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Luminescence properties of $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Ca, Sr, Ba)

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Abstract

The luminescence properties of $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Ca, Sr, Ba) as the β-aluminas type compound was investigated. Judging from the luminescence spectra and Mössbauer spectra, europium ions in these compounds were almost divalent state. The emission spectra of $A_{1-x}Eu_xAl_{12}O_{19}$ consist of broad and single peaked emission bands. The peak position was shifted from 425 to 439 nm with the increase of x ($x = 0.05$ to 0.5). However, two emission peaks were recognized at ca. 390 and 530 nm for $Sr_{1-x}Eu_xAl_{12}O_{19}$, and at ca. 435 and 485 nm for $Ba_{1-x}Eu_xAl_{12}O_{19}$. Although the intensity of two peaks varied with x, the peak position almost fixed. ^{151}Eu Mössbauer spectra of $Ca_{1-x}Eu_xAl_{12}O_{19}$ show that Eu^{2+} was present in sites with isomer shifts in the range from −12.2 to −11.7 mm/s. For $Sr_{1-x}Eu_xAl_{12}O_{19}$ and $Ba_{1-x}Eu_xAl_{12}O_{19}$, the isomer shift values were −9.7 and −10.1 mm/s, respectively.

Keywords: $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Ca, Sr, Ba); Luminescence; Divalent europium ion; ^{151}Eu Mössbauer spectra

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1. Introduction

There are some important compounds between AO (A = Ca, Sr, Ba) and Al_2O_3. $AAl_{12}O_{19}$ has the magnetoplumbite structure being similar to the β-alumina, which are available for the solid electrolyte [1], catalyst and laser host materials [2,3]. In order to understand the functional properties of these compounds it is necessary to investigate the state of active centers. In this paper, $A_{1-x}Eu_xAl_{12}O_{19}$ were synthesized the direct solid-phase reaction, and we have measured the photoluminescence and the ^{151}Eu Mössbauer spectra of $A_{1-x}Eu_xAl_{12}O_{19}$. Eu^{2+} ion among many divalent cations was chosen from the following reasons. The ionic radius of Eu^{2+} ion is close to that of Sr^{2+} ion. Also, the photoluminescence of Eu^{2+} ion is unique and is affected by the crystal field surrounding Eu^{2+} ion. On the other hand, Mössbauer spectroscopy has proved quite useful in characterizing the valence state and coordination of cations because the isomer shift is caused by small changes in the electronic charge density at nucleus. Europium is ideal in this respect.

2. Experimental

$A_{1-x}Eu_xAl_{12}O_{19}$ (A=Ca, Sr) were prepared by solid state reaction using $Al(OH)_3$, $A(OH)_2$ and Eu_2O_3 at 1373K for 2 h under a mixture gas atmosphere (20% H_2/N_2). Because the luminescence of $Ba_{1-x}Eu_xAl_{12}O_{19}$ vary slightly depending on the methods of calcinations, the mixture of $Al(OH)_3$, $Ba(OH)_2$ and Eu_2O_3 heated at 1373 K for 1 h and then at 1573 K for 1 h in a same reducing atmosphere. The emission spectra were measured with a HITACHI recording absolute spectrofluorophotometer (F-4500) at room temperature. Mössbauer spectra were recorded at room temperature using a Mössbauer spectrometer (VT-6000), which was calibrated with EuF_3. A $^{151}Sm(SmF_3)$ source (1.85 GBq) was used.

2.1. Photoluminescence of $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Ca, Sr, Ba)

The photoluminescence spectra of $Ca_{1-x}Eu_xAl_{12}O_{19}$ under excitation at 325 nm are shown in Fig. 1. The spectra consist of broad, single peaked emission band. These bands were assigned to the Eu^{2+} ions ($4f^7$–$4f^65d^1$ transition), judg-

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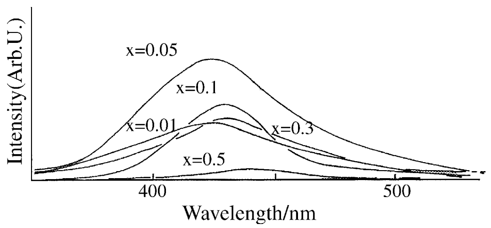


Fig. 1. Emission spectra of $Ca_{1-x}Eu_xAl_{12}O_{19}$.

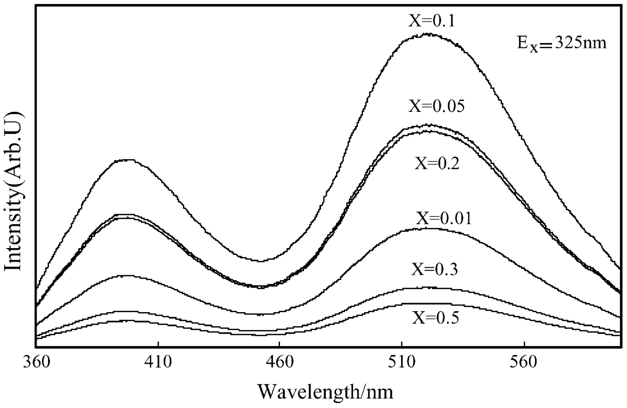


Fig. 2. Emission spectra of $Sr_{1-x}Eu_xAl_{12}O_{19}$.

ing from the range of wavelength. The peak position slightly shifted higher wavelength with the increase of Eu^{2+} ions. The emission spectra of $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Sr, Ba) are given in Figs. 2 and 3, respectively. Two emission peaks were recognized at ca. 390 and 530 nm for $Sr_{1-x}Eu_xAl_{12}O_{19}$, and at ca. 435 and 485 nm for $Ba_{1-x}Eu_xAl_{12}O_{19}$. The ratio of two peaks and peak position almost fixed, although the intensity of two peaks varied with x. The effect of varying the Eu^{2+} ion concentration on the emission band is presented in Fig. 4. The intensity with different concentration of Eu^{2+} ions shows a specific pattern. The intensity reached a maximum at ca. $x = 0.05$ for $Ca_{1-x}Eu_xAl_{12}O_{19}$ and ca. $x = 0.1$ for $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Sr, Ba). Thus, the peak position and intensity vary depending on the kind of alkaline earth ion or the concentration of Eu^{2+} ions. $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Ca, Sr, Ba) has a magnetoplumbite structure and is β-alumina type material. It is well known that there are four possible occupying positions for optically active ions in β-alumina [4]. That is, these positions are Beevers-Ross (BR) and mid-oxygen (mO) sites in the conduction plane, and four-fold Al(2), (3) and six-fold Al(1) and (4) within the spinel block. The position of these alkaline earth ions in the conduction plane of β-alumina is generally determined by short-range Coulomb interaction according to ionic radius. Accordingly, Ba ions are only located at the BR site by Coulomb interaction due to large ionic radius, whereas Sr ions can be located at both BR and mO sites due to intermediate ionic radius. Therefore the emission spectra with two peaks for $Sr_{1-x}Eu_xAl_{12}O_{19}$ can be easily understood. However, the emission spectra for $Ba_{1-x}Eu_xAl_{12}O_{19}$ are not composed of one peak. It would suggest that the structure of β-alumina is not consistent with the structure of $A_{1-x}Eu_xAl_{12}O_{19}$ [5].

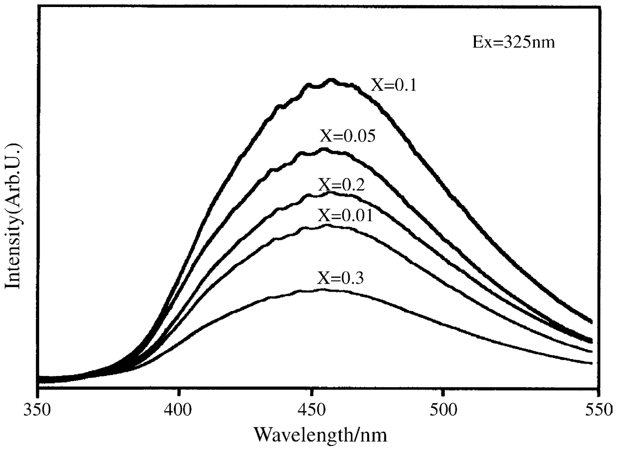
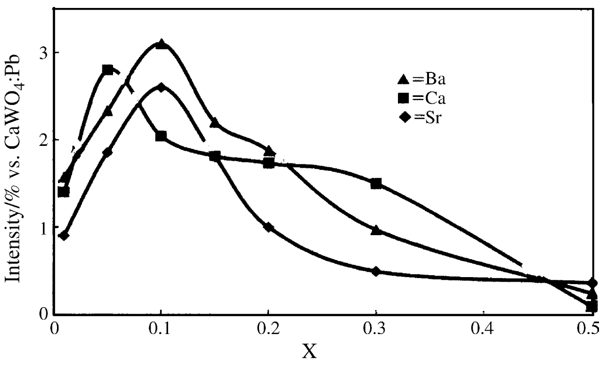


Fig. 3. Emission spectra of $Ba_{1-x}Eu_xAl_{12}O_{19}$.



The intensity of CaW_4:Pb was taken as unity.

Fig. 4. Dependence of the intensity of the emission band for Eu^{2+} on x. The intensity of $CaWO_4$:Pb was taken as unity.

2.2. ^{151}Eu Mössbauer spectra of $A_{1-x}Eu_xAl_{12}O_{19}$

Fig. 5 shows the Mössbauer spectra of $A_{1-x}Eu_xAl_{12}O_{19}$ (A = Sr, Ba). The isomer shift value of $Ca_{1-x}Eu_xAl_{12}O_{19}$ was −11.7 mm/s for $x = 0.05$ and −11.2 mm/s for $x = 0.5$ as reported elsewhere [6]. For $Sr_{1-x}Eu_xAl_{12}O_{19}$ and

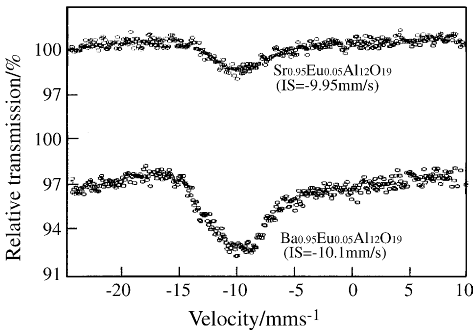


Fig. 5. ^{151}Eu Mössbauer spectra of $A_{0.95}Eu_{0.05}Al_{12}O_{19}$ (A = Sr, Ba) at room temperature.

$Ba_{1-x}Eu_xAl_{12}O_{19}$ ($x = 0.05$), the isomer shift values were −9.7 and −10.1 mm/s, respectively. As results, there is a difference of the isomer shift with x of $Ca_{1-x}Eu_xAl_{12}O_{19}$ and A ion of $A_{1-x}Eu_xAl_{12}O_{19}$. ^{151}Eu Mössbauer spectra of Eu_2NbO_3, which occurred in divalent and trivalent oxidation state, show that Eu^{2+} was present in sites with isomer shift value in the range of −13 to −12 mm/s [7]. Also, the isomer shift values of Eu^{2+} ions for $Eu_3V_2O_7$ and Eu_2VO_4, which demonstrates the presence of both divalent and trivalent Eu ions, were respectively observed at −12.53 and −11.86 mm/s [8]. It is evident from Fig. 5 that europium ions of $A_{1-x}Eu_xAl_{12}O_{19}$ are present in divalent state because this is well within the range of isomer shift reported for divalent europium compounds. Whereas the Eu^{2+} resonance line of $A_{1-x}Eu_xAl_{12}O_{19}$ is broad compared with EuF_2 as reported by Coey et al. [9]. The reason for broadening of the Eu^{2+} line would be considered as follows: (1) a distribution of isomer shifts corresponding to Eu^{2+} in sites with different coordination numbers and different Eu–O bond lengths, (2) unresolved electric quadrupole interaction, (3) $Eu^{2+} \Leftrightarrow Eu^{3+}$ electronic charge fluctuations. (3) can be neglected because there is no corresponding Eu^{3+} line. In the case of (2), linewidth of the crystalline europium compounds are usually of the order of 2.5–3.5 mm/s as reported elsewhere [7,8]. However, since linewidth of $A_{1-x}Eu_xAl_{12}O_{19}$ was slightly larger than 3.5 mm/s, the broadening of these compounds may be slightly affected by (2). The most reasonable explanation of the Eu^{2+} line is a variety of cation sites with isomer shifts in the range of isomer shift of −12.2 to −9.7 nm/s. It is reported that the range of Eu–O bond length corresponding to the range of isomer shift of −11.3 to −13.5 mm/s is found to be 0.26 to 0.30 nm [10]. Therefore, it is thought that there is a difference in Eu–O bond length of $A_{1-x}Eu_xAl_{12}O_{19}$.

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