Pyrolytic synthesis and $Eu^{3+} \rightarrow Eu^{2+}$ reduction process of blue-emitting perovskite-type $BaLiF_3$:Eu thin films

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Abstract

Perovskite-type barium lithium fluoride ($BaLiF_3$) was synthesized by pyrolysis of metal trifluoroacetates. The reaction temperature necessary for producing a single-phase material was found to be 600°C, which was lower than that for a conventional solid-state reaction or a melting method. Eu-doped $BaLiF_3$ was also prepared and characterized to examine the suitability of trifluoroacetates for precursors in synthesizing homogeneous complex metal fluoride materials. It was demonstrated that trivalent Eu^{3+}, which was used as acetate for a starting material, was reduced to divalent Eu^{2+} in the pyrolysis process of $BaLiF_3$, as indicated by a broad blue emission due to an allowed $4f^65d \rightarrow 4f^7$ transition at 408 nm with a ultraviolet excitation at 254 nm. The concentration quenching of the blue emission occurred at 5 at% of Eu in $BaLiF_3$, indicating that Eu was homogeneously dispersed in the $BaLiF_3$ host lattice. Mechanisms of the formation and reduction process of $BaLiF_3$ were discussed based on pertinent chemical reactions.
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1. Introduction

Barium lithium fluoride ($BaLiF_3$) has an inverted perovskite structure where monovalent Li^+ ions occupy the center of fluorine octahedra [1]. Doped, as well as undoped, $BaLiF_3$ materials have been investigated aiming at practical applications to X-ray storage phosphors [2], vacuum ultraviolet (UV) optical materials [3], lasers [4], and ion conductors [5]. Because electrical and optical properties of $BaLiF_3$ are greatly dependent on defect structures as well as dopants, a number of researches have been reported focusing on the development of synthetic methods by which high-quality samples can be produced.

While melting of a powder mixture of BaF_2, LiF, and dopant fluorides at high temperatures in a HF atmosphere has been generally utilized to produce doped $BaLiF_3$ single crystals [6,7], the pyrolytic synthesis starting from mixed metal-organofluorine compounds is expected as an attractive alternative for preparing fine powders and thin films [8]. This synthetic method is advantageous in that the mixing of metal constituents at an atomic level can be achieved in precursor solutions and the resultant samples are expected to have high homogeneity. In the present work, $BaLiF_3$ films were successfully prepared from mixed metal trifluoroacetates that were dissolved in an organic solvent. Eu was doped in $BaLiF_3$ to examine the homogeneity of samples as well as the potential use as phosphors. It was found that Eu^{3+} ions, which were used as acetate for a raw material, were reduced to Eu^{2+} in the pyrolysis process at temperatures as low as 600°C. This contrasts with the high-temperature $Eu^{3+} \rightarrow Eu^{2+}$ reduction which has been accomplished in oxide and fluoride materials so far [9,10]. The Eu-doped $BaLiF_3$ films exhibited efficient blue photoluminescence (PL), which could be used as a spectroscopic probe for the sample homogeneity. Mechanisms of the formation and reduction of $BaLiF_3$:Eu prepared from the trifluoroacetates were discussed based on pertinent chemical reactions.

2. Experimental procedure

Metal acetates, $Ba(CH_3COO)_2$, $LiCH_3COO$, and $Eu(CH_3COO)_3 \cdot 4H_2O$, were dissolved in isopropanol to which trifluoroacetic acid (CF_3COOH) and water

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were added. Dopant concentrations of Eu were varied between 0, 1, 2, 3, 5, 10, and 15 at%. After stirring for 2 h, the resultant solutions were spin-coated on quartz glass substrates at 2000 rpm. The coated substrates were then immediately placed in a furnace kept at 400–700°C and heated for 10 min in a flowing nitrogen atmosphere, followed by quenching. This coating/heating procedure was repeated two additional times to increase the film thickness up to ∼200 nm. This increase was necessary to analyze the films accurately.

Phase identification of the films was performed with an X-ray diffractometer equipped with a thin-film attachment using CuKα radiation (Rigaku). Thermal analysis of the solution that was dried at 90°C for 4 days was done by thermogravimetry-differential thermal analysis (TG-DTA) (Mac Science, type TG-DTA2020S thermal analyzer). A heating rate of 5°C/min was adopted. PL spectra were measured at room temperature with a spectrofluorophotometer (Shimadzu, type RF-5300PC) using a Xe lamp (150 W) as a light source. Emission scans were performed with 5 nm bandpass emission slits. A filter was used to remove a second-order peak of the excitation light.

3. Results and discussion

3.1. Pyrolytic synthesis of $BaLiF_3$

The thermal decomposition of metal trifluoroacetates generally occurs at temperatures higher than 300°C, which results in the formation of metal fluorides [8]. Thus alkaline earth (MgF_2, CaF_2, SrF_2, and BaF_2) and rare-earth fluorides (LaF_3, NdF_3, EuF_3, etc.) can be prepared by the trifluoroacetate method. In case of complex metal fluorides containing two or more metal constituents, the trifluoroacetates should be pyrolysed at relatively higher temperatures because of differences in decomposition temperatures of each individual metal trifluoroacetate [11]. Fig. 1 shows the X-ray diffraction (XRD) patterns of the $BaLiF_3$ films obtained by heating the coated solution at 400–700°C for 10 min in the flowing nitrogen. Sharp diffraction peaks appearing at $2\theta = 22.2°$, $31.7°$, $39.0°$, $45.4°$, $51.1°$, and $56.4°$ are assigned to (100), (110), (111), (200), (210), and (211) planes, respectively, of $BaLiF_3$ with a cubic structure and a lattice constant of $a = 3.9950$ Å according to JCPDS No. 18-715. While the film that was heated at 600°C is a single-phase $BaLiF_3$, the films heated at the lower temperatures of 400°C or 500°C contain BaF_2 as an impurity phase. A possible formation of LiF was not confirmed by XRD because of its lower detectability for light elements. The film heated at 700°C is contaminated with unknown crystalline phases, which are supposed to be decomposition products of $BaLiF_3$.

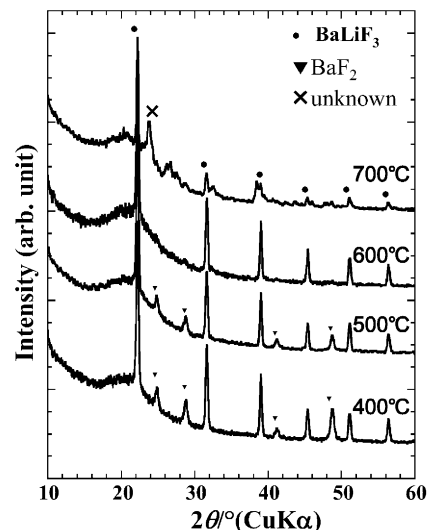Fig. 1. XRD patterns of thin films obtained by the pyrolysis of trifluoroacetates at 400–700°C for 10 min in the flowing nitrogen; $BaLiF_3$, BaF_2, and unknown peaks are labelled (●), (▼) and (×), respectively.
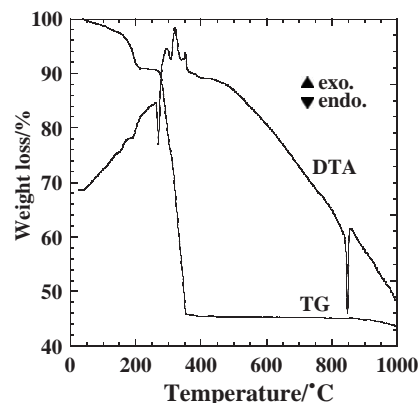

Fig. 2. TG-DTA curves of the dried trifluoroacetate precursor solution.

Fig. 2 shows the TG-DTA curves of the dried trifluoroacetate solution. A weight loss and an endotherm around 200°C are due to dehydration of the trifluoroacetates and vaporization of organic compounds such as isopropanol, trifluoroacetic acid, and acetic acid that were derived from the solvent and starting materials. The DTA curve exhibits exothermic peaks that are characteristic of the decomposition of the trifluoroacetates. The three peaks at 299°C, 320°C, and 352°C are ascribed to the formation of LiF, BaF_2, and $BaLiF_3$, respectively. These exotherms accompany a large weight loss. A sharp endothermic peak at 850°C is due to melting of $BaLiF_3$. The formation reaction of $BaLiF_3$ from the trifluoroacetates is nominally expressed by

$$Ba(CF_3COO)_2 + LiCF_3COO \rightarrow BaF_2 + LiF \rightarrow BaLiF_3$$

$$(1)$$
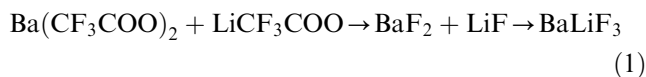
referring to the suggestion by Rillings and Roberts [12]. The weight loss observed around 300°C is 51.1%, which agrees roughly with a calculated weight loss, 58.3%, for the above reaction. The results of the thermal analysis explain the crystallization behavior of the films shown in Fig. 1. The heating temperature should be enough high to avoid the separate formation of each constituent fluoride (BaF_2 and LiF) and to produce the single-phase $BaLiF_3$ samples.

3.2. Eu-doped BaLiF₃

Fig. 3 shows the XRD patterns of the Eu-doped $BaLiF_3$ films that were heated at 600°C. Almost single-phase samples are obtained with the Eu concentration up to 5 at%. At 10 and 15 at%, peaks due to the perovskite phase become weaker, indicative of lower crystallinity. Thus the solubility limit of Eu in $BaLiF_3$ is suggested to be 5 at%. The valence state of Eu in $BaLiF_3$ cannot be estimated from the XRD data. In oxide perovskite materials, doped Eu ions generally exist in the trivalent state [13–16]. In contrast, Couto dos Santos et al. [17] have suggested that the solution energy for the Eu^{3+} ions in the $BaLiF_3$ matrix is highly positive, implying that the incorporation of Eu^{3+} into the Ba^{2+} sites has a low probability. Because Eu^{2+} and Ba^{2+} have similar ionic radii as well as the same configuration of outermost electrons ($5s^2 5p^6$), it is reasonable to think that the Eu ions are doped in $BaLiF_3$ in the divalent state. Even so, the XRD analysis seems to be incapable of examining the structural difference induced by the Eu-doping because no appreciable change in lattice constants was observed for the Eu-doped $BaLiF_3$
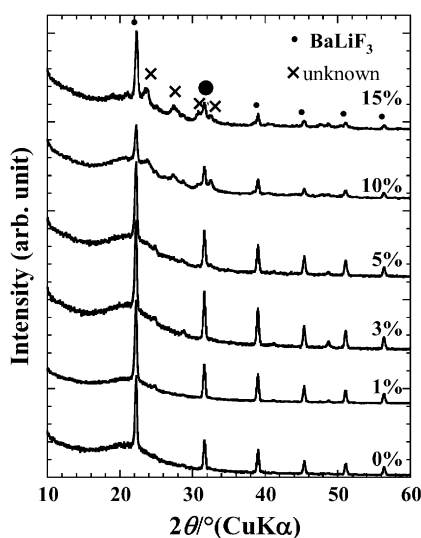
samples. Very recently, Hua et al. [18] have reported the synthesis of the Eu-doped $BaLiF_3$ through a solvothermal process and have found the similar lattice constants between the doped and the undoped sample. The case is such that Eu^{2+}-doped and undoped $BaMgF_4$ have similar lattice constants and the same space group [19].

The divalent europium ion, which has a $4f^7\ ^8S_{7/2}$ electronic configuration in the ground state, shows a broad absorption band in a long-wavelength UV region due to an allowed $4f^7 \rightarrow 4f^6 5d$ transition. Emission wavelengths for transitions from the excited to the ground state ($4f^6 5d \rightarrow 4f^7$) can vary from long-wavelength UV to yellow depending on crystal fields of host lattices [20]. Fig. 4 shows the PL spectra of the $BaLiF_3$:Eu (3 at%) film that was heated at 600°C in the flowing nitrogen atmosphere. The excitation wavelength used was 254 nm, which would provide efficient blue luminescence in $BaLiF_3$:Eu^{2+} [10]. The spectra in Fig. 4 are typical of the Eu^{2+} ions doped in the $BaLiF_3$ crystal of which the Ba^{2+} site symmetry is O_h. A broad blue emission with a peak wavelength of 408 nm is due to the $4f^6 5d \rightarrow 4f^7$ transition. A narrow peak at 360 nm is ascribed to a $^6P_{1/2} \rightarrow ^8S_{7/2}$ transition. Thus the presence of the optically active Eu^{2+} ions in $BaLiF_3$ has been demonstrated.

The $Eu^{3+} \rightarrow Eu^{2+}$ reduction is generally achieved by firing materials at high temperatures in a reducing atmosphere or air. When a reducing H_2 gas is used, a reduction mechanism can be easily explained as follows:

$$2Eu^{3+} + H_2 \rightarrow 2Eu^{2+} + 2H^+. \qquad (2)$$
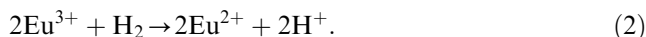
The Eu^{3+} ions are efficiently reduced by reacting with H_2. In contrast, the reduction in air should be caused by chemical interactions between Eu^{3+} and constituents of host lattices. For example, Peng et al. [9] have explained
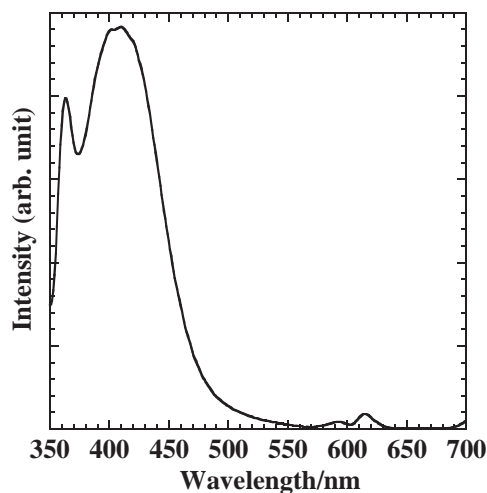

Fig. 3. XRD patterns of Eu-doped $BaLiF_3$ thin films obtained by the pyrolysis of trifluoroacetates at 600°C for 10 min in the flowing nitrogen; $BaLiF_3$ and unknown peaks are labelled (●) and (×), respectively. The Eu concentration was varied between 0 and 15 at%.

Fig. 4. PL spectra of the $BaLiF_3$:Eu (3 at%) film. The excitation wavelength used was 254 nm.

the reduction of Eu in $Sr_4Al_{14}O_{25}$ based on a charge compensation model where strontium vacancies play a key role. The Eu reduction seems to be more feasible in fluoride lattices due to chemical interactions between Eu^{3+} and F^-. When Eu^{3+} is doped in the $BaLiF_3$ lattice through a solid-state reaction between BaF_2, LiF, and EuF_3, it is reduced to Eu^{2+} by a following reaction:

$$Eu^{3+} + F^- \rightarrow Eu^{2+} + F. \quad (3)$$

This reduction was actually achieved at 750°C in the flowing nitrogen atmosphere [10]. Electrons of the F^- ions are trapped by the Eu^{3+} ions forming Eu^{2+}. The F^- ions, which lose electrons, form interstitial F atoms. The inverse reaction of (3) can naturally occur because fluorine is a strongly oxidizing species. Therefore, it is thought that reaction (3) is possible only in a special case where Eu^{2+} can be stabilized in the solid state of $BaLiF_3$. In the present case, the Eu-doped $BaLiF_3$ has been prepared from the trifluoroacetates. Because reaction (1) actually involves the generation of gaseous phases such as $(CF_3CO)_2O$, CF_3COF, and COF_2 [12], it seems that F^- can be supplied from these organofluorine species. Reminding that the film formation was achieved by placing the coated substrates immediately in the furnace kept at the heat-treatment temperature, it is highly possible that several reaction steps proceed almost simultaneously such as the dehydration, the vaporization of the organic components, the decomposition of the trifluoroacetate, the generation of the gases, and the formation of the Eu-doped $BaLiF_3$. In the presence of water, F^- ions can be supplied by hydrolysis of CF_3COF and COF_2 [12]. Thus the $Eu^{3+} \rightarrow Eu^{2+}$ reduction process is regarded as a solid–gas reaction.

Fig. 5 shows the dependence of the PL intensity (the 408 nm emission) on the Eu concentration in the $BaLiF_3$:Eu films. The intensity increases with increasing concentration up to 3 at% and then decreases. Because the crystallinity of $BaLiF_3$:Eu (10 and 15 at%) is relatively low as indicated in Fig. 3, the decreased
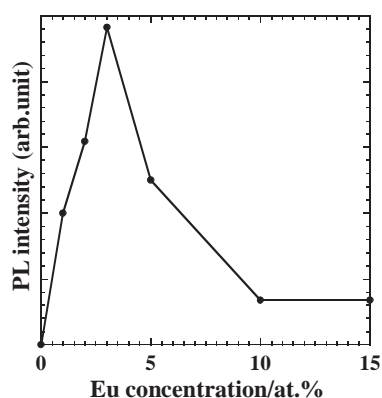

Fig. 5. Dependence of the PL intensity (the 408 nm emission) on the Eu concentration in the $BaLiF_3$:Eu thin films.

intensity cannot be ascribed only to the higher Eu concentrations. The concentration quenching, however, is clearly demonstrated for the film with 5 at% of Eu which has well crystallinity as judged from Fig. 3. Therefore the critical concentration, x_c, is suggested to be equal to $x = 0.03$ in $Ba_{1-x}Eu_xLiF_3$.

The concentration quenching of the luminescent Eu^{2+} ions doped in host crystals occurs by energy transfer between them [21]. According to Blasse [22], the critical transfer distance, R_c, can be estimated by

$$R_c \approx 2\left(\frac{3V}{4\pi x_c N}\right)^{1/3}, \quad (4)$$

where N is the number of ions, which can be replaced by the luminescent ions, in the unit cell and V is the unit cell volume. For $BaLiF_3$, N is the number of the Ba^{2+} ion and equals to 1. V is calculated to be 63.76 Å^3. By taking x_c of 0.03, R_c is found to be 16 Å. This value is close to those of other Eu^{2+}-activated phosphors [21,23], implying that the Eu^{2+} ions are well dispersed in the $BaLiF_3$ host. If Eu-aggregations, clusters, or EuF_2 were formed, the x_c value would be much smaller and the R_c value would not agree with the appropriate one. Thus the present experiments demonstrate that the high-quality, blue-emitting Eu-doped $BaLiF_3$ can be prepared from the metal trifluoroacetates by pyrolysis.

4. Conclusions

The undoped and Eu-doped $BaLiF_3$ films were prepared from the metal trifluoroacetates. The crystallization of the metal fluorides from the trifluoroacetate was influenced by the decomposition temperature, and the single-phase $BaLiF_3$ film was obtained by pyrolysis at 600°C. The Eu-doped $BaLiF_3$ films exhibited blue PL, which indicated the reduction of Eu^{3+} to Eu^{2+} during pyrolysis and $BaLiF_3$-formation process. Such the reduction was explained by the generation of F^- species, the reaction between Eu^{3+} and F^-, and stabilization in the $BaLiF_3$ lattice. The concentration quenching of the 408 nm PL emission was observed with the Eu concentrations over 5 at%, which demonstrated the well dispersion of the Eu^{2+} ions in $BaLiF_3$.

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