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The size effect on luminescence properties of praseodymium doped LuAG prepared by Pechini method

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ABSTRACT

Nano crystalline Pr^{3+} (1 mol%) doped lutetium aluminium garnet was prepared by the Pechini method in the temperature range of 800–1200 °C. The size of the grains was controlled by the annealing temperature of the samples. The crystal structure was analyzed by XRD. The results showed that LuAG:Pr^{3+} nano crystalline powder starts to crystallize at about 850 °C, and the particle size increased with the annealing temperature. The morphology of the nano crystalline powder was investigated by TEM and showed the grains of the samples well-structured but with a tendency to agglomerate. The average size of the grains was determined to be about 10–45 nm. The EDX spectroscopy was done to identify what those particular elements are and their relative proportions in the nano crystalline powder. The pure garnet phase of the obtained materials and the contamination from OH groups were studied by the FTIR analysis. Absorption, excitation and emission spectra of LuAG:Pr^{3+} nano crystalline powder were measured. The effects of heat-treatment temperature on the luminescent properties were investigated. An enhancement of the absorption ratio of 260 nm peak to 213 nm peak with increasing grain size was observed. The quantum efficiency also increased with increasing grain size. It was found that the decay times of the Pr^{3+} luminescence depends on the grain size and quenching parameter such as OH group. The decay time was increased from 12 nm to 23 nm grain size and then decreased from 23 nm to 31 nm. For a comparison study, Pr^{3+} doped LuAG powders were also prepared by the co-precipitation method.

1. Introduction

The combination of scintillator materials and photo detectors are used for detection of high energy photons and charge particles. For example, in diagnostic and therapeutic devices such as X-ray CT scan, PET, SPECT and high energy physics are used [1–3]. The scintillators are essentially a luminescent material which absorbs high-energy photons and then emit visible light. Researchers have been interested more to study the new scintillator materials due to its high absorption coefficient of photons, fast response time and high light yield [4,5]. Among the scintillator materials, lutetium aluminium garnet is a good candidate due to its high density, shock resistivity and chemical radiation stability [2,6–8]. The study of the Ce as an activator in this host was reported by Huili et al., Prusa et al., and Onderisinova at al., which confirmed its fast decay time because of the allowed 5d-4f transitions of the Ce^{3+} ion and its high light yield [1,4,9]. The Pr^{3+} ion also shows fast 5d-4f emission and it can be another candidate for high performance scintillator [2,7]. But, lutetium aluminium garnets with activator Pr as nano crystalline powders and investigation of luminescence properties of them were less reported.

In recent decade, lutetium aluminium garnets with activator Pr was developed and prepared by various methods and shapes. More studies were done on LuAG:Pr^{3+} with different concentration of activator and in the form of single crystal [6–8]. The preparation of the LuAG:Pr^{3+} single crystals is an arduous and expensive process. As an alternative, polycrystalline LuAG:Pr^{3+} nano powders can be used, if high density and transparency are made possible. Pechini and co-precipitation methods can be used to synthesize nanosized LuAG:Pr^{3+} powders. Actually, the aim of this study is to prepare nanosized LuAG:Pr^{3+} nano phosphors by the Pechini and co-precipitation methods and to study the luminescence properties of the nano phosphors with different grain sizes.

The Change of the available energy levels in nano structure materials causes different optical properties of nano phosphors. Also, it is well known that the different annealing temperatures can cause production of different nano scale sizes from the same precursor material [10,11]. So we concentrated here on investigating the effect of different annealing temperature and grain sizes on luminescence properties of

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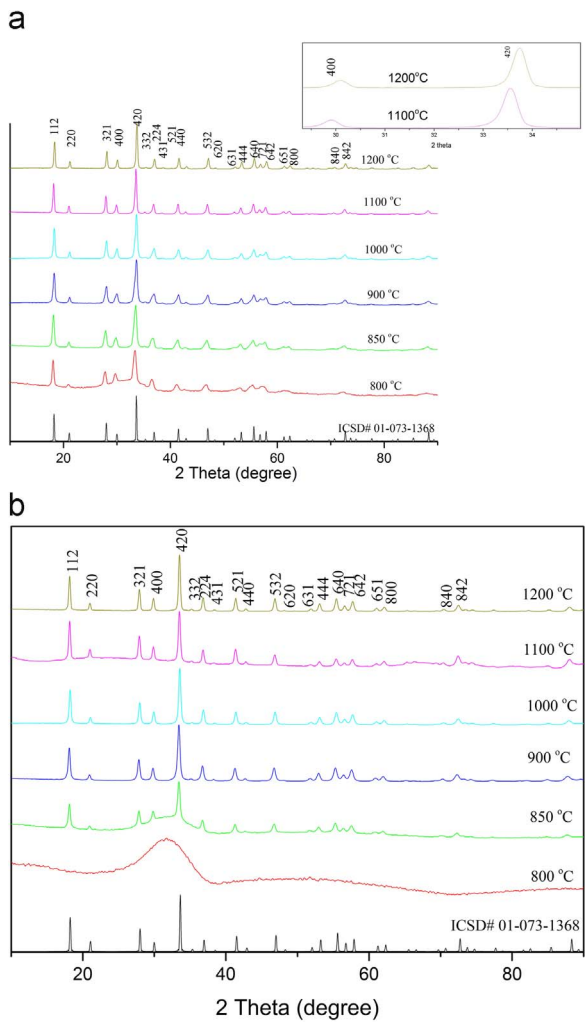

Fig. 1. X-rays diffraction pattern of LuAG:(1 mol% Pr^{3+}) nanocrystalline powder samples prepared by (a) Pechini (In the inset, the comparison of the enlarged strongest diffraction peak of LuAG:(1 mol% Pr^{3+}) was shown for two different annealing temperatures) and (b) co-precipitation methods.

Table 1
Cell parameters of Pr^{3+} doped different LuAG nanocrystalline powders annealed at different temperatures, (a) Pechini and (b) co-precipitation methods.

Sample	Cell parameters					
	a (Å)	b (Å)	c (Å)	α,β,γ	Volume (Å^3)	Grain size (nm)
(a)						
Standard	11.906	11.906	11.906	90°	1687.71	–
850 °C	12.054	12.054	12.054	90°	1751.67	12
900 °C	12.005	12.007	12.007	90°	1731.253	12
1000 °C	11.982	11.982	11.982	90°	1720.419	15
1100 °C	11.946	11.946	11.946	90°	1705.041	23
1200 °C	11.934	11.934	11.934	90°	1699.981	31
(b)						
Standard	11.906	11.906	11.906	90°	1687.71	–
900 °C	11.964	11.964	11.964	90°	1712.832	35
1000 °C	11.961	11.961	11.961	90°	1711.473	40
1100 °C	11.951	11.951	11.951	90°	1706.965	45
1200 °C	11.944	11.944	11.944	90°	1704.265	49

LuAG:Pr^{3+}. The prepared LuAG:Pr^{3+} nano phosphors were characterized by XRD, TEM, EDX, FTIR and UV–visible. In addition, the photoluminescence spectra of the nano phosphors excited by UV were investigated. Luminescence decay time and quantum efficiency was also reported.

2. Experimental

2.1. Method of preparation

2.1.1. Pechini method

Nano-crystalline powders of praseodymium (1 mol%) doped lutetium aluminium garnet (LuAG:Pr^{3+}) were prepared by Pechini method. At the start, lutetium and praseodymium nitrate were prepared. Stoichiometric amount of lutetium oxide (99.99%, Standard material) and praseodymium oxide (99.99%, Standard material) were dissolved in a diluted nitric acid (HNO_3, AR grade). Then, the stoichiometric aluminium nitrate nonahydrate solution (99.99%, PoCH S. A.), citric acid and ethylene glycol (AR grade, Alfa Aesar) were added to the mixture of aqueous nitrate solution of lutetium and praseodymium with molar ratio of 3:27:27:1. At the end, the mixed solution was heated at the 90 °C for 1 week to obtain a brownish resin. The dried resin was heated at different temperature from 800 °C to 1200 °C for 16 h.

2.1.2. Co-precipitation method

Nano-crystalline powders of praseodymium (1 mol%) doped lutetium aluminium garnet (LuAG:Pr^{3+}) were prepared by co-precipitation method. At first step, lutetium oxide (99.99%, Standard material) and praseodymium oxide (99.99%, Standard material) were dissolved in an aqueous nitric acid (HNO_3, AR grade) to obtain lutetium and praseodymium nitrate. The obtained nitrate solution was mixed with the appropriate amount of aluminium nitrate nonahydrate (99.99%, PoCH S. A.) solution. Next, the aqueous mixed solution of all nitrates was added dropewisely to mixture precipitant of ammonia hydrogen carbonate solution (AHC) and ammonia water (2 N, AR grade) on the stirrer. The measured pH was a little more than 10. The rate of the dropwisely adding solution to precipitant was 1 ml/min. Then the mixture was stirred for 1 h. At final, the precipitation was centrifuged and washed several times. Next, the precipitation was dried at the 90 °C for 24 h and then was heated at different temperature from 800 °C to 1200 °C for 2 h.

2.2. Characterization

X-ray diffraction (PANalytical, The Netherlands) with Cu Kα radiation was done at room temperature and compared with available standard data. All characterization such as the lattice parameters and average crystallite size of samples were calculated by the Rietveld method. The morphology of the prepared powders was examined by TEM (FEI Tecnai G2 20 X-TWIN). The EDX spectrum was obtained by a scanning electron microscope VEGA (TESCAN, Brno, Czech Republic) equipped with the XMU unit for energy dispersive X-ray spectroscopy to confirm the presence of impurities in the samples. FTIR analysis was done with the FTIR spectrometer (Nicolet iS50 FT-IR, Thermo Scientific, spectrometer) and its result was studied. The absorption measurement of all nano crystalline powders prepared by Pechini were calculated by the analysis of UV–vis–NIR (Cary Varian 5E) spectra at room temperature. Then the emission and excitation spectra were measured with FLS980 Fluorescence Spectrometer from Edinburgh Instruments at room temperature for all nano crystalline powders. Also, the luminescence decay time profiles were collected using LeCroy WaveSurfer 400 oscilloscope for the main emission and excitation peaks.