Preparation of nanostructures LaPO$_4$ films using sol-gel reaction with different annealing temperature

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Abstract. Thin films of lanthanum phosphate (LaPO$_4$) nanostructures were fabricated on quartz substrate using sol-gel spin coating method subsequent with drying and annealing process. Increase of annealing temperature will increase the intensity of diffraction peaks; reveal that the particle size and crystallinity increase with temperature. A monoclinic structure was shown to be present in LaPO$_4$ thin films after first anneal at 200°C. The LaPO$_4$ nanostructures of average size 30 – 50 nm were observed with field emission scanning electron microscopy. While the crystallize size were measured with x-ray diffraction (XRD). The images of LaPO$_4$ nanostructure films show uniformity of samples with homogenously close-packed morphology.

1. Introduction

Lanthanide compounds have been applied in many applications of luminescence and display such as lighting, cathode ray tubes, and field emission display [1]. One of the lanthanide compounds are Lanthanum phosphate (LaPO$_4$) also known as monazite had been used widely as a phosphor and proton conductor due to properties such as very low solubility in water, high thermal stability, high index of refraction [2] high chemical stability and high light yields of the doped materials. LaPO$_4$ has a monoclinic phase of monazite structure where La$^{3+}$ ion is nine-coordinated to oxygen atoms, four oxygen forming a distorted tetrahedron interpenetrating a quasiplanar pentagon formed by other five [3]. It expected smaller size with nanosize lanthanum phosphate can increase the luminescent quantum efficiency and display resolution as a result of both their marked shape-specific and quantum confinement effect [4]. At nanometer phase, the material will consist of high surface to volume ratio and enhanced structural, electronic and optical properties compare to the other phases. Many methods had been used to synthesis LaPO$_4$ nanostructure such as solid-state reaction, sol-gel, precipitation, micro emulsion, hydrothermal and mechano chemical method [5],[6],[7]. The fabrication of LaPO$_4$ nanostructured films could be achieve such as by several coating techniques, layer-by-layer (LbL) assembly method, spin coating, electrospinning, ink-jet printing and sol-gel process [8].
Generally, LaPO$_4$ is one of the oxide material that has an excellent host to fabricate the luminescent material. Sol-gel process is one of the promising candidate for fabricating optical devices [9] due to many advantages, such as low processing temperature, easy coating of large surface, homogenous multicomponent oxide films and simple with cheap experimental setup. In this study, we adopted the sol-gel process to prepare LaPO$_4$ with good morphologies and fine crystal structures. The present paper reports the phase of obtained thin films with different annealing temperature through X-ray diffraction (XRD). Their morphology was acquired by field emission scanning electron microscope (FESEM).

2. Experimental

2.1. Preparation of LaPO$_4$ thin film by sol-gel method

Preparation of the LaPO$_4$ nanostructure was followed by the method similar to Gao et al [10]. All chemical reagents are of analytic pure without further purification. In a typical procedure, 0.01 mol of ethylenediamine tetraacetic acid (EDTA) solution was dissolved in 1 M ammonia solution under vigorous stirring. Then, 0.45 M La(NO)$_3$ solution was added dropwise to the 1 M Citric Acid solution with strong stirring. This mixed solution with 0.5 M of NH$_4$H$_2$PO$_4$ solution were added to the already EDTA and ammonia solution. The solution was heated with 90°C in water bath with strong stirring until transparent mix solution obtained. The solution was leave at room temperature for ageing time. The films were prepared from this solution on glass quartz by spin coating with three step shown below.

| Table 1. Three step of coating solution. |
|-----------------|----------------|----------------|
| Step | Duration | Spin Rate |
| 1   | 10 s     | 1500 rpm   |
| 2   | 30 s     | 3000 rpm   |
| 3   | 30 s     | 1500 rpm   |

The following step was used in other to ensure the solution will coat smoothly on the quartz glass substrate. The films were pre-baked (dry) at 100°C for 1 hour and post-baked (anneal) at different temperature for 2 hours.

2.2. Characterization

The formation phase of films was confirmed by X-ray diffraction measurement in other to investigate the purity of samples and also it crystallite size. X-ray diffraction was done using high resolution Philips X’Pert MRD diffractometer with Cu Ka radiation ($\lambda$= 0.15406 nm) in scan range of 20° – 70°. The morphology of the film was studied by field-emission scanning electron microscope (FESEM). But before that, the LaPO$_4$ films were sputtered with platinum in other to increase the conductivity of the films.

3. Results and discussion

3.1. Phase of LaPO$_4$ films

The composition and phase purity of sample were firstly characterized using Philips X’pert Pro MPD X-ray Diffractometer (XRD). The Cu anode X-ray was operated at 40 kV and 30 mA in combination with a Ni filter to give monochromatic Cu Ka radiation. The XRD data were processed using PANanalytical X’pert PRO software to examine the peak position and its corresponding intensity. Particle size can be obtained using X-ray diffraction (XRD) technique as the particle size is correlated to the diffraction peak broadening.
Diffraction can occur when electromagnetic radiation interacts with a periodic structure whose repeat distance is about the same as the wavelength of the radiation. Figure 1 shows the typical X-ray diffraction (XRD) patterns of pure LaPO₄ figure 1(a) and as-prepared LaPO₄ figure 1(b), 1(c), 1(d), at different annealing temperature. LaPO₄ nanostructure consist of monoclinic phases (space group P21/n) which refer to the high-temperature phases [8]. The XRD patterns were found to be match well with monoclinic phase of LaPO₄ JCPDS card files no. 01-084-0600 data. The high and shape peaks indicate that the solutions are well crystallized on the film. The main peak was found around 27°–30° corresponding to the LaPO₄ reported by Y.S.Patil [11]. The grain sizes of nanostructure were calculated using Scherrer equation (1) below from value FWHM (full width half maximum). The crystalline sizes are around 5 - 30 nm for nanostrured LaPO₄ thin films respectively.

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \tag{1} \]

Where \( \beta \) represent full width at half maximum (FWHM) of XRD lines
\( \lambda = \) Wavelength of the X-rays
\( \theta = \) Braggs angle of the XRD peak

Figure 1. X-ray diffraction patterns of (a) pure LaPO₄ without annealing and as-prepared (b) 200°C (C) 400°C and (d) 600°C.

Table 2. Crystallite size and FWHM of nanostructure LaPO₄ films anneal at different temperature

| Sample | FWHM   | Crystallize size (nm) |
|--------|--------|-----------------------|
| (a)    | 0.08055| 27.68                 |
| (b)    | 0.08940| 11.45                 |
| (c)    | 0.09804| 10.45                 |
| (d)    | 0.19532| 5.24                  |

Table 2 show the crystallite size of as-prepared LaPO₄ nanostructure films. From crystallize size above it show the intensity of sample were increase with increase of anneal temperature.
3.2. Morphology of LaPO$_4$ films

Figure 2 show Field Emission Scanning Electron Microscope (FESEM) images of rod-like nanostructures LaPO$_4$ for different annealing temperature on quartz substrate. The top view of film illustrates a homogenous flat surface with covering glass quartz well. The magnification (50K X) was constant for all samples. The deposit solution on substrate typically composed of uniform nanorods with length 30 - 50 nm. In this study, Ethelynediamine tetraacetic acid (EDTA) was used as it will form constant coordination compound when respond with metal ions in neutral aqueous solution. Thus, lanthanide ($\text{Ln}^{3+}$) which divided into three (La, Ce, Tb) were dissolve in EDTA solution. Therefore, $\text{La}^{3+}$ possibly will co-exist with $\text{PO}_4^{3-}$ without forming any precipitation as shown in equation below [2].

$$\text{Ln}^{3+} + \text{PO}_4^{3-} = \text{LnPO}_4$$  \hspace{1cm} (2)

The formation of rod like nanostructure is due to the amount of EDTA solution [12]. The pH value of 10 was prepared with amount 0.01 mol of EDTA. Increasing concentration of EDTA have great effect on morphologies and sizes of product due to the result that not shown here. It can be seen that long nano-wire with 30 - 40 nm in width and about 100nm in length are observed.

![Figure 2. FESEM images of LaPO$_4$ anneal at (a) 200°C (b) 400°C (c) 600°C and without anneal (d) Pure LaPO$_4$](image-url)
The increasing of annealing temperature do promote the formation of LaPO₄. Figure 3 (b) show an enlarged FESEM image rod like nanostructure which assembled by abundant of nanoparticles fig 3(a). The thick rod was constructed by the smaller rod as shown in Figure 3. Each of samples were annealed for at least 2 hours and above [13]. No obvious precipitation were found when solution only react for 1 hour. But when the time of reaction is increase, the yield of phosphate will gradually increased. This is understand-able. When the reaction was short, only small amount of PO₄³⁻ were produced, thus led to the low yield of phosphate and vice versa. From the FESEM observation, the product were similar to rod like nanostructure in all cases (different annealing temperature) unless for the pure LaPO₄ [13].

![Figure 3](image_url)

*Figure 3.* FESEM images of LaPO₄ films : top view obtained from annealed at 400°C with (a) low magnification, 10K x (b) high magnification, 50K x.

4. Conclusion

LaPO₄ films were successfully synthesis using sol-gel spin coating method. La(NO)₃ was used as a precursors to fabricate LaPO₄ films while concentration of EDTA play a main role on the morphology of films. The main peak in XRD pattern was found between 27° - 30° corresponding to the previous research [11]. Based on XRD results, monoclinic phase of LaPO₄ was identified. FESEM images also revealed homogenously quite long rod like nanostructures with length of around 30 – 50 nm. From the experiment, the reaction could not be initiated until the temperature is in a proper range. In this study, the annealing temperature started with 200°C till 600°C.

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6. References

[1] Hui Wang, Run Liu, Liying Liu, Xiaofang Shi, Z. Xu, Electrodeposition of high aspect ratio LaPO4 and LaPO4:Ln3+ (Ln3+ = Ce3+, Tb3+ ) nanostructures, Electrochemistry Communications, 17 (2012) 79-81.
[2] V. Pankratov, A.I. Popov, L. Shirmane, A. Kotlov, C. Feldmann, LaPO4:Ce,Tb and YVO4:Eu nanophosphors: Luminescence studies in the vacuum ultraviolet spectral range, Journal of Applied Physics, 110 (2011) 053522-053527.
[3] H.-K. Jung, J.-S. Oh, S.-I. Seok, T.-H. Lee, Preparation and luminescence properties of LaPO4:Er,Yb nanoparticles, Journal of Luminescence, 114 (2005) 307-313.
[4] K. Kömpe, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Möller, M. Haase, Green-Emitting CePO4:Tb/LaPO4 Core–Shell Nanoparticles with 70 % Photoluminescence Quantum Yield, Angewandte Chemie International Edition, 42 (2003) 5513-5516.
[5] M.T. Colomer, S. Gallini, J.R. Jurado, Synthesis and characterisation of a green NiO/La(Sr)PO4−δ cermet anode for phosphate based solid oxide fuel cells, Journal of the European Ceramic Society, 27 (2007) 4237-4240.

[6] K. Rajesh, P. Shajesh, O. Seidel, P. Mukundan, K.G.K. Warrier, A Facile Sol–Gel Strategy for the Synthesis of Rod-Shaped Nanocrystalline High-Surface-Area Lanthanum Phosphate Powders and Nanocoatings, Advanced Functional Materials, 17 (2007) 1682-1690.

[7] S. Gallini, J.R. Jurado, M.T. Colomer, Synthesis and characterization of monazite-type Sr:LaPO4 prepared through coprecipitation, Journal of the European Ceramic Society, 25 (2005) 2003-2007.

[8] Sangmoon Park, Zhao Zhen, D.H. Park, Preparation of Eu-doped LaPO4 films using successive-ionic-layer-adsorption-and-reaction, Materials Letters, 64 (2010) 1861-1864.

[9] B.Y. Ahn, S.I. Seok, S.-I. Hong, J.-S. Oh, H.-K. Jung, W.J. Chung, Optical properties of organic/inorganic nanocomposite sol-gel films containing LaPO4:Er,Yb nanocrystals, Optical Materials, 28 (2006) 374-379.

[10] R. Gao, D. Qian, W. Li, Sol-gel synthesis and photoluminescence of LaPO4:Eu3+ nanorods, Transactions of Nonferrous Metals Society of China, 20 (2010) 432-436.

[11] Y.S.Patil, K.G.Chaudhari, N.V.Poornachandra Rao, K.V.R.Murthy, Effect of Erbium Doping on Structural and Photoluminescence Properties of LaPO4:Eu Phosphor, Advances in Applied Science Research, 2 (2011) 303-309.

[12] H. Dong, Y. Liu, P. Yang, W. Wang, J. Lin, ChemInform Abstract: Controlled Synthesis and Characterization of LaPO4, LaPO4:Ce3+ and LaPO4:Ce3+, Tb3+ by EDTA Assisted Hydrothermal Method, ChemInform, 41 (2010) no-no.

[13] K. Mi, Y. Ni, Y. Xu, X. Ma, J. Hong, A simple mixed-solvothermal route for LaPO4 nanorods: Synthesis, characterization, affecting factors and PL properties of LaPO4:Ce3+, Journal of Colloid and Interface Science, 356 (2011) 490-495.