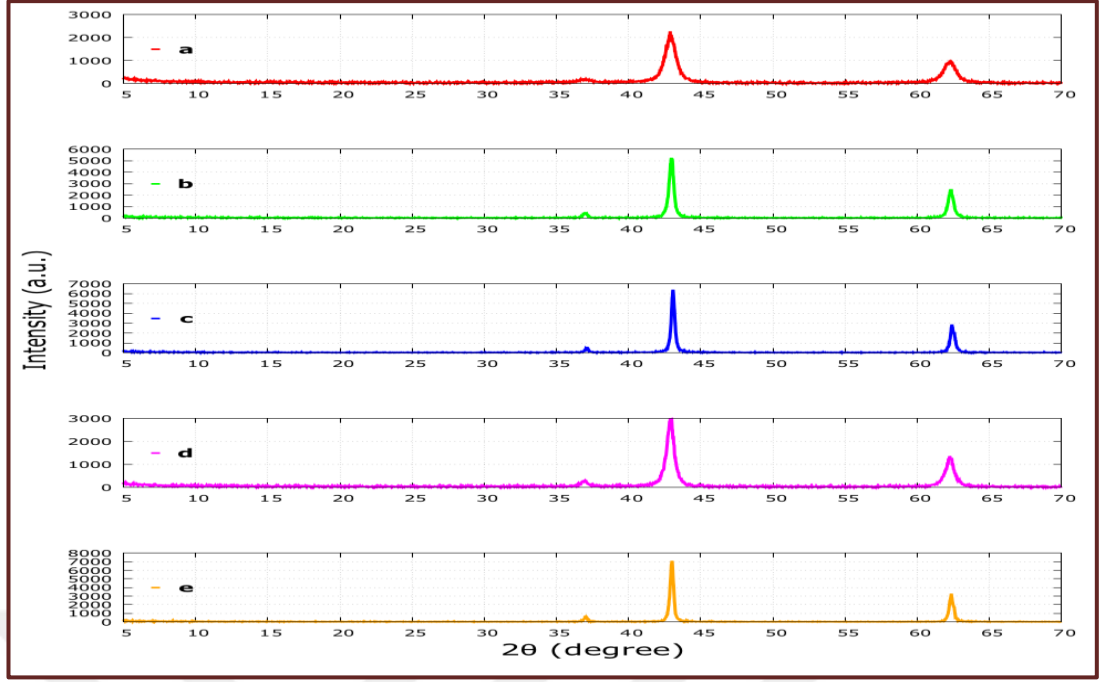


Figure 4. 3. XRD patterns of undoped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

The crystallite size (D) of the products that were synthesized with different fuels were calculated from the XRD pattern according to Scherrer formula (See Table 4.2);

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

where λ is the X-ray wavelength (0.15406 nm), β is the full-width at half maximum, θ is the diffraction angle and K is the constant. Table 4.2 prove that all synthesized MgO with five different fuels are nanoscale except U at 400°C, 10 min. While the crystallite size of MgO synthesized with TA and U decreases with increasing temperature, the HMDA decreases. Besides, crystallite sizes increased at 400°C, 1h for HMTA and CA then decreased at 500°C, 1h.

Table 4.4. Undoped MgO crystallite size changing with the temperature

FUELS	Crystallite size,nm (400°C, 10 min.)	Crystallite size,nm (400°C, 1h)	Crystallite size,nm (500°C, 1h)
TA	18.05	16.50	15.17
HMDA	23.72	27.12	34.45
HMTA	47.44	54.08	47.47
CA	19.95	47.60	18.95
U	125.75	63.29	54.07

4.1.2 Infrared Spectroscopy Studies of Undoped MgO

Figure 4.4, 4.5 and 4.6 show the FT-IR spectra of the products. The vibrational absorptions at $440\text{--}700\text{ cm}^{-1}$ which may be assigned to the stretching vibrations of Mg-O. Further, the peak at $550\text{--}890\text{ cm}^{-1}$ is higher frequency of MgO stretching and $410\text{--}450\text{ cm}^{-1}$ is lower frequency stretching. The bands appeared at $840\text{--}900\text{ cm}^{-1}$ may be due to stretching vibrations between magnesium and oxygen (Nassar et al., 2017). Also, the bands appeared at $3290\text{--}3670$ and $1300\text{--}1800\text{ cm}^{-1}$ can be attributed to the stretching and bending vibrational frequencies of the hydroxyl groups of the surface adsorbed waters bond. Also, the absorption at $\sim 3440\text{ cm}^{-1}$ indicates the presence of hydroxyl groups (O-H mode), which was probably due to the fact that the spectra was not recorded in situ and some water re-adsorption from the ambient atmosphere as occurred. After all, it is clearly seen that water and organic compound disappeared with the temperature increasing.

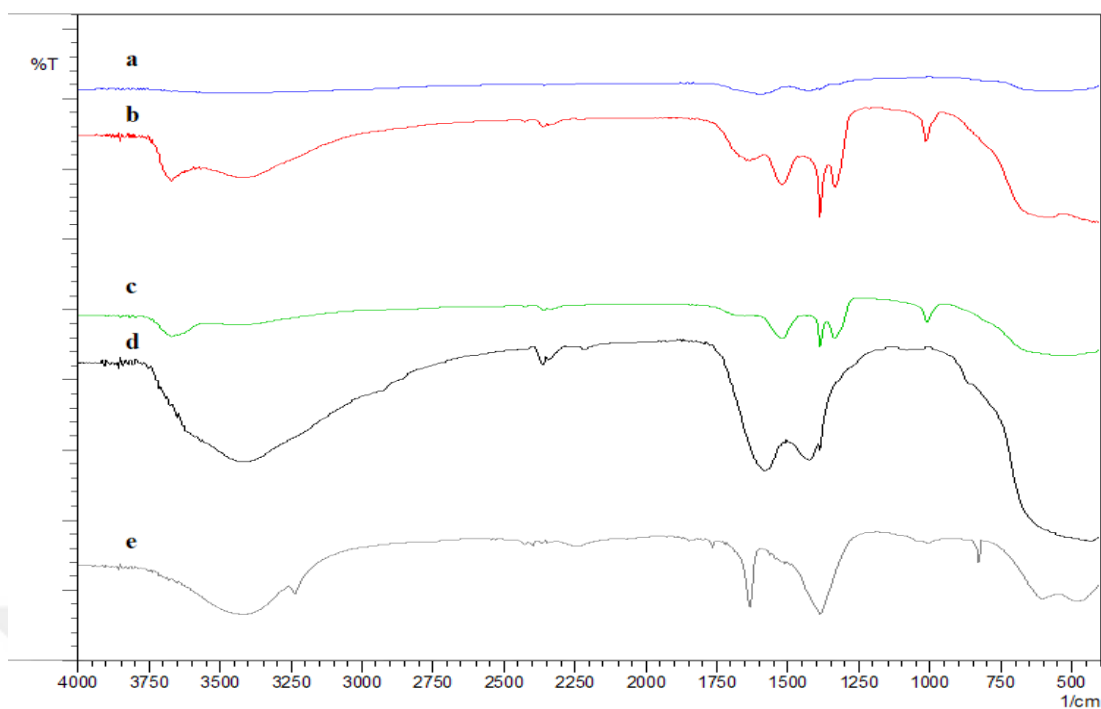


Figure 4. 4. IR spectra of of undoped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

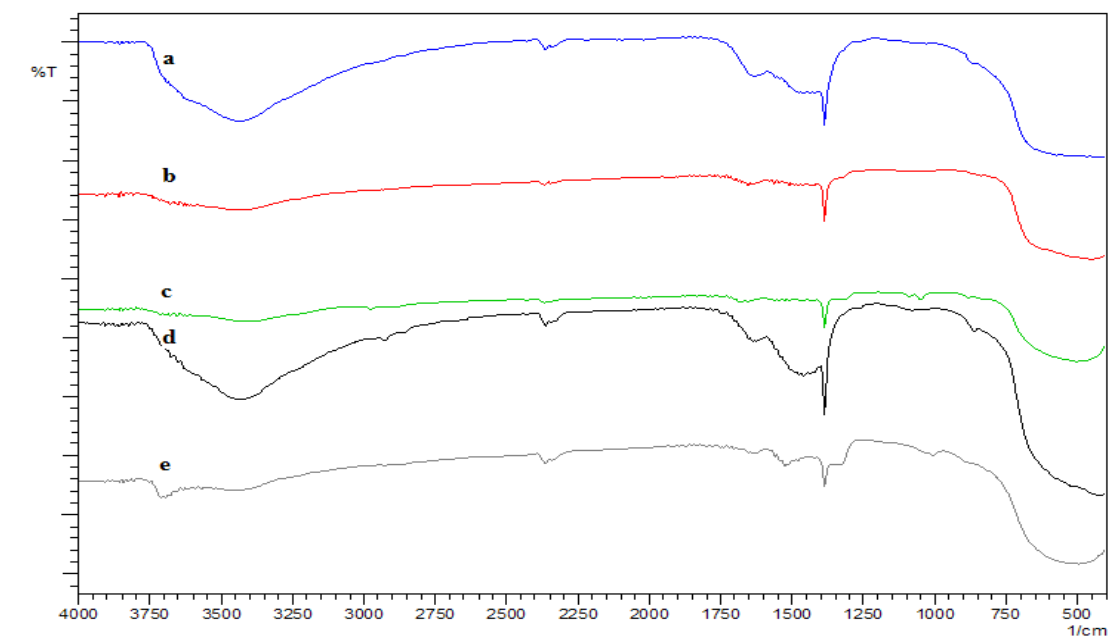


Figure 4. 5. IR spectra of of undoped MgO heated at 400°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

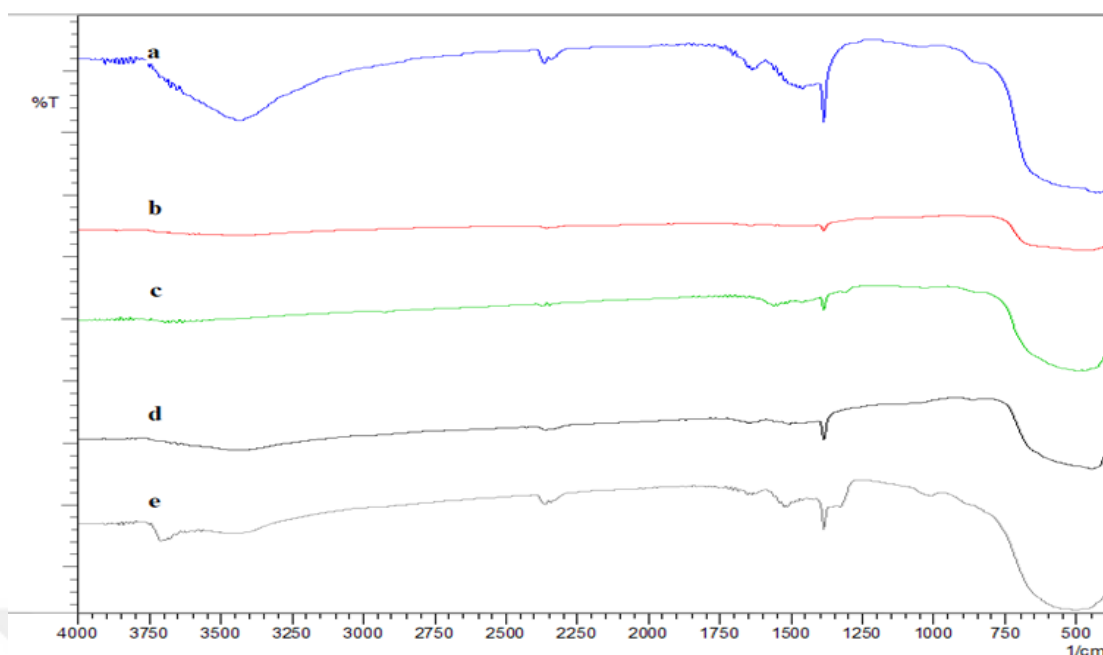


Figure 4. 6. IR spectra of of undoped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

4.2 Undoped MgO from β -Alanine, Glycine and Carbohydrazide Fuels

4.2.1 β -Alanine

β -Alanine was synthesized twice at hot plate at 370°C. In both synthesis process, three significant explosions occurred. The great majority of the sample was lost. Only a little amount of sample could be obtained for IR measurement. IR spectra of the sample is as shown below Figure 4.1. So, because of the unefficient results, it was not continued to work with β -Alanine fuel.

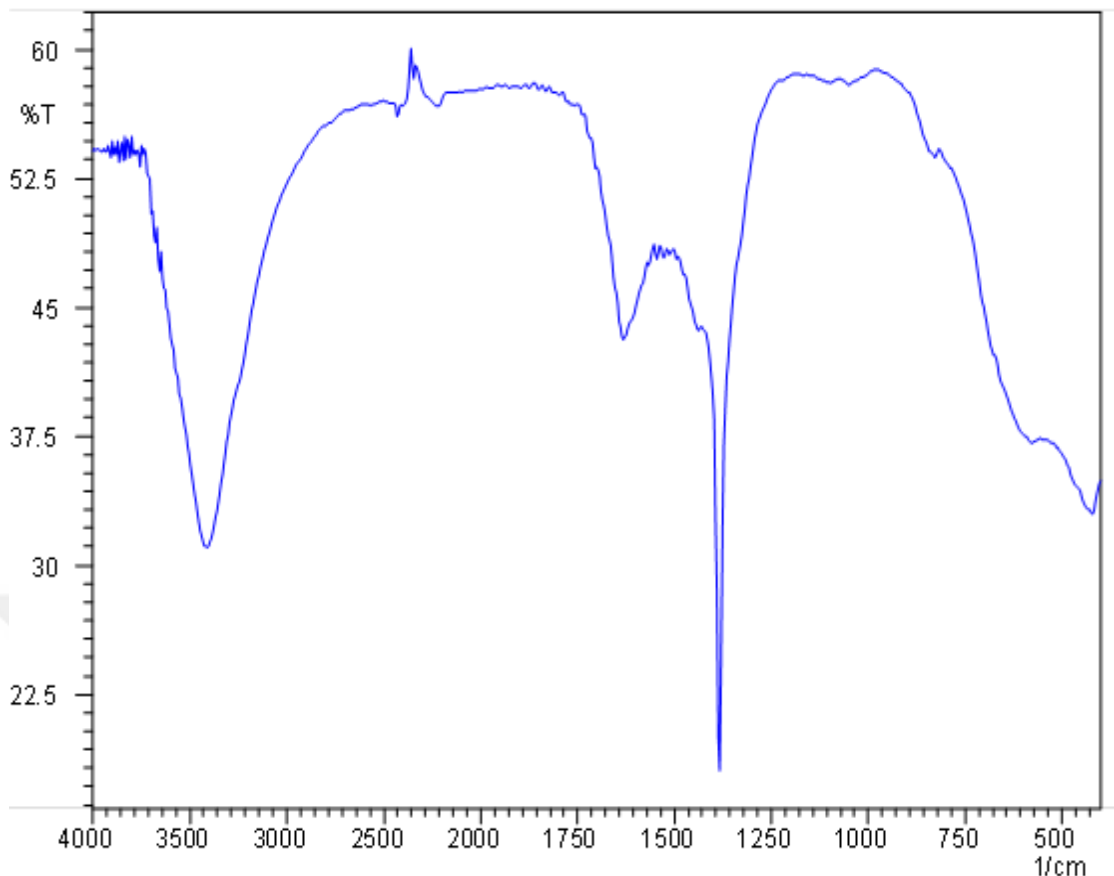


Figure 4. 7. IR spectra of MgO synthesized using β -Alanine fuel

4.2.2 Carbohydrazide and Glycine

Carbohydrazide (CH) and glycine (Gly) were both synthesized at hot plate (370°C) and furnace (400 °C). CH was firstly synthesized in furnace and a loudly explosion occurred. It could not been obtained any substance for FTIR and XRD. CH was secondly synthesized at hot plate in a beaker and evaporating dish. Gas evolution was observed without no combustion. While the heating process, substance remained as gel. Thus, powder substance could not been obtained. Glycine was also synthesized two times; at hot plate and furnace. The process carried out in the oven was a large loss of matter. When the process was performed at hot plate, three significant explosions were observed. After explosions, some parts of substance remained as gel and no considerable amount of substance was obtained. After all, CH

and Gly were introduced to drying oven and let them to dry for a week. End of the process, surprisingly ultra light and fluffy substances were obtained as shown in Figure 4.5. Finally, XRD (see Figure 4.6) and FTIR (see Figure 4.7, Figure 4.8) analysis were carried out for these substances. As a result; due to the insufficient results like yield and crystallinity, it was not continued to work with these two fuels. XRD patterns of CH and Gly show that they have amorphous crystal structure. FT-IR spectra of the products exhibit vibrational absorptions at $440\text{--}700\text{ cm}^{-1}$ which may be assigned to the stretching vibrations of Mg-O. Besides, the peaks at 420 cm^{-1} and 435 cm^{-1} for carbohydrazide and glycine fuels show the lower frequency stretching of Mg-O. Dhananjaya et al. (2012) study is also proved that glycine is more reactive than citric acid. In other words, the fuel consisting of the -NH_2 group like glycine is a more reactive fuel than citric acid containing -OH and -COOH group. Thus, glycine has higher heat of combustion and it is more violent and difficult to control when it is compared to other fuels.



a



b

Figure 4. 8. The images of the products prepared with a) CH and b) Gyl

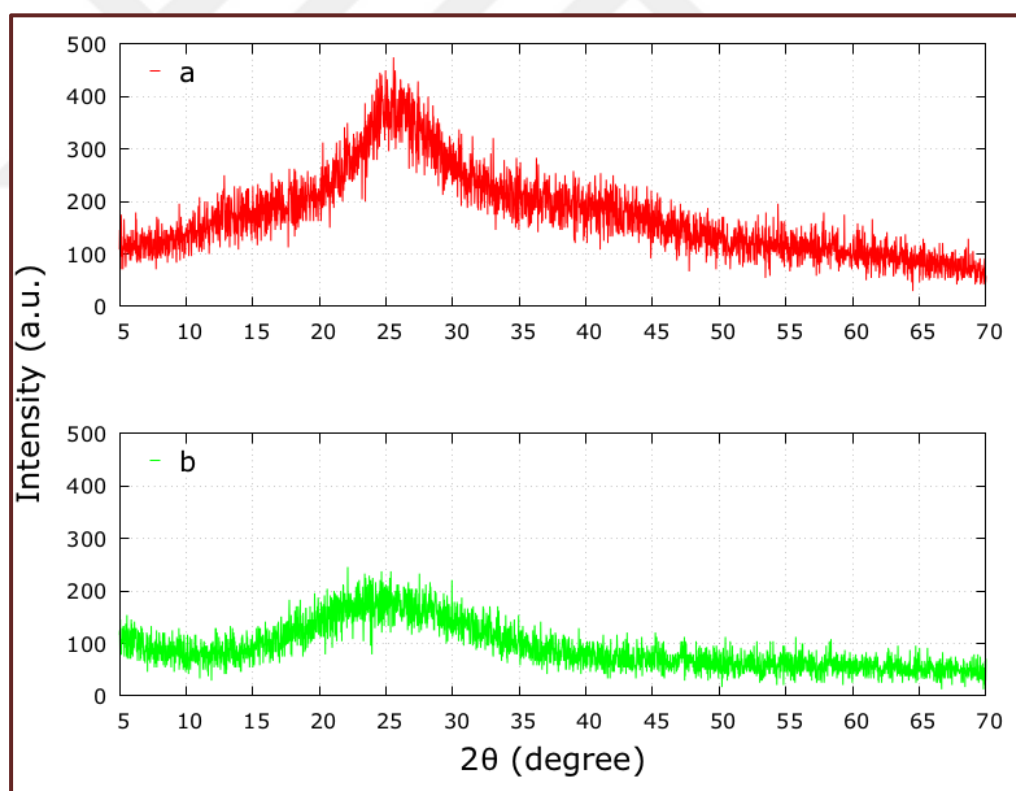


Figure 4. 9. XRD patterns of the products prepared at 400°C for 10 min. using a) CH, b) Gly.

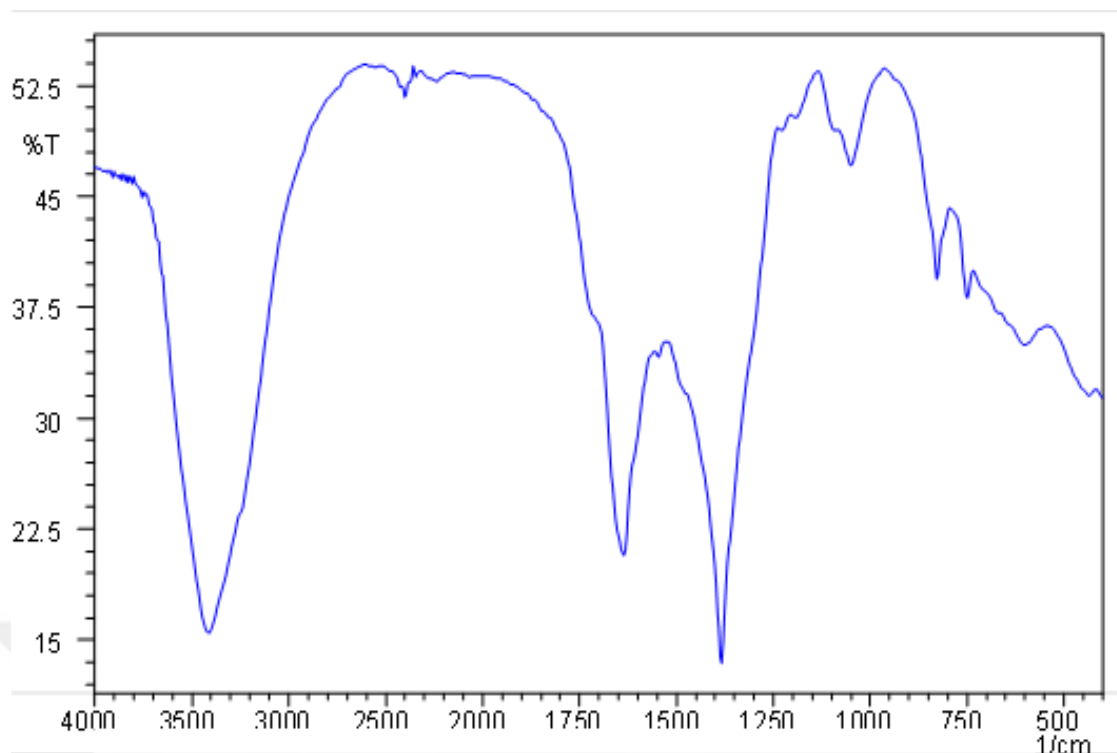


Figure 4. 10. IR spectra of the products prepared using carbohydrazide fuel

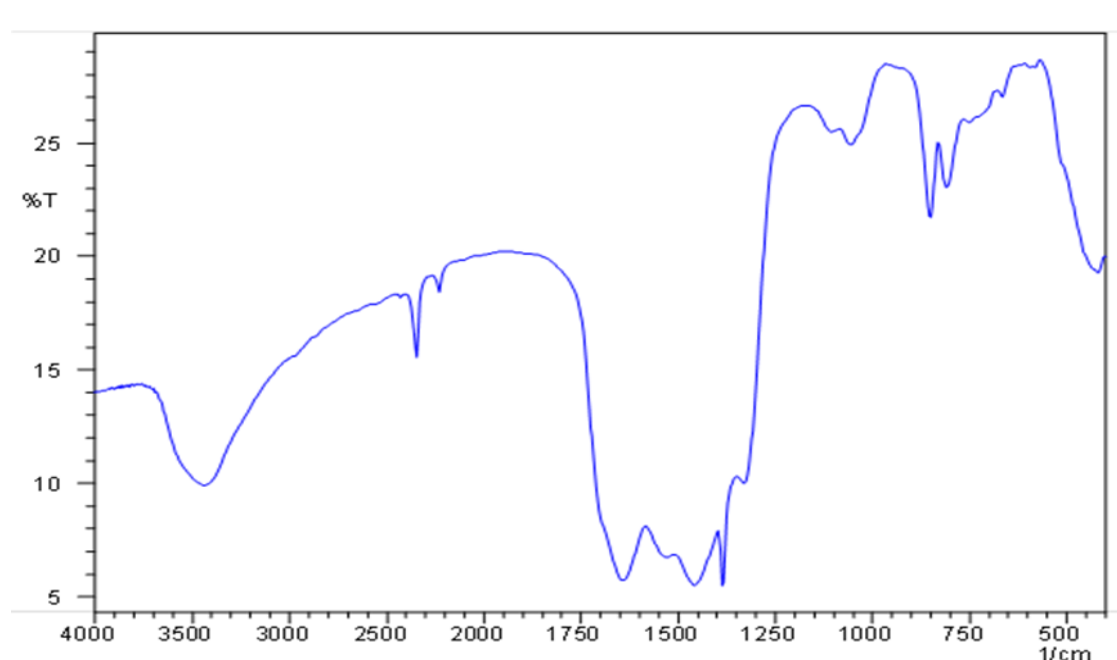


Figure 4. 11. IR spectra of the products prepared using glycine fuel

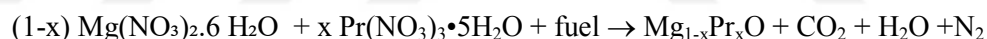
4.3 Rare Earth (RE: Pr^{+3} , Ho^{+3} , Tb^{+3}) doped MgO from TA, HMDA, HMTA, CA, U fuels

MgO:Rare Earth (RE: Pr^{+3} , Ho^{+3} , Tb^{+3}) nanostructures were prepared via a solution combustion method utilizing magnesium nitrate and different fuels such as TA, HMDA, HMTA, CA, U. In this investigation, it was figured out that the type of fuel has a remarkable influence on the structure, crystallinity and morphology of the products. Moreover, the effect of different types and concentrations of RE metal dopants were also examined on the structural features of the products.

4.3.1 Pr doped MgO

A series of MgO: Pr^{3+} (0.005, 0.01, 0.03 mol) nanoparticles were synthesized by solution combustion method and its crystal morphology was examined under FT-IR, XRD, SEM and EDX.

The general reaction is predicted with different fuels;



(x = 0, 0.005, 0.01, and 0.03)

The color of the MgO that was synthesized with the TA fuel was getting darker from light brown to dark brown with increasing temperature in 0.01, 0.03 mol Pr^{3+} concentrations. It turned from light brown to dark brown. But in the 0.005 mol concentration the color turned from cream to beige. The obtained substance was soft and porous. The color of the MgO synthesized with citric acid changed from dark brown to light cream and it was fluffy and soft after combustion process. When the HMDA was used as fuel, a dense gas evolution was observed during heating period at hot plate. The color of the MgO was light cream. It was observed that there is no significant change in the color with the heating and concentration changing. Lastly, as it is shown in the Figure 4.12, amount of MgO from HMTA and U fuels are not much as synthesized MgO that was used TA and CA fuels.

The images that are shown in Figure 4. 12 are the products after the 400°C 10 min.



a



b



c



d



e

Figure 4. 12. The images of $\text{Mg}_{0.99}\text{Pr}_{0.01}\text{O}$ samples was synthesized with a) TA, b) HMDA, c) HMTA, d) CA, e) U

4.3.2 XRD Studies of Pr doped MgO

The results exhibited that the used different fuels gave MgO products with different morphologies and crystallinity. MgO synthesized with HMTA fuel has the highest crystallinity and lowest yield in all three Pr^{+3} concentrations (0.005, 0.01, 0.03 mol) after the combustion process at 400°C 10 min. Unlike HMTA fuel, MgO synthesized with TA has the lowest crystallinity and highest yield in different three Pr^{+3} concentrations and temperatures.

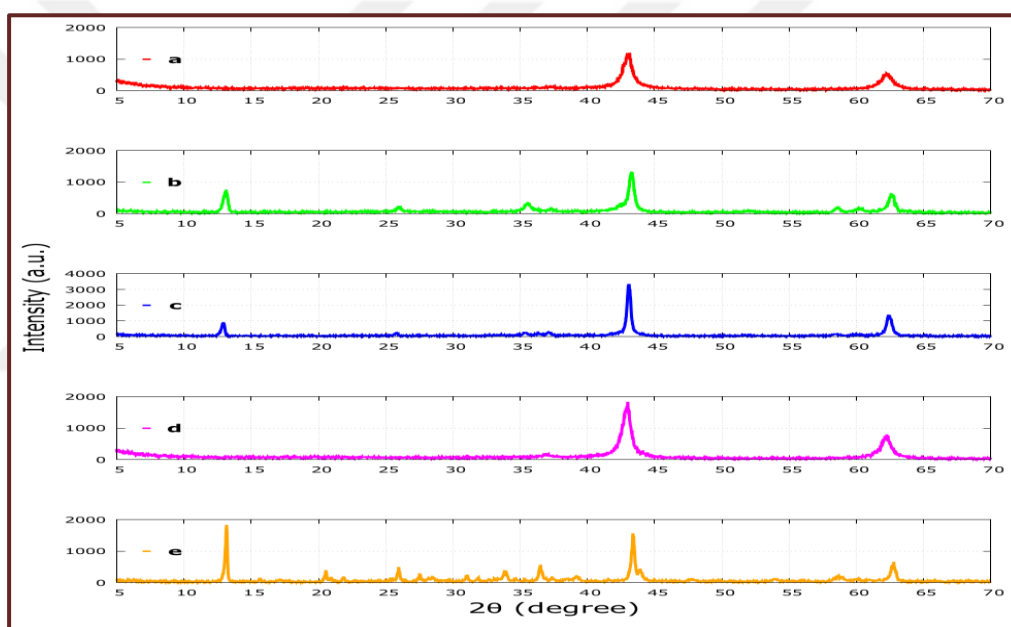


Figure 4. 13. XRD patterns of 0.005 mol Pr doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

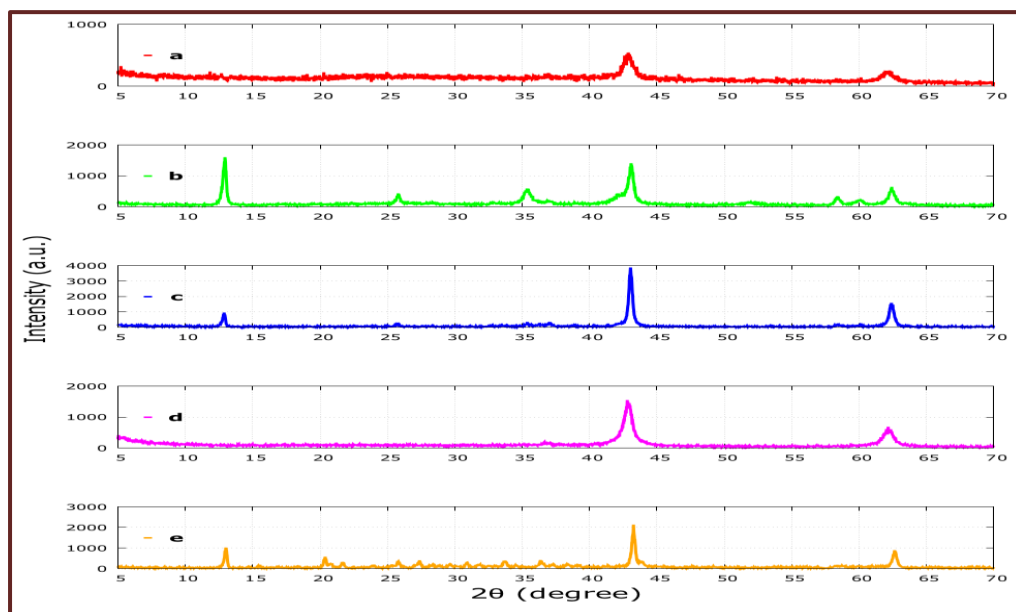


Figure 4.14. XRD patterns of 0.01mol Pr doped MgO heated at 400°C 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

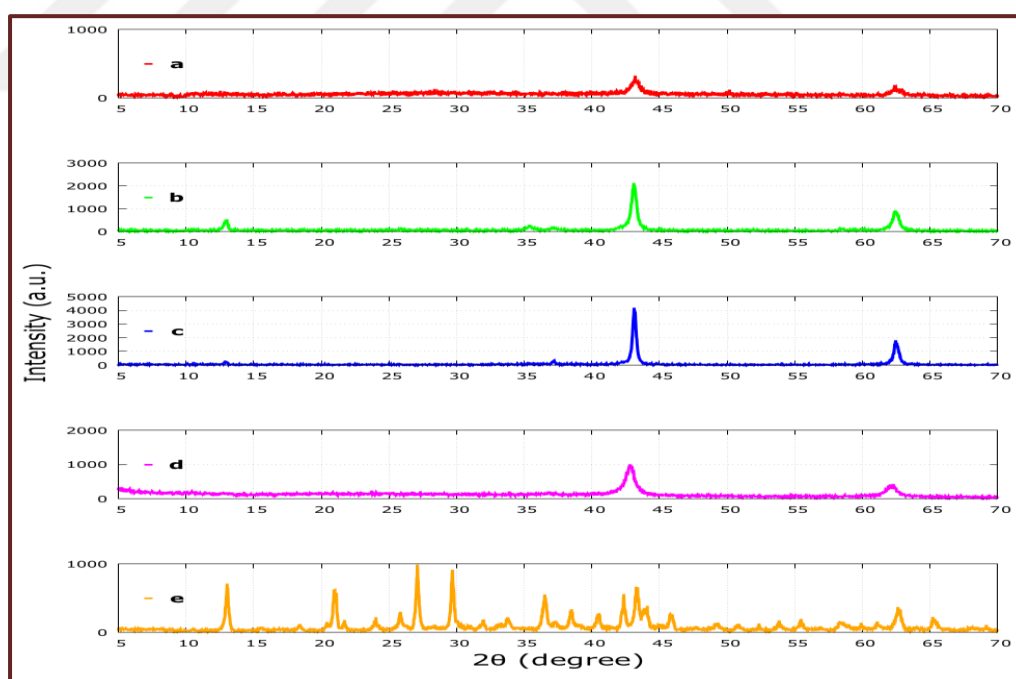


Figure 4.15. XRD patterns of 0.03 mol Pr doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

Figure 4.16, 17, 18 show the XRD patterns of 0.005, 0.01, 0.03 mol Pr^{+3} doped MgO at 400°C, respectively.

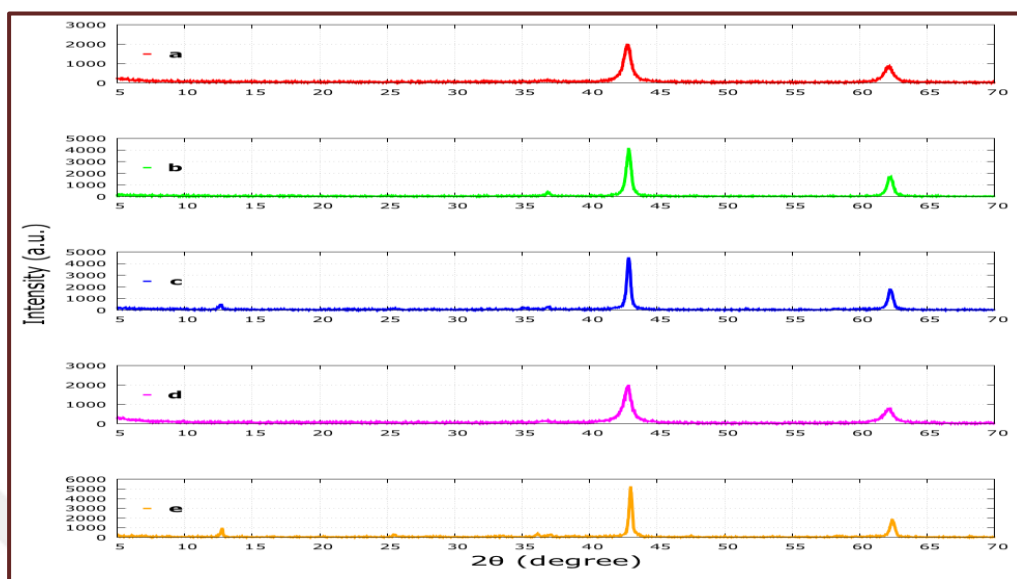


Figure 4. 16. XRD patterns of 0.005 mol Pr doped MgO heated at 400°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

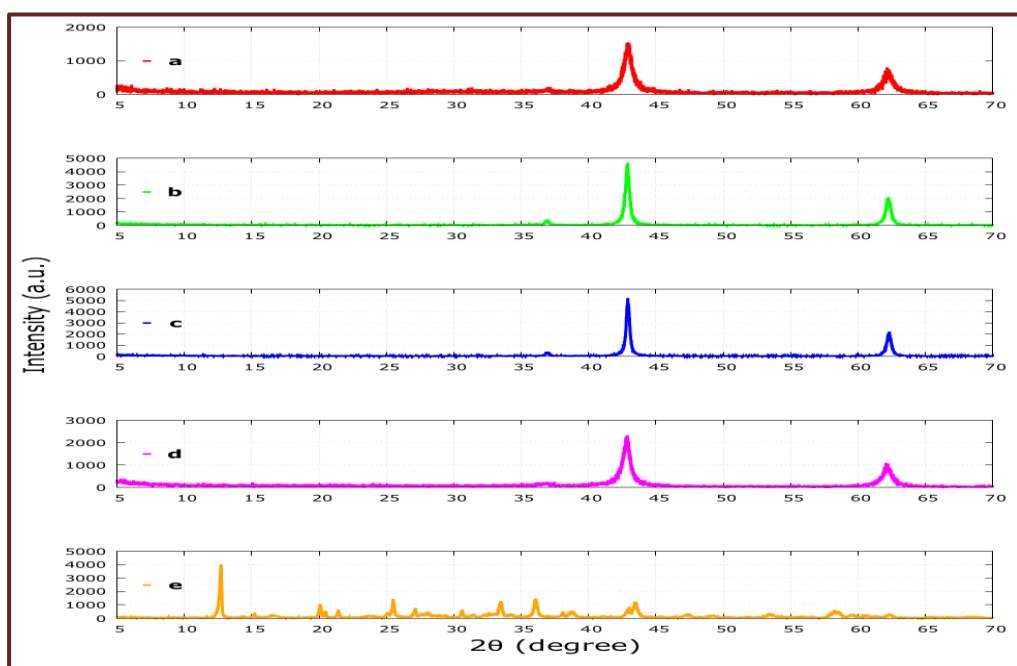


Figure 4. 17. XRD patterns of 0.01 mol Pr doped MgO heated at 400°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

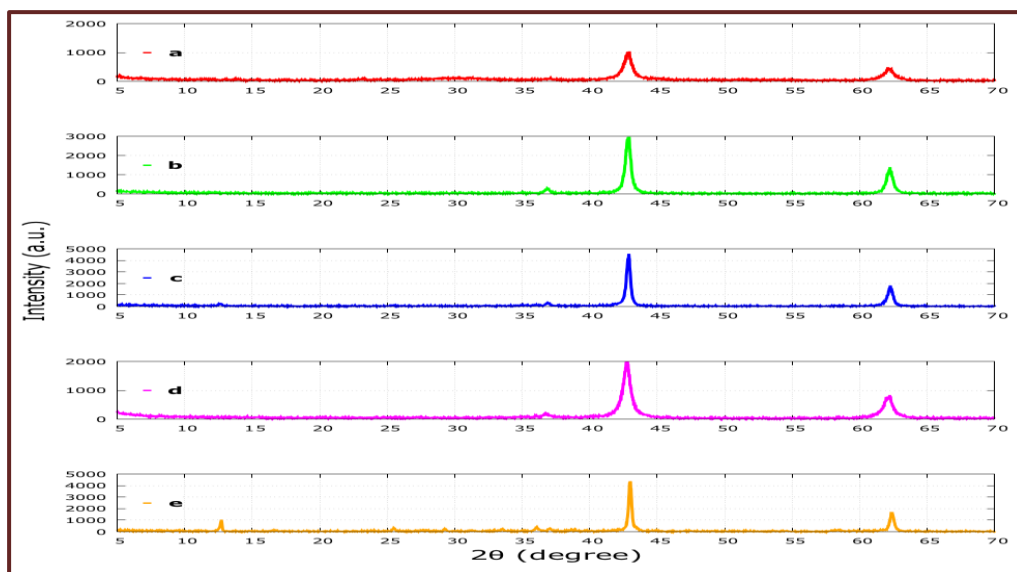


Figure 4. 18. XRD patterns of 0.03 mol Pr doped MgO heated at 400°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

Also, the urea fuel produced pure MgO nanoparticles has the highest crystallinity at 500°C in all three Pr^{+3} concentrations. The highest intensities of MgO synthesized with urea fuel are 7908 cps at 42.800 (2theta) for 0.005 mol, 7270 cps at 42.840 (2theta) for 0.01 mol Pr ,6513 cps at 42.866 (2theta) for 0.03 mol Pr. Additionally, the intensity of the undoped MgO synthesized with U is 7104 cps at 43.000 (2theta).

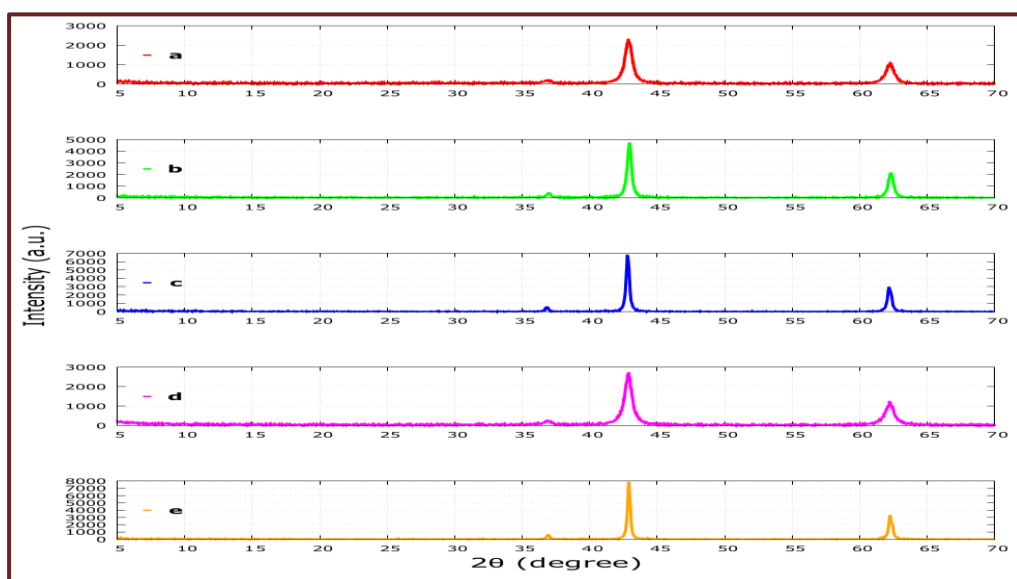


Figure 4. 19. XRD patterns of 0.005 mol Pr doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

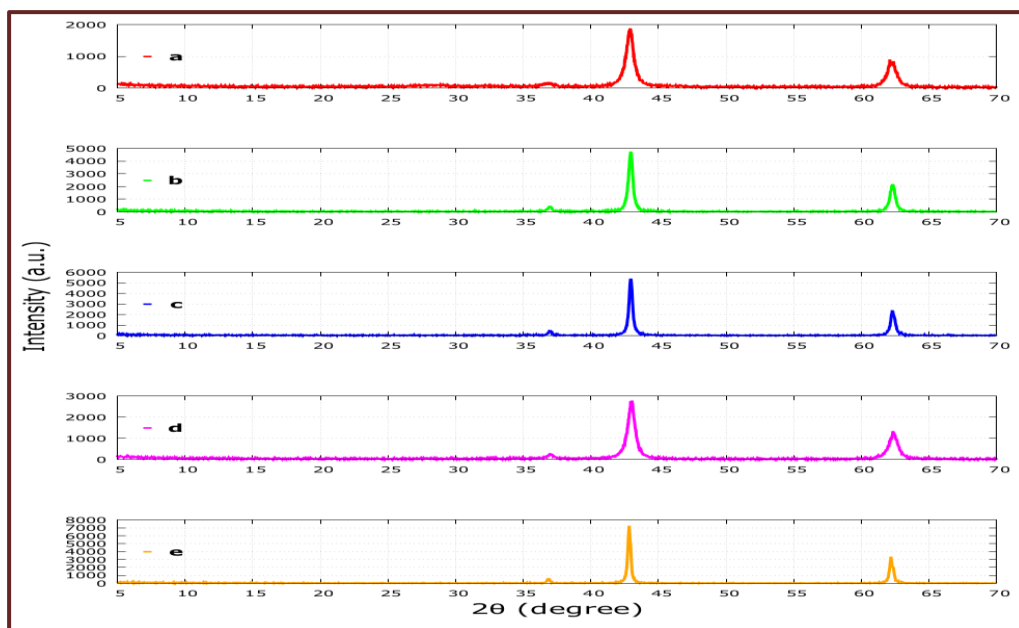


Figure 4. 20. XRD patterns of 0.01 mol Pr doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

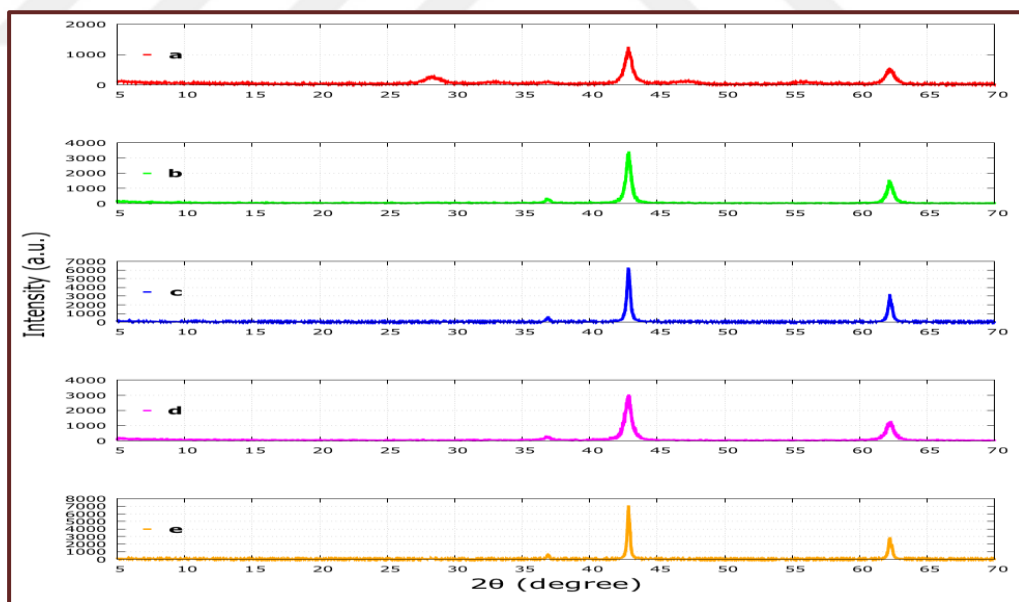


Figure 4. 21. XRD patterns of 0.03 mol Pr doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

The crystallite sizes of the products were calculated from the XRD pattern according to the Scherrer formula as mentioned in 4.1.1. Table 4.3 shows 0.03 mol Pr doped magnesium oxide's prepared with different fuels are nanoscale at 400°C and 500°C.

Table 4. 2. MgO:0.03Pr⁺³ crystallite size changing with temprerature

FUELS	Crystallite size,nm (400°C, 10 min.)	Crystallite size,nm (400°C, 1h)	Crystallite size,nm (500°C, 1h)
TA	27.13	21.13	47
HMDA	31.65	27.10	28.67
HMTA	125.71	47.44	38.27
CA	18.93	23.71	29.13
U	120.26	42.08	70.86

Figure 4.22 shows the effect of dopant and dopant concentration at 500°C. When the intensities compare with undoped MgO, 0.005 mol Pr doped MgO synthesized with urea has highest value corresponding to best crystallinity. It is clear that the crystallinity decreases as the concentration of dopant increases while it increases with rising temperature. Also, a small shift in the position of highest peak to the lower side of 2θ is observed for Pr doped samples (See Fig. 4.22). Consequently, 2θ shifting to the lower side increases with decreasing concentration.

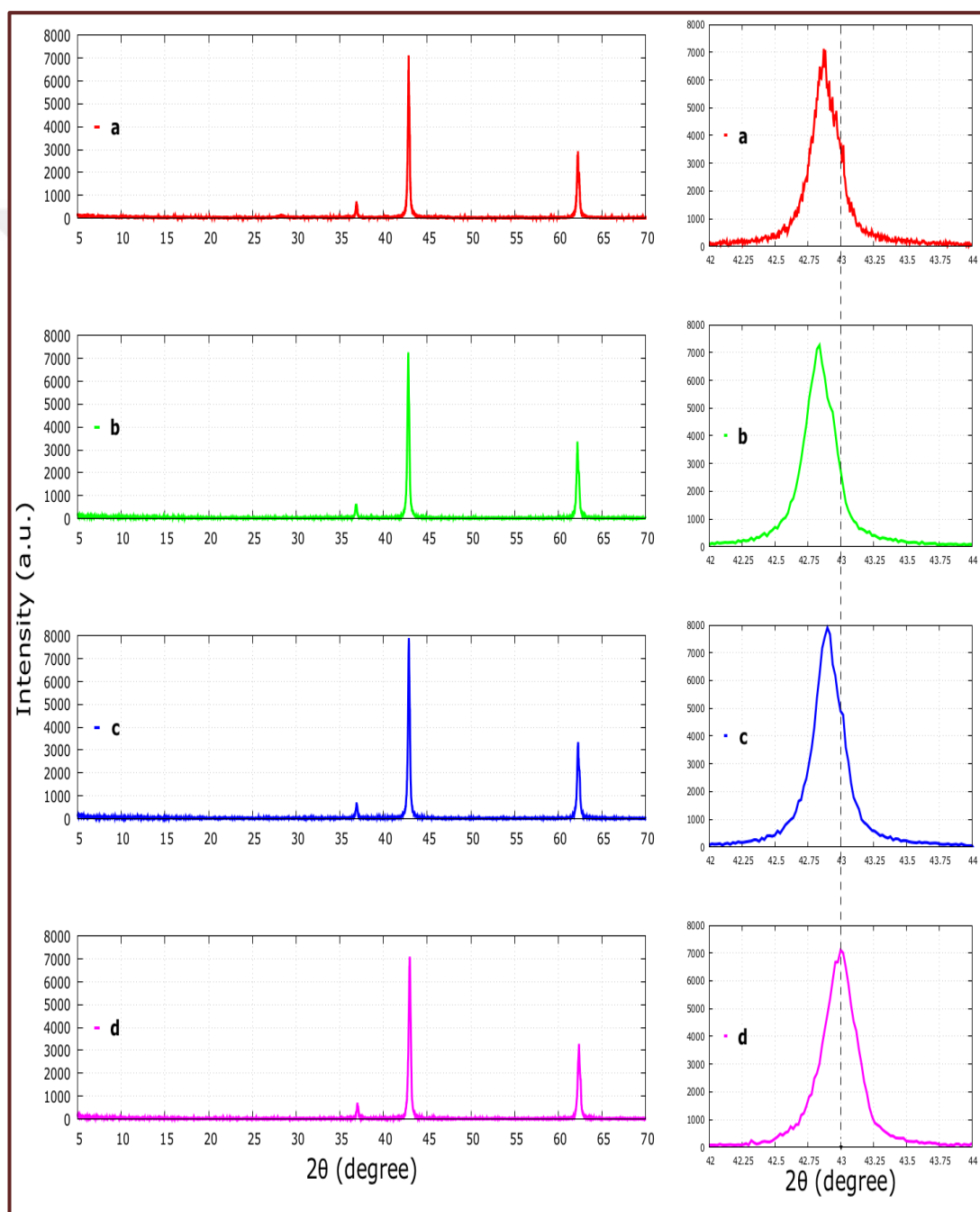


Figure 4. 22. XRD patterns of as-prepared and Pr doped MgO synthesized with urea fuel, at 500°C 1 hour, a) 0.03 , b) 0.01, c) 0.005 mol Pr, d) undoped

4.3.3 Infrared Spectroscopy Studies of Pr doped MgO

IR spectra of $\text{Mg}_{(1-x)}\text{Pr}_x\text{O}$ ($x=0.005, 0.01, 0.03$ mol) samples at 400°C for 10 min. and 500°C 1 h. were shown Figure 4.23-28. It is clearly seen that most of the vibrational bands due to organic impurities and water are disappeared with increasing temperature. The bands observed at 420 and 550 cm^{-1} are attributed to the higher and lower frequency of MgO stretching bands (Borghei et al., 2011). The OH stretching vibrations of water molecules appeared at the broad vibration band at $3440\text{--}3450\text{ cm}^{-1}$ while those at $1630\text{--}1645\text{ cm}^{-1}$ are associated with their bending mode (Devaraja et al., 2016) The absorption bands at $1630, 1450$ and 1010 cm^{-1} are assigned to the carbonate species. However, these carbonates are chemisorbed on the surface of the MgO (Kiran et al., 2017).

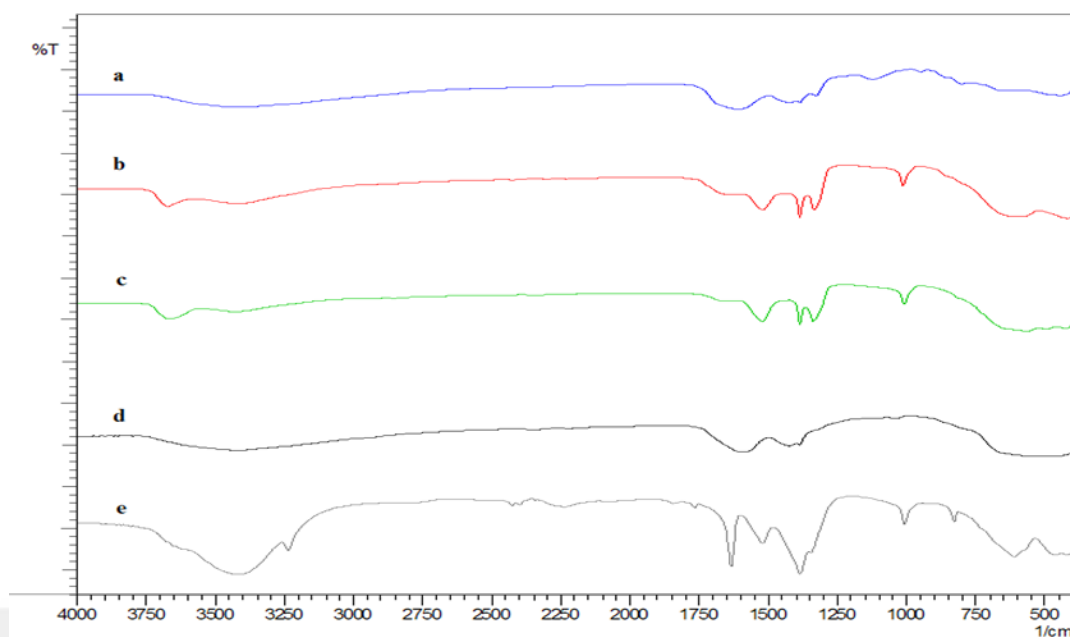


Figure 4. 23. IR spectra of as-prepared 0.005 mol Pr doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

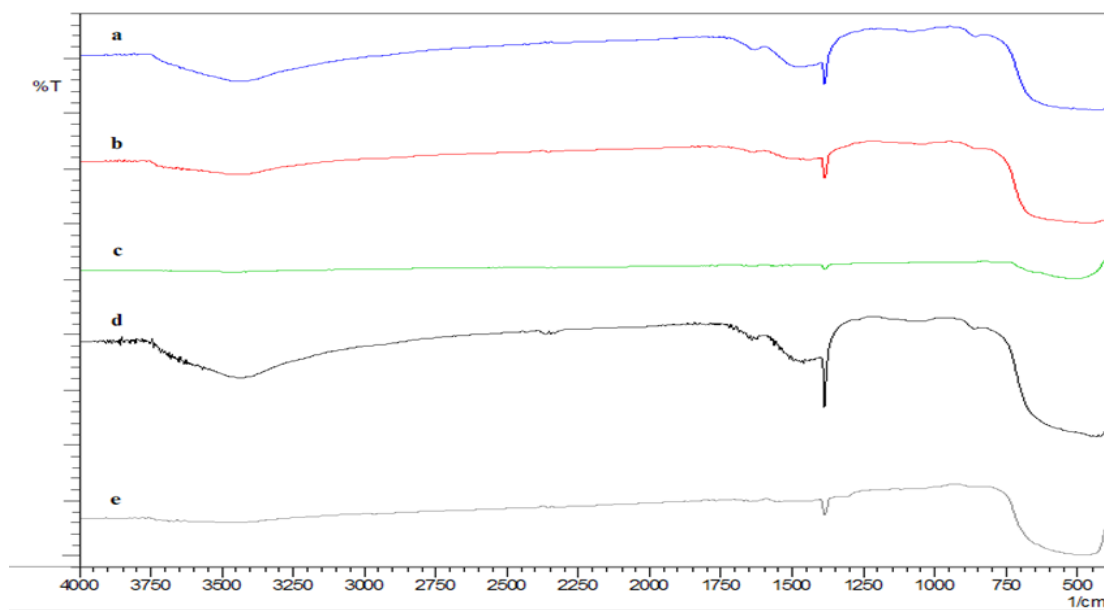


Figure 4. 24. IR spectra of 0.005 mol Pr doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

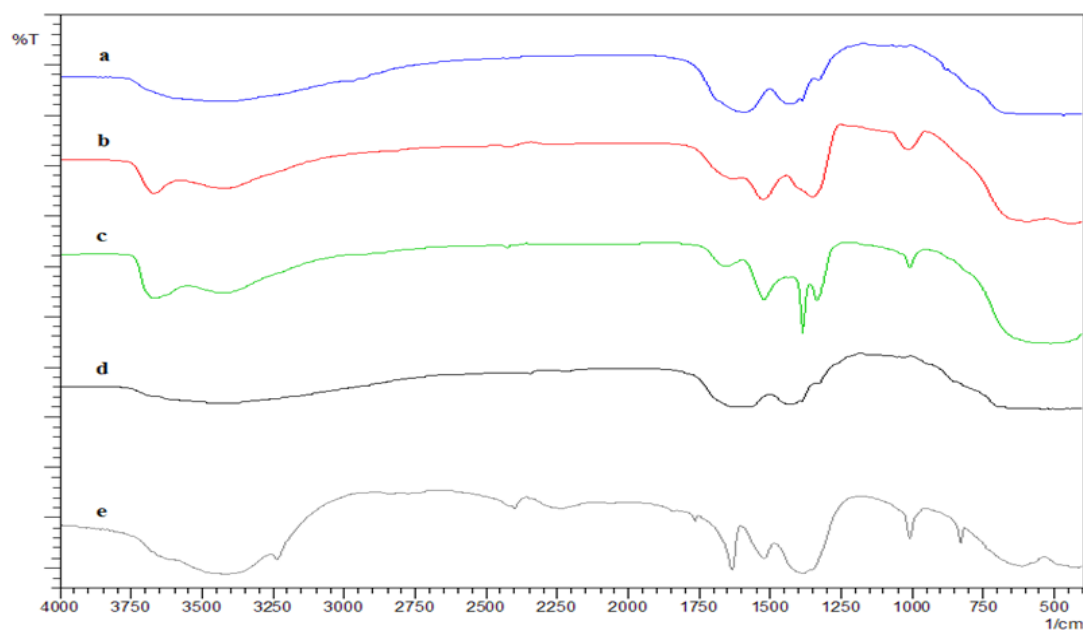


Figure 4. 25. IR spectra of as-prepared 0.01 mol Pr doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c)HMTA, d) CA, e) U

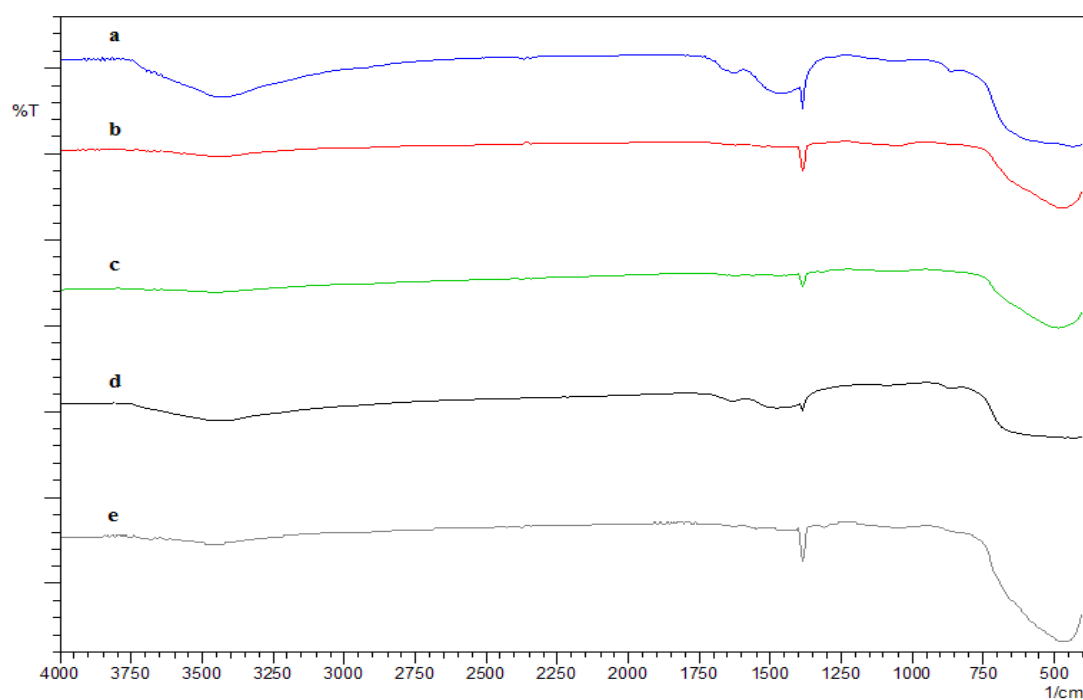


Figure 4. 26. IR spectra of 0.01 mol Pr doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

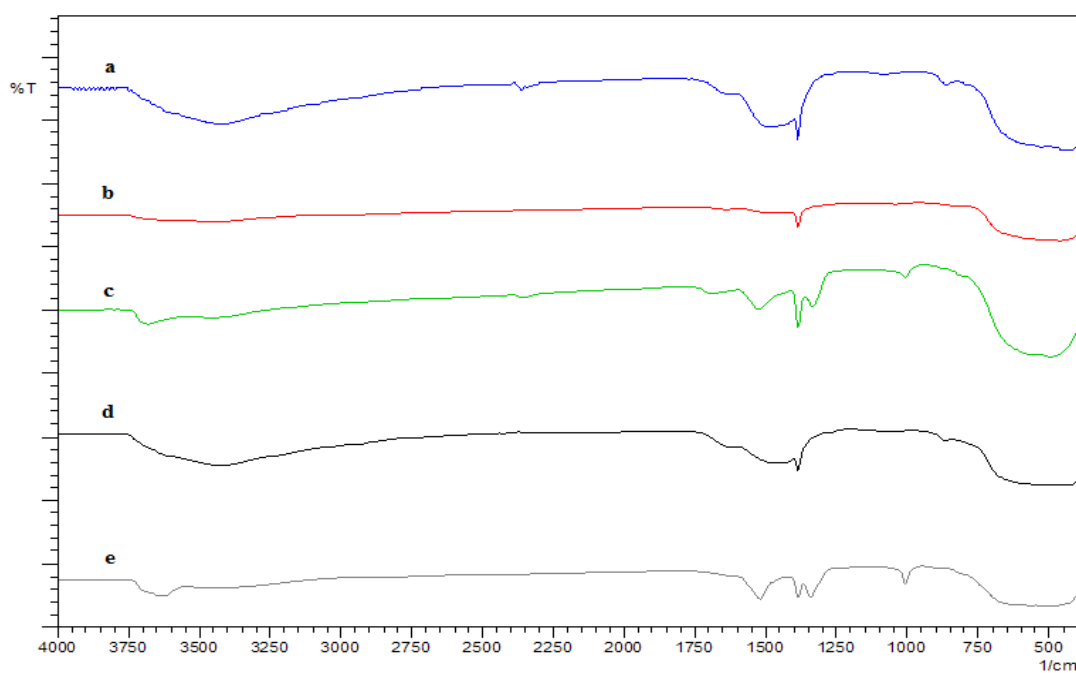


Figure 4. 27. IR spectra of as-prepared 0.03 mol Pr doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c)HMTA, d) CA, e) U

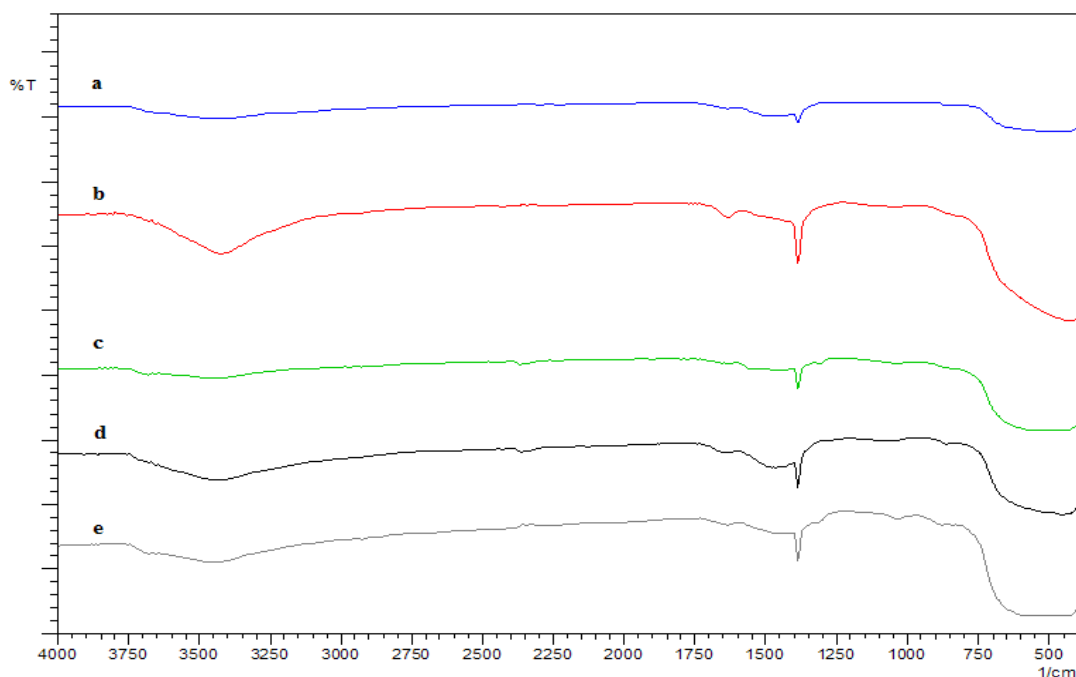


Figure 4. 28. IR spectra of 0.03 mol Pr doped MgO heated at 500°C for 1 hour using a)TA, b) HMDA, c) HMTA, d) CA, e) U

4.3.4 SEM and EDX Studies of Pr doped MgO

MgO:Pr³⁺ samples were synthesized with TA, HMDA, HMTA, CA, U fuels respectively. Fig. 4.29 shows the typical electron micrograph of the combustion derived MgO:Pr³⁺ (0.03mol) nanoparticles were calcined at 500°C for 1 hour. The images give information about the particle size and the morphology of products. Magnesium oxide products might be resulted with different size and morphologies because of that the employed fuels in the synthesis procedure produced different quantities of heat and gases during the combustion step. In this study, agglomerated spherical particles with porous morphology were observed in all samples. All the MgO nanoparticles obtained with different fuels are seen very similar to each other, but MgO that is synthesized with urea shows larger particles. This feature agreed with XRD pattern because it has the highest intensity with good crystallinity. Also, the MgO:0.03Pr³⁺ at 500°C estimated crystallite sizes were calculated using Scherrer equation as 28-71 nm for five different fuels shown in Table 4.3.

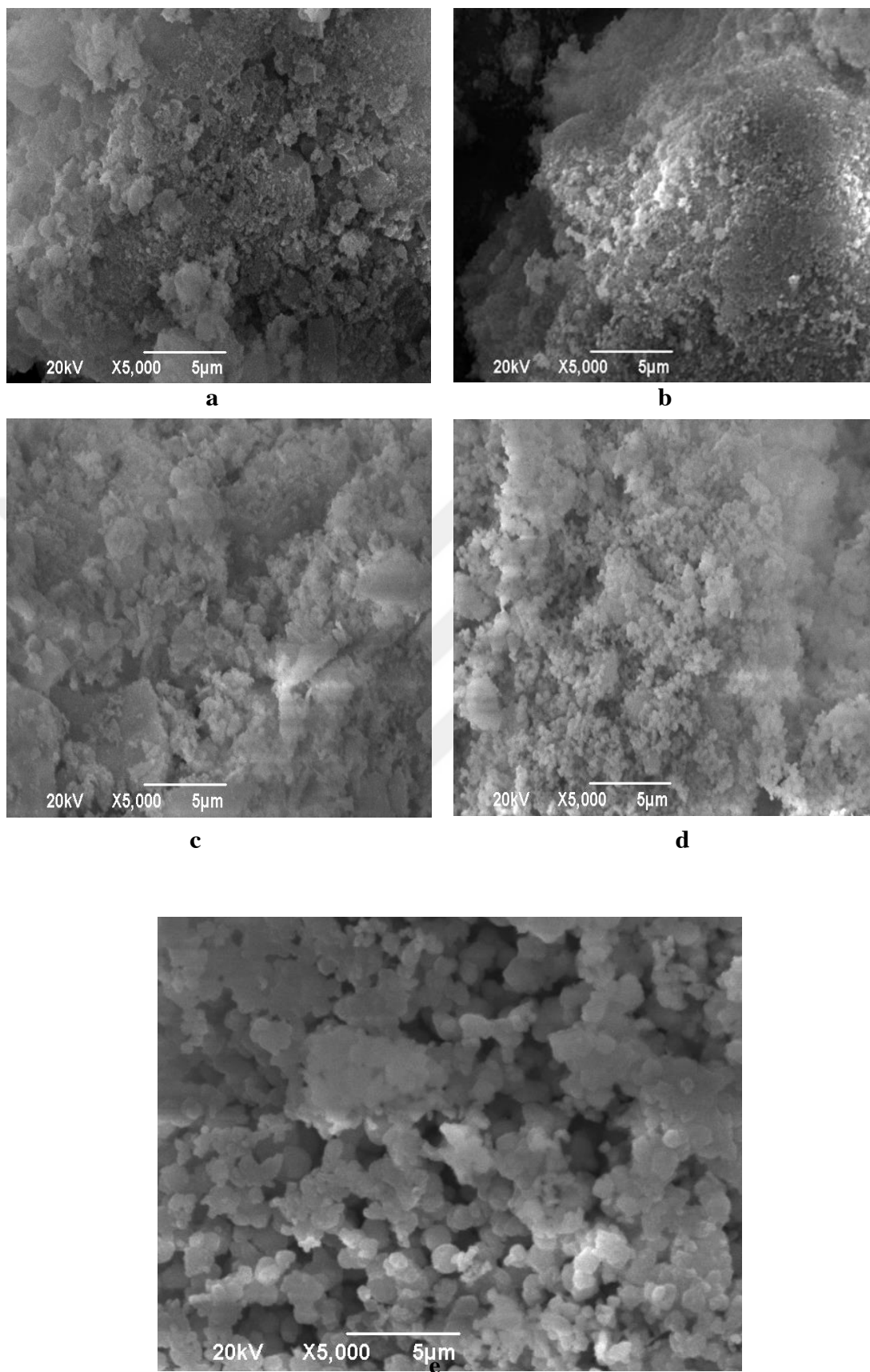


Figure 4. 29. SEM images of $\text{Mg}_{0.97}\text{Pr}_{0.03}\text{O}$ synthesized with a) TA, b) HMDA, c) HMTA, d) CA, e) U

Through EDX analysis, shown in Figure 4.30 (a-e) it was detected that the peaks attributed to praseodymium ion for each fuel used in the synthesis of $\text{Mg}_{0.97}\text{Pr}_{0.03}\text{O}$. The EDX spectra also detected the presence of magnesium and oxygen atoms. Any other elements were not detected in EDX spectra. Figure 4. 30-e shows the atomic weight measurement of Pr^{+3} ion and MgO .

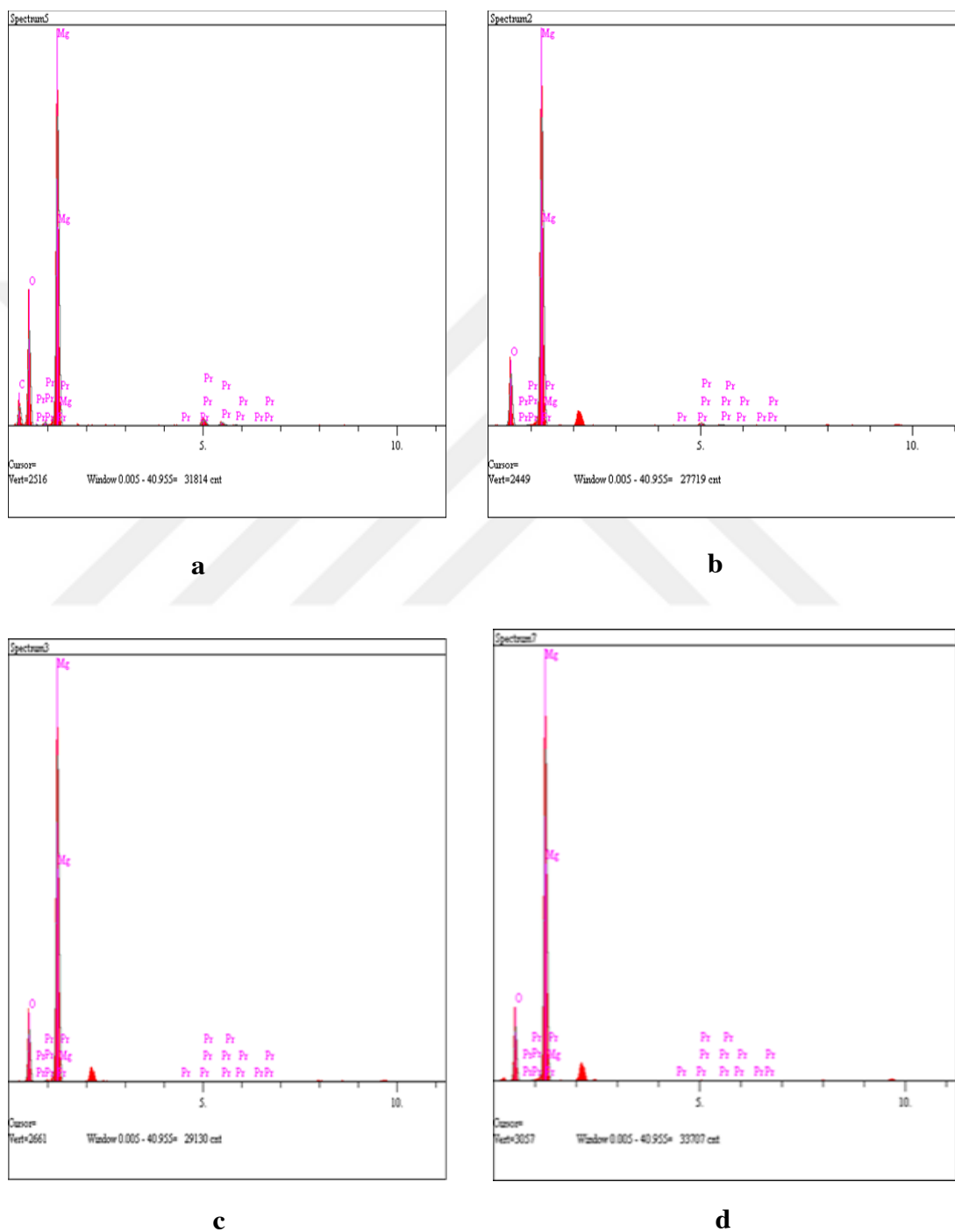
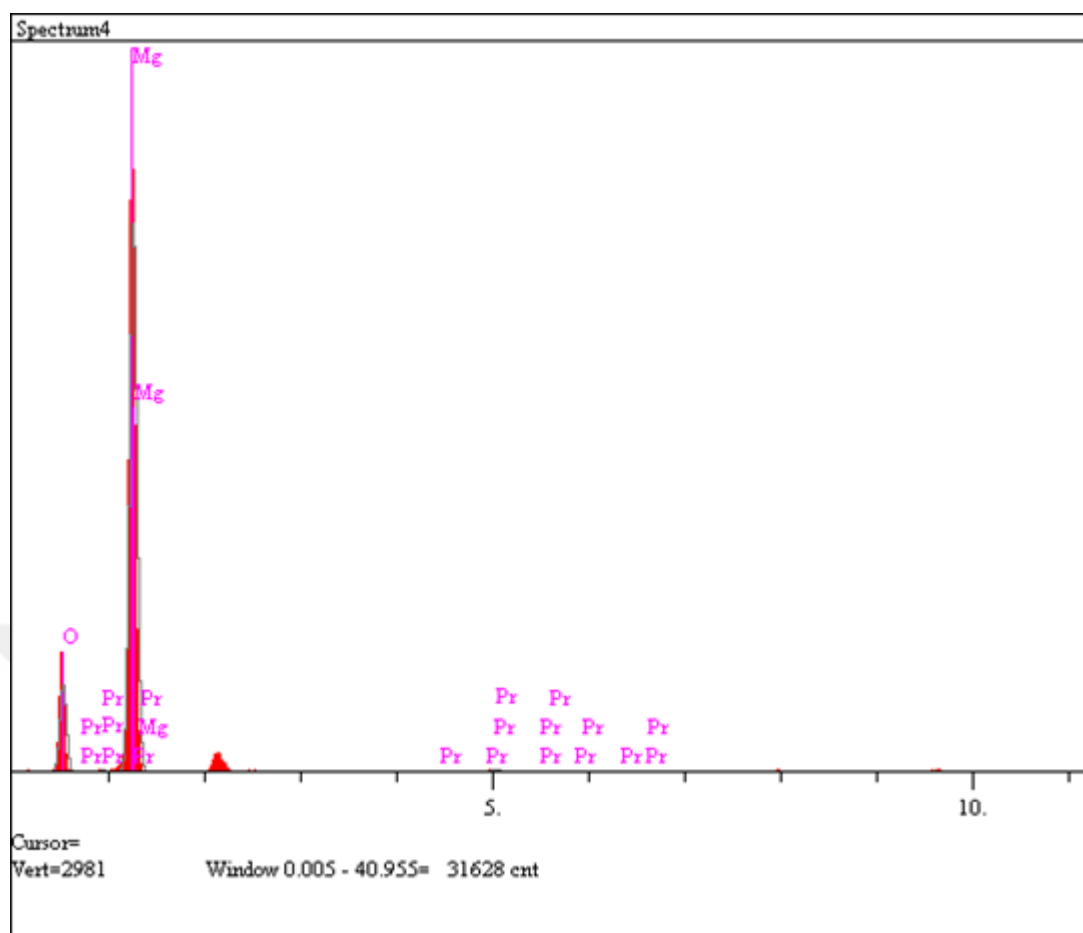


Figure 4. 30. EDX of $\text{Mg}_{0.97}\text{Pr}_{0.03}\text{O}$ synthesized with a) TA, b) HMDA, c)HMTA, d) CA, e)U



e

Element	Line	Intensity (c/s)	Error 2-sig	Conc	Units
O	Ka	77.48	2.783	35.880	wt.%
Mg	Ka	550.78	7.421	61.014	wt.%
Pr	La	4.25	0.652	3.107	wt.%
Total				100.000	wt.%

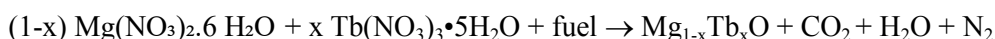
e

Figure 4. 31. EDX of $\text{Mg}_{0.97}\text{Pr}_{0.03}\text{O}$ synthesized with a) TA, b) HMDA, c)HMTA, d) CA, e)U (cont'd)

4.4 Tb doped MgO

The stoichiometric mixture of reactants, $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, fuel and distilled water were mixed and heated at 370°C until the gel form is produced to obtain $\text{Mg}_{1-x}\text{Tb}_x\text{O}$ ($x = 0, 0.05, 0.01, \text{ and } 0.03 \text{ mol}$). Then it was placed into furnace at 400°C , 10 min. After that, it was heated at 400°C for 1 hour, then 500°C for 1 hour to get rid of the organic impurity and analyze the temperature effect on crystallinity.

The general reaction is suggested with different fuels;



($x = 0.005, 0.01 \text{ and } 0.03$)

In the synthesis of MgO, product yield was so high when the TA and CA were used as a fuel. The product color was cream with TA and brown with CA, but it turned to lighter color with increasing temperature. Also, they were fluffy and soft. When the HMDA was used as a fuel, too much gas evolution was observed and MgO product was slightly soft and light cream. Unlike the other fuels, when the HMTA and U were used, magnesium oxide was white color and hard. On the other hand, after combustion process at 400°C for 10 min., MgO that was synthesized with urea was still wet. Because of this, it was heated again at the furnace for a couple minutes. Moreover, in 0.03 mol Tb doped concentration the color was turned to light brown from white at 500°C .

4.4.1 XRD Studies of Tb Doped MgO

The XRD patterns of Tb^{+3} doped MgO show that while the dopant concentration and temperature were significantly affected the crystallinity of MgO synthesized with urea fuel, other fuels were affected slightly. MgO:Tb prepared using HMTA has highest intensity at low temperature, 400°C for 10 min. When the HMDA and HMTA fuels are compared to other fuels, MgO synthesized with HMDA and HMTA have high intensities at 400°C for 10 min. The crystallinity of the MgO synthesized with HMTA increased with the temperature but slightly decreased with the increasing Tb concentration. However, the XRD spectra belong to organic fuel were detected at 12.780 and 12.580 (2theta).

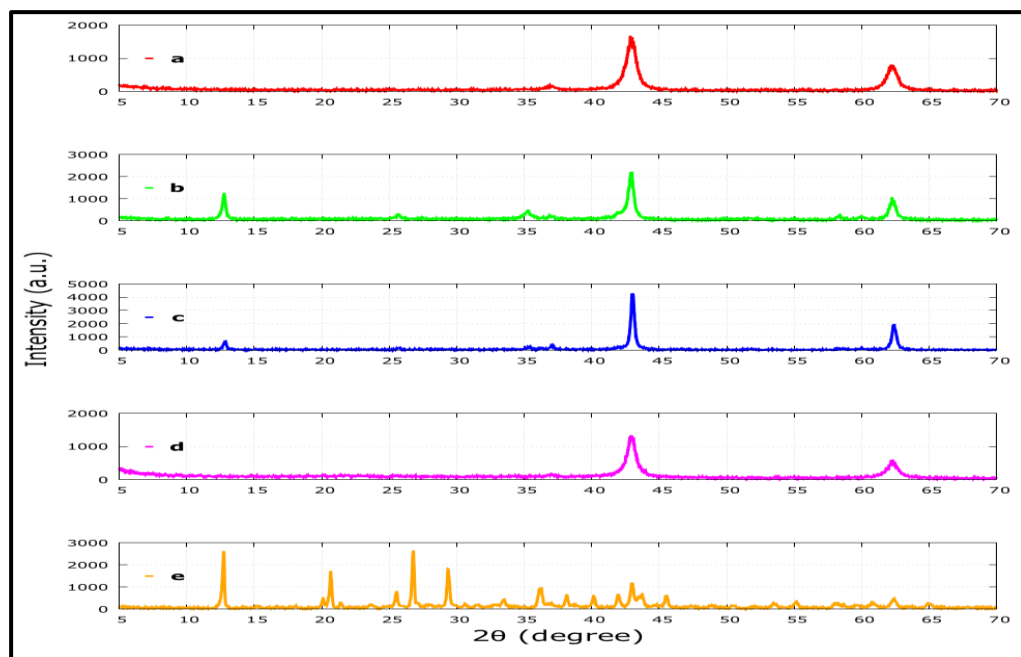


Figure 4.32. XRD patterns of 0.005 mol Tb^{+3} doped MgO heated at 400°C for 10min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

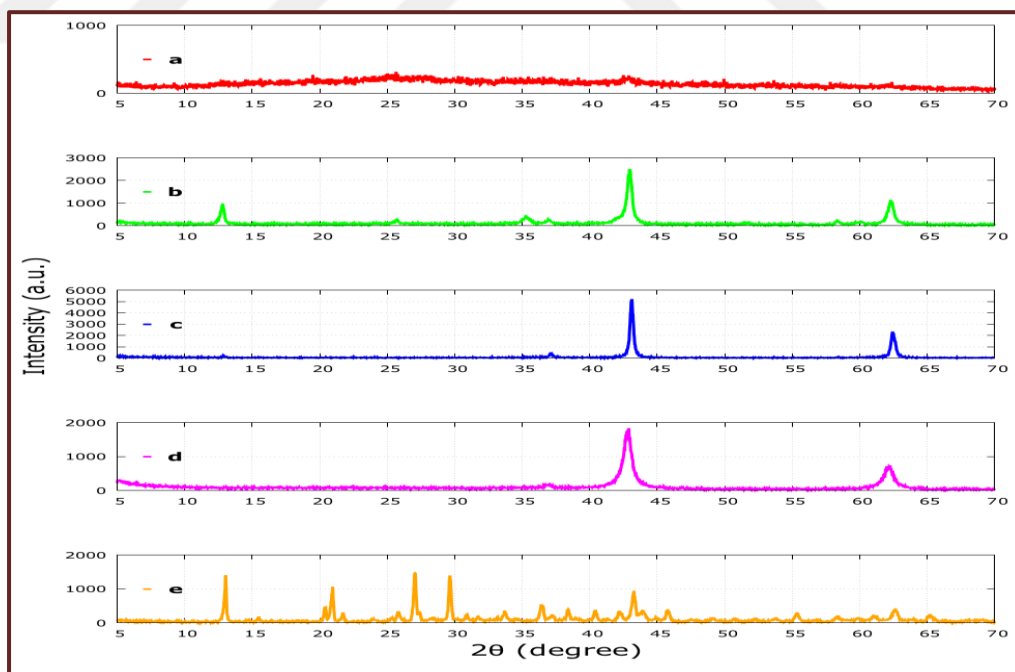


Figure 4.33. XRD patterns of 0.01 mol Tb^{+3} doped MgO heated at 400°C for 10min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

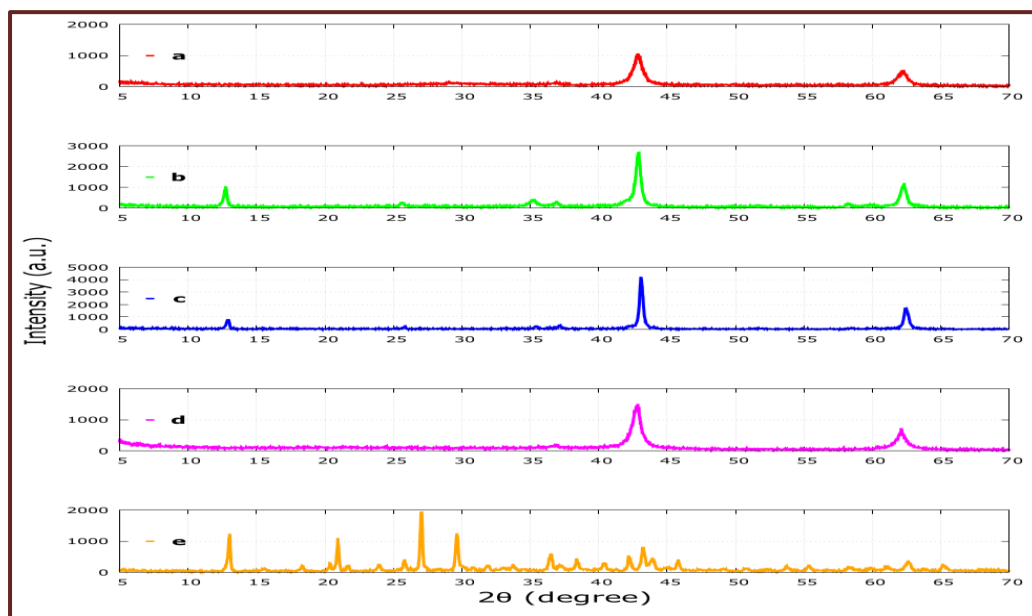


Figure 4. 34. XRD patterns of 0.03 mol Tb⁺³ doped MgO heated at 400°C for 10min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

MgO obtained with TA has lowest crystallinity at 400°C and 500°C with 0.005, 0.01, 0.03 mol Tb. When the HMDA fuel was used, it was observed that crystallinity increased with the temperature but stayed the same with different Tb concentrations. In the use of citric acid fuel, no significant change is observed with the variation of crystallinity temperature and concentration. Lastly, MgO from urea has highest intensity at 500 °C for 0.005 and 0.01 concentrations. It is 8793 cps at 42.920 (2θ) for 0.005 mol Tb, 6908 cps at 43.020 (2θ) for 0.01 mol Tb, 4287 cps at 43.240 (2θ) for 0.03 mol Tb.

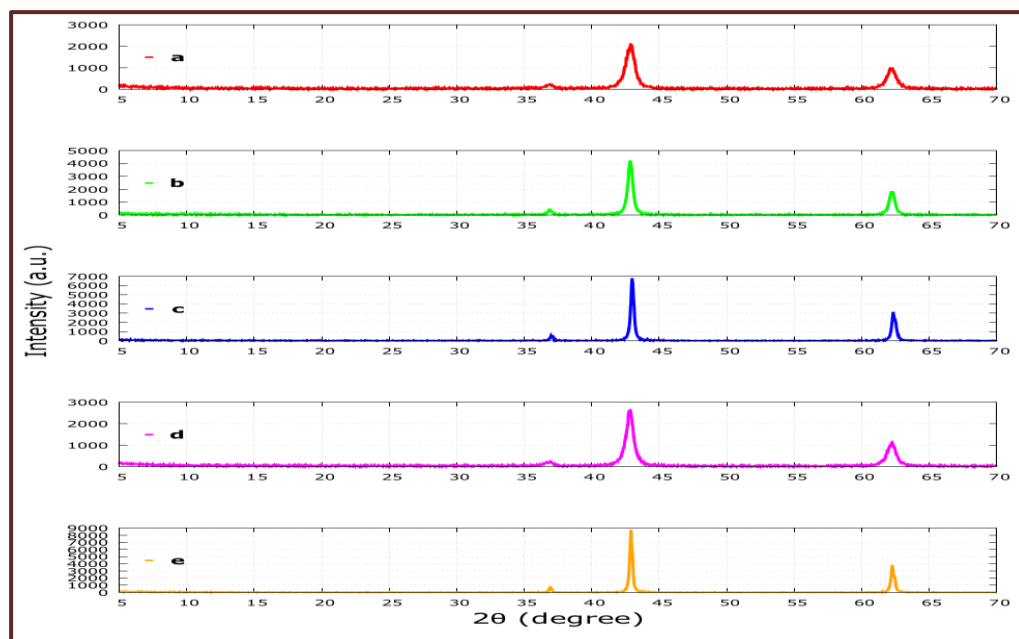


Figure 4. 35. XRD patterns of 0.005 mol Tb^{+3} doped MgO heated at 500°C for 1 h using a) TA, b) HMDA, c) HMTA, d) CA, e) U

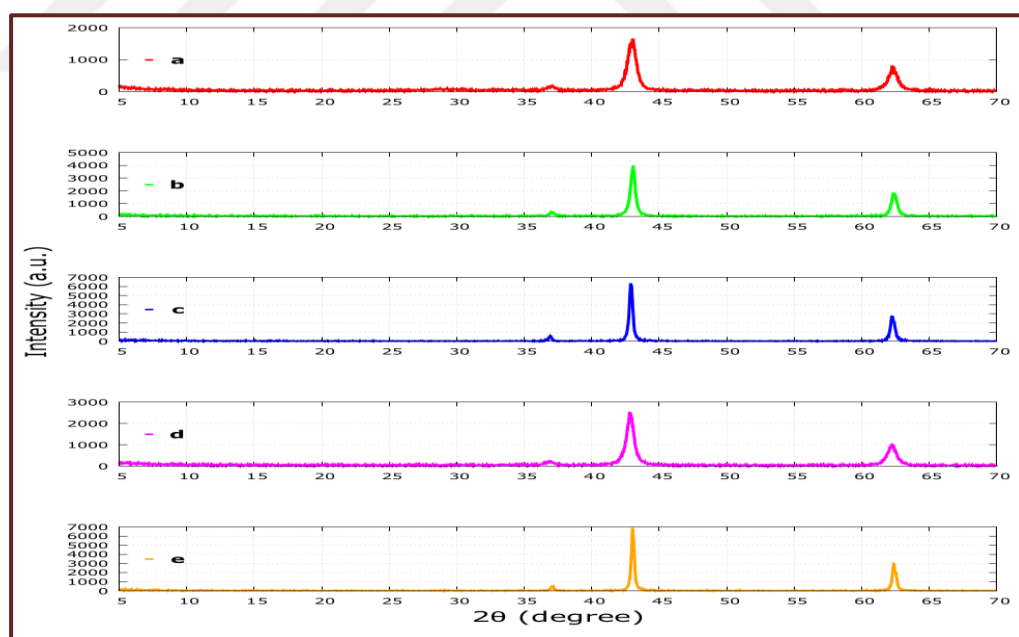


Figure 4. 36. XRD patterns of 0.01 mol Tb^{+3} doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e)

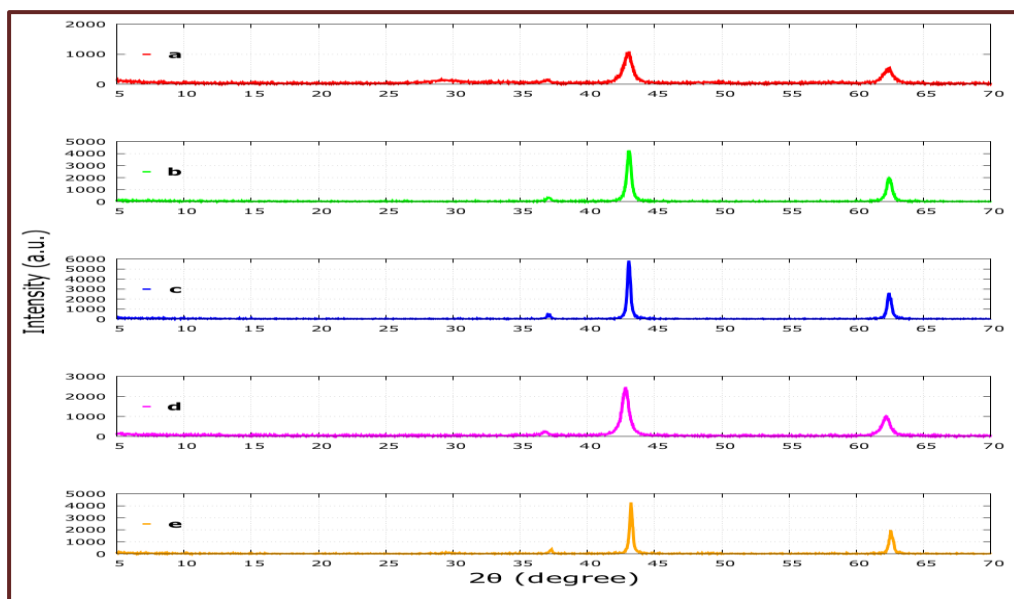


Figure 4. 36. XRD patterns of 0.03 mol Tb+3 doped MgO heated at 500°C for 1 hour, using a) TA, b) HMDA, c) HMTA, d) CA, e) U

Figure 4.37 shows the XRD patterns of undoped and 0.003 mol Tb doped MgO prepared with urea fuel after heating step at 500°C. It was observed that as the dopant concentration increases, the position 2 theta changes. Also, Figure 4.37 clearly shows that crystallinity decreases with increasing dopant concentration.

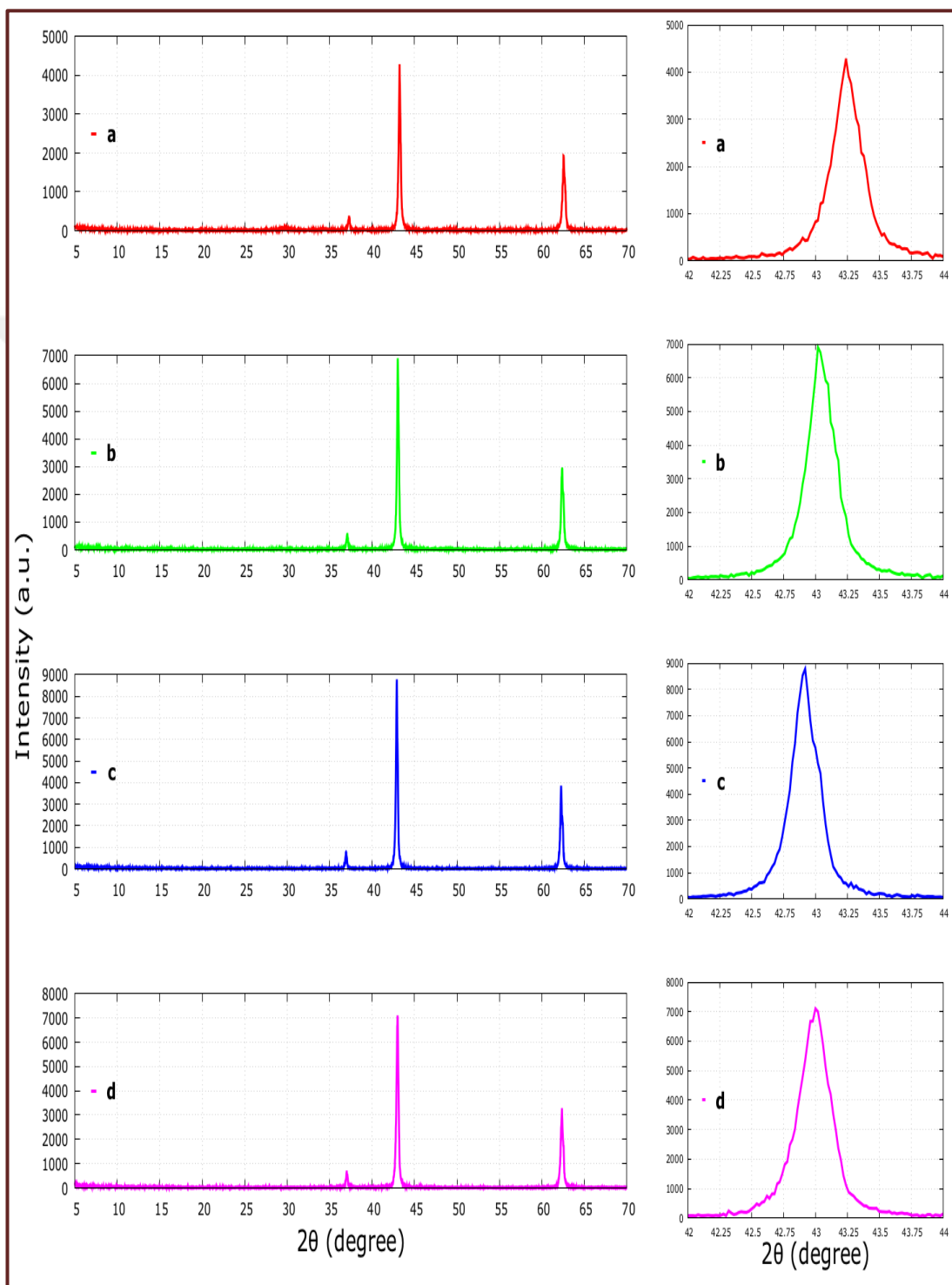


Figure 4. 37. XRD patterns of as-prepared and Tb doped MgO was synthesized with U fuel, at 500°C for 1 hour, a) 0.03 , b) 0.01 , c) 0.005 mol Pr, d) undoped

4.4.2 Infrared Spectroscopy Studies of Tb doped MgO

The room temperature Fourier transform infrared (FTIR) spectra of pure and Tb³⁺ doped MgO samples synthesized via solution combustion method was recorded in the range 300–4000 cm⁻¹ using KBr pellets. Peaks at 3700–3300cm⁻¹ are corresponding to the O–H stretching mode of Hydroxyl groups present on the surface due to moisture. A broad band at 1460–1400 cm⁻¹ in each pattern corresponds to Mg–O stretching vibrations. Peaks at 850–900 cm⁻¹ corresponds to vibrations of metal oxygen bond. The major peaks in the range of 440–690 cm⁻¹ are due to Mg–O stretching vibrations.



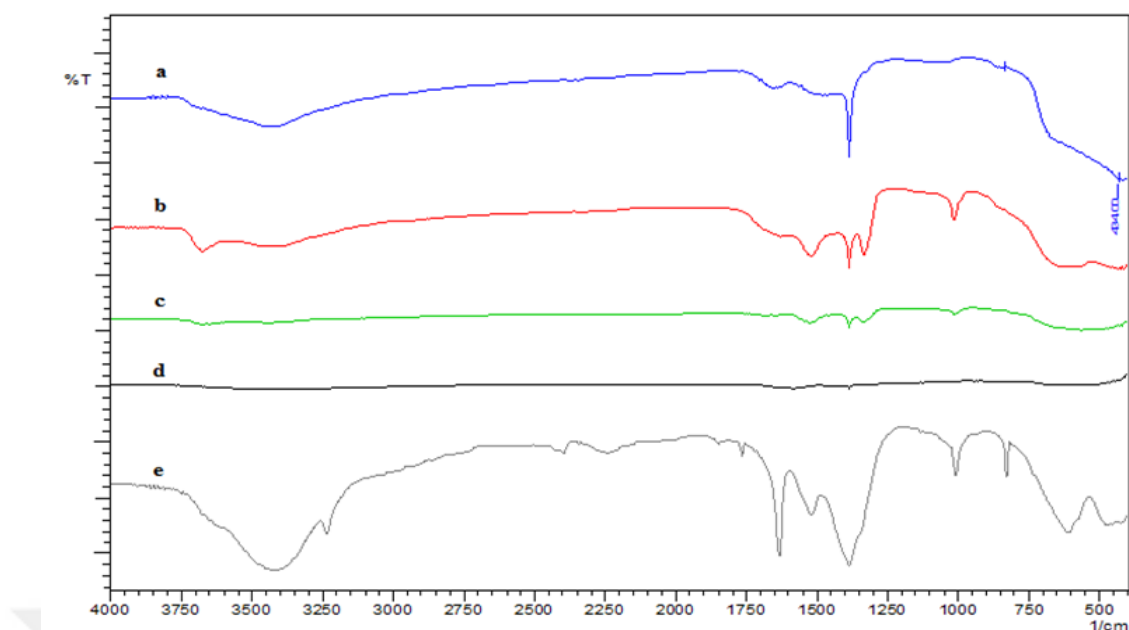


Figure 4. 37. IR spectra of as-prepared 0.005 mol Tb³⁺ doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

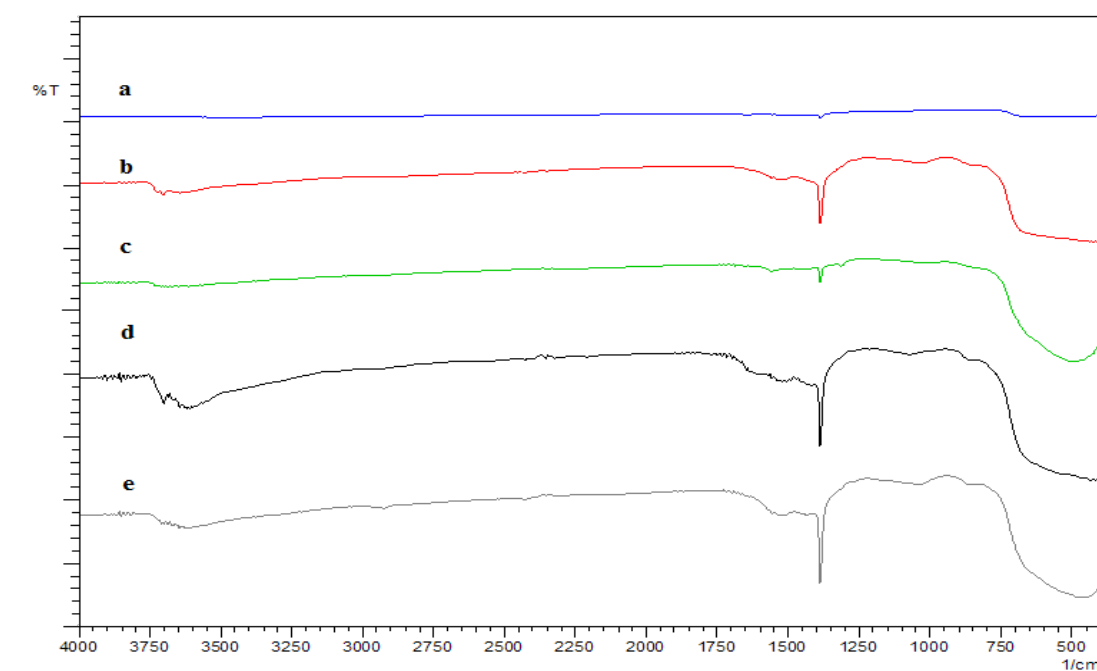


Figure 4. 38. IR spectra of as-prepared 0.005 mol Tb³⁺ doped MgO heated at 500°C for 1 h. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

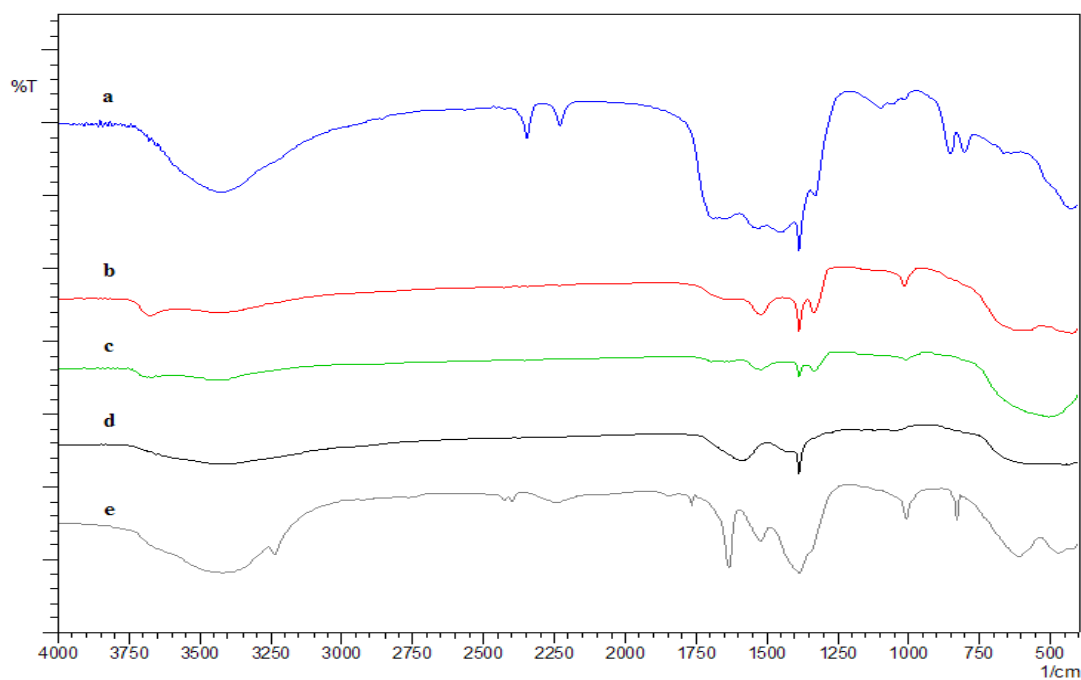


Figure 4. 39. IR spectra of as-prepared 0.01 mol Tb³⁺ doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e)U

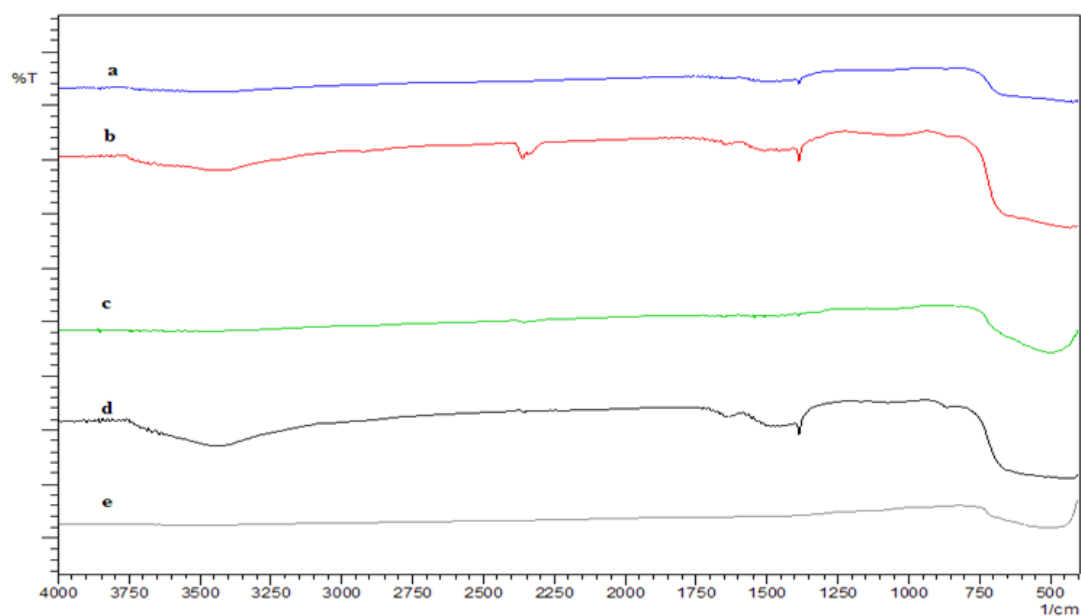


Figure 4. 40. IR spectra of 0.01 mol Tb³⁺ doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

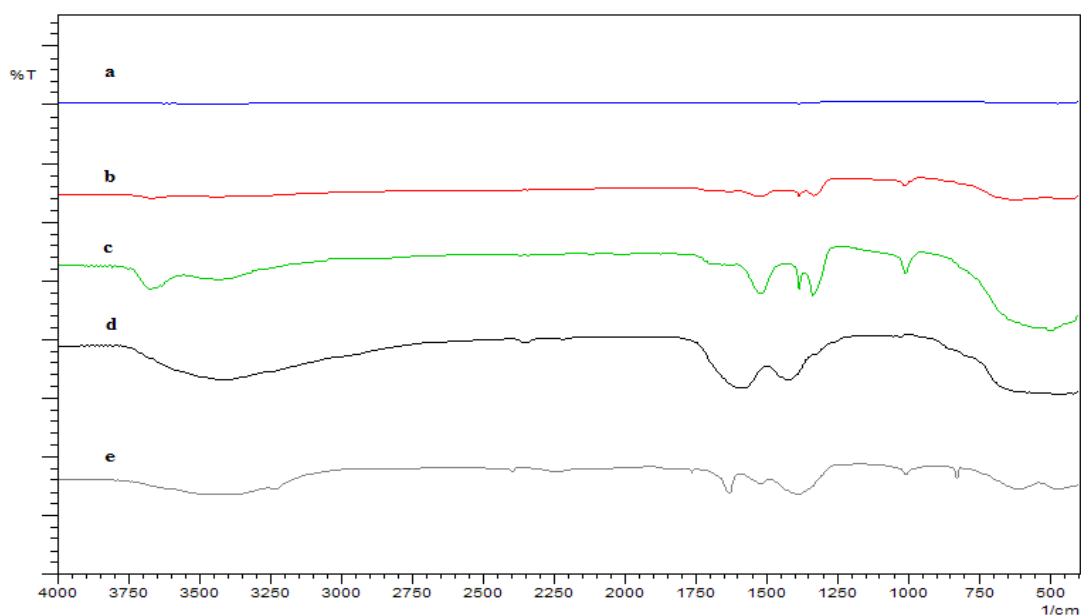


Figure 4. 41. IR spectra of as-prepared 0.03 mol Tb³⁺ doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

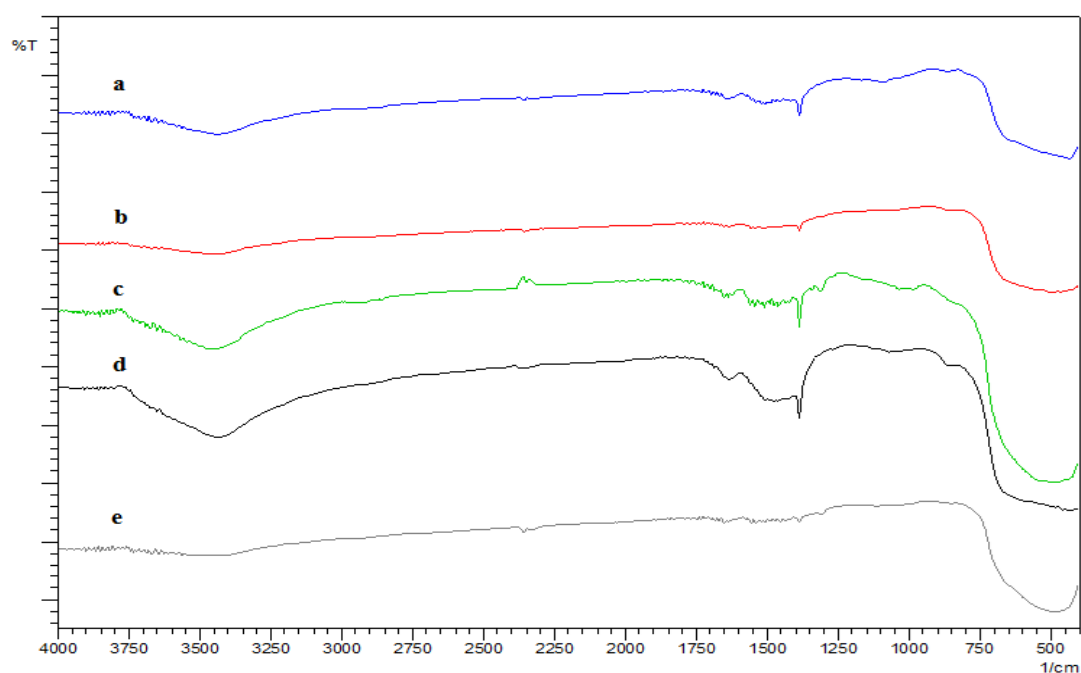
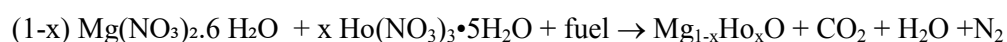


Figure 4. 42. IR spectra of as-prepared 0.03 mol Tb³⁺ doped MgO heated at 500°C for 1 h. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

4.5 Ho doped MgO

Mg_{1-x}Ho_xO (x = 0, 0.05, 0.01, and 0.03 mol) samples were synthesized via SCS method. After combustion process was carried out at 400°C for 10 min. it was placed into furnace at 400°C for 1 hour, then 500°C for 1 hour to get rid of the organic impurity and analyze the temperature effect on crystallinity.

The general reaction with different fuels;



(x = 0, 0.05, 0.01, and 0.03)

When the TA was used as fuel, gas evolution was observed. The product that changed its color from dark brown to light cream has high yield and soft. In the solution mixture, more water was used to dissolve the HMDA fuel. A dense gas evolved when it was heating at 370°C. The MgO product was fluffy and soft and its color turned from light yellow to white. Unlike the HMDA, MgO that was synthesized with HMTA and U was white and hard and its yield was low. Like TA, urea made the MgO fluffy and soft. Also, its product that color changed from dark brown to light cream was high yield and soft.

4.5.1 XRD Studies of Ho Doped MgO

The XRD patterns of the as-formed and calcined (400°C for 1 h, 500°C for 1h) $\text{Mg}_{1-x}\text{Ho}_x\text{O}$ ($x = 0, 0.05, 0.01$, and 0.3) samples prepared by different fuels are shown below. MgO synthesized with TA fuel has lowest crystallinity at 400°C, 10 min. and 500 °C at all Ho concentrations and especially has amorphous structure in the 0.005 and 0.01 mol Ho concentrations at 400°C 10 min as shown in Figure 43 and 44.

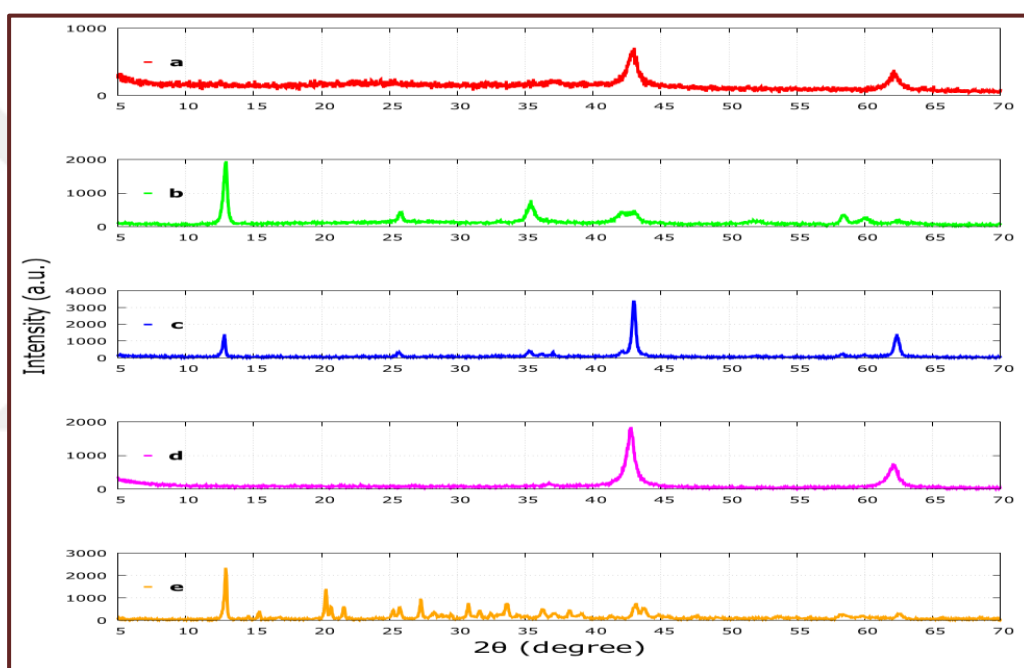


Figure 4. 43. XRD patterns of 0.005 mol Ho doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

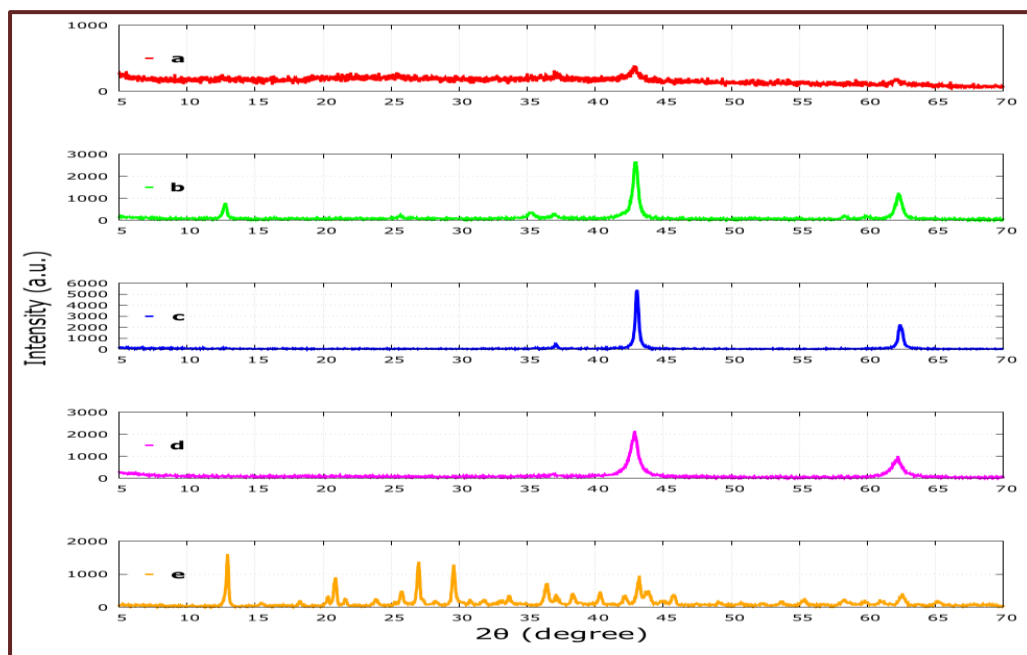


Figure 4. 44. XRD patterns of 0.01 mol Ho doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

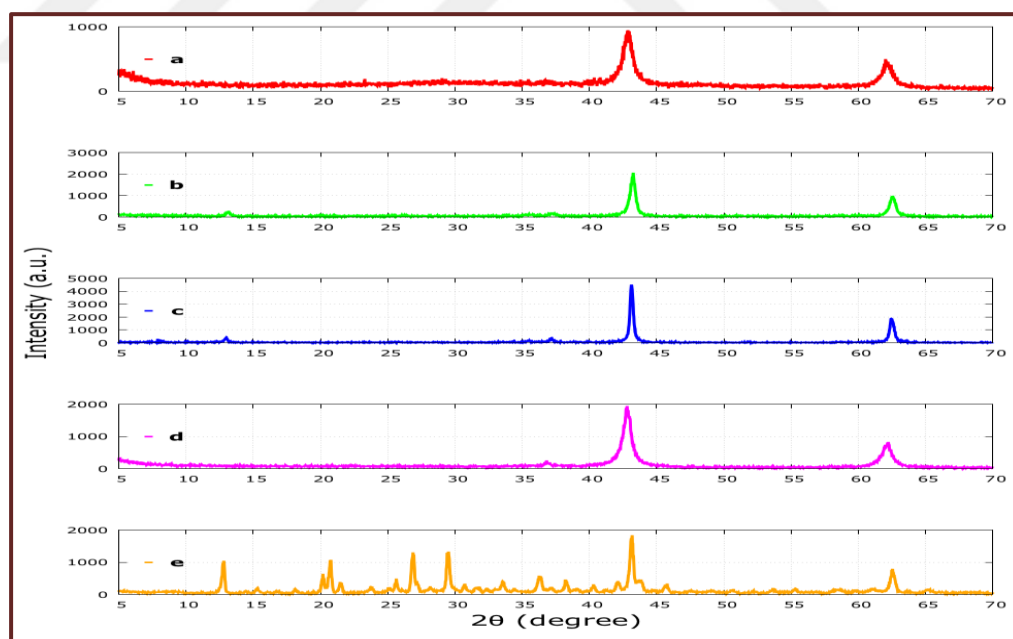


Figure 4. 45. XRD patterns of 0.03 mol Ho doped MgO heated at 400°C for 10 min., using a) TA, b) HMDA, c) HMTA, d) CA, e) U

When the HMDA and CA fuels were used, it was observed that crystallinity slightly increased with the temperature but stayed the same with different Ho concentrations. Also, HMTA has highest intensity at low temperature (400°C, 10 min.) at all three concentrations. However, the XRD lines belong to organic fuel was detected at 13.060 and 13.160 (2theta) for 0.005, 0.03 mol Ho. Also, it was observed crystallinity significantly changes with increasing temperature. In the use of urea fuel, MgO has highest crystallinity at 500°C in all Ho concentrations. It is 7529 cps at 42.940 (2θ) for 0.005 mol Tb, 6725 cps at 42.980 (2θ) for 0.01 mol Tb, 7462 cps at 42.980 (2θ) for 0.03 mol Tb (see Figure 4.49). Finally, a very small shift in the position of highest peak to the lower side of 2θ is observed for Ho doped samples. The X-ray diffraction peaks of the samples were well matched with ICDD card No. 77-2179.

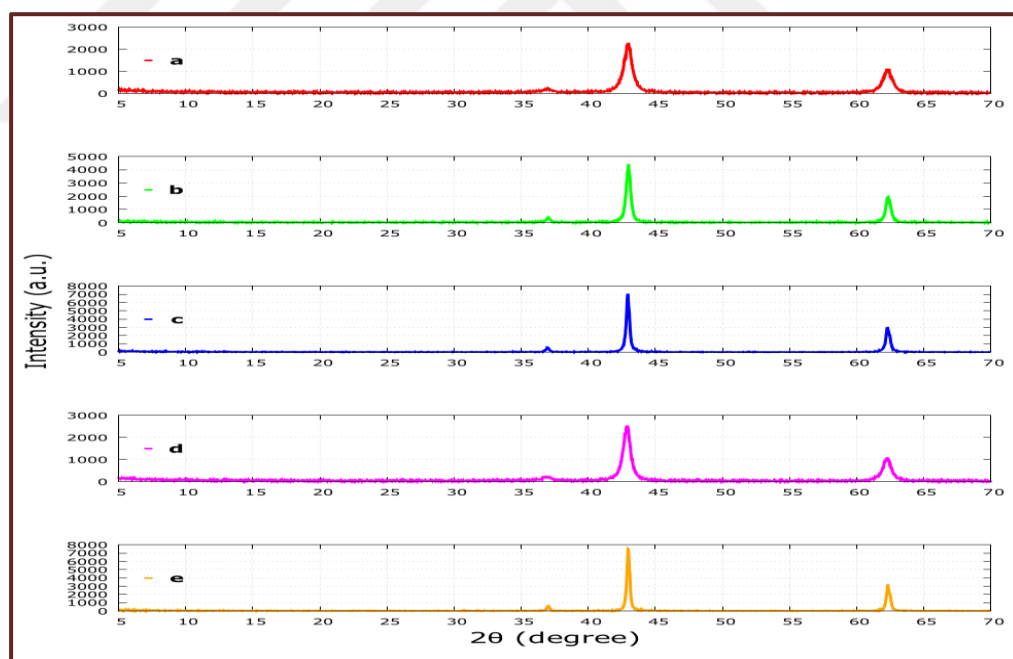


Figure 4. 46. XRD patterns of 0.005 mol Ho doped MgO heated at 500°C for 1 hour, using a) TA, b) HMDA, c) HMTA, d) CA, e) U

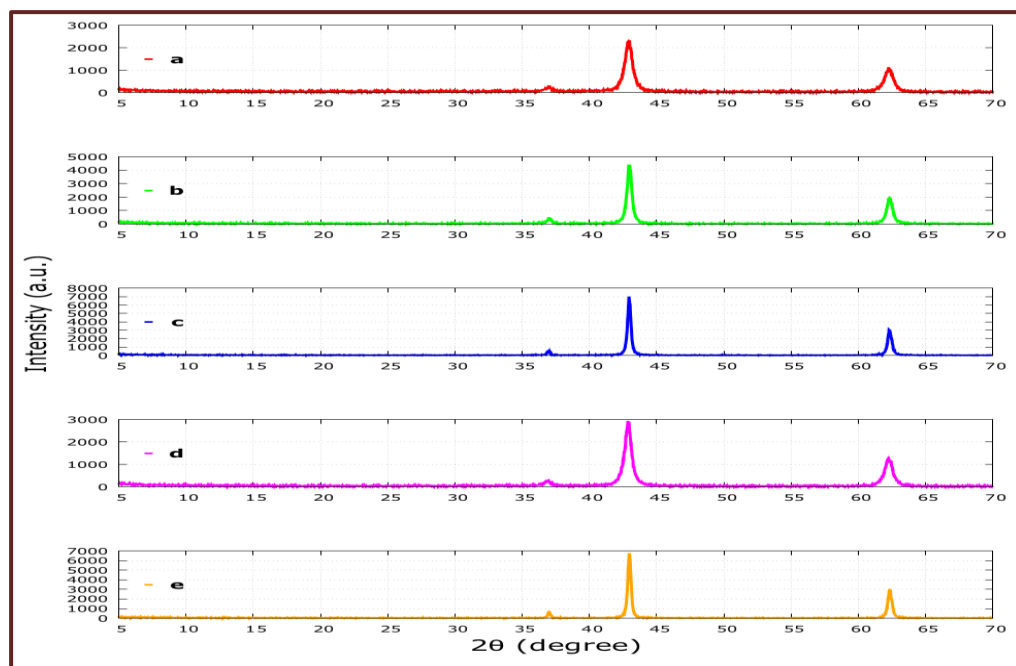


Figure 4. 46. XRD patterns of 0.01 mol Ho doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c) HMTA, d) CA, e) U

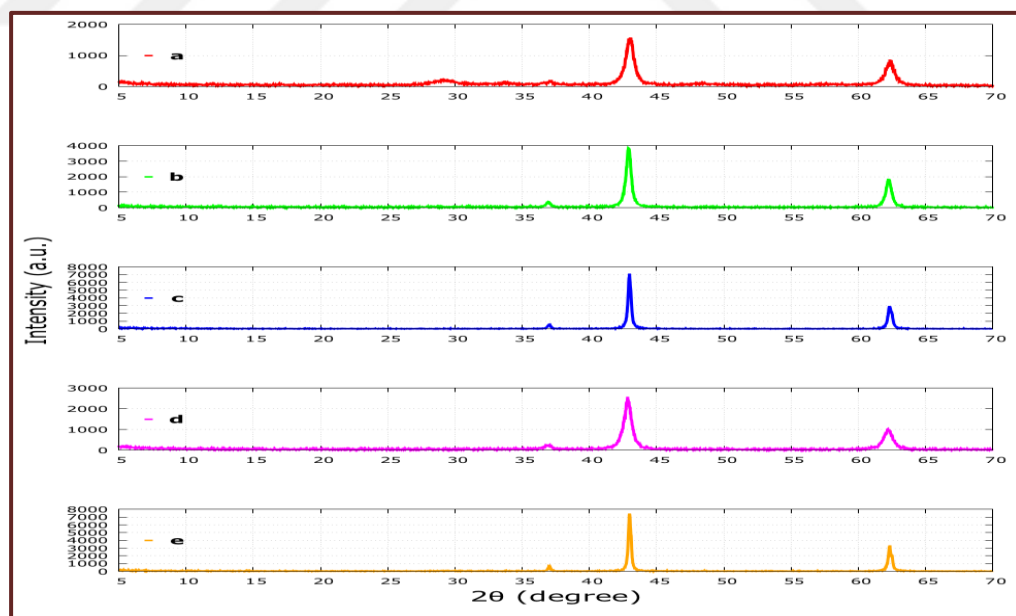


Figure 4. 47. XRD patterns of 0.03 mol Ho doped MgO heated at 500°C for 1 hour, using a) TA, b) HMDA, c) HMTA, d) CA, e) U

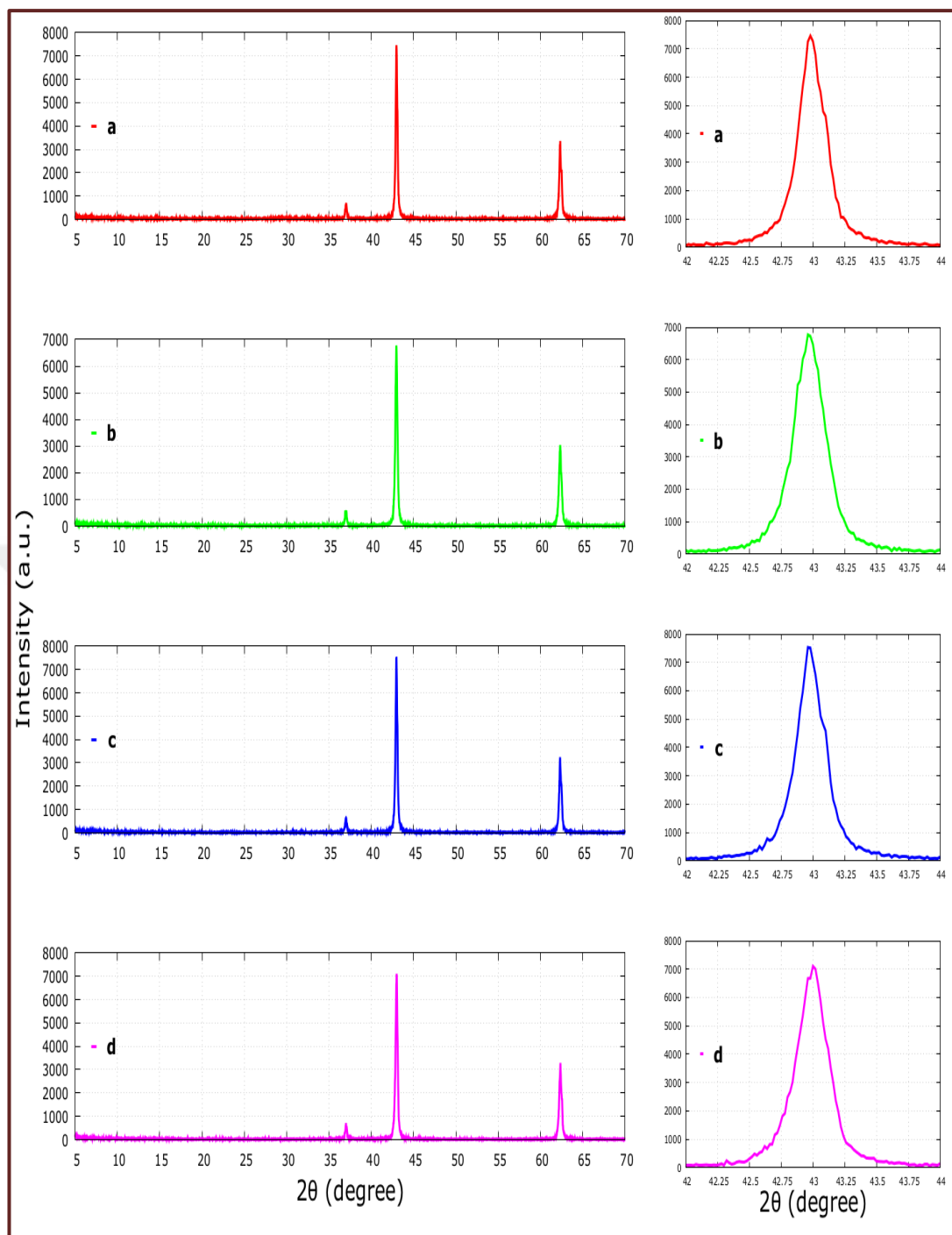


Figure 4. 48. XRD patterns of as-prepared and Ho doped MgO that was synthesized with urea fuel heated at 500°C 1 hour, a) 0.03, b) 0.01, c) 0.005 mol Ho doped, d) undoped MgO

4.5.2 IR Studies of Ho doped MgO

The Fourier transformed spectrum of 0.005, 0.01, 0.03 mol Ho doped MgO at low and high temperature shown in Figure 50-55. The spectrum was recorded between the range 4000 and 400 cm^{-1} . The vibrational absorptions at 440–700 cm^{-1} which may be assigned to the stretching vibrations of Mg-O. Further, the peak at 550–890 cm^{-1} is higher frequency of MgO stretching and 410–450 cm^{-1} is lower frequency stretching. The bands appeared at 840–900 cm^{-1} may be due to stretching vibrations of the magnesium oxygen (Nassar et al., 2017). Also, the bands appeared at 3290–3670 and 1300–1800 cm^{-1} are associated with OH⁻ group vibrations due to H₂O bound on the surface of the sample. Previous studies supported the idea that when the organic substances exist in synthesis, it is possible to find the radicals bonded to the surface of the vacant sites (Lopez et al., 1991). After all, it is clearly seen that water and organic compounds disappeared with increasing temperature.

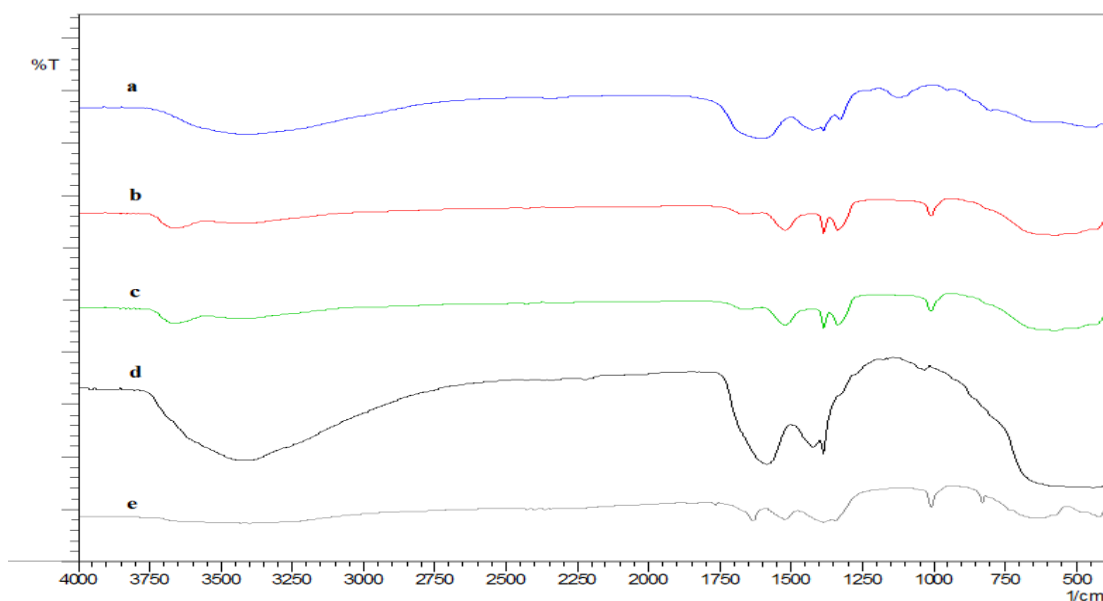


Figure 4. 49. IR spectra of as-prepared 0.005 mol Ho doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c) HMTA, d) CA, e) U

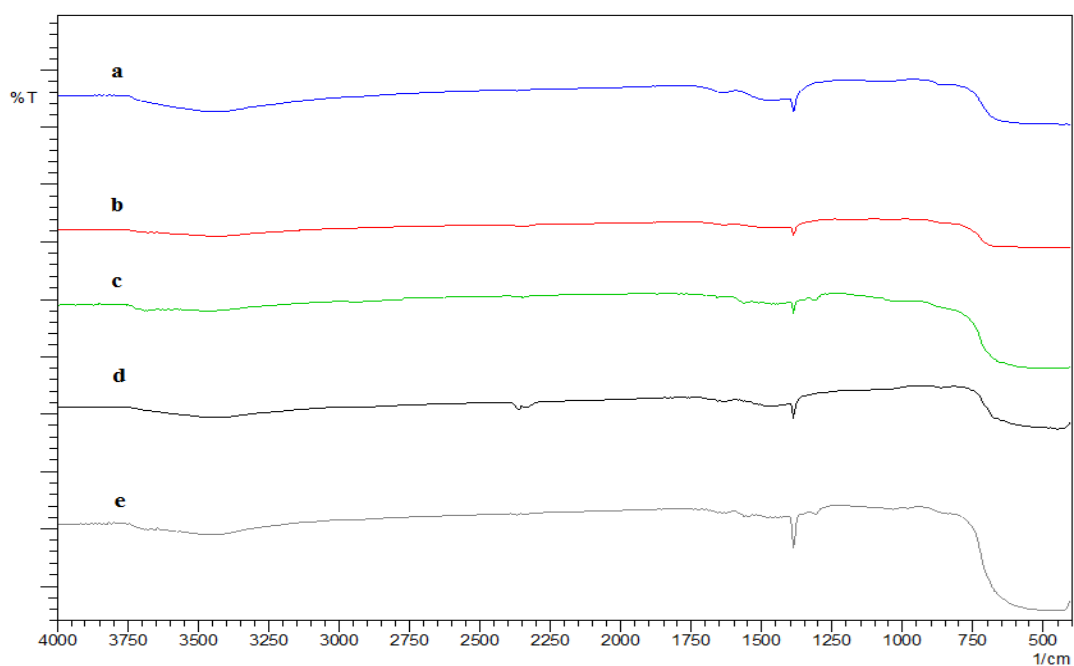


Figure 4. 50. IR spectra of as-prepared 0.005 mol Ho doped MgO heated at 500°C for 10 min. using a) TA, b) HMDA, c)HMTA, d) CA, e) U

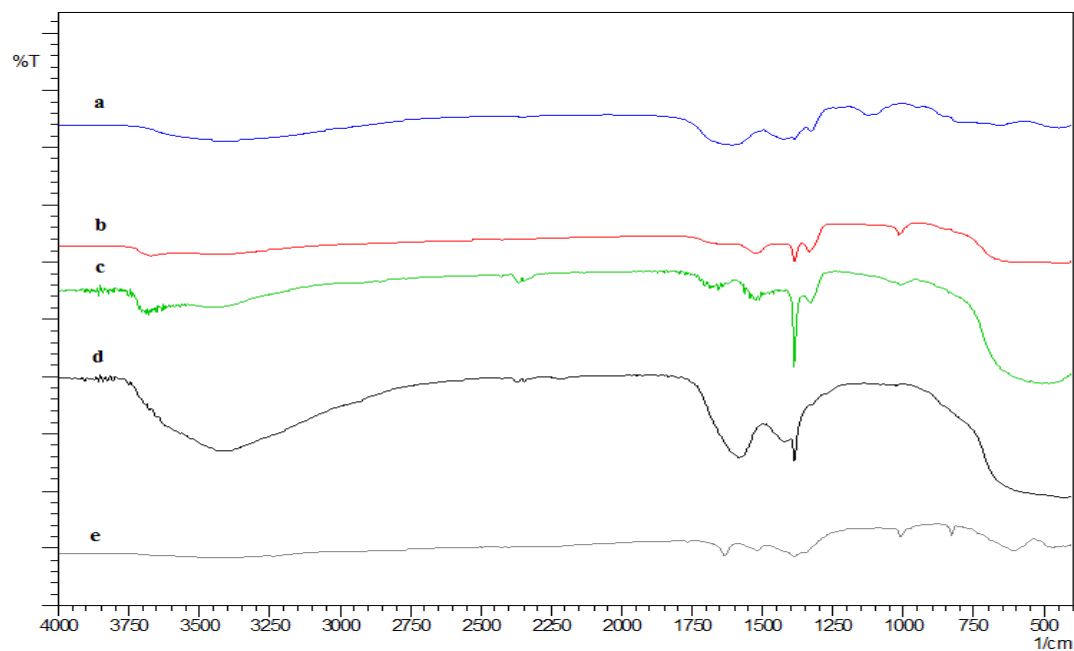


Figure 4. 51. IR spectra of as-prepared 0.01 mol Ho doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c)HMTA, d) CA, e) U

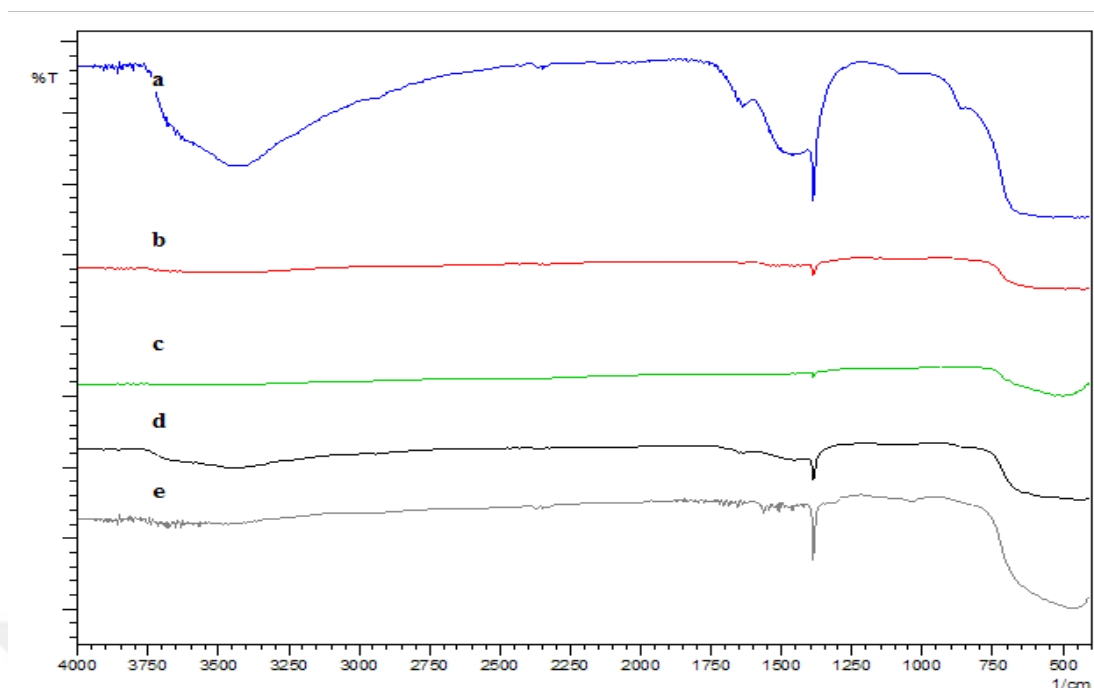


Figure 4. 52. IR spectra of as-prepared 0.01 mol Ho doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c)HMTA, d) CA, e) U

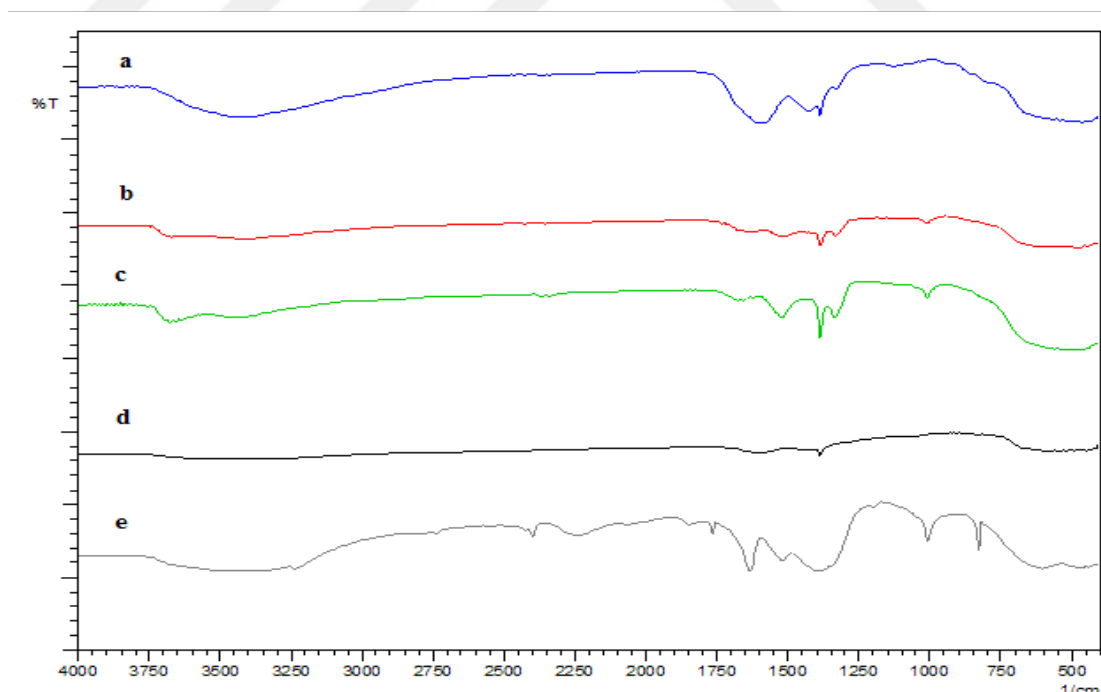


Figure 4. 53. IR spectra of as-prepared 0.03 mol Ho doped MgO heated at 400°C for 10 min. using a) TA, b) HMDA, c)HMTA, d) CA, e) U

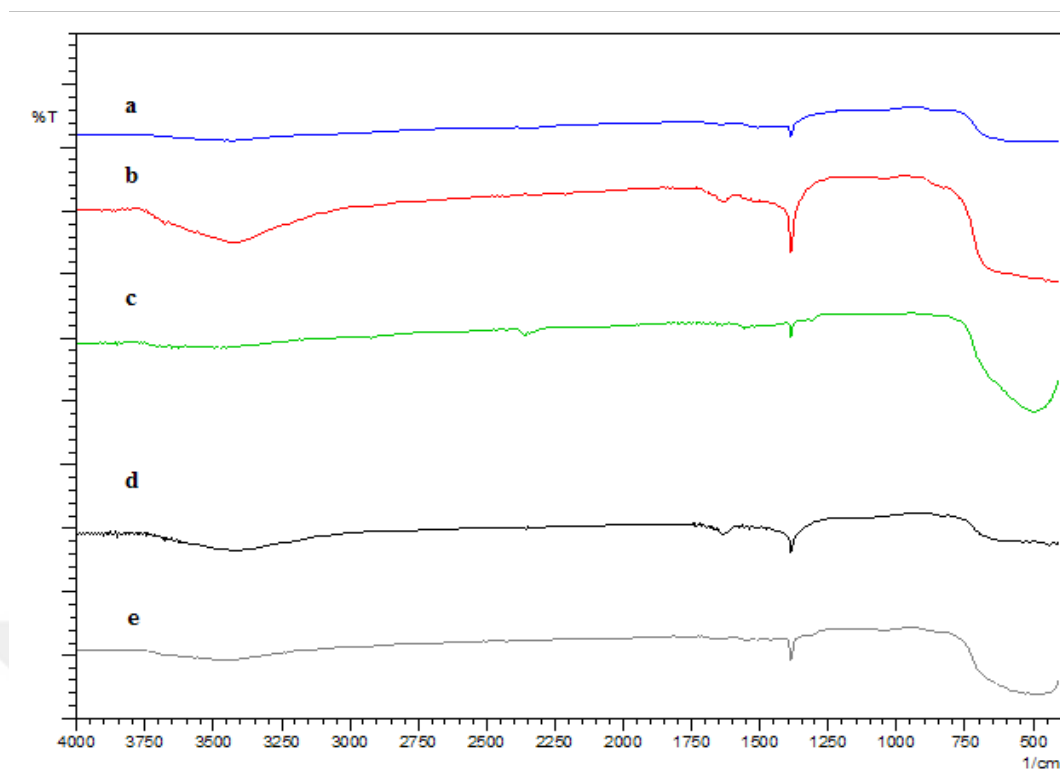


Figure 4. 54. IR spectra of as-prepared 0.03 mol Ho doped MgO heated at 500°C for 1 hour using a) TA, b) HMDA, c)HMTA, d) CA, e) U

5. CONCLUSION

Magnesium oxide nanostructures were successfully prepared employing a solution combustion method using various fuels such as tartaric acid, 1,6-diaminohexane, hexamethylenetetramine, citric acid, and urea. This method offers wide range of advantages such as high purity at low temperature, simple experimental setup, time and energy saving, when compared to the other methods. Studing of XRD, IR, SEM and EDX of these MgO nanopowders obtained in this thesis led to following conclusions.

In the first part of this study, undoped MgO nanoparticles were synthesized with eight different fuels as TA, HMDA, HMTA, CA, U, CH, Gly and β -Alanine. It was found that tartaric acid, urea, citric acid, 1,6-diaminohexane, hexamethylenetetramine fuels were suitable while β -alanine, glycine and carbohydrazide fuels were not suitable because of causing very low amount of yield of the products in the synthesis of MgO nanoparticles.

Temperature and fuel effects were examined on the structural parameters of undoped MgO nanoparticles. The XRD results reveal that crystallinity of magnesium oxide prepared as single phase with TA, CA, HMDA increased regularly with temperature while remained constant of HMTA, and decreased slightly of U. Also, HMTA has the highest crystallinity at low temperature (400°C, 10 min.) and urea has the highest crystallinity at 400°C and 500°C.

In the next step, single phase MgO:RE (Pr, Tb, Ho) nanoparticles were synthesized and the effect of RE metal type and concentration (0.005, 0.01, 0.03), temperature and type of fuel on the structural features of MgO materials were investigated. Pr doped MgO synthesized with HMTA has highest crystallinity in all concentrations at low temperature while TA has lowest intensity in all concentrations at low and high temperature. Urea has the highest crystallinity at all concentrations at high temperature.

In the following step, Tb doped magnesium oxide XRD datas show that TA has the lowest crystallinity but highest yield at all temperatures and concentrations when compared to other fuels. HMTA has the highest crystallinity at low

temperature in all concentrations and at high temperature in 0.03 mol Tb concentration. Urea has the highest crystallinity at 500°C at concentrations of 0.005 and 0.01 Tb. On the other hand, crystallinity increases with temperature, but decreases with increasing dopant concentration.

The XRD datas of Ho doped MgO synthesis show that MgO prepared with TA has the lowest crystallinity at all temperatures and the lowest crystallinity is detected at 0.01 mol Ho concentration as does Pr doped MgO. HMTA has the highest crystallinity at all concentrations with a significant difference at low temperature. Besides, U has the highest crystallinity at all concentrations and temperatures. MgO synthesized with U has the highest crystallinity at 500°C for each concentration. Although a steady increase or decrease at crystallinity was not observed depending on small concentration change, it was observed that the crystallinity of MgO:Ho synthesized with all fuels increased with the temperature.

Consequently, the results showed that temperature, fuel, type of RE metal, concentration of RE metal had a significant effect on the properties of synthesized undoped and RE doped MgO nanoparticles such as crystallinity, purity and morphology. Also, the crystallite size calculations from Scherrer equation proved that all synthesized MgO's through solution combustion technique are in nanoscale. IR data also agreed all the XRD patterns for MgO nanoparticles synthesized in this thesis.

6. REFERENCES

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