

Eu²⁺ doped calcium aluminate coatings by sol–gel methods

T. Aitasalo ^{a,b}, J. Hölsä ^a, H. Jungner ^c, M. Lastusaari ^a, J. Niittykoski ^{a,b,*}, J. Saarinen ^a

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

^b Graduate School of Materials Research, Turku, Finland

^c Dating Laboratory, University of Helsinki, P.O. Box 64, FI-00014 Helsinki, Finland

Available online 7 April 2005

Abstract

Eu²⁺ doped calcium aluminate coatings were prepared by the dip- and spin-coating methods on α -alumina substrates. This kind of persistent luminescent coatings may replace the luminous paints used in many applications. If sol–gel methods are used the expense of preparing the coatings is relatively low. Annealing at 1050 °C yielded the CaAl₂O₄:Eu²⁺ coatings with similar luminescence and thermoluminescence properties than those of the CaAl₂O₄:Eu²⁺ powders. At higher annealing temperatures, CaAl₄O₇ and CaAl₁₂O₁₉ were formed due to the diffusion of alumina from the substrate. The persistent luminescence was, however, relatively weak and thus more work is needed to optimize the multitude of parameters affecting the properties of the coatings.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Calcium aluminate; Europium; Sol–gel; Coating

1. Introduction

The Eu²⁺ doped alkaline earth aluminates, MAl₂O₄:Eu²⁺ (M = Ca, Sr), are efficient blue/green emitting persistent luminescence materials used e.g. in luminous paints [1]. Traditionally, the luminous paints are prepared by mixing the luminescent powders into a resin [2]. In this treatment, it is important that the paint does not quench luminescence intensity but binds strongly the powders. In applications, the luminous paints can be replaced by luminous coatings. The Eu²⁺ doped alkaline earth aluminate coatings have earlier been prepared by sputtering [3], pulsed laser deposition [4] and ion-beam evaporation [5] techniques, but the expense of preparing the coatings by such methods is high. If simple sol–gel methods, e.g. dip- and spin-coating [6], can be used for

the preparation, the capital expenses will be considerably reduced.

In this work, Eu²⁺ doped calcium aluminate (CaAl₂O₄:Eu²⁺) coatings were prepared by dip- and spin-coating methods. The preparation conditions were optimized and the structure as well as the luminescence and thermoluminescence properties of the coatings were studied. The properties were compared to those of the corresponding powder materials.

2. Experimental

The CaAl₂O₄:Eu²⁺ gels were prepared using stoichiometric amounts of aluminium isopropoxide (Al(OC₃H₇)₃) and calcium nitrate (Ca(NO₃)₂·4H₂O) as well as europium oxide (Eu₂O₃, 0.5 mol%) as starting materials [7,8]. The aluminium isopropoxide was refluxed at approximately 90 °C in water with stirring for 1 h. Calcium nitrate was dissolved in water and europium oxide in nitric acid. The aqueous calcium-europium nitrate solution was then slowly added to the aluminium sol.

* Corresponding author. Address: Department of Chemistry, University of Turku, FI-20014 Turku, Finland. Tel.: +358 2 3336734; fax: +358 2 3336700.

E-mail address: japeni@utu.fi (J. Niittykoski).

The resultant sol was refluxed with stirring for an additional hour and further concentrated slowly until a gel was formed. As-prepared gels were then used for the coating.

Alumina (α -Al₂O₃) plates were used as substrates. This material was used because of the high thermal stability, good adherence (because being an oxidic material), and the slightly uneven surface (when compared to metals). Lab-made dip- and spin-coating devices were used. In the dip-coating method, the speed of vertical movement, the number of the dipping cycles and in the spin-coating method, the rotating speed were controlled by a PC. In this work dipping speed values from 0.1 to 2 mm s⁻¹ were used. The dipping was repeated from one to seven times. In the spin coating, the rotating speed and time range were 500–5000 rpm and 10–60 s, respectively. The prepared coatings were dried slowly at room temperature and further annealed for 1–2 h at 1050–1250 °C in a dynamic N₂ + 12% H₂ atmosphere with the flow rate of approximately 10 cm³ min⁻¹.

X-ray powder diffraction (XPD) patterns were collected at room temperature between 25 and 40 degrees (in 2θ) with a Philips PW 3710 diffractometer with CuK α radiation, $\lambda = 1.5418$ Å.

UV excited and persistent luminescence spectra were measured at room temperature with a Perkin Elmer LS-5 spectrometer. The wide band excitation ($\lambda_{\text{exc}} = 330$ nm) source was a xenon lamp. The materials studied were irradiated with a conventional tricolour fluorescent lamp prior to the persistent luminescence measurements.

Thermoluminescence (TL) glow curves were measured with an upgraded Risø TL/OSL-DA-12 system between 25 and 400 °C with a linear heating rate of 5 °C s⁻¹. The global TL emission from UV to 600 nm was monitored. Three minutes prior to the TL measurements, the materials were exposed for 10, 30 and 60 s to the radiation from a combination of the Philips TL 20 W/05 (maximum 360 nm) and TL 20 W/03 (420 nm) UV lamps.

3. Results and discussion

3.1. Preparation

In addition to the dipping/spinning speed and time as well as the composition of the gel, the quality of the CaAl₂O₄:Eu²⁺ coatings was observed to be also affected by several other factors, e.g. the surface tension (diameter of the decanter), evaporation of the gel (during and after the coating), viscosity of the gel as well as the drying and annealing rate, temperature and duration. The dip-coating was observed to be easier to control than the spin-coating. Therefore, the main emphasis at the present stage of this work is placed upon the dip-coated

materials. The results presented below were obtained with the following dip-coating setup parameters: the vertical up and downward speeds 1 mm s⁻¹ and dipping for 5 times. These parameters affect mainly the adhesion and thickness of the CaAl₂O₄:Eu²⁺ thick film. Also the cracking during annealing was dependent on these experimental parameters.

When the dip-coated CaAl₂O₄:Eu²⁺ was annealed at 1050–1150 °C, the main phase is the monoclinic high temperature form of CaAl₂O₄:Eu²⁺ (Fig. 1). In addition, CaAl₄O₇:Eu²⁺ impurity is also observed in the XPD patterns. The widths of the Bragg reflections of all compounds are relatively large indicating low crystallinity. The intensity of the Bragg reflections of CaAl₄O₇ are enhanced and those of CaAl₂O₄:Eu²⁺ are hardly observed with the high temperature annealing. When the coating was annealed at higher temperatures up to 1250 °C, CaAl₁₂O₁₉:Eu²⁺ was found as the main phase. This is quite a different observation compared to the usual sol-gel (and solid state) synthesis with a powder as the end product, since the amount of the impurities has been observed to diminish when high temperature annealing has been used [8–10]. Therefore the impurities are probably formed at the substrate-coating interface due to diffusion of Al₂O₃ from the substrate. This is both an advantage and a disadvantage, since the adhesion of the coatings is clearly stronger in the cases where the interface compounds are formed. On the other hand, the control of the phase formation is more complicated, since the substrate will take part in the reaction. The hexagonal low temperature form of CaAl₂O₄:Eu²⁺ was not formed at 850 °C in contrast to the powder sol-gel synthesis [8], where it was observed that impurities from the sol-gel process stabilized the hexagonal CaAl₂O₄ form.

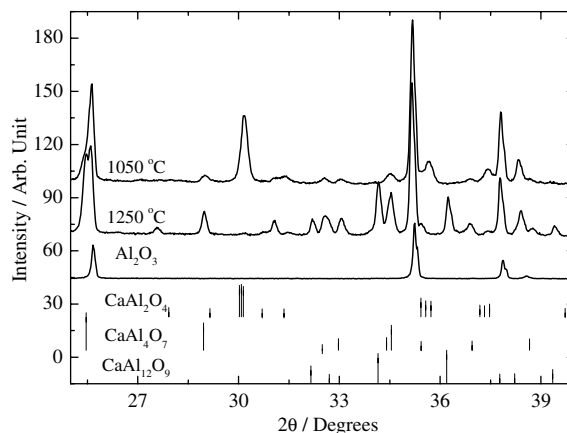


Fig. 1. X-ray diffraction patterns of the dip-coated CaAl₂O₄:Eu²⁺ annealed at 1050 and 1250 °C in N₂ + 12% H₂ (CuK α radiation, 1.5418 Å). The patterns of the α -Al₂O₃ substrate as well as the calculated [14] patterns of CaAl₂O₄, CaAl₄O₇ and CaAl₁₂O₁₉ [15] are shown for reference.

Download English Version:

<https://daneshyari.com/en/article/10633208>

Download Persian Version:

<https://daneshyari.com/article/10633208>

[Daneshyari.com](https://daneshyari.com)