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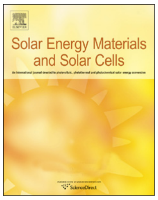

Directionally solidified Al_2O_3–$Yb_3Al_5O_{12}$ eutectics for selective emitters

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ABSTRACT

Al_2O_3–$Yb_3Al_5O_{12}$ eutectic rods were directionally solidified using the laser floating zone method at rates between 25 and 750 mm/h. The microstructure consisted of an interpenetrated network of both eutectic phases for all the growth rates. The size of the phases was strongly dependent on the growth rate, the eutectic interspacing decreasing from 4.5 μm at the lowest growth rate to 600 nm at 750 mm/h. The optical transmission of the sample with coarser microstructure was measured and compared with that of an $Yb_3Al_5O_{12}$ single crystal grown “ad hoc” using the same method. The apparent “oscillator strength” of the single $^2F_{7/2}\rightarrow{}^2F_{5/2}$ Yb^{3+} absorption band was larger in the eutectic sample than in the single crystal, which was attributed to the increase in the light path caused by multiple refractions at the eutectic interphases. The thermal emission of the eutectic rod was studied between 1000 °C and 1500 °C. An intense and relatively narrow emission band at about 1 μm corresponding to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ Yb^{3+} electronic transition was observed in the whole temperature range. The intensity of the band increased with the temperature up to about 1300 °C. At higher temperatures a saturation of the selective emission was observed which was attributed to the competition between the increase in the thermal population of the excited state and the enhancement of the non-radiative de-excitation channels with the temperature.

1. Introduction

Thermofotovoltaic (TPV) energy conversion allows obtaining electricity from the thermal emission of a hot body [1]. The electromagnetic radiation emitted by the hot body excites a photovoltaic cell, which transforms the photon into electrical energy. The emitter may be a black/grey body, with a broad and continuous emission spectrum, or a selective emitter, that is, a material emitting light at high temperature in narrow bands. In order to increase the efficiency of the device, the emission band of the selective emitter should match with the energy gap of the photovoltaic cell with a negligible emittance outside the sensitive region of the cell to minimise the non-convertible radiation.

Materials containing rare-earth ions are good candidates as selective emitters because of their narrow emission bands even at solid-state densities. Er^{3+} and Yb^{3+} are the ions most studied for TPV devices as their emission bands match with the active region of several photovoltaic cells [2,3]. Different rare-earth compounds have been studied for their use as selective emitters. Early work on high temperature selective emission was performed on oxides of erbium, samarium, neodymium and ytterbium [4].

When making the selective emitter, it must be taken into account the extreme conditions of use. Emitters in TPV devices have to work in air atmosphere at high temperatures during long times and under severe thermal shock conditions, which limits the use of monolithic ceramics. Different geometries have been explored for TPV devices. Small diameter filaments improved the response to thermal shock and reduced radiation outside the active region of the cell [5]. Chubb et al. [6] developed selective emitters based on different rare earth aluminium garnets in planar geometries.

Among the materials that can meet the thermo-structural challenge in TPV converters, directionally solidified eutectic (DSE) ceramics stands out. Growth from the melt of DSE ceramics allows producing in situ composites with a homogenous and fine microstructure and strong and clean interfaces that result in improved functional and structural properties [7]. In particular, DSE ceramics based on Al_2O_3 shows unpaired chemical and thermal stability and excellent mechanical properties that are retained up to temperatures close to the melting point [8–10]. If rare earth oxides were incorporated into the eutectic composition, in addition to the good thermo-structural behaviour and microstructural stability [11–13], the material would also show selective emission. At that point, it should be noted that the thermo-structural performance in these materials is largely dependent on the microstructure. It has been reported a significant increase of the mechanical strength of the DSE ceramics with the finer microstructure

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[10,13]. However, eutectics with smaller phase sizes are more likely to undergo phase coarsening processes for long time permanence at high temperature [12]. To the contrary, eutectics with coarser microstructures are very stable after long treatments and coarsening does not appear even in extreme conditions [9,12]. A compromise between microstructure stability and mechanical performance at high temperature should be reached to make a material suitable for TPV devices. In addition, light propagation and emission strongly depends on the material microstructure. Morphology, structure, size and alignment of the component phases are also a matter of study for a material in a TPV converter.

In spite of the interest, there are still very few studies in the literature on DSE ceramics for TPV applications and all of them have been focused on erbium-based eutectics. Sai et al. [14] and Nakagawa et al. [15] have produced a selective emitter consisting of directionally solidified Al_2O_3–$Er_3Al_5O_{12}$ ceramic eutectics. Recently, the thermal emission of the binary and ternary eutectics of the Al_2O_3–Er_2O_3–ZrO_2 system has also been investigated [16]. In that study, selective emission at 1.55 μm matching with the sensitive region of the GaSb photovoltaic cell was observed in both Al_2O_3–$Er_3Al_5O_{12}$ and Al_2O_3–$Er_3Al_5O_{12}$–ZrO_2 eutectics. The relation between microstructure and optical properties was studied. In addition, a good thermal shock resistance of these eutectics at cooling rates on the surface as large as 400 °C/s from 1500 °C to room temperature was established.

The aim of this work is to investigate the thermal emission of DSE containing Yb^{3+} ions, in particular of directionally solidified Al_2O_3–$Yb_3Al_5O_{12}$ ceramic eutectics as selective emitters. It is interesting to notice that Yb_2O_3-based eutectics have been scarcely studied. To our knowledge, only one preliminary study on the microstructure of Al_2O_3–$Yb_3Al_5O_{12}$ DSE has been reported [17]. The addition of Yb^{3+} ions to the eutectic ceramics is of large interest as these ions show an emission band that matches very well to the spectral sensitivity of the widely used silicon cells [3,18].

From the point of view of emission properties, Yb^{3+} is an only-one-channel de-excitation ion with the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ as only emission band, which matches the optical band gap of GaAs, InP and Si PV cells. In addition, the nearly two-level Yb^{3+} optical system may add some interesting information about thermo processes, in particular, about emission efficiencies.

Al_2O_3–$Yb_3Al_5O_{12}$ ceramic eutectics have been processed using the laser assisted floating zone (LFZ) technique. The use of the LFZ method has allowed studying the microstructure of these eutectics in a wide range of processing rates. The optical properties (absorption and thermal emission) have been investigated in the eutectic with the largest phase size in order to have larger microstructure stability at high temperatures, a requirement for the proposed TPV application.

2. Material and methods

Eutectic rods of Al_2O_3–$Yb_3Al_5O_{12}$ were obtained by directional solidification with the LFZ method. Ceramic powders were prepared using a mixture of commercial powders of Al_2O_3 (Aldrich, 99.99%) and Yb_2O_3 (Aldrich, 99.9%) with the eutectic composition (Table 1) [17]. Cylindrical precursors were fabricated isostatically pressing the powder for 3 min at 200 MPa and sintered at 1250 °C during 12 h. Sintered precursor rods had a typical diameter of around 2.5 mm.

Eutectic rods were directionally solidified using a continuous wave CO_2 laser as heating source. Processing was performed in a nitrogen atmosphere with a slight overpressure of 0.1–0.25 bar respect to ambient pressure in order to avoid the presence of voids in the solidified rods [19]. To eliminate the precursor porosity, different densification stages were applied at a low growth rate (100–250 mm/h). The final directional solidification was always performed with the grown crystal travelling downwards and without rotation of the crystal or the precursor. Processing rates between 25 and 750 mm/h were used. The solidified rods had a final diameter in the range 1–1.5 mm. $Yb_3Al_5O_{12}$ single crystals were grown in air using the same procedure and a growth rate of 50 mm/h. The commercial powders of the oxides were mixed in the compositions given in Table 1.

Table 1
Composition, volume fractions, Yb^{3+} concentration and experimental oscillator strengths of Yb^{3+} in $Yb_3Al_5O_{12}$ and Al_2O_3–$Yb_3Al_5O_{12}$.

Sample	Composition	Volume fractions	Yb^{3+} ions cm^{-3}	f_{EXP} (10^{-8})
				${}^2\mathbf{F}_{7/2} \rightarrow {}^2\mathbf{F}_{5/2}$
$Yb_3Al_5O_{12}$	62.5% mol Al_2O_3 37.5% mol Yb_2O_3	100% $Yb_3Al_5O_{12}$	$1.41 \cdot 10^{22}$	151
Al_2O_3–$Yb_3Al_5O_{12}$	81.5% mol Al_2O_3 19.5% mol Yb_2O_3	46.2 ± 2.1% Al_2O_3 53.8 ± 2.1% $Yb_3Al_5O_{12}$	$7.59 \cdot 10^{21}$ (in $Yb_3Al_5O_{12}$)	356

Microstructural characterisation was performed in polished transverse and longitudinal cross-sections of rods by means of back-scattered electron images obtained in a Scanning Electron Microscope (SEM) (model 6400, Jeol, Tokyo, Japan) and a Field Emission SEM (model Carl Zeiss MERLIN). Specimens for this characterisation were prepared using conventional metallographic methods.

The optical absorption spectra of the eutectics were measured at room temperature by transmission in a transverse cross-section of 100 μm thickness in the 300–2600 nm optical range using a CARY 500 Scan from VARIAN spectrophotometer. In the case of $Yb_3Al_5O_{12}$ transparent single crystals, samples of 1 mm thickness were used for absorption measurements.

Thermal emission spectra were measured on the as-grown rods by heating the samples with the CO_2-laser focused annularly on the sample surface. Emitted light was collected using an optical fibre and the emission spectrum was measured in the 900–2500 nm range using an NIR 256-2.5 from Ocean Optics spectrophotometer and in the 250–900 nm using an Ocean Optics USB-2000 spectrophotometer. The spectral sensitivity of the spectrometer was calibrated using an halogen lamp with the brightness temperature of 2968 K. Temperature of the sample was measured using a two-colour pyrometer (Impac, ISR12-LO MB33) and varied from 1000 °C to 1500 °C by changing the laser power.

3. Results and discussion

3.1. Microstructure

Al_2O_3–$Yb_3Al_5O_{12}$ eutectic rods were directionally solidified at different growth rates. SEM micrograph analysis was used to study the evolution of the microstructure with the processing rate. Samples were found to be free of voids and cracks. Fig. 1 shows back-scattered electron images of transverse cross-sections of the eutectic rods processed at (a) 25 mm/h, (b) 100 mm/h and (c) 750 mm/h growth rates. In all cases, the microstructure consists of a three-dimensional interpenetrated network of both eutectic phases, Al_2O_3 (dark contrast) and $Yb_3Al_5O_{12}$ (bright contrast). This microstructure with strongly faceted phases is usually referred to as Chinese Script microstructure. The volumetric fractions of the eutectic phases were estimated from the area analysis