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Comparison of sol–gel and solid-state prepared Eu^{2+} doped calcium aluminates[*]

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The Eu^{2+} doped calcium aluminate ($CaAl_2O_4:Eu^{2+}$) was prepared by the sol–gel method. The structure and luminescence properties of the title compound were studied and compared to the corresponding properties of the materials prepared by a conventional solid state reaction. The use of the sol–gel method in preparation lowered the reaction threshold temperature by c.a. 200 °C. An unusual hexagonal form of $CaAl_2O_4:Eu^{2+}$, which cannot be prepared by the solid state reaction, was obtained by the sol–gel method. The UV excited luminescence and afterglow bands of the hexagonal $CaAl_2O_4:Eu^{2+}$ were observed at a slightly longer wavelength than that of the normal monoclinic phase due to small differences in the crystal field effect on the splitting of the excited $4f^6 5d^1$ configuration of the Eu^{2+} ion. The afterglow lifetime of the hexagonal phase was slightly longer than that of the monoclinic one due to deeper traps.

Key words: Eu^{2+} doped calcium aluminate, sol–gel method, persistent luminescence

1. Introduction

The Eu^{2+} doped alkaline earth aluminates, $MAl_2O_4:Eu^{2+}$ (M = Ca, Sr) are potential persistent luminescence materials to replace the traditional ZnS:Cu used, e.g. in luminous paints [1]. The aluminates yield strong luminescence at the blue/green region [2, 3] that is characterized by a rapid initial decay from the Eu^{2+} ion followed by extremely long afterglow. The afterglow can be enhanced even more by co-doping the

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aluminates with some RE^{3+} ions (e.g. Dy^{3+} and Nd^{3+}) [4–7]. Although the overall mechanism of the persistent luminescence of $MAl_2O_4:Eu^{2+}$ is now quite well agreed on [4-7], the details involved are largely unknown. The search for new persistent luminescence materials would be facilitated greatly if the underlying mechanisms were known.

The solid state reaction of monoclinic $CaAl_2O_4$ must be carried out at high temperatures (around 1300 °C) since impurities as $Ca_3Al_2O_6$ are formed at lower temperatures [8]. On the other hand, the successful preparation of the $CaAl_2O_4$ powders at low temperatures (900 °C) by the sol–gel synthesis has been reported [9]. With the sol–gel method a metastable phase of $CaAl_2O_4$, which can not be prepared by the solid state reaction, has been obtained [10, 11]. In this work, studies on the sol–gel preparation, structure and luminescence of $CaAl_2O_4:Eu^{2+}$ are reported and compared to those of the material prepared by the solid state route.

2. Experimental

The polycrystalline $CaAl_2O_4:Eu^{2+}$ was prepared with the sol–gel method [8] using stoichiometric mixtures of aluminum isopropoxide ($Al(OC_3H_7)_3$), calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and europium oxide (Eu_2O_3, 0.5 mole-%) as starting materials. The gel was heated at 180 °C for 10 h to remove water and then at 850 °C for 20 h under a N_2 + 12% H_2 gas mixture. The solid state reaction between calcium carbonate ($CaCO_3$), aluminum oxide (Al_2O_3) and europium oxide was carried out at 1250 °C for 6 h.

The thermogravimetric (TG) curves were measured with a TA Instruments SDT 2960 Simultaneous DTA-TGA thermoanalyzer. The sol–gel and solid state reactions were studied in the temperature range between 25 and 1400 °C. The heating rate was 10 $°C min^{-1}$ and the gas (N_2 + 12% H_2) flowing rate was 100 $cm^3 min^{-1}$. Sample weights were ca. 10 mg.

The X-ray powder diffraction patterns were measured with an Enraf-Nonius PDS120 diffractometer ($CuK_{\alpha 1}$ radiation; λ = 1,5406 Å) equipped with an INEL CPS120 position sensitive detector. The measurements were carried out at room temperature between 5 and 125 degrees using a flat rotating sample holder. The angular resolution of the apparatus was better than 0,018 degrees in q. A mixture of silicon (NIST standard #640b) and fluorophlogopite (NIST #675) powders was used as an external standard.

The luminescence and afterglow spectra were measured at room temperature using a Perkin Elmer LS-5 spectrometer. The UV-excitation from a xenon lamp was centered sharply at 350 nm. Prior to the afterglow measurements materials were exposed to radiation from a conventional tricolor fluorescent lamp for 10 s. The delay between the initial irradiation and afterglow measurements was 3 min. The thermoluminescence glow curves were measured with a Risø TL/OSL-DA-12 system between 25 and 400 °C monitoring globally emission up to 600 nm using a heating rate of 5 $°C \cdot s^{-1}$.

3. Results and discussion

A 52% loss of weight was observed in the TG curve of CaO-Al_2O_3 gel at the temperature range between 200 and 600 °C (Fig. 1). This was due to the loss of organic solvent and the decomposition of nitrate. No loss of water below 200 °C was observed because the gel was heated at 180 °C before measurements. The sol–gel method lowered the reaction threshold temperature for $CaAl_2O_4$ by ca. 200 °C compared to the solid state reaction. With the sol–gel method, the pure monoclinic $CaAl_2O_4$ phase was not formed below 1200 °C because the byproducts as $CaAl_4O_7$, $Ca_3Al_2O_6$ and $Ca_{12}Al_{14}O_{33}$ were also formed.

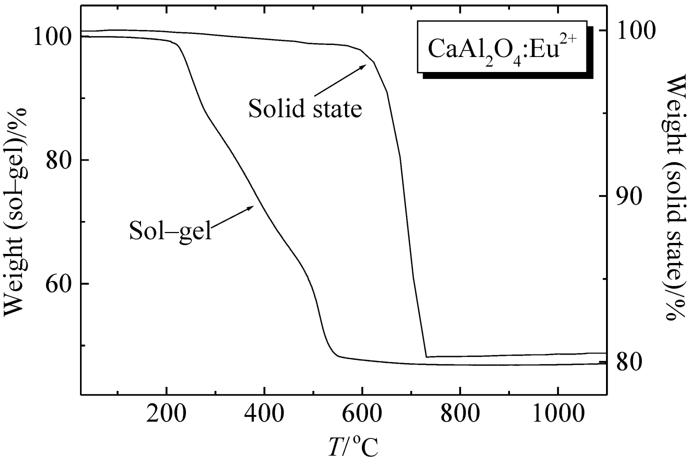

Fig. 1. Thermogravimetric curves of the sol–gel and solid-state prepared $CaAl_2O_4:Eu^{2+}$ materials; heating rate – 10 °C·min^{-1}, gas (N_2 + 12% H_2) flow rate: – 100 $cm^3 \cdot min^{-1}$, sample weight – ca. 10 mg)

The metastable $CaAl_2O_4:Eu^{2+}$ phase, probably stabilized by impurities, was obtained with the sol–gel method by heating at 850 °C. Other products or starting materials were not observed. The X-ray diffraction patterns of the sol–gel hexagonal and the solid state prepared monoclinic phases were very similar (Fig. 2). The higher structural symmetry of the hexagonal phase can be seen in the less complicated pattern, however. The structure of the metastable $CaAl_2O_4:Eu^{2+}$ was determined as hexagonal with the space group $P6_3$ ($Z = 6$), in contrast to earlier data [10] reporting an orthorhombic structure. The calculated lattice parameters were as follows: $a = 8.74$ and $c = 8.08$ Å.

The UV excited luminescence and afterglow spectra of the monoclinic $CaAl_2O_4:Eu^{2+}$ phase consist of a single wide band peaking in the blue region ($l_{max} = 440$ nm) as reported earlier [1]. The band in the luminescence and afterglow spectra of the hexagonal $CaAl_2O_4:Eu^{2+}$ occurred at a slightly longer wavelength compared to that of the monoclinic phase (Fig. 3). The luminescence of the Eu^{2+} ion originates from the transitions between the $4f^65d^1$ and $4f^7$ configurations and can easily vary, in general, from UV to red depending on the host lattice [12]. A shift in the luminescence band position for the different $CaAl_2O_4$ phases can be explained by a small change in the crystal field effect on the Eu^{2+} ion because the splitting of the excited $4f^65d^1$ configuration is very strongly affected by the environment.

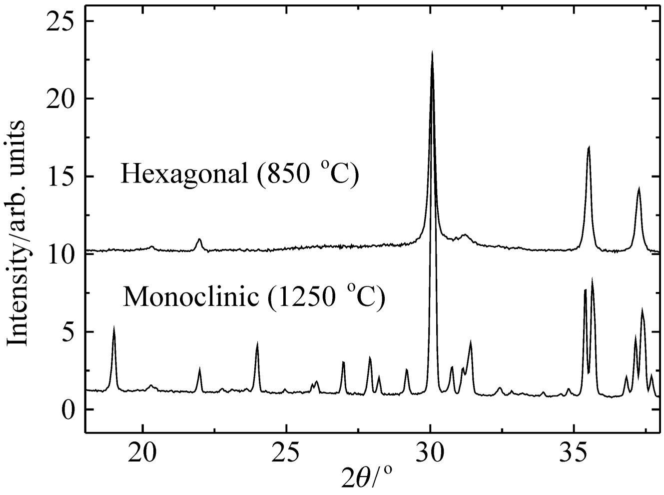

Fig. 2. X-ray diffraction patterns of the hexagonal and monoclinic $CaAl_2O_4:Eu^{2+}$ materials at room temperature ($CuK_{\alpha 1}$ radiation)

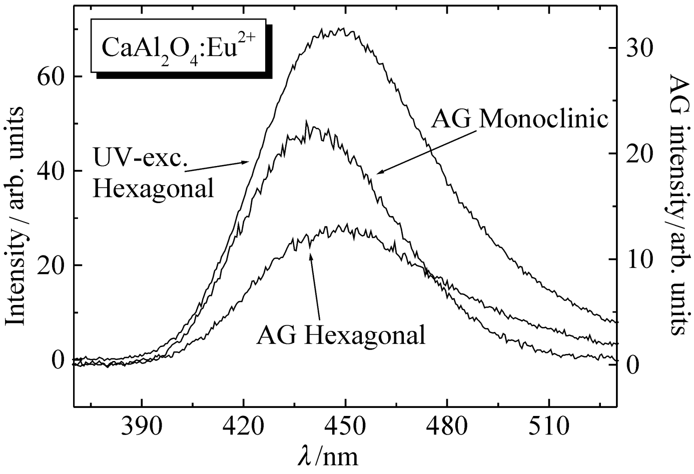

Fig. 3. UV-excited luminescence and afterglow spectra of the hexagonal and monoclinic $CaAl_2O_4:Eu^{2+}$ materials at room temperature

The afterglow spectra of the both polymorphs have the same band position, shape and width than those of the UV excited spectra indicating the same Eu^{2+} luminescent center. The initial afterglow from the hexagonal phase was weaker than that from the monoclinic one, but the difference was not as clear than as the case of the UV-excited spectra. The Eu^{2+} ion seems to favour only one site of the three Ca sites available in the structure of the monoclinic $CaAl_2O_4$ [13]. There are two six co-ordinated sites where the Ca–O distances (average 2.4 Å) are rather short for the Eu^{2+} ion whereas the third nine co-ordinated site, which has longer Ca-O distances (average 2.8 Å) [14] has thus enough space for the Eu^{2+} ion. The sum of the ionic radii $r(Eu^{2+}) + r(O^{2-})$ is 2.57 and 2.7 Å for the Eu^{2+} co-ordination numbers six and nine, respectively [15]. That supports also the preferred occupation of the nine co-ordinated Ca^{2+} site.

The afterglow lifetime of the hexagonal phase was slightly longer than that of the monoclinic one. After the initial nanosecond normal emission of the Eu^{2+} ion, the afterglow decay curves consisted of at least two additional processes, a rapid one prior to 20 min and further on a very slow one. The thermoluminescence glow curves of both the hexagonal and monoclinic $CaAl_2O_4:Eu^{2+}$ phases have a main maximum at about 80 °C followed by a tail extending up to 250 °C. The intensity of the main peak of the hexagonal phase was lower but the high-temperature tail was more intense than that of the monoclinic one. The existence of the high-temperature tail corresponding to deeper traps could explain the longer afterglow decay of the hexagonal phase.

4. Conclusions

The sol–gel method lowered the reaction threshold temperature by ca. 200 °C compared to the conventional solid state reaction. The pure monoclinic $CaAl_2O_4:Eu^{2+}$ phase was not, however, formed below 1200 °C. The metastable $CaAl_2O_4:Eu^{2+}$ phase was successfully prepared by the sol–gel method at 850 °C. The structure of this unconventional $CaAl_2O_4$ phase was determined as hexagonal.

The luminescence of both $CaAl_2O_4:Eu^{2+}$ phases was blue. The luminescence band of the hexagonal phase had the maximum at a slightly longer wavelength than that of the monoclinic one. The initial afterglow of the hexagonal phase was weaker but the lifetime was longer than that of the monoclinic one. The nature, number and depth of the traps as well as the overall persistent luminescence mechanisms are studied at the moment.

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