Shape Transition Effect of Temperature on MgO Nanostructures and its Optical Properties

K. Tamizh Selvi M. Rathnakumari M. Priya P. Suresh Kumar

Abstract— In this paper we report the synthesis of various morphologies of MgO nanomaterials such as nanoflakes, nanoflowers and nanoparticles using magnesium acetate tetra hydrate as a precursor and refluxed at a suitable temperature. The refluxed powder sample is calcined at three different temperatures. The white powder product obtained was characterized by TG/DTA, XRD, HRSEM and photoluminescence (PL). The results showed that the synthesized powder is pure cubic MgO and the grain size increases with increasing temperature. The micro-strain is calculated using Williamson-Hall plot method. HRSEM picture showed that shape changes from nanoflakes to nanoparticle by increasing temperature.

Key words: MgO nanomaterial, TG/DTA, XRD, HR-SEM with EDAX, TEM, PL, Micro-strain.

1. Introduction:

Researchers have been focused much attention to the one dimensional nanostructure of nanomaterials for their applications in nano-electronic devices. MgO is typical wide band gap (7.2eV) semiconductor, represents an important class of functional metal oxides with a broad range of properties. They also find tremendous application in catalysis, refractory industries, electronics, cosmetics and waste water remediation [1]. MgO performs excellently in high temperature, particularly in the creation of electrical insulation. Other properties of MgO include effective corrosion resistance and that it is transparent to IR light. It has a high thermal and low electrical conductivity [2]. MgO is thermodynamically stable and wide band gap material; it has application as a buffer layer in superconductor and ferroelectric materials [3]. The vast applications of MgO nanomaterial inclined to work on this material. Here for, various morphologies of MgO such as nanorods, nanobelts, nanowires, nanosheets, and nanoplates [4-9] have been synthesized via a variety of different chemical routes.

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In this paper, we present synthesis of MgO nanoparticle by sol-gel route under reflux condition and the effect of annealed temperature on the particle size, morphology and luminescent properties of the MgO nanomaterial were studied.

2. Experimental:

Analytical grade Magnesium acetate tetra hydrate $(CH3COO)_2Mg.4H_2O$ is used as a starting material; AR grade ethanol is used as a solvent. Acetic acid is taken as a gelling agent.

1M of Magnesium acetate tetra hydrate is dissolved with 50ml ethanol. 0.5M of acetic acid is added with this solution and stirred for 1/2hour. Then, this solution is transferred into round bottom flask and refluxed for 1h. The obtained powder sample is heat treated with 90^0C for 6h. The as-synthesized powder sample is calcined at three different temperatures 400^0C, 500^0C and 600^0C for 2h. These three samples labeled as sample-A (400^0C), sample-B (500^0C), sample-C (600^0C).

3. Results and Discussions:

3.1 Characterization:

The samples A, B and C respectively were characterized by X-ray diffractometer (XRD) with CuKα radiation in the range of 10-80^o (λ=0.154nm). Thermal decomposition temperature was studied by using TG/DTA. HRSEM was recorded using FEI Quanta FEG 200 High Resolution Scanning Electron Microscope coupled with EDX and TEM (Philips Model: CM-20). The photoluminescence (PL) spectra of MgO were recorded by the Perkin-Elmer lambda 900 spectrophotometer with a Xe lamp as the excitation light source.

3.2 TG/DTA Analysis:

Fig. 1 shows the TG/DTA curve of as-synthesized MgO precursor after refluxed. TGA measures weight changes as a function of temperature. In this case we can see three peaks at 155.96, 329.11 and 359.12°C. The first weight loss of 9.234% below the temperature 155.96°C can be attributed to the evaporation of physically absorbed water in the air.

The second weight loss of 42.92% observed around 300-360°C corresponds to the decomposition of organic compounds in the precursor; Fig 1 indicates that the weight loss is terminated at 369.33°C, this is due to the decomposition of the precursor could be terminated at about 369.33°C. This is consistent with the previous report [10]. Therefore, we annealed the samples above 400°C, and the sample annealed at three temperatures 400°C, 500°C and 600°C to study its morphology, crystallite size and luminescence property.

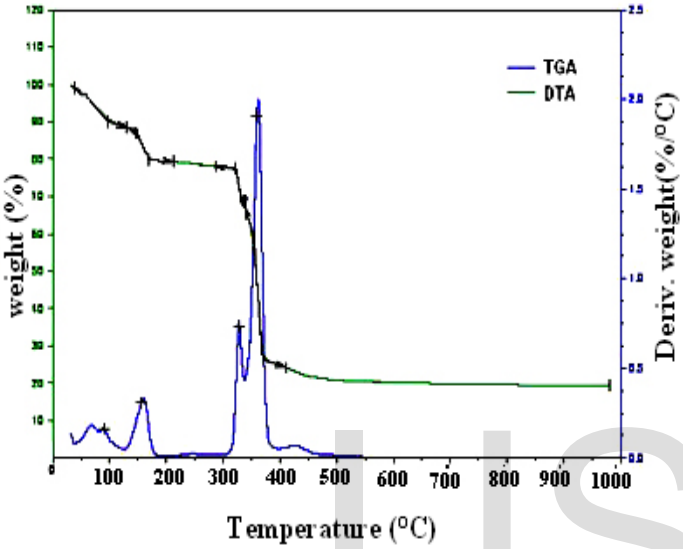

Fig. 1 TG/DTA pattern of as- synthesized MgO precursor after refluxed

3.3 Phase analysis:

Fig. 2 Shows the XRD spectra of sample-A, sample-B and sample-C respectively. The entire sample exhibits four major peaks with (hkl) planes (111), (200), (220), (222) at around 37.06°, 42.94°, 62.49°, and 78.71° respectively can be well indexed to the cubic MgO structure (JCPDS:04-0829). Lattice parameters are almost coincidence for all samples prepared with different temperatures (in good agreement with JCPDS). Is in excellent agreement with the reference pattern [14, 15]. No other peaks were found in the spectra. This indicates the high purity of the products. The average grain size is calculated using Scherer formula [11]. The lattice constant and the particles size of each sample are listed in table1. We also used the Williamson-Hall equation [12, 13] to calculate micro-strain (which is listed in table 1). Micro-strain and small size of the particle is one of the reasons for the broadness of the peak. The Williamson-Hall equation is,

$$B\cos\theta = \frac{k\lambda}{t} + 4\varepsilon\sin\theta$$

Where B is Full-width at half maxima, θ is the angle of diffraction, t is the particle size calculated from X- ray diffraction spectra, ε is the micro-strain and λ is the wavelength of CuKα radiation[λ=1.54056Å]. The dislocation density is calculated using the relation $\delta=1/D^2$ (lines/Sq.meter), where D is the particle size. Table 1 show that micro-strain increases and dislocation density decreases with increasing temperature.

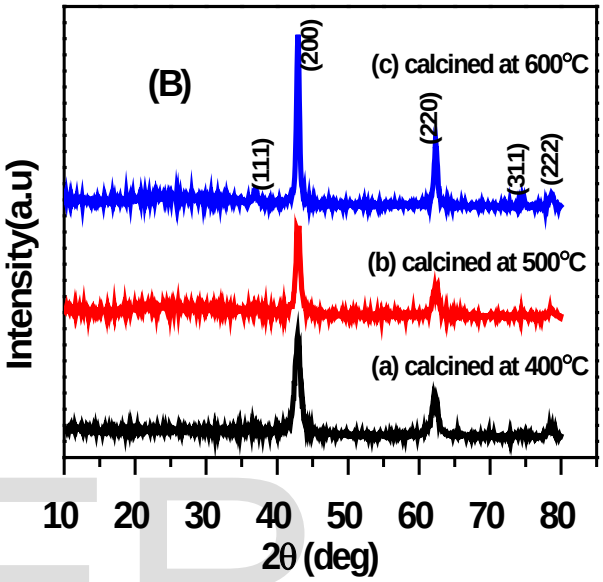

Fig. 2 XRD spectra of (a) sample-A, (b) sample-B and (c) sample-C.

Table 1: Lattice constant, Particle Size, micro-strain and dislocation density Variation with different Annealing Temperature

sample	Lattice constant (Å)	Particle size (nm)	Micro strain ($\times10^{-4}$)	δ (lines/Sq. meter)
Sample A	4.22	8.38	-0.00832	0.0142
Sample B	4.208	10.95	-0.00460	0.0083
Sample C	4.21	15.85	-0.00043	0.00368

3.4 HR-SEM and EDX analysis:

Fig 3 Shows the HRSEM pictures of MgO samples. In fig 3, sample-A and sample-B shows the morphology of nano

sheets, nano-flakes and nanosheets are assembled to form a smooth surface flower like structure of MgO. A smooth layered surface may be ideal for building flat electrical components, such as photovoltaic devices, batteries and fuel cells. The drastic change has been observed at 600°C, uniform, spherical nanoparticles of MgO are formed shown in fig (4e, 4f). This shows that morphology strongly depends on annealed temperature. The energy dispersive X-ray spectra (EDX-not shown here) of MgO samples assures the existence of Mg and O at appropriate concentration without any impurities. The measured atomic concentrations of the elements with respect to the annealed temperature and solvent were given in Table 2.

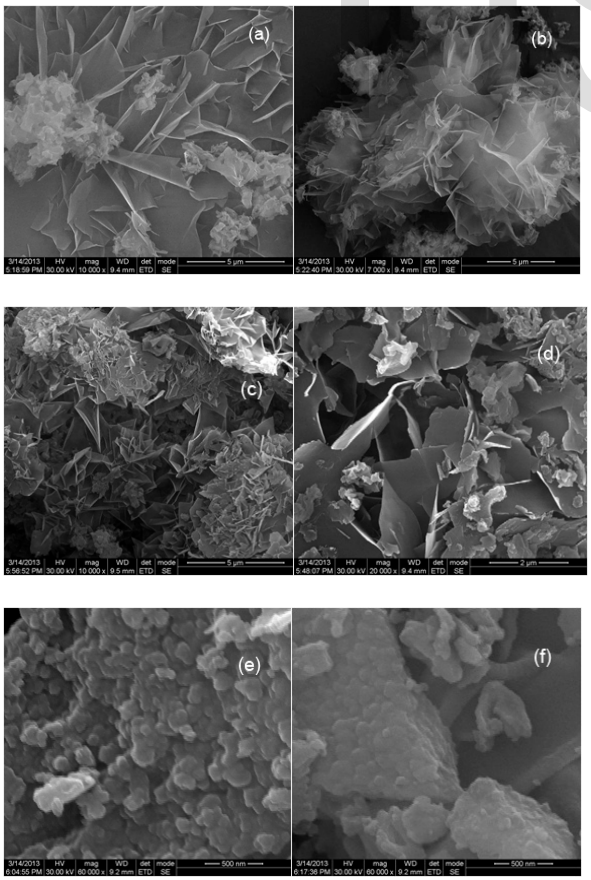

Fig. 3 SEM image of (a,b) sample A, (c,d) sample B, (e,f) sample C

Table 2 Atomic concentration of elements for MgO nanocrystals measured from the EDS analysis

Sample	Atomic % of Mg	Atomic % of O
Sample A	42.78	57.22
Sample B	50.53	49.47
Sample C	50.24	49.76

3.5 TEM analysis:

TEM was employed for further investigation of MgO nanosheet. Fig 4 shows the TEM pictures of MgO nanosheets formed after annealing 400°C (sample-B). TEM images reveals that the synthesized nanosheets having different lengths and breadths, such as, 609.98nm length and 601.12nm wide. A long nano sheet has been observed whose length and breadth is 4.074µm and 1.1176µm

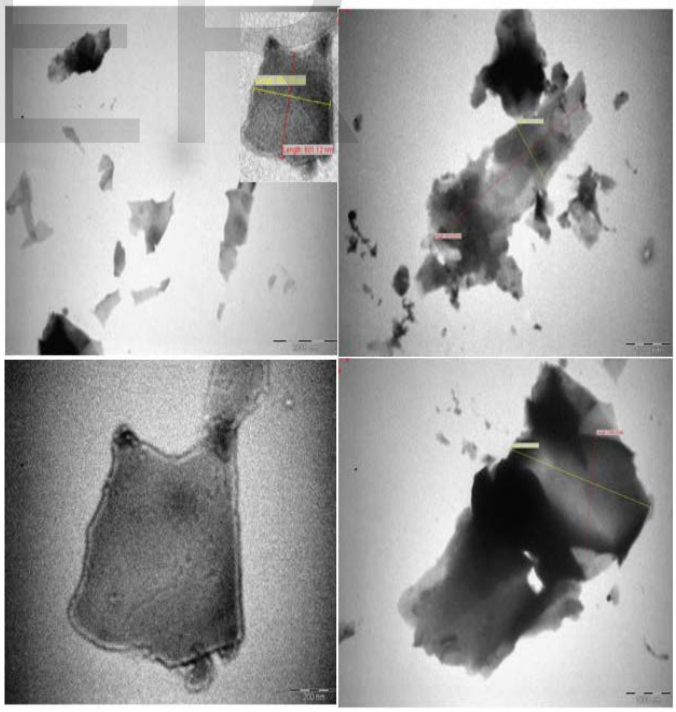

Fig. 4 TEM image of sample B (annealed at 400°C)

3.6 Photoluminescence spectra analysis:

For a characterization of the optical properties of the MgO nanomaterial Photoluminescence spectra (PL) were recorded shown in Fig 5. From the PL spectra, we can see the strong UV emission peak at 287nm, 291nm and 278nm for sample-A, sample-B and sample-C due to the direct recombination of holes and electrons in the energy band. All the samples shows the broad emission band appears in the visible region at 370-430nm is due to oxygen vacancies, Mg vacancies or Mg interstitials[16-17] which induce new energy levels in the band gap of MgO. Oxygen vacancies that might be the common defect in the nano samples induce distortion of the lattice in its direct surrounding and act as radiative centre in luminescence processes. The larger surface area with oxygen defect on the surface is an added advantage for the MgO nanosheet to act as an excellent photocatalyst.

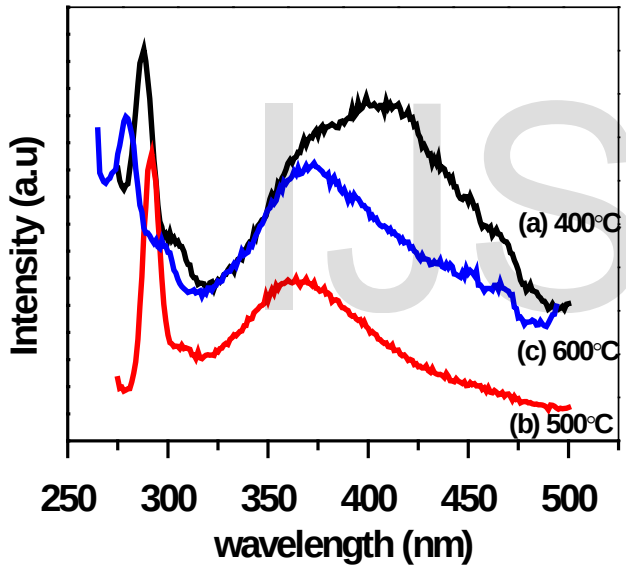

Fig. 5 PL- spectum of (a) sample-A, (b) sample-B and (c) sample-C

4. Conclusion:

We successfully synthesized different morphologies of MgO nanomaterial by a simple reflux method. The XRD pattern shows the MgO nanosamples were pure cubic MgO. A HRSEM and TEM picture evidences the 2D nanostructure such as nano flake, nanosheets and nanoflower morphology with smooth surfaces which is highly useful for photovoltaic devices and superconductors. High intense UV emission and a broad visible emission band in PL spectra further demonstrates that the potential applications of the material in optoelectronic devices.

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