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Co-Dopant Influence on the Persistent Luminescence of $BaAl_2O_4$:Eu^{2+},R^{3+}

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ABSTRACT

The R^{3+} (rare earth) co-dopants may have a surprisingly important role in persistent luminescence – enhancement of up to 1–3 orders of magnitude may be obtained in the performance of these phosphor materials – depending strongly on the R^{3+} ion, of course. In this work, the effects of the R^{3+} co-dopants in the $BaAl_2O_4$:Eu^{2+},R^{3+} materials were studied using mainly thermoluminescence (TL) and synchrotron radiation XANES methods. In $BaAl_2O_4$, the conventional and persistent luminescence both arise from the $4f^7 \rightarrow 4f^65d^1$ transition of Eu^{2+}, yielding blue–green emission color. The former, in the presence of humidity, turns to more bluish because of creation of an additional Eu^{2+} luminescence centre which is not, however, visible in persistent luminescence. The trap structure in the non-co-doped $BaAl_2O_4$:Eu^{2+} is rather complex with 4–5 TL bands above room temperature. With R^{3+} co-doping, this basic structure is modified though no drastic change can be observed. This underlines the fact that even very small changes in the trap depths can produce significant modifications in the persistent luminescence efficiency. It should be remembered that basically the persistent luminescence performance is controlled by the Boltzmann population law depending exponentially on both the temperature and trap depth.

Some mechanisms for persistent luminescence have suggested the presence of either divalent R^{2+} or tetravalent R^{IV} during the charging of the Eu^{2+} doped materials. The present XANES measurements on $BaAl_2O_4$:Eu^{2+},R^{3+} confirmed the presence of only the trivalent form of the R^{3+} co-dopants excluding both of these pathways. It must thus be concluded, that the energy is stored in intrinsic and extrinsic defects created by the synthesis conditions and charge compensation due to R^{3+} co-doping. Even though the effect of the R^{3+} co-dopants was carefully exploited and characterized, the differences in the effect of different R^{3+} ions with very similar chemical and spectroscopic properties could not be explained in a satisfactory manner. More work is – and perhaps a completely new approach may be – needed.

1. Introduction

In persistent luminescence, which is nominally an isothermal case of thermally stimulated luminescence, the material continues to emit light for several hours after ceasing the irradiation [1,2]. These materials can be applied in emergency signalization, micro defect sensing, optoelectronics for image storage, detectors of high energy radiation, thermal sensors, *in vivo* imaging, *etc.* [1–3]. The recent progress in the research of persistent luminescence materials is related to the discovery of the $SrAl_2O_4$:Eu^{2+},Dy^{3+} phosphor [2] in 1996. The initial innovation was soon followed by a family of new efficient persistent luminescence materials based mainly on different aluminates and silicates with higher chemical stability, *e.g.* $CaAl_2O_4$:Eu^{2+},Nd^{3+} [1], $Sr_4Al_{14}O_{25}$:Eu^{2+},Dy^{3+} [4] and $Sr_2MgSi_2O_7$:Eu^{2+},Dy^{3+} [5]. Presently, the best materials can continue to emit light in excess of 24 h in the dark. Among the aluminate materials, $BaAl_2O_4$:Eu^{2+},R^{3+} have a special advantage that europium can be reduced and kept in the divalent state without the use of any reducing atmosphere [6–8] which facilitates the preparation of these persistent luminescence materials.

According to the present understanding, in persistent luminescence the excitation energy is stored to traps and then released with the stimulation by thermal energy available at room temperature [1]. In most – if not in all – Eu^{2+} doped persistent luminescence materials the traps' properties can be modified by

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using different trivalent rare earth (R^{3+}) co-dopants [1,9]. In order to improve the intensity and duration of the persistent luminescence, it is important to know genuinely the role of the R^{3+} co-dopants in the mechanism of the phenomenon, not just to note that this happened to be the outcome of co-doping. The genuine knowledge is very important to reduce the amount of human and financial resources dedicated to the development of new materials. This work was thus aimed to study the role of the R^{3+} co-dopants in modifying the trap structure in $BaAl_2O_4:Eu^{2+},R^{3+}$ and how these modifications affect the efficiency of persistent luminescence.

2. Experimental

2.1. Materials preparation

The $BaAl_2O_4:Eu^{2+},R^{3+}$ materials were prepared using the combustion synthesis route starting with the metal nitrates and urea as the reactants and the fuel, respectively. The rare earth nitrate hydrates were obtained from the respective rare earth oxides (R_2O_3, Pr_6O_{11} or Tb_4O_7; 99.99% CSTARM) or from $Ce_2(CO_3)_3$ (99.99% Aldrich) with a reaction with concentrated nitric acid. The precursors were then dissolved into a smallest possible amount of distilled water. A silica capsule filled with the homogeneous solution was inserted into a furnace pre-heated to 500 °C [6,10–12]. The reaction began *ca.* 5 min after the introduction of the capsule into the furnace. The mixture was then self-ignited with a white flame and produced a white powder. After the completion of the reaction, the furnace was turned off and allowed to cool freely. The products were removed from the oven when the temperature had decreased to *ca.* 25 °C. The nominal concentrations of Eu^{2+} and R^{3+} were 1 and 2 mol-% (of the Ba^{2+} amount), respectively. The formation of Eu^{2+} using Eu^{3+} as a source without the use of reducing atmosphere has been explained to result from the evaporation of the interstitial oxygen at high temperatures [6].

2.2. Methods of characterization

The crystal structure and phase purity of the $BaAl_2O_4:Eu^{2+},R^{3+}$ materials were routinely verified with the X-ray powder diffraction measurements using a Rigaku Miniflex diffractometer with $CuK_{\alpha 1}$ radiation (1.5406 Å) between 3 and 90° (in 2θ) with 0.02° and 1 s as the 2θ step and step time, respectively.

The luminescence spectra and persistent luminescence decay times were measured with a SPEX Fluorolog-2 spectrofluorometer equipped with two 0.22 m SPEX 1680 double grating monochromators. A 450 W Xenon lamp was used as the excitation and irradiation source. The CIE color coordinates were calculated based on the emission spectra using the SpectraLux v2.0 software [13].

The thermoluminescence (TL) glow curves of the $BaAl_2O_4:Eu^{2+},R^{3+}$ phosphors were recorded with a Daybreak TL Reader 1100 thermoluminescence system with a linear heating rate of 5 °C s^{-1} in the temperature range between 25 and 400 °C. The global TL emission from UV to 650 nm was monitored using the bialkali EMI 9235QA photomultiplier and the Corning 7-59 and Schott BG-39 filters. Prior to the TL measurements, the materials were exposed to radiation from a 6 W Cole-Parmer UV lamp (emission maxima at 254 and 365 nm). Exposure and delay times were 2 and 3 min, respectively. The analysis of the TL glow curves was carried out by deconvoluting the TL curves with the program TLanal v.1.0.3 [14,15]. The fitted bands were considered to be of either the 1st or 2nd order kinetics depending on the asymmetry of the band profile.

The X-ray Absorption Near-Edge Structure (XANES) measurements of the rare earth elements in $BaAl_2O_4:Eu^{2+},R^{3+}$ persistent luminescence materials were carried out at room temperature using the beamline I811 at MAX-lab in Lund, Sweden [16]. The data were collected in the fluorescence mode over the rare earth L_{II} and L_{III} edges using the Si(111) double crystal monochromator with a 7 element Gresham Si(Li) detector. The energy resolution $\Delta E/E$ was 10^{-4} and the measured energy range was from 100 eV both before and after the edge.

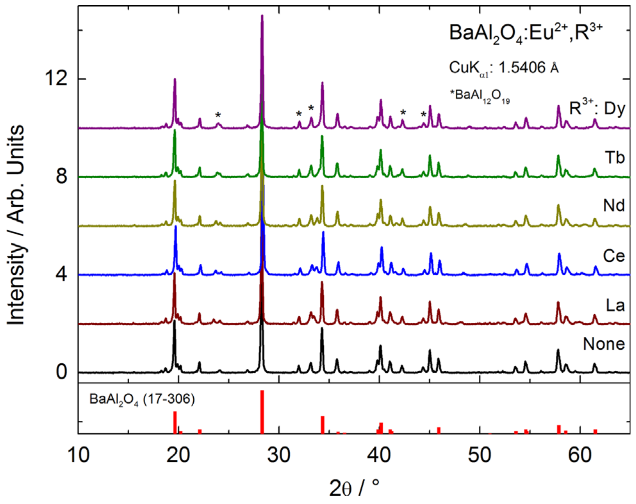

Fig. 1. X-Ray diffraction patterns of the $BaAl_2O_4:Eu^{2+},R^{3+}$ materials.

3. Results and discussion

3.1. Formation and phase purity

The X-ray diffraction patterns (Fig. 1) confirm the formation of the hexagonal $BaAl_2O_4$ phase though usually with a small amount of $BaAl_{12}O_{19}$ as a sole impurity phase [17]. The presence of this impurity is mainly due to the high temperature achieved locally and for a short period of time during the combustion synthesis; estimates range from up to at least 1600 °C [18] but, depending on the fuel and oxidizer, temperatures as high as 3000 °C may be achieved. The local temperature may clearly exceed that required for the formation of $BaAl_2O_4$, as low as 1300 °C. No significant differences were observed in either the 2θ positions or FWHM values of the XRD reflections between materials with different co-dopants, most probably due to the low dopant concentrations used.

3.2. Photoluminescence of $BaAl_2O_4:Eu^{2+},R^{3+}$

The UV excited luminescence spectra of $BaAl_2O_4:Eu^{2+},R^{3+}$ confirm the role of Eu^{2+} as the emitting ion, since only the broad $4f^65d^1 \rightarrow 4f^7$ emission bands are observed with the maxima at 430 and 500 nm (Fig. 2), yielding a bluish-green emission with the CIE color coordinates x, y of 0.128, 0.414 (Fig. 2, inset). The emission spectra of the materials with different co-dopants are very similar, irrespective of the R^{3+} co-dopant, in agreement with previous work [19]. The 430 nm band arises from the creation of a new Eu^{2+} site due to water exposure [20,21]. Since this band is not observed in the persistent luminescence spectrum of *e.g.* the Dy^{3+} co-doped material, it may be due to a new compound rather than a modification of the existing $BaAl_2O_4$.

Despite the close similarity of the emission spectra, the persistent luminescence decay times are strongly influenced by the co-dopant. The materials with Dy^{3+} and Nd^{3+} as the co-dopant show the longest duration of persistent luminescence, followed by