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Short communication

Effect of annealing on photoluminescence properties of combustion synthesized ultraviolet-emitting cerium-ion-doped $LiAl_5O_8$ phosphor

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ABSTRACT

$LiAl_5O_8$ doped with varying concentrations of Ce^{3+} were synthesized by a combustion route. Powder X-ray diffraction and scanning electron microscopy techniques were used to characterize the as-prepared and annealed phosphors. The luminescence intensity decreased after annealing the samples at 800 °C for 2 h in air. These results indicate the possibility of fabrication of high quality Ce^{3+} doped $LiAl_5O_8$ phosphor even at furnace temperature 500 °C via a simple process.

1. Introduction

Lanthanide doped inorganic phosphors especially aluminate hosts have found considerable interest owing to their wide range of applications in the fields of solid-state lighting [1–3]. Over the last two decades, lithium aluminates have been widely studied for a variety of applications, such as color emitting phosphors, solid electrolytes, supports for catalysts and humidity sensors [4–7]. The $LiAl_5O_8$ crystal has an inverse spinel structure with cubic lattice. $LiAl_5O_8$ doped with Fe is known as an efficient phosphor material and reported by different groups [8]. Raj et al. [9] studied synthesization condition of Co^{2+} and Ni^{2+} doped $LiAl_5O_8$ powder. Singh et al. [10] reported electron paramagnetic resonance and photoluminescence properties of $LiAl_5O_8$:Cr. Recently, some work focused on rare earths doped $LiAl_5O_8$ has been reported. For example, Singh et al. [11] investigated up-conversion luminescence of $LiAl_5O_8:Er^{3+}$ co-doped with Yb^{3+} and Zn^{2+}. Dhabhekar et al. [12] reported thermoluminescence, optically stimulated luminescence and electron spin resonance properties of $LiAl_5O_8$:Tb. Mu et al. [13] presented luminescence and energy transfer in $LiAl_5O_8:Ce^{3+},Dy^{3+}$ phosphor. Singh et al. [4] studied defects in $LiAl_5O_8:Eu^{3+}$ phosphor. Nevertheless, little attention has been drawn towards luminescence properties of Ce^{3+} doped $LiAl_5O_8$ phosphor. It is a well-known fact that the efficient absorption and luminescent properties of Ce^{3+} ions are due to their parity allow f → d transitions. Trivalent cerium ions serve as sensitizers for transferring energy to other co-doped luminescent centers. In Ref. [14], it was reported that the stabilization of Ce^{4+} ions in the host matrix reduces the luminescence output by depleting Ce^{3+} ions and by quenching the luminescence of Ce^{3+} ions through a non-radiative pathway provided by Ce^{4+} ions. It is to be noted that the reduction of Ce^{4+} to Ce^{3+} was reported during synthesis in oxidizing atmosphere. The thermal treatment can be done at atmospheric pressure or under different values of pressure. Also some studies show that the repeated sintering

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Table 1
Detailed information of sample code, and starting materials.

Sample code		Starting materials			
as-prepared	annealed				
LI1	LI1-H	Al = 5 g	U = 2.1341 g	Li = 0.1841	Ce = 0.0115
LI2	LI2-H	Al = 5 g	U = 2.1341 g	Li = 0.1849	Ce = 0.0349
LI3	LI3-H	Al = 5 g	U = 2.1341 g	Li = 0.1860	Ce = 0.0702
LI4	LI4-H	Al = 5 g	U = 2.1341 g	Li = 0.1875	Ce = 0.1181
LI5	LI5-H	Al = 5 g	U = 2.1341 g	Li = 0.1890	Ce = 0.1667
LI6	LI6-H	Al = 5 g	U = 2.1341 g	Li = 0.1914	Ce = 0.2411

Al = $Al(NO_3)_3{\cdot}9(H_2O)$, U = $CO(NH_2)_2$, Li = $LiNO_3$, Ce = $Ce(NO_3)_3{\cdot}6H_2O$.

operations and milling are necessary during the preparation. There are indeed several reports on the luminescence studies of Ce^{3+} doped systems where these materials were prepared under reducing atmosphere [15–17]. However, in the present study, we have not used any reducing atmosphere. Previous work has shown that the luminescent properties of cerium doped systems are relatively sensitive to the preparation conditions and these systems behave differently when annealed with and without reducing atmosphere.

Keeping in view of this, we have synthesized $LiAl_5O_8$ doped with varying concentrations of Ce^{3+} phosphor and luminescent characteristics were investigated on the as-prepared and annealed samples. Also, combustion derived as-prepared and annealed samples were characterized by X-ray diffraction (XRD) and scanning electron microscopic (SEM) techniques.

2. Experimental

$LiAl_5O_8$ doped with Ce^{3+} ions by varying concentrations were prepared by solution combustion method. For the preparation of samples, lithium nitrate ($LiNO_3$) and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) were used as the source of Li^+ and Al^{3+}. Cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) was used as doping material of Ce^{3+}. Also, urea (CH_4N_2O) was added as a fuel for combustion. Table 1 shows the details of the sample code, and starting materials. The starting materials were dissolved in a minimum quantity of deionized water and heated at 95 °C for 20 min in a porcelain dish with 100 ml capacity to obtain a homogeneous solution. Then the solution was introduced into a muffle furnace preheated to 500 ±10 °C. Combustion took place with the introduction of the solution along with the evolution of gases. The mixture then froths and swells forming foam, rupturing with a flame and glows to incandescence. The entire combustion process was completed within 5 min. The combustion reaction produced a fluffy resultant. The resulting fluffy product was gently ground using a mortar and pestle. Afterwards, the product was divided in two parts. The first part was directly used for characterization (LI1 to LI6). Second part was placed in 50 ml alumina crucible to be heat-treated to 800 °C for 2 h in air (LI1-H to LI6-H). After that, the sample was cooled down to room temperature and used for characterization. For the series of samples same synthesis route was followed.

The powders XRD patterns of the samples were recorded using RIGAKU Miniflex-600 diffractometer operating in the Bragg-Brentano focusing geometry. Cu-Kα radiation ($\lambda = 1.5406$ Å) has been used as X-ray source. The instrument was operated at 40 kV and 30 mA. The XRD patterns were taken in the 2θ range of 10–80°. Morphology details were obtained by scanning electron microscopy (SEM) (S-3400, Hitachi, Japan). Photoluminescence measurements were carried out at room temperature using a Shimadzu RF-5301PC, spectrofluorophotometer equipped with a Xenon flash lamp.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the powder XRD patterns of the as-prepared (Fig. 1 (a)) samples and the samples annealed (Fig. 1 (b)) at 800 °C for 2 h in air, respectively. All the diffraction peaks observed for the as-prepared and the annealed samples matched well with the standard data for $LiAl_5O_8$ (JCPDS No. 71–1736), confirming the formation of cubic $LiAl_5O_8$ phase. These diffraction peaks can be indexed as (110), (111), (210), (211), (220), (221), (311), (222), (320), (400), (410), (331), (421), (422), (511), (520), (521), (440), (531), (620) and (533). The crystallite size (D) of the samples was calculated using the Debye Scherrer formula $D = 0.9\,\lambda/\beta\cos\theta$, where λ is the wavelength of incident X-ray, θ is the corresponding Bragg's diffraction angle, and β is the FWHM of the (311) peak. The crystallite size calculated from this method was found to be in the range 20–35 nm. Table 2 shows the FWHM and crystallite size of all the samples. It was noticed that as the Ce^{3+} content increases, the diffraction peak at $2\theta = 37.758$ (311) exhibits the most noticeable change with its decreased intensity. However, comparing the results in Fig. 1, except variations in the peak intensities, no other phase specific changes were observed and the corresponding diffraction lines of all the samples can be assigned to $LiAl_5O_8$ only. At these high concentrations with large lattice distortions, there is no evidence of secondary phases in the XRD patterns. It was observed that with increasing Ce^{3+} concentration, the diffraction peaks (311) for all the samples slightly shifted towards lower angle (Fig. 1), suggesting increased inter planar spacing. However, there is no systematic movement in the position of reflection peaks observed.