Journal of Luminescence 136 (2013) 411–414

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Synthesis and characterization of Mn-activated lithium aluminate red phosphors

Masahiro Aoyama [a], Yusuke Amano [a], Koji Inoue [b], Sawao Honda [a], Shinobu Hashimoto [c], Yuji Iwamoto [a,*]

[a] *Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*
[b] *Department of Electrical Material Science, Mie Industrial Research Institute, 5-5-45, Takatyaya, Tsu-city, Mie 514-0819, Japan*
[c] *Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

ARTICLE INFO

Article history:
Received 1 June 2012
Received in revised form
12 October 2012
Accepted 4 December 2012
Available online 13 December 2012

Keywords:
Lithium aluminate
Sol–gel method
Mn^{4+}-activated red phosphor
ESR spectroscopic analyses

ABSTRACT

Mn-doped $LiAlO_2$ powders were synthesized by the sol–gel method. The crystalline phase of the sol–gel-derived host lithium aluminate could be successfully controlled as α-$LiAlO_2$ single phase by heat treatment at 700 °C. The results of electron spin resonance spectroscopic analyses revealed that Mn ions existed as isolated Mn^{4+} and clustered cations in the host α-$LiAlO_2$ matrix, and a part of the isolated Mn^{4+} were thought to substitute the Al^{3+} octahedral sites. The red emission peaks derived from d–d transitions of the Mn^{4+} ($3d^3$) configuration from ^2E to $^4A_2$ were observed around 670 nm. The emission intensity increased consistently with the Mn-doping concentration, and the highest intensity was achieved at the Mn-doping of 0.10 mol. At and above 0.10 mol Mn-doping, the concentration quenching was observed. Based on these results, the relationships between the crystalline phases of the $LiAlO_2$ phosphor matrix, amount of the doped-manganese, and the photoluminescence properties were discussed from a viewpoint to develop a novel α-$LiAlO_2$:Mn^{4+} red phosphor.

1. Introduction

The compounds in the ternary Li–Al–O system are known to exist in three phases of $LiAl_5O_8$, $LiAlO_2$ and Li_5AlO_4 as shown in Fig. 1 [1]. A lot of researchers have reported many different processes to synthesize lithium aluminates and their various properties [2–4]. Lithium aluminates have a wide field of application.

$LiAlO_2$ has existed in three allotropic forms, namely hexagonal α-$LiAlO_2$, monoclinic β-$LiAlO_2$ and tetragonal γ-$LiAlO_2$. The most stable polymorph is γ-$LiAlO_2$, and α- or β-$LiAlO_2$ is transformed to γ-$LiAlO_2$ at elevated temperature [5]. The γ-$LiAlO_2$ is one of the candidate materials as an irradiation blanket for nuclear fusion reactors because this material exhibits good thermochemical and irradiation stability [6]. Apart from this application, γ-$LiAlO_2$ has been well known as an electrolyte matrix of molten carbonate fuel cells (MCFC) [7]. Furthermore, in other applications, $LiAlO_2$ has been recently reported as a good luminescent material [8,9]. γ-$LiAlO_2$:Fe^{3+} was especially found to be attractive as a red phosphor for artificial illuminations [10]. Because of the lower fabricating temperatures below 1000 °C, $LiAlO_2$ is attractive as a low-cost host matrix of luminescent materials. The activators of transition metal ions such as Fe^{3+} and Mn^{4+} also have potential to develop inexpensive rare earth-free red-emitting phosphors for warm white light generation such as tri-color phosphors.

Thus, in this study, attentions have been focused on $LiAlO_2$ as the phosphor matrix and transition metal cation as the activator. Mn^{4+} ion exhibits luminescence in the visible regions (around 620–700 nm). In the ternary Li–Al–O material system, Mn^{4+} doped $LiAl_5O_8$ has been reported [11]. However, luminescence properties of Mn^{4+} doped $LiAlO_2$ have not been reported yet. In this study, Mn-doped $LiAlO_2$ powders were synthesized by the sol–gel method using aluminum isoproxide, lithium nitrate and manganese (II) chloride. The oxidation state of the manganese cation in the $LiAlO_2$ matrix was studied by the electron spin resonance spectroscopy, and the relationships between the crystalline phase of the $LiAlO_2$ phosphor matrix, amount of the doped-manganese, and the photoluminescence properties were studied and discussed from a viewpoint to develop a novel α-$LiAlO_2$:Mn^{4+} red phosphor.

2. Experimental

Lithium aluminate powders were synthesized by the sol–gel method. Aluminum isoproxide ($Al(OiPr)_3$, 99.9%, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan) and lithium nitrate ($LiNO_3$, 99.9%, Wako Pure Chemical Industries Ltd., Osaka, Japan) were used as starting materials, and manganese (II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 99.9%, Kojundo Chemical Laboratory Co. Ltd.,

---

[*] Corresponding author. Tel.: +81 52 735 5276.
E-mail address: iwamoto.yuji@nitech.ac.jp (Y. Iwamoto).

0022-2313/$ - see front matter
http://dx.doi.org/10.1016/j.jlumin.2012.12.012

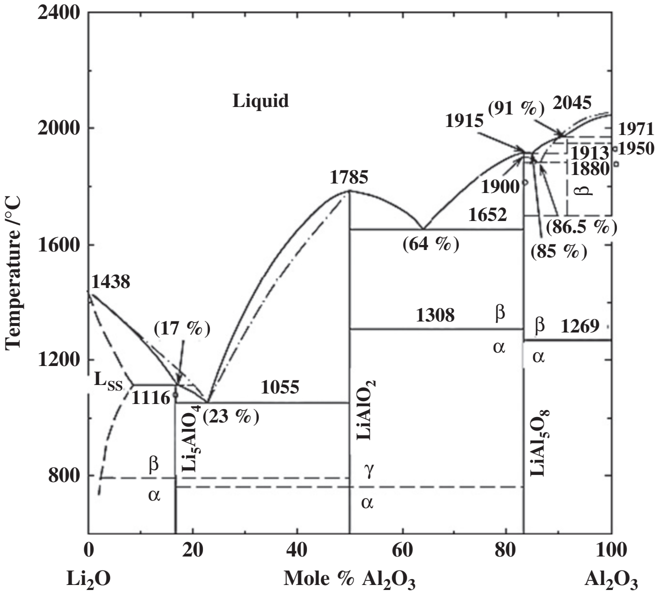

Fig. 1. Phase diagram of lithium aluminates.

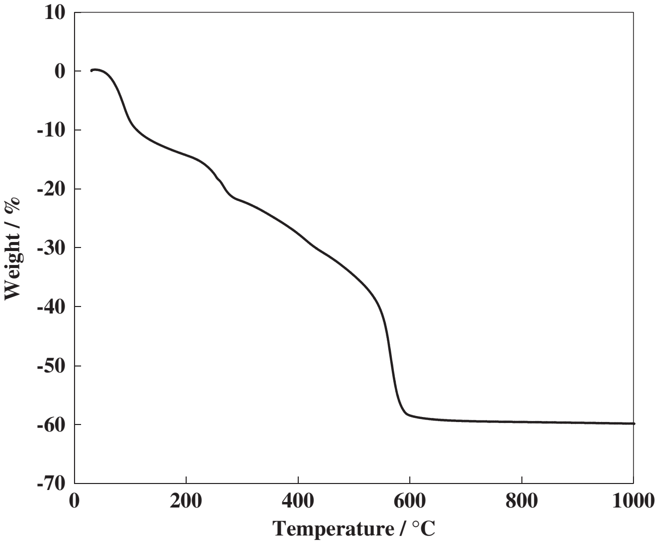

Fig. 2. TG curve of the dried Li–Al–O gel precursor sample.

Saitama, Japan) was selected as a source of Mn cation. Distilled water was mixed with the metal alkoxide to produce white solution, which was stirred at 90 °C to complete hydrolysis. $LiNO_3$, $MnCl_2 \cdot 4H_2O$ and concentrated HNO_3 were added to the solution. The Li/Al molar ratios were 1/1. After drying, the gel precursor powders were converted into the lithium aluminate powders by heat treatment at various temperatures ranging from 600 to 900 °C.

Thermogravimetric and differential thermal analysis (TG–DTA) were used to determine the weight loss at high temperature (TG8120, Rigaku, Japan). X-ray diffraction (XRD, Philips, X'pert Pro α1, Japan) measurements were performed on the heat treated samples with CuKα radiation ($\lambda = 0.15406$ nm) using an automated powder diffractometer equipped with monochrometer. Electron spin resonance (ESR) measurements of the sample powders were carried out at the X-band on a JEOL JES-RE1X spectrometer. The ESR X-band spectra were recorded at R.T. The microwave frequency was 9.13 GHz, and a 100 kHz field modulation was used. The *g* values were calculated from the measurements of the magnetic field and the microwave frequency parameters. UV–vis absorption spectra were measured at room temperature using ultraviolet and visible spectrophotometer (V-570, JASCO, Japan) with a deuterium lamp (190–340 nm), W-I2 lamp (340–2500 nm). The photoluminescence (PL) emission and excitation spectra were measured at room temperature using fluorescence spectrometer (F-7000, Hitachi, Japan) with a Xe lamp. The PL internal and external quantum efficiencies for the light emission materials were measured through PL measurements using 60 mm integrated sphere.

3. Results and discussion

The result of TG analysis for the dried gel precursor powders is shown in Fig. 2. The TG curve shows two distinct steps. In the first step, the weight loss occurs over a temperature range from room temperature to approximately 100 °C, which is due to dehydration of adsorbed water. In the second step, the weight loss occurs between 300 °C and 500 °C. It is due to the denitration and dehydro-condensation reactions. These reactions were observed in the same temperature range as shown in the previous report [12]. From this TG result, gel precursor powders were heat-treated in air at various temperatures ranging from 600 to 900 °C.

XRD patterns of the powder samples are shown in Fig. 3. The α-$LiAlO_2$ crystallization from the Mn-free dried gel precursor powder started at 600 °C, and then subsequent α/γ-$LiAlO_2$ phase transformation started at 750 °C. After the heat treatment at 900 °C, the XRD pattern was identical to γ-$LiAlO_2$ single phase (Fig. 3(a)). To study the luminescent properties stepwise, low temperature phase of α-$LiAlO_2$ was selected. Then, the Mn-doped samples were heat-treated at 700 °C, and α-$LiAlO_2$ sample powders with the Mn-doping range from 0.05 to 0.15 were successfully synthesized (Fig. 3(b)).

The ESR spectrum of the 0.10 mol Mn-doped α-$LiAlO_2$ is shown in Fig. 4. Two typical signals derived from Mn ions were observed. The sextet ESR signal (labeled as I, $g = 3.726$) is assigned to isolated Mn^{4+} ions [13]. The other one (labeled as II) is two overlapping ESR signals; broadening line due to the exchange–coupled Mn ions clusters ($g = 1.983$) [14], and the characteristic sextet signal derived from isolated Mn^{2+} or Mn^{4+} ions ($g = 2.022$) [15]. During the heat treatment to 700 °C, most of the $MnCl_2$-derived Mn (II) ion in the gel precursor powder could be oxidized to Mn (IV). The existence of the isolated Mn^{4+} strongly suggests that a part of Mn^{4+} ions could substitute the Al^{3+} octahedral sites in α-$LiAlO_2$. As shown in Fig. 3(b), the XRD peak shift was not observed for all the Mn-doped samples. This result could be predicted due to the similar ionic radius of Al^{3+} ($r_{Al}^{3+} = 0.535$ Å) and Mn^{4+} ($r_{Mn}^{4+} = 0.530$ Å). For example, the Mn^{4+} ions substituted the Al^{3+} sites in the calcium aluminates ($CaAl_{12}O_{19}$) [16]. It was also reported that Mn^{4+} ions could substitute the six-oxygen coordinated Ge^{4+} sites in the $3.5MgO \cdot 0.5MgF \cdot GeO_2$ matrix because Mn^{4+} and Ge^{4+} ions have the same valence state, and ionic radius ($r_{Mn}^{4+} = r_{Ge}^{4+} = 0.530$ Å) [17].

Fig. 5 shows the excitation and the absorption spectra of the 0.10 mol Mn-doped α-$LiAlO_2$. The maximum intensity of the excitation spectrum was determined to be 300 nm. Then, the emission spectra ($\lambda_{ex} = 300$ nm) of the Mn-doped α-$LiAlO_2$ were recorded and the results are shown in (Fig. 6(a)). The spectra revealed red emission peaks around 670 nm derived from d–d transitions of the Mn^{4+} ($3d^3$) configuration from ^2E to $^4A_2$. The relation between the amount of doped Mn and the dominant PL emission peak intensity at 670 nm is shown in Fig. 7. The emission intensity at the 0.10 mol Mn doping was the highest among the Mn-doped α-$LiAlO_2$ in this study. At and above