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RAPID COMMUNICATION

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Transparent cobalt-doped yttrium aluminum garnet (Co^{2+}:YAG) ceramics—An innovatory fast saturable absorber

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Abstract

Highly transparent $Y_3Al_5O_{12}$ (YAG) ceramics doped with 0.025 and 0.05 at.% Co ions were prepared for the first time by the freeze granulation process and reaction sintering. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were performed to analyze the microstructure and crystal structure of the samples. The absorption spectra of the Co^{2+}:YAG ceramics were measured at room temperature, and significant absorption bands at 600 nm, as well as at 1535 nm, were observed. The nonlinear behavior of the received material was experimentally demonstrated. Due to the short relaxation time of investigated ceramics, we considered them as fast saturable absorbers. The influence of the postsintering annealing process was examined. The values of saturation intensities of YAG ceramics with different concentrations of cobalt were estimated by fitting experimental data to the theoretical model for fast saturable absorbers.

KEYWORDS

Co:YAG ceramics, fast saturable absorber, freeze granulation, transparent ceramics

1 | INTRODUCTION

Transparent ceramics are a very promising alternative to single crystals as optical materials, for example, in laser technology or in solid-state lighting.[1,2] They have similar or better thermal and mechanical properties, appropriate spectroscopic properties, and offer considerable economic advantages. It is possible to manufacture materials with a gradient concentration of dopants. Moreover, the manufacturing processes enable one to control grain size (micro and nano are possible), porosity, and shape.[3] Transparent ceramics have attracted much attention for their integration in high power laser systems. In literature, applying fast and slow ceramic saturable absorbers in passive mode-locking and Q-switching are widely discussed.[4,5]

Yttrium aluminum garnet (YAG) plays an important role as a matrix for both: laser materials with rare-earth (RE) ions doping (for example with ytterbium, erbium, thulium, or holmium) and saturable absorbers with transition metal (TM) ions doping (eg, with chromium or vanadium).[6,7] In recent years, there has been increasing interest in the fabrication and investigation of the optical properties of transparent ceramics. However, we found only a few papers reporting on cobalt-doped YAG (Co^{2+}:$Y_3Al_5O_{12}$, Co^{2+}:YAG) materials. Satapathy[8] considered adding cobalt oxide only as a sintering aid to densify YAG ceramics. In turn, Sun[9] described single-phase nanopowders obtained by the sol-gel method and proposed that the received material can be used to fabricate transparent ceramics working as nonlinear absorber. K. Hamamoto[10] reported on the absorption spectra of Co^{2+}:YAG at different temperatures, but did not describe the process of ceramic fabrication. H. Yagi et al.[11] produced Co^{2+}:YAG ceramics by slip casting and the vacuum sintering method, and they analyzed absorption spectra near the 808 and 1064 nm region. Sarnecki[12] presented the fabrication of epitaxial layers of Co^{2+}:YAG from the liquid phase on a substrate made out of pure YAG. Based on spectroscopic studies, they concluded that layers could be used as nonlinear saturable absorbers in a wavelength range safe for the human eye.

In this paper, we report on the elaboration of Co^{2+}:$Y_3Al_5O_{12}$ ceramics. We utilized freeze-granulation process which allows improved material homogenization. Further on we describe the investigation of nonlinear saturable absorption of obtained samples near 1535 nm. To the best of our knowledge, this is the very first time when high-quality transparent polycrystalline Co^{2+}:YAG is shown, as previous articles did not discuss the optical quality of investigated samples.[11] Transparent YAG ceramics have great potential to replace single crystals in many applications being either a cheaper substitute or material more suited for microlaser application when it is fabricated with dopants separated from each other (eg, Nd^{3+}, Cr^{4+}). Therefore, continuous effort is needed to improve this material to the point of its industrial application.

We discuss the nonlinear properties of the obtained ceramics as saturable absorbers. Based on absorption spectra, we indicate the prospective applications for laser systems generating wavelengths from 1250 to 1560 nm. It could be used, for example, together with: 1320 nm Nd:YAG, 1340 nm Nd:YVO, 1350 nm Nd:KGW, 1440 nm Nd:YAG, and 1540 nm erbium glass lasers operating in the spectral region where Co:YAG is characterized by increased absorption. In particular, the possibility of implementing such material for eye-safe lasers applications is desirable. The values of saturation of the Co^{2+}:YAG ceramics were estimated using the Keyes model for fast saturable absorbers based on absorption saturation measurements performed at 1535 nm.

2 | EXPERIMENTAL PROCEDURE

Our goal, during the fabrication process, was to manufacture transparent YAG ceramics doped with tetrahedrally coordinated Co^{2+} ions. We obtained Co^{2+}:$Y_3Al_5O_{12}$ with two different Co doping level: 0.025 and 0.050 at.% using the freeze granulation process and reaction sintering. First, aqueous slurries of pure yttria (99.99% purity), alumina (99.99% purity), and cobalt oxide (99.9% purity) were prepared through mixing the powders in a planetary mill in water with Duramax B-1000 as a binder, DolapixCE 64 as a dispersing agent, and laboratory-prepared octaanion as a sintering aid. Aqueous slurries were sprayed into liquid nitrogen in order to form granules, which afterwards were immediately transferred to a lyophilizer and freeze-dried overnight. The obtained granulates were pressed (under both uniaxial and isostatic pressure) into 20 mm pellets. The samples were calcined at 950°C in order to remove organic additives and afterward sintered under vacuum at 1715°C. Subsequently, some samples were annealed in the air at 1600°C for 2 hours in order to compare their properties with as-sintered materials. The received ceramics were ground and polished to obtain disks with a thickness of 0.87 mm with mirror-like parallel surfaces. After machining, some samples were annealed again in order to reveal grain boundaries. Thermal etching took place in the air at 1600°C for 30 minutes.

Qualitative phase analysis of the ceramics was carried out using X-ray powder diffraction. The measurements were carried out on a Rigaku SmartLab 3kW X-ray diffractometer equipped with a copper lamp and D/tex Ultra 250 solid-state detector. The operating parameters of the lamp were: 40 kV and 30 mA. The measurements were made on bulk samples in continuous mode in the Bragg-Brentano geometry (θ/2θ scan) in an angular range of 5-120° (2θ) with a scanning step of 0.01° and a speed of 1.2°/min. The PDXL2 software package, cooperating with the crystallographic database PDF4 + 2018 and the XRayan program (created by H. Marciniak, R. Diduszko, M. Kozak), was used in order to analyze the obtained data. After thermal etching, the microstructures of ceramics were observed with a scanning electron microscope (SEM) (Carl Zeiss CrossBeam Workstation AURIGA). All measurements were carried out at room temperature. The optical transmission of Co^{2+}:YAG ceramics was measured in the range 0-3300 nm by a Varian Carry 500 spectrophotometer. The nonlinear optical properties of transparent Co^{2+}:YAG ceramics were evaluated by experiments of saturated absorption/transmission using Er^{3+}:glass laser (Kigre) generated at 1535 nm. The pump pulse duration was 7 ns (FWHM) in single-shot mode. The measuring set consisted of: set of filters, beam splitter, and two energy detectors. The knife-edge method was applied to determine the radius of the laser beam.

3 | RESULTS AND DISCUSSION

In Figure 1, a photograph of 0.87-mm-thick ceramic Co^{2+}:YAG samples is shown. One can observe that the intensity of the blue color increased with a higher amount of dopant, as the slightly blue color of the ceramics changed to a deeper blue.

Figure 2 shows the X-ray diffraction patterns of the samples with two different concentrations of Co^{2+} ions: 0.025 and 0.05 at.%. No secondary phases were identified. According to the position of diffraction peaks, the obtained ceramics can

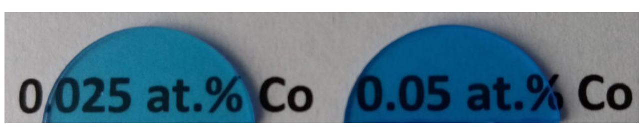

FIGURE 1 Photograph of 0.025 and 0.050 at.% Co:$Y_3Al_5O_{12}$ transparent ceramics after grinding and polishing, with an approximate diameter of 1.5 cm [Color figure can be viewed at wileyonlinelibrary.com]

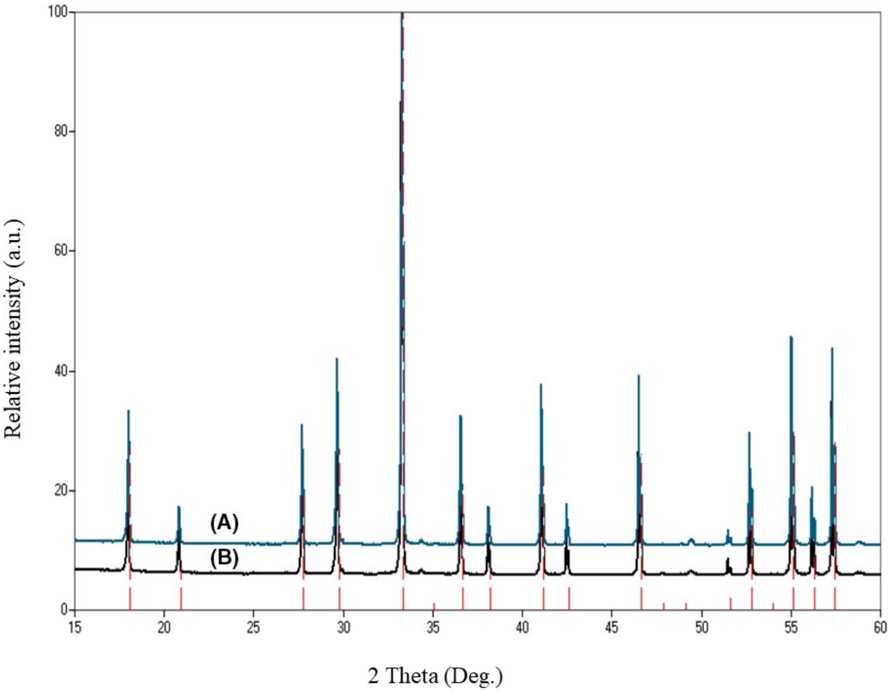

FIGURE 2 X-ray diffraction patterns of $Y_3Al_5O_{12}$ transparent ceramics doped with: (A) 0.025 at.% Co^{2+}, (B) 0.050 at.% Co^{2+} [Color figure can be viewed at wileyonlinelibrary.com]

be well identified as pure YAG phase. Calculations of unit cell dimensions proved that all-ceramic samples were close to stoichiometric. The obtained lattice constants for 0.025 and 0.050 at.% Co concentration dopants equaled 1.20089 and 1.20091 nm, respectively, whereas the lattice constant of pure YAG is equal to 1.2053 nm. The density of the produced ceramics, determined using the Archimedes principle, was $\rho = 4.553$ g/cm^3, which is the same as the theoretical model.

The Co:$Y_3Al_5O_{12}$ samples with a nominal doping of 0.025 and 0.050 at.% Co had almost the same surface morphology as is shown in Figure 3. A large grain size was obtained. It is desirable for transmission reasons. It was obtained by adding octaanion as a sintering aid. The presence of cobalt oxide (melting point of Co_3O_4 = 895°C) as a substrate may also contribute to a better sintering of the ceramics.[8] With the increase in cobalt content, a pronounced grain size increase was observed. This effect was especially visible for the sample with 0.4 at.% concentrations of Co^{2+} in $Y_3Al_5O_{12}$ which consisted of grains with a diameter of hundreds of micrometers (not shown here). The transparent ceramics have a homogeneous distribution of grain size (in the range of 5-35 μm), and clear grain boundaries are visible. These ceramics exhibit almost no porosity, which proves that fabricated Co:$Y_3Al_5O_{12}$ transparent ceramics are of very good quality.

The next goal of this research was to investigate the transmittance spectra of the produced ceramics in the infrared and visible light range at room temperature. As anticipated, we observed two broad absorption bands at approximately 600 nm, as well as in the range 1250-1560 nm (Figure 4). Co^{2+}:$Y_3Al_5O_{12}$ ceramics have been found to have significant absorption at 1535 nm, which is comparable to cobalt-doped magnesium aluminate spinel (Co^{2+}:$MgAl_2O_4$).[13] In Figure 4, the transmittance spectra are presented. The

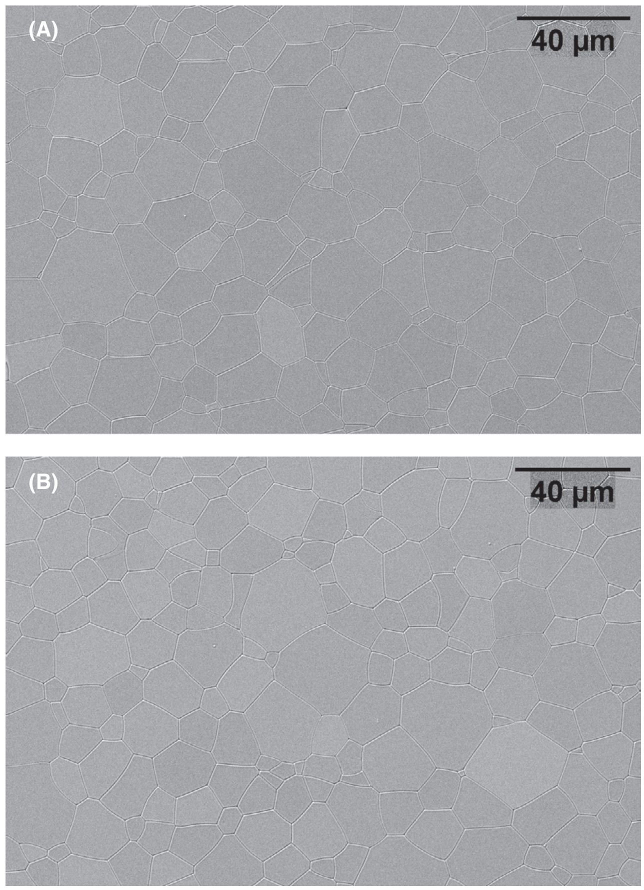

FIGURE 3 SEM images of Co:$Y_3Al_5O_{12}$ transparent ceramic microstructures with a cobalt doping of: (A) 0.025 at.% Co, (B) 0.050 at.% Co

highest transmittance was obtained for 0.025 at. % Co and was found to be 81.7% and 83.1% at 1000 nm and 2500 nm wavelength, respectively. As anticipated, in all samples, in the

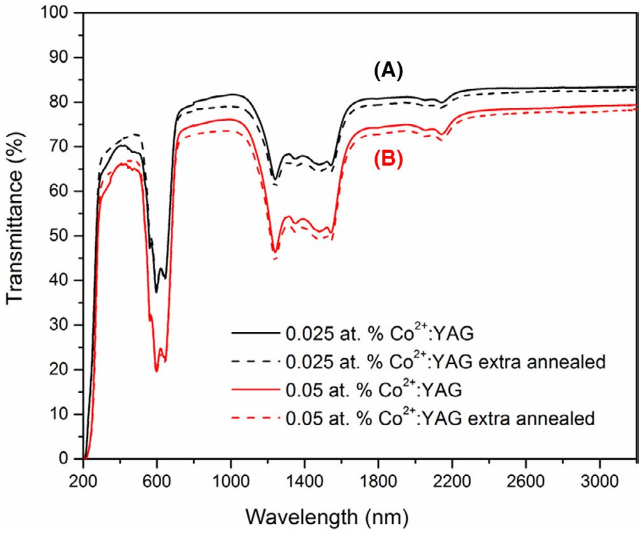

FIGURE 4 Transmission spectra of Co:YAG ceramics (A) 0.025 at.% and (B) 0.050 at.% Co^{2+}:$Y_3Al_5O_{12}$ transparent ceramics (solid lines). The dashed lines represent the spectra of extra-annealed samples at 1600°C/2 h [Color figure can be viewed at wileyonlinelibrary.com]

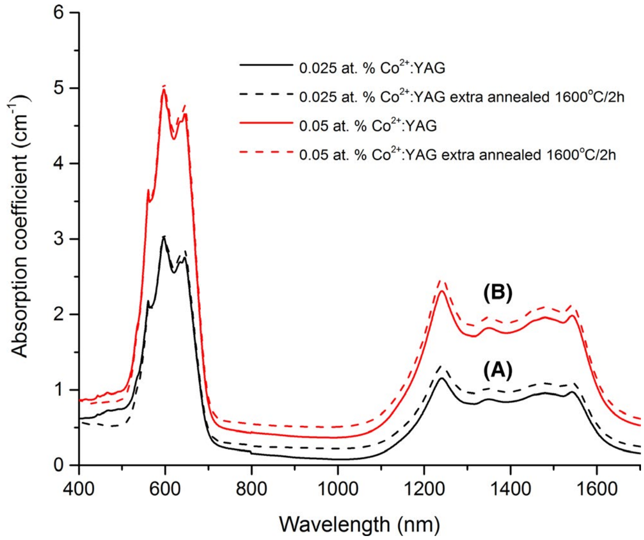

FIGURE 5 Absorption spectra of (A) 0.025 at.% and (B) 0.050 at.% Co^{2+}:$Y_3Al_5O_{12}$ transparent ceramics (solid lines). The dashed lines represent the spectra of extra-annealed samples at 1600°C/2 h [Color figure can be viewed at wileyonlinelibrary.com]

range 1250-1560 nm absorption band attributed to $^4A_2 \rightarrow {}^4T_1$ (^4F) transition of the tetrahedrally coordinated Co^{2+} ions was observed. The ceramic samples were polished, not coated, so it is obvious that during the experiments the reflectance from the surfaces has been taken place.

Another research goal was to investigate the absorption spectra of the produced ceramics in the near-infrared region at room temperature. We took into account reflectance from two surfaces of ceramic probes during the absorbance coefficients calculation. The calculated reflectance from each surface changes with the reflective index as a function of wavelength and for example at 1535 nm is equal 8.276%. In Figure 5, the calculated absorption coefficients of Co^{2+}:$Y_3Al_5O_{12}$ ceramics according to the Beer-Lambert law were presented. For samples that were additionally annealed, the values of absorption coefficients in ceramics were slightly higher than in samples not subjected to this procedure.

As previously mentioned, the nonlinear optical properties of Co^{2+}:$Y_3Al_5O_{12}$ ceramics were investigated during the experiments of saturated transmission with a 1535 nm laser. Figure 6 shows the results of a series of samples with different concentrations of Co^{2+} ions, with or without annealing. A nonlinear behavior of responses was observed. The experiments were performed as a function of the power density of transmitted laser radiation.

Due to the short relaxation time of Co^{2+}:$Y_3Al_5O_{12}$, around 1-2 ns,[14] best fit approximations were performed using the Keyes model:

$$\ln\left(\frac{T}{T_0}\right) = \left(\frac{I}{I_s}\right)(1-T), \tag{1}$$

where T_0 is the small-signal transmission, T is the measured transmission, I is the incident power density, I_s is the unknown value of saturation power density (saturation intensity). Having known the values of saturation intensities, one can calculate the absorption cross sections of the samples:

$$I_s = \frac{h\nu}{\sigma\tau}, \tag{2}$$

where $h\nu$ is the photon energy, σ is the absorption cross section, τ is the relaxation time. According to the short relaxation time in the Keyes model, only ground saturation absorption is assumed to exist.

Equation 1 was numerically solved, and the experimental data were subjected to the best-fit approximation procedure. A very good correlation between experimental and modeling data is obtained for low irradiation fluences. The discrepancies in the high fluence range are most probably related to the damage that occurred during irradiation. Similar behavior of Cobalt-doped YAG was already observed for the crystal samples.[15] Tentatively, the high ability of cobalt-doped materials to transform into a liquid phase, results in a lower laser damage threshold compared to the other types of doped ceramics. For example, Nd: YAG materials exhibit high laser damage threshold of 100 J/cm^2 at 4 ns pulses (wavelength of 1.064 μm).[16] In the case of Co:YAG samples doped 0.050 at.% of Co, observation under high-magnification optical microscope revealed visible areas of recrystallization after 3 J/cm^2 laser irradiation (6 ns pulses). However, some defect states might have occurred even below the fluence, where the damage is clearly visible. Additional sources of discrepancies between modeling and experiment data may be

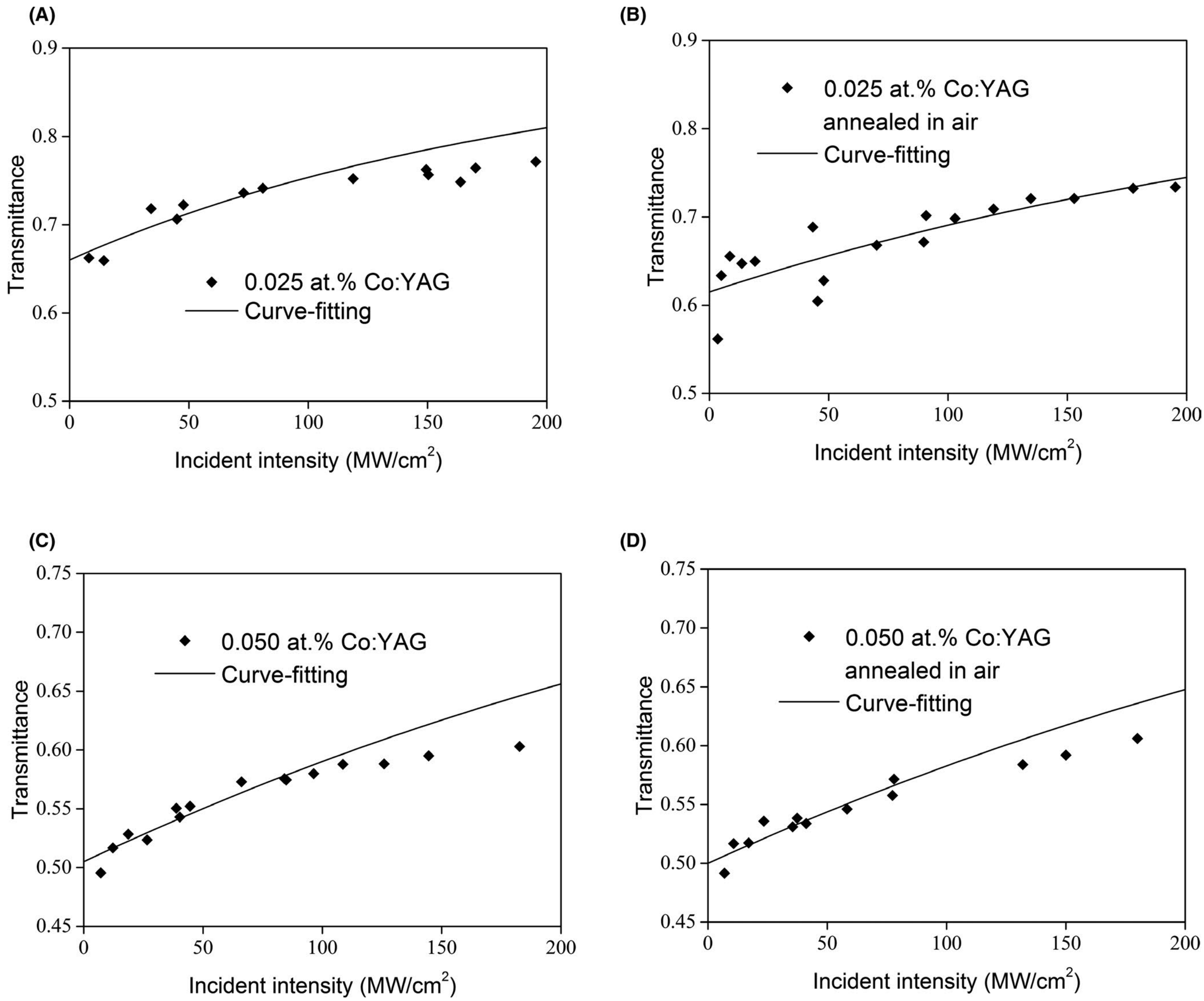

FIGURE 6 Saturation transmission measurements of Co^{2+}:$Y_3Al_5O_{12}$ ceramic samples: (A) 0.025 at.% of Co, (B) 0.025 at.% of Co annealed at 1600°C, (C) 0.050 at.% of Co, (D) 0.050 at.% of Co annealed at 1600°C. Solid lines represent the best fitting approximations

TABLE 1 Main parameters and calculated spectroscopic values of fabricated Co^{2+}:$Y_3Al_5O_{12}$ transparent ceramic samples

	Sample 1	Sample 2	Sample 3	Sample 4
Cobalt concentration [at.%]	0.025	0.025 extra-annealed in air 1600°C	0.050	0.050 extra-annealed in air 1600°C
thickness [mm]	0.87	0.87	0.87	0.87
T_0 small-signal transmittance [%] at 1535 nm (measured)	66.1	64.6	51.1	49.3
T_0 small-signal transmittance [%] at 1535 nm (calculated)	66	61.5	50	50
I_s saturation intensity [MW/cm^2] at 1535 nm	185.7	166.7	262.8	272.3
σ absorption cross section [cm^2] ($\tau = 1$ ns)	$6.969{\cdot}10^{-19}$	$4.852{\cdot}10^{-19}$	$4.314{\cdot}10^{-19}$	$4.753{\cdot}10^{-19}$
MSE mean squared error	$5.16{\cdot}10^{-4}$	$6.08{\cdot}10^{-4}$	$2.48{\cdot}10^{-4}$	$2.029{\cdot}10^{-4}$
R^2 coefficient of determination	0.8641	0.7212	0.8959	0.9333

related to the thermal effects that where not taken into account in the model.

The main parameters of the produced Co^{2+}:YAG samples and the results of the calculations, including mean squared error and coefficient of determination of the fitting curves, are presented in Table 1.

It is difficult to appraise the obtained values, because the results of saturated absorption measurements of similar material, that is, Co^{2+}:$Y_3Al_5O_{12}$, are very rarely found in literature. Nevertheless, we noticed that the absorption cross sections of thin films of Co,Si:YAG with concentrations (mole fractions) in the range from 0.0002 to 0.0054 grown on

YAG and Er,Yb:YAG substrates by means of the isothermal liquid-phase epitaxy (LPE) dipping technique were varied between $3 \cdot 10^{-19}$ to $8 \cdot 10^{-19}$ cm^2.[17] In Co^{2+}:YAG crystal with 2 at.% Co concentration grown by the Czochralski method, the value of the parameter is evaluated to be $8.6 \cdot 10^{-20}$ cm^2.[18] It should be remembered that the differences between concentrations of Co dopants in the above-mentioned materials (ceramic, thin films, and crystal) are substantial. We presume that our results, that is, absorption cross sections of $Co^{2+}:Y_3Al_5O_{12}$ ceramics between $5 \cdot 10^{-19}$ to $7 \cdot 10^{-19}$ cm^2, are promising and comparable to those in literature.

4 | SUMMARY

Transparent YAG ceramics with different Co doping concentrations of 0.025 and 0.050 at.% were obtained by the freeze granulation method and reaction sintering. To the best of our knowledge, these materials were, for the first time, obtained using this method. The obtained single-phase, homogeneous samples were characterized in terms of microstructure (XRD, SEM). The absorption spectra were measured, and the absorption spectra of transparent $Co^{2+}:Y_3Al_5O_{12}$ ceramics were investigated. The nonlinear optical properties of transparent $Co^{2+}:Y_3Al_5O_{12}$ ceramics were evaluated by experiments of saturated absorption/transmission at 1535 nm Er^{3+}:glass laser. The ground state absorption cross sections for different Co doping concentrations were determined. We observed a nonlinear behavior of transmission as a function of the power density of the transmitted 1535 nm laser radiation. Curve fitting procedures were performed to find saturation intensities and ground state cross sections of transparent Co^{2+}:YAG ceramic samples with different Co doping. This ceramic can be used as a nonlinear absorber for eye-safe lasers.

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