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DIRECTIONALLY SOLIDIFIED Al₂O₃- Yb₃Al₅O₁₂ EUTECTICS FOR SELECTIVE EMITTERS

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ABSTRACT

Al₂O₃-Yb₃Al₅O₁₂ 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 750mm/h. The optical transmission of the sample with coarser microstructure was measured and compared with that of an Yb₃Al₅O₁₂ 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 μ m 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.

Keywords: Al₂O₃/Yb₃Al₅O₁₂; Directionally solidified eutectic ceramics; Selective emission; Optical absorption; Thermophotovoltaic

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 minimize 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. Er³⁺ and Yb³⁺ 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 Al₂O₃ 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 [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 Al₂O₃-Er₃Al₅O₁₂ ceramic eutectics. Recently, the thermal emission of the binary and ternary eutectics of the Al₂O₃-Er₂O₃-ZrO₂ 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 Al₂O₃-Er₃Al₅O₁₂ and Al₂O₃-Er₃Al₅O₁₂-ZrO₂ 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 deexcitation 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.

Al₂O₃-Yb₃Al₅O₁₂ 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 Al₂O₃-Yb₃Al₅O₁₂ were obtained by directional solidification with the LFZ method. Ceramic powders were prepared using a mixture of commercial powders of Al₂O₃ (Aldrich, 99.99%) and Yb₂O₃ (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 hours. 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. Yb₃Al₅O₁₂ 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.

Microstructural characterization 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 characterization 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 μ m thickness in the 300-2600 nm optical range using a CARY 500 Scan from VARIAN spectrophotometer. In the case of Yb₃Al₅O₁₂ 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 CO₂-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

Al₂O₃-Yb₃Al₅O₁₂ 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) 25mm/h, (b) 100mm/h and (c) 750 mm/h growth rates. In all cases, the microstructure consists of a three-dimensional interpenetrated network of both eutectic phases, Al₂O₃ (dark contrast) and Yb₃Al₅O₁₂ (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 in SEM micrographs. The Yb₃Al₅O₁₂ volume fraction was 53.8±2.1%, in agreement with the value of 54.7% calculated from the composition of the starting powders.

The microstructure was highly dependent of the rate used in the solidification, the size of the phases decreasing when the processing rate increased. The eutectic interspacing, λ , was measured using linear interception methods on transverse cross-section micrographs [20]. λ decreased from 4.5 μ m to 600 nm when the growth rate increased from 25 mm/h to 750 mm/h. Figure 2 shows the dependence of the eutectic interspacing measured in Al₂O₃-Yb₃Al₅O₁₂ eutectic rods with the processing rate. The eutectic interspacing in all the range of growth rates studied was found to follow the Hunt-Jackson law [21], $\lambda^2 \cdot v = C$, with C a constant depending essentially on the phase diagram and the diffusion coefficient of the ions in the melt. The value of C =133 μ m³/s obtained from fitting the experimental data to the quadratic law (solid line in figure 2), is close to that reported for Al₂O₃-Er₃Al₅O₁₂ eutectic [14] and slightly higher than the value of 100 μ m³/s determined for Al₂O₃-Y₃Al₅O₁₂ eutectic [19, 22].

3.2. Optical absorption

Due to the good alignment of the phases and clean interfaces, DSE ceramics are translucent and optical absorption experiments can be performed. In-line transmission spectrum of the eutectic rod grown at 25 mm/h was measured at room temperature in the infrared and visible regions. For comparative purposes, the absorption spectrum of the Yb₃Al₅O₁₂ single crystal was also recorded. The recorded spectra were zeroed at the long wavelength side. Figure 3 plots the extinction coefficient, α , for both samples, calculated using $\alpha = 2.303$ *OD/t*, with *OD*, the optical density after zeroing and t, the sample thickness. When comparing both spectra, the main difference lies in an intense background extinction decreasing with increasing wavelength, only observed in the spectrum of the eutectic sample. This structureless extinction has been also reported in the case of Al₂O₃-EuAlO₃ [23] and Al₂O₃-Er₃Al₃O₁₂ [16] eutectics and it can be explained by the effect of the geometrical light scattering at the eutectic interfaces.

In addition to the scattering background, an absorption band centred at 930 nm was observed. This absorption was also present in the $Yb_3Al_5O_{12}$ single crystal spectrum and it was ascribed to the f-f electronic transition of the Yb^{3+} ion between the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state, the only excited electronic level available for this ion in the measured spectral range.

Although only one electronic transition is expected for the Yb³⁺ ion, some structure was observed in the absorption band due to the Stark components of the ground and excited levels. The structure of the band was very similar in the eutectic and in the Yb₃Al₅O₁₂ single crystal, which is expected as all the Yb³⁺ ions in the eutectic enter the garnet phase. Taking into account the Yb³⁺ local symmetry in the garnet, four Stark electronic levels are expected for the ground state and three for the excited states [24].

Following the energy level scheme proposed by Yoshikawa [24] for Yb³⁺ ion in YAG, we tentatively attributed the absorption lines in the range 880 - 980 nm to the transitions between the lowest Stark level of the ${}^2F_{7/2}$ ground state and the multiplet of the ${}^2F_{5/2}$ excited state. The line at the longest wavelength (1025 nm) would correspond to the transition from the ${}^2F_{7/2}$ first excited Stark level and the ${}^2F_{5/2}$ lowest Stark level.

Although the features of the absorption band (positions and relative intensity), are very similar in both samples, a slightly higher overall absorption was measured for the eutectic sample, despite the volume concentration of Yb³⁺ ions in the eutectic ceramics is half than in the garnet single crystal (see Table 1). In order to quantify the absorption of both samples, the experimental oscillator strengths of the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition, f_{EXP} , were calculated by measuring the room temperature integrated area of the absorption bands:

$$f_{EXP} = \frac{m c^2}{\pi e^2 N} \int \frac{\alpha(\lambda)}{\lambda^2} d\lambda$$
 (1)

m being the electron mass; e, the electron charge; c, the light velocity in vacuum; $\alpha(\lambda)$, the absorption coefficient and N, the number of Yb³⁺ ions per unit volume in the samples, given in Table 1. All the magnitudes are expressed in cgs units.

The experimental f_{EXP} of the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition for the eutectic and the Yb₃Al₅O₁₂ single crystal are presented in Table 1. As expected from the absorption spectra, the experimental oscillator strength found for the Al₂O₃-Yb₃Al₅O₁₂ is higher than that of the single crystal. It is rather unlikely that this might be due to different environments for the active ion in each case. In both samples, Yb³⁺ ions enter the Yb₃Al₅O₁₂ lattice as constituent and occupying the same symmetry site. The observed difference in the

absorption is more probably due to the eutectic microstructure than to a difference in the local ion surroundings. As shown in figure 1, the eutectic microstructure consists in an entangled pattern of two phases. The contrast in the refractive indices of Al_2O_3 and $Yb_3Al_5O_{12}$ will produce a refraction of the light when passing through an interface. Taking into account the large number of interfaces present in the eutectic sample, light will have numerous refractions inside the eutectic sample, leading to a significant lengthening of the light path. Therefore, the more intense absorption measured in the eutectic samples was not attributed to a higher oscillator strength but to a lengthening in a factor of 2.35 of the optical path.

3.3. Selective thermal emission

Thermal emission was measured from 1000°C to 1500°C using a CO₂-laser as the heating source in the Al₂O₃-Yb₃Al₅O₁₂ eutectic rods grown at 25 mm/h. Figure 4 shows the emission of the eutectic rod in the near infrared spectral region at different temperatures. The spectrum exhibits only a relatively narrow strong emission band at 1000 nm at all the temperatures, over a broad spectrum covering most of the measured spectral range. No equivalent emission bands were measured in the visible range.

The selective emission in 1000 nm was ascribed to the thermal emission of the Yb^{3+} ion from the ${}^2F_{5/2}$ excited state to the ${}^2F_{7/2}$ ground state. It should be noted that the emission spectrum differs from the absorption spectrum because the optical transitions in emission are taking place between all the levels of the excited state multiplet, which can be considered equally populated at these temperatures, and all the states of the ground state multiplet.

The increase of the selective emission intensity with the temperature was clearly observed when the temperature rose from 1000°C to 1200°C. However, at higher temperatures the emission intensity increases more noticeably in the long-wavelength radiation rather than in the narrow Yb³⁺ emission band. Figure 5 shows the variation of the thermal emission intensity of the eutectic rod measured at 1000 nm (peak of the Yb³⁺ emission) and 1200 nm (far away from Yb³⁺ emission band) as a function of the temperature. These emission intensities are compared with the expected black body radiation at 1200 nm. It can be seen that far from the Yb³⁺ emission band, thermal emission is proportional to that of the black body and increases with temperature as expected. However, at the wavelength corresponding to the maximum of the Yb³⁺ band, the emission increases with temperature and appears to saturate at temperatures above 1300 °C.

A loss in the efficiency of the selective emission at high temperatures has been also reported in Yb₂O₃ polycrystals [25]. In that case, the Yb³⁺ thermal emission was drastically reduced at high powers of the laser used for thermal excitation. Authors attributed the selectivity loss in Yb₂O₃ polycrystals to self-absorption processes, resonant with the thermal emission transition. The same self-absorption process could also be invoked here to explain the loss in selectivity, although it is not clear why this effect increases with temperature. In addition, self-absorption is expected to be important in optically thick samples, one condition difficult to meet in our case as the emitting phase is embedded in a non-absorbing transparent Al₂O₃ phase.

Likewise, this behaviour can be explained by just considering the basic principles of heat-light conversion in a two-level electronic system such as that of Yb³⁺. In fact, the heat-light conversion is triggered by the energy transfer between the hot phonon

subsystem of the matrix and the electrons of the optically active ion [26]. This energy transfer promotes the ions to high electronically excited states.

In thermal equilibrium the population in the electronic excited state $N_2\,(^2F_{5/2}\,)$ is:

$$N_2(T) = \frac{N_0}{1 + e^{\Delta E/kT}} \tag{2}$$

 N_0 being the concentration of Yb^{3+} ions and ΔE , the difference in energy between the ground and excited levels.

The excited ions relax to the ground state by two different channels. Either emitting photons, radiative transitions with probability A_{21} related with the oscillator strength of the transition, or by non-radiative multiphonon processes producing phonons and probability Γ_{21} . It is worthy to notice that in this model the mechanisms giving rise to non-radiative de-excitation are the same that induce the phonon excitation of the electronic system. Multiphonon non-radiative processes have a temperature dependence given by [27]

$$\Gamma_{21}(T) = \Gamma_{21}(0) [1 + n_{eff}]^p$$
 (3)

where it is assumed that de-excitation takes place via emission of p effective phonons of energy hv_{eff}. n_{eff} is the occupancy of the effective phonon modes given by

$$n_{eff}(T) = \frac{1}{e^{hv_{eff}/kT} - 1} \tag{4}$$

The intensity of the selective emission is then given by

$$I_{em} \propto N_2 A_{21} \eta \tag{5}$$

η-being the emission quantum yield defined as

$$\eta = \frac{A_{21}}{A_{21} + \Gamma_{21}} \tag{6}$$

It is clear that the observed increase of the selective emission with the temperature can be explained considering that the $^2F_{5/2}$ levels become more populated when thermal excitation increases (eq. 2). However, at higher temperatures the non-radiative deexcitation channel given by eq. 3 is increasingly active in reducing the quantum yield of the emission. That may produce a decrease in the rate at which thermo-emission increases with temperature at higher temperatures. It is worthy to point out here some of the crude assumptions made. In particular we neglected other non-radiative deexcitation mechanisms that may affect the emission quantum yield otherwise assumed to be temperature independent.

In spite of this, we have performed some calculations using the simple model outlined above. Taking into account that the maximum phonon energy measured in Yb₃Al₅O₁₂ is 830 cm⁻¹ [28], the non-radiative de-excitation will be a process involving at least 12 phonons. Assuming that the probability of radiative transition, A₂₁, has negligible temperature dependence, the emitted intensity can be calculated using Eqs. (2-6). Figure 6 presents the calculated emission intensity at 1000 nm as a function of the temperature in the 1000-1500°C range for different values of the quantum yield at 1000°C and considering that the multiphonon de-excitation occurs via 12 phonons of energy 833 cm⁻¹ According to observations and regardless of the quantum yield value used the calculated selective emission intensity shows a tendency to saturation at high temperatures in agreement with the experimental results.

Finally, we should note here the good thermal shock resistance presented by the eutectic rods in the thermal emission experiments. To test the performance of the

eutectic sample at rapid temperature variations, the CO_2 laser was switched on and off producing heating and cooling rates on the rod surface of ~400°C/s. The surface did not show evidence of damage after the thermal cycle.

4. CONCLUSIONS

Directionally solidified Al₂O₃-Yb₃Al₅O₁₂ eutectic rods were produced from the melt by the laser floating zone method at different growth rates. The rods presented a homogeneous microstructure consisting of an interpenetrating network of Al₂O₃ and Yb₃Al₅O₁₂ crystal phases at all processing rates. The phase interspacing decreased with the growth rate following the Hunt-Jackson law.

The optical absorption of Al₂O₃-Yb₃Al₅O₁₂ eutectic rods grown at 25 mm/h and Yb₃Al₅O₁₂ single crystal was studied at room temperature. A stronger optical extinction was observed in the eutectic, which was attributed to a lengthening of the optical path due to the light refractions at the interphases.

The thermal emission in the eutectic was studied as a function of the temperature. An intense and relatively narrow emission band corresponding to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ Yb³⁺ electronic transition was measured at 1 μ m. In this composite the thermal emission was highly selective up to 1300°C. However, a loss in the efficiency of the selective emission was observed at higher temperatures. We propose a simple model to explain the thermo-emission selectivity loss. In spite of the crude assumptions of the model it seems that the trade off between thermal excitation and multiphononic de-excitation explains the effect.

The intense selective emission band at 1 µm in addition to the good performance of the eutectic rods under severe thermal shock conditions make this material a good candidate as a selective emitter in TPV devices based on silicon photovoltaic cells.

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FIGURE CAPTIONS

Figure 1: Back-scattered scanning electron micrographs of the transverse cross section of Al₂O₃-Yb₃Al₅O₁₂ eutectic rods processed at (a) 25 mm/h; (b) 100 mm/h; (c) 750 mm/h.

Figure 2: Dependence of the lamellar interspacing, λ , with the growth rate, v, for Al₂O₃-Yb₃Al₅O₁₂ eutectic rods. Solid circles correspond to the experimental values and the line corresponds to the fitting to the Hunt–Jackson law with $C=133 \, \mu m^3 \, s^{-1}$.

Figure 3: Infrared optical absorption spectra of Al₂O₃-Yb₃Al₅O₁₂ eutectic rods grown at 25 mm/h and Yb₃Al₅O₁₂ single crystal measured at room temperature. Inset: absorption spectra in the visible range.

Figure 4: Selective emission spectra of Al₂O₃-Yb₃Al₅O₁₂ eutectic rods grown at 25 mm/h measured at several temperatures.

Figure 5: Emission intensity (in arbitrary units) measured at 1000 nm (solid circles) and 1200 nm (open circles) as a function of temperature. For comparison, the normalized blackbody emission at 1200 nm is also given (solid line).

Figure 6: Calculated emission intensity (in arbitrary units) using eqs. (2-6) in text with p = 12 and $hv_{eff} = 833$ cm⁻¹ energy for different quantum yields at 1000°C of 0.3 (solid circles), 0.5 (open circles) and 0.7 (solid triangles).

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	$f_{EXP} (\cdot 10^{-8})$ $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$	
Yb ₃ Al ₅ O ₁₂	62.5% mol Al ₂ O ₃ 37.5% mol Yb ₂ O ₃	100% Yb ₃ Al ₅ O ₁₂	$1.41 \cdot 10^{22}$	151	
Al ₂ O ₃ - Yb ₃ Al ₅ O ₁₂	81.5% mol Al ₂ O ₃	$46.2 \pm 2.1\% \text{ Al}_2\text{O}_3$	$7.59 \cdot 10^{21}$		
1 1.2 0 3 1 1 0 3 1 1 3 0 1 2	19.5% mol Yb ₂ O ₃	$53.8 \pm 2.1\% \text{ Yb}_3 \text{Al}_5 \text{O}_{12}$	(in Yb ₃ Al ₅ O ₁₂)	356	