Journal of Crystal Growth 360 (2012) 123–126

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

# Processing, microstructure and optical properties of the directionally solidified $Al_2O_3$–$EuAlO_3$ eutectic rods

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ARTICLE INFO

Available online 13 December 2011

*Keywords:*
A1. Eutectics
A1. Luminescence
A2. Floating zone technique
B1. $Al_2O_3$–$EuAlO_3$
B1. Europium compounds
B2. Phosphors

ABSTRACT

$Al_2O_3$–$EuAlO_3$ eutectic rods were directionally solidified using the Laser-Heated Floating Zone method, also known as Laser-Heated Pedestal Growth technique, with growth rates ranging between 25 and 750 mm/h. The microstructure was found to be highly dependent on the processing parameters, the size of the phases decreasing with the growth rate down 200 nm in samples grown at 750 mm/h. At low rates, an interpenetrated network of the eutectic phases was obtained whereas at high growth rates a tendency towards a nanofibrous pattern was observed. The optical absorption and photoluminescence of the eutectics grown at 100 mm/h and 350 mm/h were measured at room temperature. The Judd-Ofelt parameters, $\Omega_2$, $\Omega_4$ and $\Omega_6$, were obtained from the absorption spectra. Under a 396 nm lamp excitation, a red light emission centred in 616 nm corresponding to the $Eu^{3+}$ ion was detected. The $Eu^{3+}$ emission was stronger in the samples with the finer microstructure.



## 1. Introduction

Large investigation efforts have been devoted to directionally solidified ceramic eutectics due to their interesting properties, which result from being composites fabricated in situ with fine microstructures controlled by the solidification parameters [1]. Among them, those based in $Al_2O_3$ outstand by their microstructural stability and mechanical behaviour up to temperatures near the melting point [2–4]. In addition to their excellent performance as structural material, the unique features of the eutectic microstructure allow to extend the use of these materials to functional aplications. For instance, the contrast in the refractive index between the constituent phases allows to produce efficient light guiding in some eutectic ceramics [5]. The functional application field of these materials can be extended with the addition of rare earths (RE) to the eutectic system. In particular, the lifetime of the $Er^{3+}$ luminescence at 1.5 μm in $Al_2O_3$–$ZrO_2$ Er-doped directionally solidified eutectics has been shown to be modified by changes in the size of the microstructure [6]. More recently, $Al_2O_3$–$Er_3Al_5O_{12}$ eutectic ceramics have been investigated as selective emitters for a thermophotovoltaic generation system [7]. In the optical field, $Eu^{3+}$ ion stands out due to their interesting luminescence properties. We should note that the incorporation of europium to a large variety of materials have been investigated as potential phosphors [8,9], as $Eu^{3+}$ can be used like a red light source because of its strong red emission when exciting with UV light.

In this work, directionally solidified $Al_2O_3$–$EuAlO_3$ eutectic rods were studied. Up to our knowledge, only two preliminary studies in $Al_2O_3$–$EuAlO_3$ eutectics have been reported [10,11]. In [10] the material was grown using a very low solidification rate and presented a rather coarser microstructure than that studied here. Reference [11] corresponds to a eutectic phase identification study in different $Al_2O_3$–$RE_2O_3$ systems grown by the micro-pulling-down method. X-Ray diffraction in $Al_2O_3$/$Eu_2O_3$ system allowed to identify the eutectic phases as $\alpha$-$Al_2O_3$ and $EuAlO_3$.

The aim of this work is to study the microstructure and optical properties of the $Eu^{3+}$ ion in the $Al_2O_3$–$EuAlO_3$ eutectic ceramic. The eutectic rods were fabricated in a large range of growth rates up to 750 mm/h in order to investigate the effect of the processing parameters on the microstructure and the $Eu^{3+}$ emission. The ceramic eutectics were processed by the Laser-Heated Floating Zone method (LHFZ), also known as Laser-Heated Pedestal Growth technique. LHFZ method presents important advantages as no crucible is needed, avoiding contamination of the samples, the growth atmosphere can be modified and large axial thermal gradients at the solid/liquid interface are achieved which allows obtaining homogeneous eutectic microstructures even when high solidification rates are used [1]. The main goal of the investigation was the eutectic microstructure control in phase size and morphology using the solidification rate as the control parameter. The use of high growth rates produced a refinement of the microstructure and a stronger $Eu^{3+}$ emission in the $Al_2O_3$–$EuAlO_3$ eutectic ceramic.

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doi:10.1016/j.jcrysgro.2011.12.032

## 2. Experimental Details

Ceramic rods of the system $Al_2O_3$–$Eu_2O_3$ with the reported eutectic composition (76% mol $Al_2O_3$ and 24% mol $Eu_2O_3$) [12] were processed by the LHFZ method at solidification rates ranging between 25 and 750 mm/h in order to obtain different microstructures. A $CO_2$ laser was used as the heating source. The rods were solidified in air except the sample grown at the highest growth rate, which was processed in nitrogen in order to avoid gas inclusions in the rod during solidification. Previous studies of the effect of changing the growth atmosphere in other $Al_2O_3$-based eutectics conclude that the voids in rods grown at high pulling rates are highly reduced using a nitrogen atmosphere [13]. However, no effect of the growth atmosphere was observed in the microstructure and no different phases were found in the eutectics.

Cylindrical ceramic precursors (feed rods) of 2–2.5 diameter and 10 cm length were obtained from cold isostatic pressing. Up to two densification steps were performed previous to the final growth to reduce the precursor porosity. These steps consisted of LHFZ growths at solidification rates between 100 and 250 mm/h performed in the atmosphere used for the final crystal growth. Last stage was always performed with the solidified rod being pulled out downwards and without rotation of the crystal and precursor using the corresponding solidification rate (25–750 mm/h). Directional solidified rods with typical diameters of 1–1.5 mm were obtained.

The microstructure was studied for the different growth rates. Polished transverse and longitudinal cross-sections were observed using Scanning Electron Microscopy (SEM) (model 6400, Jeol, Tokyo, Japan). The phases present in the eutectic were identified by Energy Dispersive X-Ray Spectroscopy (EDS).

Optical properties of $Al_2O_3$–$EuAlO_3$ eutectics were studied by absorption and luminescence spectroscopy at room temperature. The optical absorption of the eutectics was measured by transmission in transverse cross-sections obtained by polishing the samples down 200 μm in the 300–2600 nm range using a CARY 500 Scan from VARIAN spectrophotometer. Photoluminescence spectra were measured on the as-grown rod surface by exciting the samples with the light of a 1000 W tungsten lamp passed through a 0.22 m SPEX double monochromator. Fluorescence was detected at 90° through a 0.5 m Jarrell-Ash monochromator with a Hamamatsu R-928 photomultiplier.

## 3. Results and discussion

### 3.1. Microstructure

Fig. 1(a), (b) and (c) show the SEM micrographs of the transverse cross sections of samples grown at 25, 350 and 750 mm/h, respectively. For all the samples a microstructure consisting of two phases, $Al_2O_3$ (dark phase) and $EuAlO_3$ (light phase), was observed. The microstructure was highly dependent on the growth rate, both the morphology and the size of the phases. For growth rates up to 100 mm/h the microstructure was homogeneous throughout the entire cross-section of the grown rod. The microstructure consisted of an interpenetrated network of both phases (Fig. 1(a)). A slight elongation was observed along the growth direction in the longitudinal cross section. However, above 100 mm/h, regions consisting of $EuAlO_3$ fibers in an $Al_2O_3$ matrix coexisted with the interpenetrated pattern (Fig. 1(b)). At 750 mm/h, a cellular microstructure with only fibrilar domains was obtained (Fig. 1(c)).

The microstructure became finer when the growth rate increased. For the interpenetrated pattern, the phase size decreased from 1 μm in samples grown at 25 mm/h up to 250 nm in samples solidified at 350 mm/h. The interspacing length, $\lambda$, was measured using the interception linear methods in the SEM micrographs of the transverse sections. Fig. 2 shows $\lambda$ as a function of the growth rate. The dependence of $\lambda$ with the solidification rate, $V$, could be fitted by the Hunt–Jackson law, $\lambda^2 V = C$ [14]. The $C$-value of 35 $\mu m^3/s$ was obtained for the $Al_2O_3$–$EuAlO_3$ eutectic from the fitting. This value is lower that those obtained for binary $Al_2O_3$-aluminum garnets eutectics [15] indicating that eutectics with perovskite structure phases tend to solidify with finer microstructures than those with garnet structures.

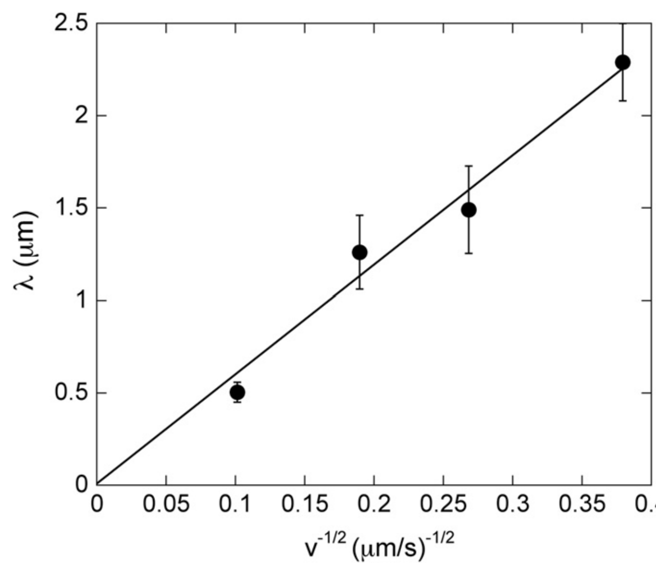


**Fig. 2.** Dependence of the interspacing with the growth rate in the of $Al_2O_3$–$EuAlO_3$ eutectic rods. Circles correspond to the experimental values and the line is the fitting of the interpenetrated microstructure data to the Hunt–Jackson law with a $C$-value of 35 $\mu m^3\,s^{-1}$.

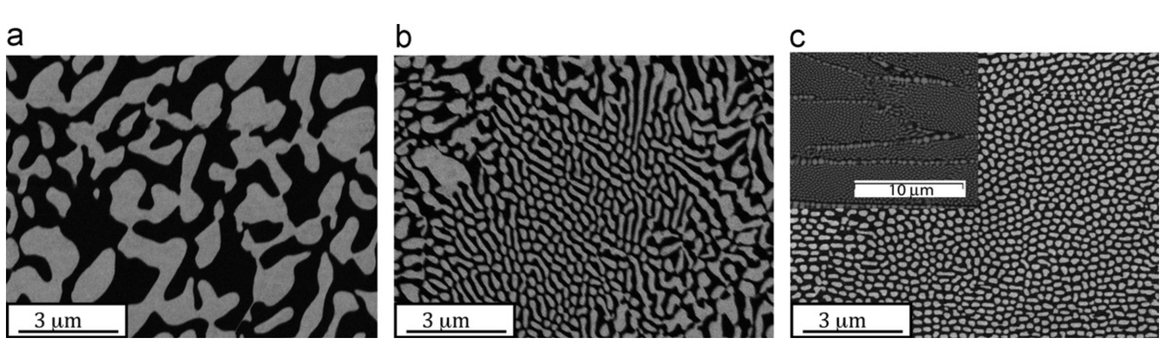


**Fig. 1.** SEM transverse cross-sections of $Al_2O_3$–$EuAlO_3$ eutectic rods grown at (a) 100 mm/h, (b) 350 mm/h and (c) 750 mm/h. $EuAlO_3$, light contrast, $Al_2O_3$, dark contrast.