Synchrotron radiation spectroscopy of rare earth doped persistent luminescence materials

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ARTICLE INFO

ABSTRACT

The electronic structure of the polycrystalline $CaAl_2O_4$:Eu^{2+},Ce^{3+} persistent luminescence materials were studied with X-ray absorption (XANES) and UV–VUV emission and excitation spectroscopy by using synchrotron radiation. Theoretical calculations using the density functional theory (DFT) were carried out simultaneously with the experimental work. The experimental band gap energy (E_g) value of 6.7 eV agrees very well with the DFT value of 6.4 eV. From the $4f^7 \rightarrow 4f^65d^1$ excitation bands of Eu^{2+}, the positions of the $4f^7$ ground as well as the $4f^65d^1$ excited levels were established. The excitonic fine structure which could act as trap levels close to the bottom of the conduction band could not be observed, however. The different processes contributing to the mechanism of persistent luminescence from $CaAl_2O_4$:Eu^{2+} were constructed and discussed.

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1. Introduction

The persistent luminescence materials have been known and exploited for hundreds of years since the beginning of the 17th century (Newton Harvey, 1957). Despite the long history of the materials, the understanding of even the mere basics of the phenomenon itself has not been at the same level. No progress occurred earlier than the mid 1990s prior to the advent of the commercial exploitation of the modern and efficient persistent luminescence materials, the Eu^{2+} doped and R^{3+} (R: rare earth) co-doped alkaline earth aluminates (MAl_2O_4:Eu^{2+},R^{3+}; M: Ca, Sr, Ba) (Matsuzawa et al., 1996). As expected, only then serious interest was awakening to the study of the mechanisms underlying the persistent luminescence in a manner not uncommon to the breakthrough of the ceramic high T_c superconducting materials.

From the rather simplistic start neither considering the energetics nor the veracity of the actual players in the phenomenon, there have been more and more elaborate models brought up as the mechanisms (e.g. Chen et al., 2006; Zhang and Wang, 2007; Dorenbos, 2005a; Aitasalo et al., 2004b, 2006). However, as it is the case with the photostimulated luminescence – possibly related to persistent luminescence – no completely convincing or proven mechanisms have yet appeared in the scientific literature. There seem to be two critical obstacles preventing the theoretical clearing up of the persistent luminescence mechanism(s). Despite the early work (Pedrini et al., 1986; Thiel et al., 2002) – later a great deal elaborated (e.g. Dorenbos, 2005b, 2007, 2008) – on the relationships between the energy levels of the $R^{2+/3+/IV}$ ions and the electronic band structure of the host lattice, the resulting energy level structures are by far too inaccurate or too painstaking to be attained in such a detail to be useful in the elucidation of persistent luminescence. In addition, not much is known about the defect energy levels in solids although it is expected that different kinds of defects may play a major role in the persistent luminescence mechanism.

As the second major obstacle, the possible changes in the valence states of the dopants (e.g. Eu^{2+}, Ce^{3+}, Eu^{3+} or Tb^{3+}) during the persistent luminescence are not known at all. The energy level positions of the $R^{2+/3+/IV}$ ions *vis-à-vis* the host band structure can give some information about these changes though experimental verification is still lacking in most cases. Already in the very beginning of the studies on the persistent luminescence mechanisms, it was assumed that such valence changes occur (e.g. Chen et al., 2006; Zhang and Wang, 2007; Dorenbos, 2005a; Aitasalo et al., 2004b, 2006). As for the veracity of these species assumed

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to be present, it may now be stated that the occurrence of such ions as the monovalent Eu^+, is not at all conceivable if common sense is used. Furthermore, such a species is not fitting to any of the energy level models referred to above. Nonetheless, the presence of tetravalent ions as Ce^{4+} may be plausible and fit into these models, too.

In the present work, the luminescence properties of the Eu^{2+} doped and R^{3+} (especially Ce^{3+}) co-doped $CaAl_2O_4$ persistent luminescence materials were investigated using synchrotron radiation (SR) UV–VUV excitation in order to establish at different temperatures the relationships between the (co-)dopants' energy levels and the electronic host band structure. In addition to the experimental determination of the host band structure, a simultaneous theoretical study was carried out with the density functional theory (DFT) calculations. Further, the presence of the $Eu^{2+/3+}$ and $Ce^{3+/IV}$ ions were probed by SR X-ray absorption methods (XANES). Eventually, a persistent luminescence mechanism was suggested based on these experimental and theoretical results.

2. Experimental

2.1. Materials preparation

The polycrystalline $CaAl_2O_4$:Eu^{2+},R^{3+} materials were prepared with a solid state reaction between stoichiometric amounts of $CaCO_3$, Al_2O_3 and rare earth oxides (Aitasalo et al., 2004a). A small amount of B_2O_3 (1 mol%) was used as a flux. The nominal concentration of both the Eu^{2+} and R^{3+} ions was 1 mol% of the calcium amount. The starting materials were ground to a homogeneous mixture in a ball mill. The mixtures were then annealed in a reducing (N_2+10% H_2) atmosphere for 1 and 4 h at 900 and 1300 °C, respectively. The structural and phase purity was confirmed by X-ray powder diffraction using a Huber 670 image plate Guinier-camera at 295 K ($CuK_{\alpha1}$ radiation, 1.5406 Å). No additional phases were found in the materials.

2.2. Synchrotron radiation measurements

The UV–VUV excitation spectra of the $CaAl_2O_4$:Eu^{2+},R^{3+} materials were measured between 3.7 and 40 eV by using the synchrotron radiation at the SUPERLUMI beamline of HASYLAB at DESY (Hamburg, Germany) (Laasch, 2009a). The samples were mounted on the cold finger of a liquid He flow cryostat. The spectra were recorded at selected temperatures between 10 and 298 K with a 2-m primary McPherson monochromator attaining a resolution between 0.02 and 0.32 nm. The emission spectra were obtained both with a Spectra Pro 300i monochromator (200–800 nm) equipped with a conventional photomultiplier and a CCD detector (200–1050 nm). Since the SR has a pulse separation of ca. 190 ns, the time resolution of the emission spectra are somewhat impaired owing to the conventional Eu^{2+} decay time being close to 1 μs.

The SR X-ray absorption (XAFS) spectra were measured between 5 and 9 keV at the E4 beamline of HASYLAB (Laasch, 2009b). The spectra corresponding to the L_{III} edge of the lanthanides were recorded at selected temperatures between 10 and 298 K with a He flow cryostat setup similar to the one described above. Due to the strong host absorption, the EXAFS/XANES measurements were carried out in the fluorescence mode using a 7 pixel Si(Li) detector. The resolution of the experimental setup was around 1 eV in the energy range used.

2.3. Density functional theory calculations

The electronic structure of the $SrAl_2O_4$ materials were calculated using the WIEN2k package (Blaha et al., 2001). WIEN2k is based on the full potential linearized augmented plane wave method, an approach which is among the most precise and reliable ways to calculate the electronic structure of solids. The generalized gradient approximation (GGA) was employed.

3. Results and discussion

3.1. Luminescence of $CaAl_2O_4$:Eu^{2+},R^{3+}

The luminescence spectra of the $CaAl_2O_4$:Eu^{2+},R^{3+} materials excited to the conduction band by SR were characterized by a strong band at ca. 440 nm (22500 cm^{-1}) due to the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ion (Figs. 1 and 2). The FWHM value of this band is quite low, 2250 cm^{-1}, which indicates that the emission originates from one Eu^{2+} centre only despite the fact that there are three different Ca^{2+} sites in the monoclinic $CaAl_2O_4$ structure (Hörkner and Müller-Buschbaum, 1976). However, there is only one nine-fold coordinated Ca^{2+} site in addition to two seven-fold coordinated ones. Only this single site has sufficient spacing to allow for the substitution by the large Eu^{2+} (ionic radii:
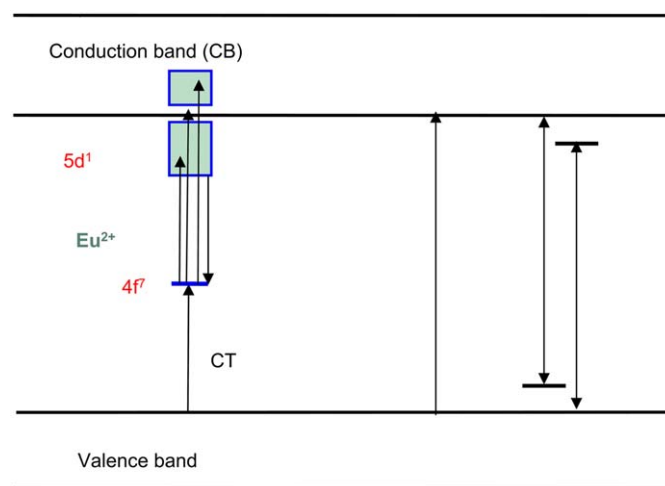

Fig. 1. Schematic energy level diagram of the emission and selected excitation processes in the Eu^{2+} doped $CaAl_2O_4$.
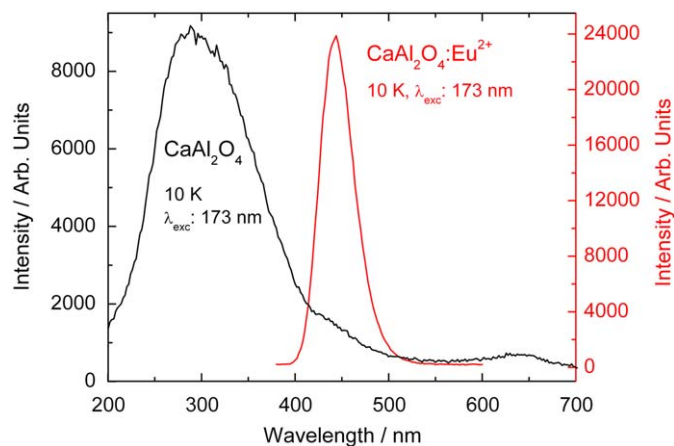

Fig. 2. Synchrotron radiation excited emission spectra of both Eu^{2+} doped and non-doped $CaAl_2O_4$ at 10 K (SUPERLUMI, HASYLAB).