



Research note

Valence and environment of rare earth ions in $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ persistent luminescence materials[☆]

Jorma Hölsä^{a,b}, Taneli Laamanen^{a,c}, Mika Lastusaari^{a,b,*}, Marja Malkamäki^{a,c}, Edmund Welter^d, Dariusz A. Zajac^d

^a University of Turku, Department of Chemistry, FI-20014 Turku, Finland

^b Turku University Centre for Materials and Surfaces (MatSurf), Turku, Finland

^c Graduate School of Materials Research (GSMR), Turku, Finland

^d Deutsches Elektronen-Synchrotron, a Research Centre of the Helmholtz Association, Notkestrasse 85, D-22607 Hamburg, Germany

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ABSTRACT

The existence of the different $\text{R}^{2+}/\text{R}^{3+}/\text{R}^{\text{IV}}$ (R: rare earth) ions as well as the modifications in the structural environment around the dopant and co-dopants in $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ persistent luminescence materials was studied by L_{III} edge X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements at Hamburger Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY) (Hamburg, Germany). The measurements were carried out at 10 and 296 K for selected rare earth (co-)dopants (Eu^{2+} ; Ce^{3+} , Nd^{3+} , Sm^{3+} , and Yb^{3+}).

The XANES results indicated the co-existence of both divalent and trivalent europium in all co-doped $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ materials, but only divalent europium in $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}$. The measurement temperature did not affect the XANES results. The interatomic distances extracted from the EXAFS data of the $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ materials indicated that co-doping creates distortions around the Eu^{2+} ions suggesting dopant aggregation.

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1. Introduction

In everyday life, persistent luminescence materials have established an invaluable position with their most obvious application: self-lit signalization. The phenomenon implies the ability of a material to store energy from (artificial) lighting, including visible and ultraviolet (UV) radiation, around it and to gradually release it as light in the dark at room temperature [1]. Although persistent luminescence has been known since the discovery of the Bologna stone in the early 1600s [2], the details behind the storage and slow release of energy are still not completely resolved. With the mechanism known, applications such as radiation detection [3], structural damage sensing [4] as well as medical diagnostics [5] could be employed in their full potential, while new and existing materials could be tailored to match a wealth of new uses.

After the advent of the new generation of persistent luminescence materials in the 1990s, i.e. the Eu^{2+} and R^{3+} (R: rare earth) co-doped alkaline earth aluminates $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}, \text{R}^{3+}$ [6] and disilicates

$\text{M}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{R}^{3+}$ [7] (M: Ca, Sr, Ba), replacing the traditional $\text{ZnS}:\text{Cu}, \text{Co}$ used exclusively earlier, the studies on the mechanism of persistent luminescence have been focused on the interplay of the rare earth ions with the host band structure and the lattice defects. Although it is known that the Eu^{2+} ion acts as the luminescence center, the origin of the enhancement (or decrease) of the persistent luminescence efficiency due to the R^{3+} co-doping has not been established.

The location of the 4f and 5d levels of the Eu^{2+} ion and the other $\text{R}^{2+}/\text{R}^{3+}/\text{R}^{\text{IV}}$ ions in the host band structure can be used to predict the ability of the rare earth species to trap electrons/holes [8], but the level positions alone cannot explain the energy storage and luminescent feeding processes [1]. This suggests a very important role for lattice defects, which may easily be produced during the reducing conditions used in the preparation of these materials. The existence of the defects has been confirmed by Electron Paramagnetic Resonance (EPR) measurements [9] and emission from undoped materials [10], but the defect chemistry of these materials still remains basically an open question.

X-ray absorption spectroscopy techniques X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) can be employed to clarify the role of both the Eu^{2+} ion and the $\text{R}^{2+}/\text{R}^{3+}/\text{R}^{\text{IV}}$ ions in the mechanism of persistent luminescence by monitoring *in situ* their valences (obtainable by XANES) and the local structures around them (EXAFS). Previous

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* Corresponding author. University of Turku, Department of Chemistry, FI-20014 Turku, Finland. Tel.: +358 2 3336736; fax: +358 2 3336700.

E-mail address: miklas@utu.fi (M. Lastusaari).

reports using these methods at room temperature have shown the co-existence of both Eu^{2+} and Eu^{3+} in the $\text{Ca}_2\text{MgSi}_2\text{O}_7$ [11] and $\text{Sr}_2\text{MgSi}_2\text{O}_7$ host materials [11,12]. Moreover, it has been reported that the Dy [11,12] and other R co-dopants [12] are only in the trivalent form indicating that no net changes in the co-dopant valences occur during the persistent luminescence process.

This work focuses on the blue emitting persistent luminescence materials $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$. From this series, $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ is already in commercial use. The *in situ* XANES and EXAFS measurements were carried out both at 10 K and room temperature. At the former temperature, only the energy storage is supposed to take place whereas at the latter, also the energy release should be observed.

2. Structural considerations

The crystal structure of CaAl_2O_4 is related to the stuffed tridymite (SiO_2) with the monoclinic space group $\text{P}2_1/\text{n}$ (No. 14), $Z: 12$ [13]. The structure consists of channels built up of rings formed by six corner-sharing AlO_4 tetrahedra and Ca^{2+} cations situated within the channels. There are three different Ca^{2+} sites. Two of them (Ca1 and Ca2) are six- and one (Ca3) is nine-coordinated. The coordination polyhedra of CaO_6 and CaO_9 are distorted octahedra and tri-capped antiprisms, respectively. The average Ca–O distances 2.42 and 2.43 Å for the six-coordinated Ca^{2+} ions are clearly shorter than that for the nine-coordinated one (2.78 Å).

In this structure, only the Ca sites are large enough to accommodate the rare earth ions [14]. Thus, following the Kröger–Vink notation, $\text{R}_{\text{Ca}}^{\cdot\cdot}$, $\text{R}_{\text{Ca}}^{\cdot}$ and $\text{R}_{\text{Ca}}^{\cdot\cdot\cdot}$ may be created by the di-, tri- and tetravalent rare earths, respectively, upon substitution for the Ca^{2+} ions in the lattice. As reported before [9,10], oxygen vacancies $\text{V}_{\text{O}}^{\cdot\cdot}$ will be formed, as well, due to the reducing preparation conditions. For charge compensation, also cation vacancies $\text{V}_{\text{Ca}}^{\prime\prime}$ with a negative net charge should be created, when R^{3+} and R^{IV} ions are inserted in the Ca^{2+} sites.

Empirically, complete solid solubility is expected when the difference between the radii of the participating ions is smaller than about 15% (Vegard's law) [15]. This is providing the same charges and at least similar structures for the pure components of the solid solutions. In the CaAl_2O_4 host, the statistical size [14] difference of all the studied trivalent co-dopants to that of Ca^{2+} falls within the 15% limit with Yb^{3+} very close to it (13–15% difference). On the other hand, for the Eu^{2+} ion, the difference decreases from 16 (coordination number, CN: 6) to 10% (CN: 9) with increasing coordination number. Thus, problems with the solubility of the (co-)dopants to the host lattices may be possible, but the low concentration will greatly facilitate the solid solubility.

3. Experimental

3.1. Materials preparation

The polycrystalline $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$ (R^{3+} : none, Ce^{3+} , Nd^{3+} , Sm^{3+} , and Yb^{3+}) materials were prepared with a solid state reaction between stoichiometric amounts of CaCO_3 , Al_2O_3 as well as R_2O_3 or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. 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 mixtures of starting materials were annealed in a reducing ($\text{N}_2 + 12\% \text{H}_2$) atmosphere for one and 10 h at 700 and 1350 °C, respectively. The structural and phase purity was confirmed by X-ray powder diffraction using a Huber G670 image plate Guinier-camera at 295 K ($\text{CuK}\alpha_1$ radiation, 1.5406 Å). No additional phases were found.

3.2. X-ray absorption measurements

The valence and environment of selected rare earth dopants in $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$ (Eu^{2+} ; Ce^{3+} , Nd^{3+} , Sm^{3+} , and Yb^{3+}) persistent luminescence materials were studied by XANES and EXAFS measurements at 10 K and room temperature. Beamline E4 at Hamburger

Synchrotronstrahlungslabor (HASYLAB) at Deutsches Elektronen-Synchrotron (DESY) (Hamburg, Germany) was used. Data was collected on the L_{III} edges using a Si(111) double crystal monochromator. The measurements were carried out in fluorescence mode using a Canberra 7 pixel High Purity Germanium (HPGe) detector. The beam size on the sample (thickness: 1.5 mm) was ca. $1.5 \times 8.5 \text{ mm}^2$. The energy was calibrated using the K edge of Fe (7111 eV), and XANES spectra of freshly annealed rare earth oxides were measured for reference.

The energy range studied was from -100 to 600 (EXAFS) or 100 eV (XANES) with respect to the absorption edge. Steps of 0.3 eV and 0.04 \AA^{-1} were used for data collection at the near edge and extended regions, respectively. The total time per measurement was ca. 1 h (EXAFS) or 20 min (XANES) from which one minute took place before the edge.

The data treatment and extraction of interatomic distances from the EXAFS data was carried out by the EXAFSPAK program package [16]. For the Fourier transforms, photoelectron wave vector ($k = [0.2625 \times (E - E_0)]^{1/2}$, where E_0 is the edge energy) ranges starting from 3 \AA^{-1} were used to avoid the increasing multiple scattering contributions at lower energies. The end value was set as high as allowed by the data, usually to 11 \AA^{-1} .

4. Results and discussion

4.1. Valences of europium

In several mechanisms presented for persistent luminescence, it has been suggested that there occurs, at some stage of the process, changes in the valence of the Eu^{2+} dopant. Since the X-ray absorption measurement can be considered as a first irradiation step of the persistent luminescence mechanism, the measurement can be an *in situ* probe of the changes in the valence of Eu^{2+} .

For the $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$ materials, the room temperature *in situ* XANES data (Fig. 1) shows that in the co-doped samples both Eu^{2+} and Eu^{3+} are present. These are observed as the white lines peaking at ca. 6980 and 6988 eV due to the final states $2\text{p}4\text{f}^75\text{d}^*$ and $2\text{p}4\text{f}^65\text{d}^*$ (2p denotes a hole in the 2p shell and 5d^* an excited electron in the 5d band) [11]. The divalent form is clearly dominant. On the other hand, for the singly doped material, only Eu^{2+} was observed. At low temperatures as 10 K, persistent luminescence does not take place since there is not enough thermal energy available to bleach the traps and thus only the storage of energy occurs. The number of species in their temporary valence state should then increase and facilitate their observation. However, decreasing the temperature from 296 K down to 10 K had no effect on the results.

Previously, it was reported for the $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{R}^{3+}$ materials that the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio decreases as a function of time during the X-ray irradiation, whereas no such oxidation was observed for the

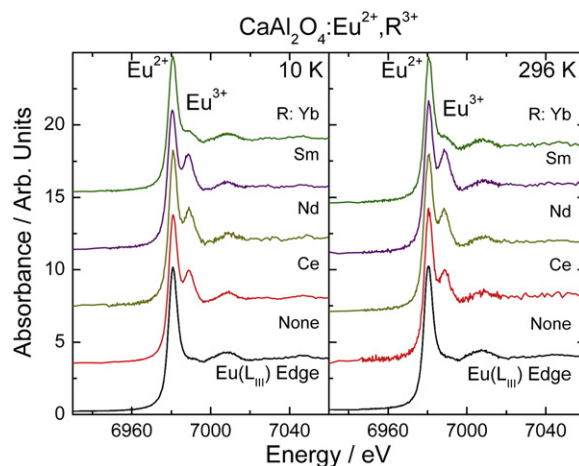


Fig. 1. $\text{Eu}(\text{L}_{\text{III}})$ edge XANES spectra for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{R}^{3+}$ at 10 and 296 K.

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