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Fabrication and characterization of new Er-doped yttrium-scandium-aluminum garnet ceramics

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Abstract: We report the fabrication and characterization of the yttrium aluminum garnet (Er:YAG) and yttrium scandium aluminum garnet (Er:YSAG) ceramics for implementing analysis as an active medium for 1500 nm lasing. High erbium content Er:YAG and Er:YSAG ceramics have been fabricated from Er:YAG and Er:YSAG powders, respectively. All ceramic samples belong to the garnet-type cubic structure (space group *Ia3d*) without any traceable impure phases. Including Sc^{3+} in the Er:YAG crystal structure leads to improving mechanical characteristics and elastic-plastic properties of the materials. The optical transmittance of ceramics is affected strongly by the including Sc^{3+} and increasing up to 60% at about 1500 nm.

Keywords: YAG, ceramics, transparency

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1. Introduction

The rare-earth-doped yttrium aluminum garnet, RE^{3+}:$Y_3Al_5O_{12}$ (RE^{3+}:YAG), is well-known as active media for high power lasers [1-3]. Transparent ceramics were initially developed to replace single crystals in case of disk geometry [4], multilayer and concentration gradient architectures. We have synthesized $(Y_{0.5}Er_{0.5})_3Al_5O_{12}$ (Er^{3+}:YAG) and $(Y_{0.5}Er_{0.5})_3(Al_{0.8}Sc_{0.2})_5O_{12}$ (Er^{3+}:YSAG) ceramics and investigated their microstructure and transmittance in dependence on the presence of Sc^{3+} ion.

2. Materials and Methods

Precursor powders were synthesized by reverse precipitation of metals chlorides ($MeCl_3 \cdot 6H_2O$, where *Me* are Al, Sc, Y, Er) into a cooled aqueous ammonia solution of 25 % through spraying [5, 6]. The disaggregated oxyhydrate powders were annealed at 1200 °C for 2 hours in an oven. Additionally, a part of them were annealed at 1600 °C. TEOS were used as a sintering addition at milling powder stage. Then the ceramic powders were processed by uniaxial pressing, cold isostatic pressing, and sintering in a vacuum at 1760-1780 °C for 10 hours. After vacuum sintering the samples were processed through lighting annealing and polished on both sides.

The phase composition and unit cell parameters of ceramic powders were deter-

mined with the Empyrean X-ray diffractometer (*PANalytical*, Netherlands) using *CuKα* radiation (1.5406 Å). The experimental powder diffraction patterns were compared with the XRD pattern of $Y_3Al_5O_{12}$ from the ICSD database (№ 01-072-1853).

Particle-size distribution of the oxyhydrate powders was measured with laser diffraction technique using the Analysette 22 MicroTecPlus laser particle sizer (Fritsch, Germany).

A microstructure of the ceramic surfaces was scanned on electron microscope EVO 10 from GmbH Zeiss Microscopy (Jena, Germany). The samples were examined at 20 kV accelerating voltage with 9 mm working distance in low vacuum operation (EP = 70 Pa); cathode LaB6. Digital images were captured in tiff format with resolution 1024x768 px (0.09nm/px).

Before SEM imaging the samples of dry particles were placed onto carbon adhesive tape. The observations of samples were carried out with a beam current on the samples of 370 pA. The images were captured in backscattered electron mode (BSE).

Examination of chemical composition was carried out on detector SmartEDX(AMETEK, USA) with a beam current of 626 pA for analyses and at 20 kV accelerating voltage with 9 mm working distance.

Refractive index was determined with the total internal reflection method with the Metricon refractometer for three wavelengths.

The room-temperature transmittance spectra of the Er^{3+}:YAG and Er^{3+}:YSAG ceramics were recorded in the wide range of 250 to 1700 nm on the Shimadzu UV-3101PC spectrophotometer controlled by a desktop computer.

3. Results and Discussion

Characteristics of the Er^{3+}:YSAG ceramic powder are summarized in Table 1. The average grain size has been evaluated as d_{50} = 0.88 μm. X-ray diffraction data (Figure 1) point to presence of Y_2O_3 as an impurity phase after annealing at 1200 °C. To exclude the impurity phase the samples have been annealed at higher temperature of 1600 °C. X-ray data of the repeatedly annealed powders include picks corresponding to YSAG only and point to compliance of the initial cationic composition with stoichiometric one. Moreover, difference in unit cell parameters of the powders before and after annealing at 1600 °C implies particular formation of garnets at 1200 °C and full formation at 1600 °C. The average crystallite size d_{XRD} is about 66 nm, and the ceramic powder may be classified as nanocrystalline one.

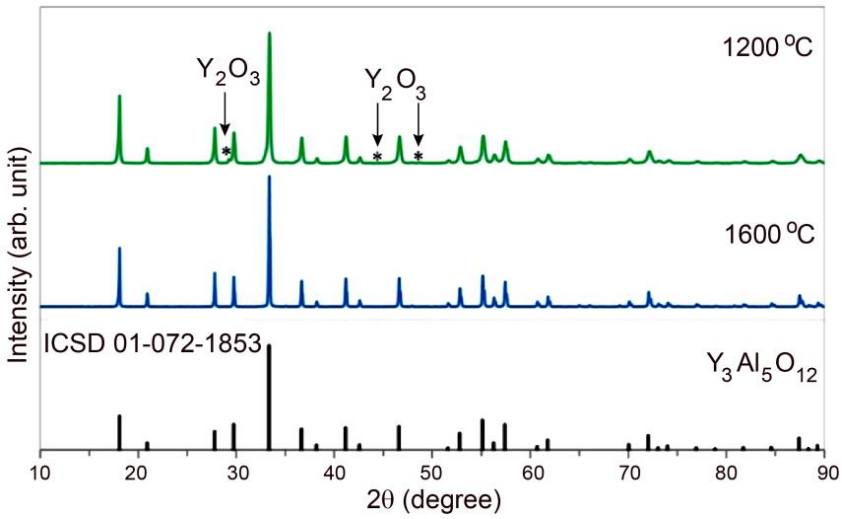

Figure 1. X-ray diffraction pattern of the ceramic powder annealed at 1200 °C and 1600 °C in comparison with the XRD pattern of $Y_3Al_5O_{12}$ from the ICSD database (№ 01-072-1853)

Table 1. Characteristics of the Er^{3+}:YSAG ceramic powder obtained with calcinations at 1200 °C and 1600 °C.

Annealing temperature	Particle-size distribution, μm			Phase composition		d_{XRD}, nm	YSAG unit cell parameters, *a*, *Å*
	d_{10}	d_{50}	d_{90}	Er:YSAG	Y_2O_3		
1200 °C	0.22	0.88	2.13	99.2 %	0.8 %	66 ± 2	11.9904(2)
1600 °C	-	-	-	100 %	-	>500	11.9958(2)

Experimental data of refractive indices for three wavelengths (Table 2) were subsequently fitted using a least-squares fitting program to the Sellmeier's dispersion equation (Figure 2): $\frac{1}{n^2-1} = -\frac{A}{\lambda^2} + B$.

where $(-A)$, the slope of the plot of $(n^2\text{-}1)^{-1}$ versus λ^{-2}, gives a measure of dispersion and B, the intercept of the plot at $\lambda = \infty$, gives $n_\infty = (1+1/B)^{1/2}$.

Table 2. Measured refractive indices of the ceramic samples and coefficients in the Sellmeier's dispersion equation.

Ceramic samples	Refractive indices			Coefficients in the Sellmeier's dispersion equation	
	633.5 nm	969.0 nm	1539.5 nm	*A*	*B*
Er:YAG	1.8386(5)	1.8259(5)	1.8167(5)	$6.9(1.4)\cdot10^3$	$4.36(2)\ 10^{-1}$
Er:YSAG	1.8487(5)	1.8359(5)	1.8257(5)	$6.9(1.1)\ 10^3$	$4.30(2)\ 10^{-1}$

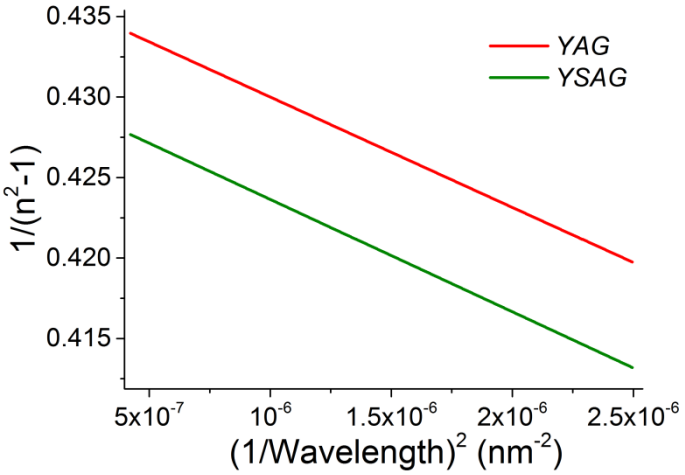

Figure 2. Refractive index (n)–wavelength (λ) dependence.

Figures 3 *a*, *b* show the SEM micrographs of the Er^{3+}:YAG and Er^{3+}:YSAG ceramics, respectively. Er^{3+}:YAG includes many pores that might be scattering centers. The surfaces of Er^{3+}:YSAG ceramics demonstrates homogenious texture, the number of pores decreases significantly.

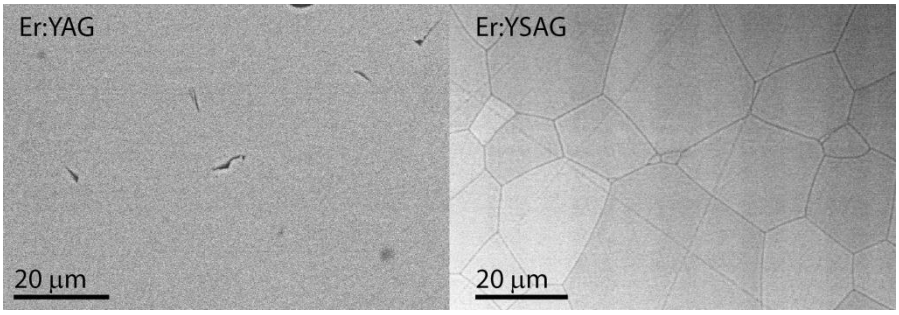

Figure 3. SEM micrographs of the Er:YAG and Er:YSAG ceramic surface.

Probably, presence of Sc^{3+} in the YAG crystal structure leads to decreasing melting temperature and improving elastic-plastic properties of the materials. As a result, Er:YSAG ceramic sample has more perfect microstructure and higher optical transmittance (Figure 4).

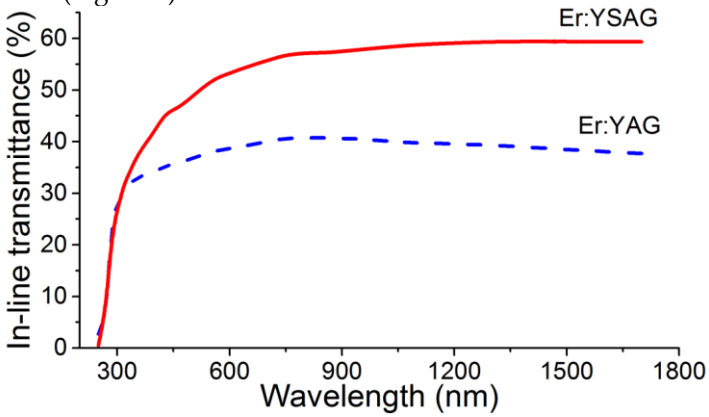

Figure 4. In-line transmittance of the Er^{3+}:YAG (blue one) and Er^{3+}:YSAG (red one) samples

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Conflicts of Interest: The authors declare no conflict of interest.

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