

Persistent luminescence of Eu^{2+} and Dy^{3+} doped barium aluminate ($\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$) materials

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ARTICLE INFO

Article history:

Received 17 July 2008

Accepted 14 December 2008

Available online 17 May 2009

PACS:

78.60

83.80.Pc

Keywords:

Persistent luminescence

Phosphors

Barium aluminate

Europium

Dysprosium

ABSTRACT

Polycrystalline Eu^{2+} and Dy^{3+} doped barium aluminate materials, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$, were prepared with solid state reactions at temperatures between 700 and 1500 °C. The influence of the thermal treatments on the stability, homogeneity and structure as well as to the UV-excited and persistent luminescence of the materials was investigated by X-ray powder diffraction, SEM imaging and infrared spectroscopies as well as by steady state luminescence spectroscopy and persistent luminescence decay curves, respectively. The IR spectra of the materials prepared at 250, 700, and 1500 °C follow the formation of BaAl_2O_4 composition whereas the X-ray powder diffraction of compounds revealed how the hexagonal structure was obtained. The morphology of the materials at high temperatures indicated important aggregation due to sintering. The luminescence decay of the quite narrow Eu^{2+} band at ca. 500 nm shows the presence of persistent luminescence after UV irradiation. The dopant (Eu^{2+}) and co-dopant (Dy^{3+}) concentrations affect the crystallinity and luminescence properties of the materials.

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1. Introduction

Persistent luminescence, or afterglow, is the phenomenon observed when a phosphor after exposure to UV-radiation or even to light shows visible luminescence in the dark for a long time, preferably for tens of hours. Persistent luminescence materials are widely used in different displays, but their applications are being expanded to optoelectronics for image storage and detectors of high energy radiation [1].

The alkaline earth aluminates $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ [2] and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$, [2,3] are efficient blue and green emitting persistent luminescence materials that are already in commercial use. The mechanism of persistent luminescence in these aluminates is, however, not fully understood. The Eu^{2+} ion is agreed to be the luminescent center and the R^{2+} and R^{3+} ions have been suggested to trap holes and electrons, respectively [4–6]. The mechanism is considered to include the photoionization of the Eu^{2+} ion and a subsequent transfer of the electrons to traps formed by the lattice defects as oxide ion vacancies and possibly also the auxiliary R^{3+} ion co-dopants. The thermal bleaching of the electrons from the

traps followed by the process reverse to the storage of the excitation energy leads to the Eu^{2+} emission [7].

The $\text{Eu}^{2+},\text{R}^{3+}$ co-doped barium aluminates as $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ [4] have been studied only infrequently, even if they also show persistent luminescence. The reasons may be due to the rather complicated structural chemistry of the MAL_2O_4 host as well as the considerable size mismatch between the host (Ba^{2+}) and the main dopant (Eu^{2+}) cations. These factors may affect the efficiency of the Eu^{2+} luminescence when compared to that from the Ca^{2+} and Sr^{2+} aluminates.

In the present work, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ materials are prepared at different temperatures and with different Eu^{2+} and Dy^{3+} concentrations. The effects on the stability, homogeneity and structure as well as to the persistent luminescence are presented and discussed based on the analyses of the X-ray powder diffraction, SEM imaging as well as infrared and luminescence spectroscopic studies.

2. Experimental

2.1. Materials preparation

The polycrystalline $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ materials were prepared with a solid state reaction between stoichiometric amounts of

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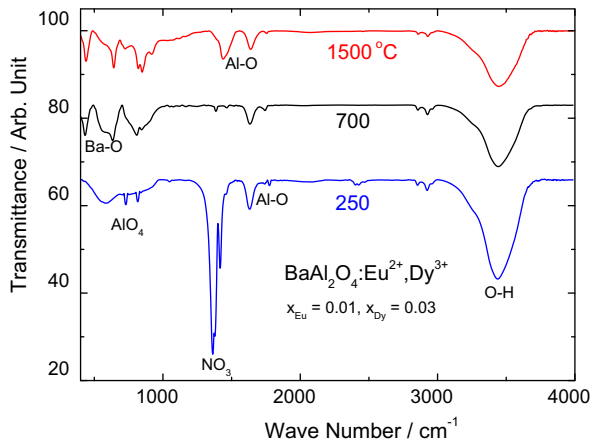


Fig. 1. FT-IR spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ prepared at different temperatures.

$\text{Ba}(\text{NO}_3)_2$, Al_2O_3 , $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The rare earth nitrates were obtained from the respective oxides. The starting materials were heated at 250, 700, 1150 and 1500 °C in air using heating times between two and five hours. The materials were

doped with the nominal concentrations of $\text{Eu}^{2+}/\text{Dy}^{3+}$ (in mole% of the barium amount): 0.50/0.50; 0.25/0.25; 0.25/0.50; 0.10/0.10; 1.0/2.8 and 1.0/2.0.

2.2. Experimental techniques

The purity and structure of the materials was checked with X-ray powder diffraction (XRD) recorded on a Rigaku Miniflex diffractometer using the $\text{FeK}_{\alpha 1}$ radiation (wavelength: 1.9360 Å) in the 2θ range of 2–90° using a data collection time of one second for each step of 0.02°. In this report, the powder diffraction patterns were calculated to correspond to the $\text{CuK}_{\alpha 1}$ radiation (wavelength: 1.5406 Å) in order to facilitate comparison to the patterns available in the literature. The infrared absorption spectra of the materials were recorded by using the standard KBr pellet techniques with a Bomem Model MB-100 spectrometer in the range of 400–4000 cm^{-1} . The electron microscopic analyses were carried out with a JEOL JSM-740 1F (Field Scanning Electron Microscope). Photoluminescence measurements were performed with a SPEX-Fluorolog 2 spectrofluorimeter equipped with 0.22 m SPEX 1680 double grating monochromators. A 450 W xenon lamp was used as an excitation source. The excitation and emission spectra at room temperature were collected at an angle of 22.5° (front face).

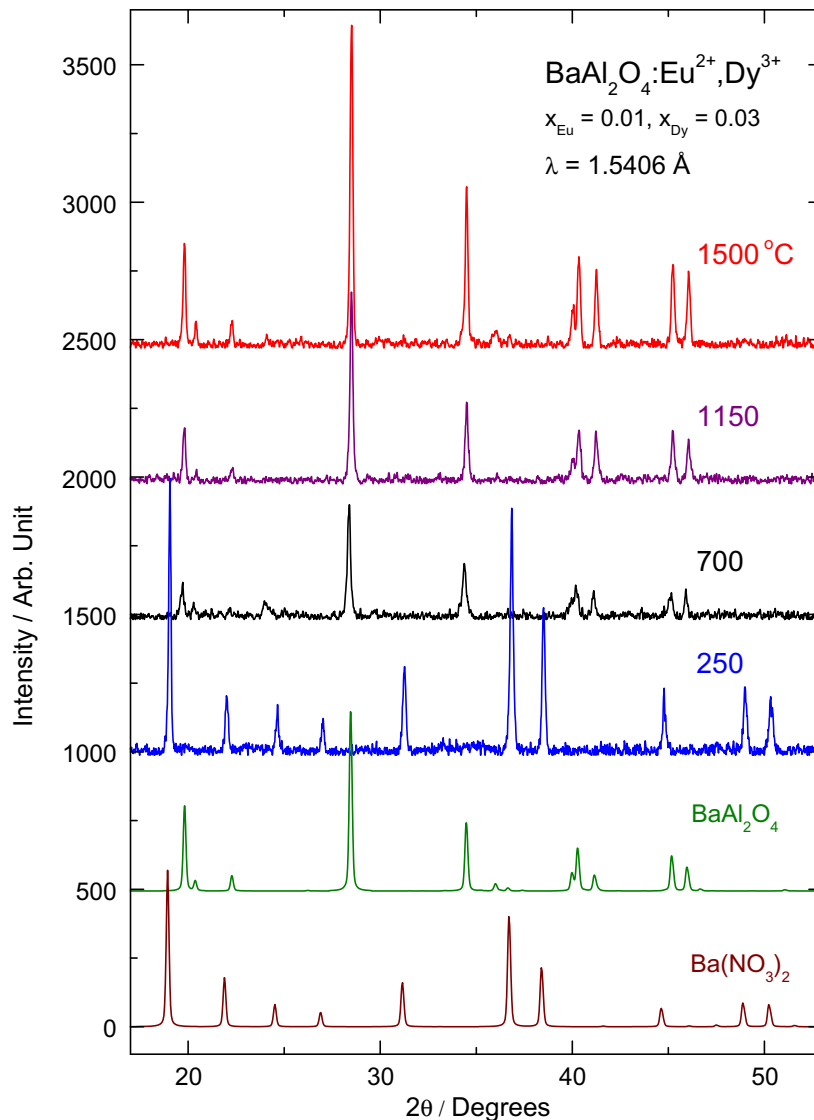


Fig. 2. X-ray powder diffraction patterns of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ prepared at different temperatures.

3. Results and discussion

3.1. Formation and phase purity

The FT-IR absorption spectrum of the material heated at 250 °C (Fig. 1) shows intense nitrate absorption bands at *ca.* 1365 and 1430 cm^{-1} indicating that the decomposition of $\text{Ba}(\text{NO}_3)_2$ has not started. The Al–O stretching vibration at 1630 cm^{-1} and the other vibrations assigned to the AlO_4 unit at 500–900 cm^{-1} are rather broad due to the poor crystallinity of the Al_2O_3 starting material. At 700 °C, traces of the nitrates still persist, while the Al–O vibrations, especially that at 1440 cm^{-1} , indicate the formation of the BaAl_2O_4 phase though the Al_2O_3 vibrations still dominate. The Al–O vibrations are fully developed and reasonably sharp only at 1500 °C. The absorption bands below 500 cm^{-1} can be assigned to the Ba–O vibrations. The strong absorption at the 3000–3750 cm^{-1} range is most probably due to the humidity absorbed by the KBr during the preparation of the pellets.

The X-ray diffraction patterns (Fig. 2) confirm the observations made from the FT-IR spectra. The heating temperature 250 °C is definitely too low to decompose $\text{Ba}(\text{NO}_3)_2$, since the pattern corresponds exactly to the calculated one [8] for the cubic $\text{Ba}(\text{NO}_3)_2$ with the space group $\text{P}2_13$ (No. 198 [9]) [10] or $\text{Pa}\bar{3}$ (No. 205 [9]) [11]. The reflections of Al_2O_3 are very weak and broad indicating low crystallinity. At 700 °C, only the desired hexagonal BaAl_2O_4 phase with the space group $\text{P}6_3$ (No. 173 [9]) [12] is observed. However, there is a weak reflection at *ca.* 30°, which may indicate unreacted Al_2O_3 disappearing at still higher temperatures.

The crystallinity of the BaAl_2O_4 phase is greatly improved with increasing temperature as shown by the X-ray diffraction patterns of the materials annealed at 1150 and 1500 °C. Moreover, important aggregation of the phosphor material due to sintering was observed by SEM. The hexagonal BaAl_2O_4 phase remains stable even up to 1500 °C and no formation of other more complex aluminate phases can be observed, either.

3.2. Luminescence properties

Two maxima, peaking at 435 and 500 nm, were observed in the luminescence spectra of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ (Fig. 3). These are due to the transitions from the lowest ^2D level of the excited $4f^65d^1$ configuration to the ground $^8\text{S}_{7/2}$ level of the $4f^7$ configuration of the Eu^{2+} ion. There are two Ba^{2+} sites in the BaAl_2O_4 structure

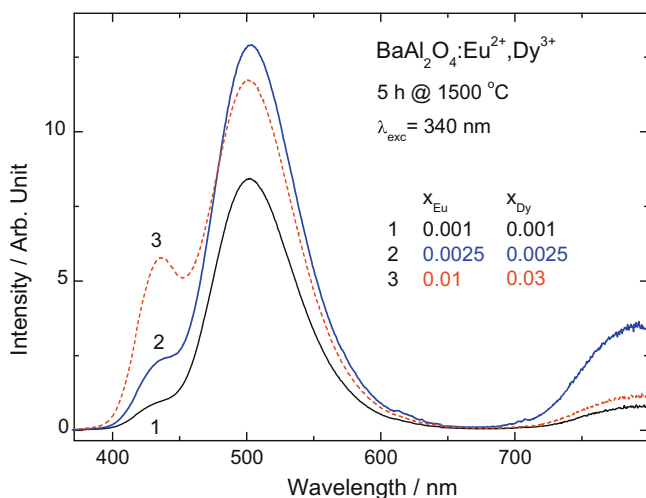


Fig. 3. Effect of dopant and co-dopant concentration on the photoluminescence emission of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$.

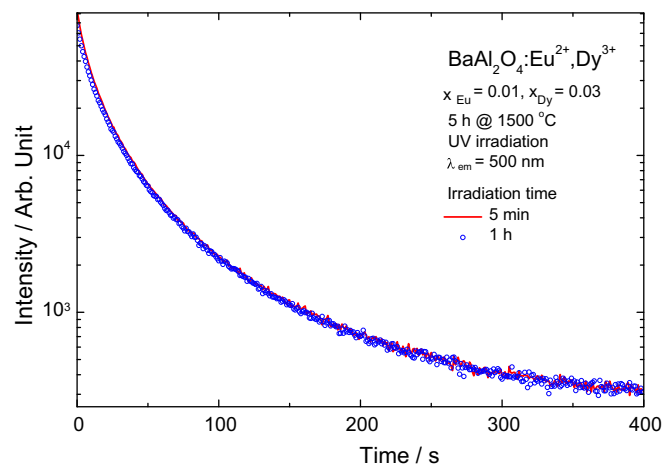


Fig. 4. Effect of irradiation time on the luminescence decay of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$.

and thus the two maxima correspond to emission from the two sites. The relative intensity of the emission at 435 nm was observed to increase with increasing dopant and co-dopant concentration (Fig. 3). This indicates that one of the Ba^{2+} sites is preferentially occupied by the Eu^{2+} ions and that the second site is filled only with higher dopant concentrations. According to the crystal structure, the first Ba^{2+} site (2a) has the multiplicity of two and a site symmetry of C_3 while the second one (6c) has six and C_1 . Both Ba^{2+} sites have nine-coordination and the sites are similar in average size ($d(\text{Ba}-\text{O})_{\text{Ave}} = 2.86$ and 2.87 Å). However, the lower symmetry site has also shorter Ba–O distances (2.69 Å) corresponding to those typical of $\text{Eu}^{2+}-\text{O}$ (2.68 [13]). It would therefore seem reasonable that this 6c site is filled preferentially. This is also supported by the higher PL intensity as a result of contribution from six instead of two Eu^{2+} ions.

The luminescence decay characteristics investigated for the 500 nm emission indicate that the material emits light far longer than the typical microsecond lifetime of Eu^{2+} [14] (Fig. 4). This indicates the presence of persistent luminescence. In the time scale chosen, no conventional Eu^{2+} emission can be observed. Instead, the decay consists of many overlapping components. The decay characteristics show no significant changes with different irradiation times.

4. Conclusions

The polycrystalline $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ material was successfully prepared with a solid state reaction. The product was obtained in hexagonal form at temperatures above 700 °C. At higher temperatures, the crystallinity increases and the crystallites aggregate due to sintering. The main emission was observed from the Eu^{2+} ion at 500 nm, but the intensity of the second band at 435 nm increased with increasing dopant/co-dopant concentration. The luminescence decay characteristics indicated that the material shows persistent luminescence. In the future, the preparation conditions and the dopant/co-dopant content need further studies to optimize the persistent luminescence performance of $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$. Moreover, the optical properties will be studied in more detail and combined with theoretical calculations to obtain more information on the mechanism of persistent luminescence.

Acknowledgments

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Rede de Nanotecnologia Molecu-

lar e de Interfaces (RENAMI) and Instituto do Milênio de Materiais Complexos (IM²C) for financial support. Financial support to JH from the Graduate School of Materials Research (GSMR, Turku, Finland) is acknowledged, too.

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