

Effect of Raw Material on the Properties of LuAG:Cr⁴⁺ Ceramics¹

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Abstract—Samples of Cr⁴⁺:LuAG ceramics have been synthesized using commercial and reprecipitated Lu₂O₃ powders. The optimum conditions for the synthesis of the reprecipitated Lu₂O₃ powder have been established, a dilatometric analysis of the ceramics has been carried out, and the effect of the initial Lu₂O₃ powder on the optical properties of the ceramics has been studied.

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INTRODUCTION

The saturable absorbers based on Cr⁴⁺-doped crystals have been known for several decades. It all started with Nd³⁺- and Cr⁴⁺-doped gadolinium scandium gallium garnet (GSGG) crystals. A little later, the applicability of this concept was confirmed by the investigations of Cr⁴⁺:YAG saturable absorber crystals synthesized by the Czochralski method. Subsequently, YAG saturable crystal-based absorbers found wide application in Q-switched lasers. However, the production of crystals growing from melt, including Cr⁴⁺:YAG, is an expensive and time-consuming process. Another drawback of the crystal growth from melt is the limited range of dopant concentrations and the impossibility of obtaining composite structures in a single process. The first Cr⁴⁺:YAG saturable absorbers manufactured by ceramic technology were obtained in 1995 [1]. In 1996, several reports [2, 3] on the Cr⁴⁺:LuAG saturable absorbers in the form of single crystals grown from melt were published. It was established [2] that these saturable absorbers have an absorption cross section of $\sigma_{\text{esa}} < 3 \times 10^{-20} \text{ cm}^2$ from the excited state and $\sigma_{\text{gsa}} = (1.0 + 0.2) \times 10^{-18} \text{ cm}^2$ from the ground state. Consequently, their ratio is $\gamma = \sigma_{\text{gsa}}/\sigma_{\text{esa}} > \approx 30$, while the Cr⁴⁺:YAG adsorbers have $\gamma \approx 10$. Since we are not aware of any published studies on Cr⁴⁺:LuAG ceramic saturable absorbers, we started synthesizing and studying this material in order to compare them with our Cr⁴⁺:YAG samples. In this

study, we examined the effect of the initial Lu₂O₃ powder on the properties of the synthesized ceramics.

1. EXPERIMENTAL

High-purity commercial Lu₂O₃ (LyuO-L, Russia), Al₂O₃ (AKP-50, Sumitomo Chemical, Japan), Ca(NO₃)₂, and Mg(NO₃)₂ materials were used as raw materials. For reprecipitation, the initial commercial Lu₂O₃ powder was dissolved in nitric acid and then precipitated with the NH₄OH and NH₄HCO₃ mixture. The resulting precipitate was washed several times, first with deionized water and then with isopropyl alcohol. After washing, the powder was dried at a temperature of 50°C until completely dry. The dried powder was passed through a 180-mesh sieve (83- μm mesh), after which it was calcined in portions at different temperatures to establish the optimum synthesis temperature. Sintering additives MgO and CaO, which are used to promote shrinkage, acted also as charge compensators for Cr ions. The total sintering additive concentration was chosen to be 0.1 mol %, analogously to the Cr doping level, and the CaO/MgO molar ratio was 1/1.

In addition, we fabricated the Cr⁴⁺:LuAG samples with the same additives using reprecipitated Lu₂O₃ to study its effect on the characteristics of the final sample. After mixing the initial powders in stoichiometric ratios, they were ground in a planetary mill in anhydrous isopropanol for 15 h. The powders prepared in this way were uniaxially pressed in a stainless steel mold into compacts 10 mm in diameter at 100 MPa

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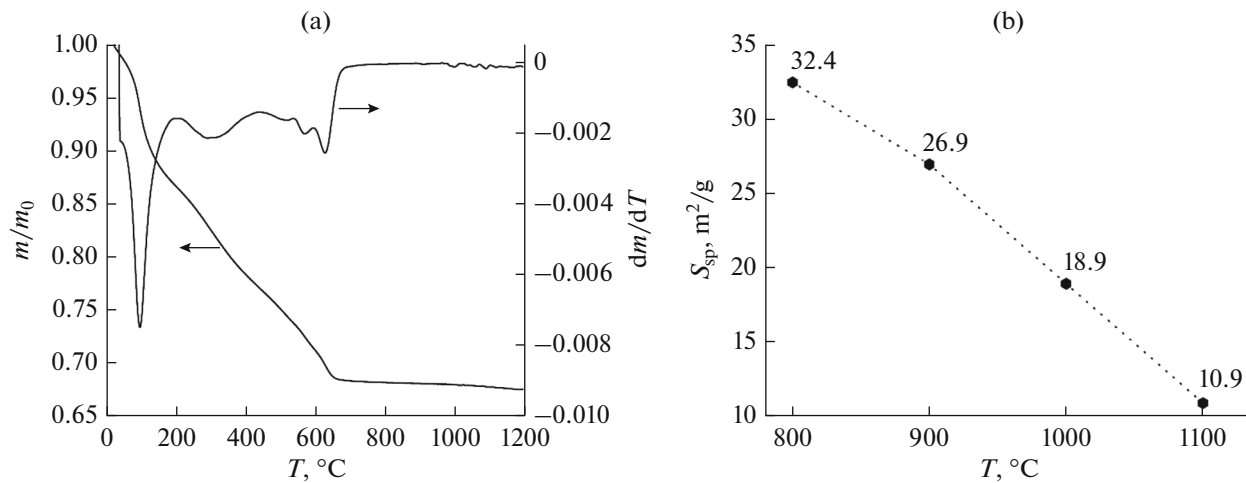


Fig. 1. (a) Measured TGA/DTGA curves and (b) specific surface area of the reprecipitated Lu_2O_3 powder as functions of synthesis temperature.

and then subjected to clean-in-place (CIP) processing at 250 MPa. To remove volatile substances, the compacts were calcined at 1000°C in air for 5 h. Then, they were sintered at 1850°C for 8 h in a vacuum furnace with tungsten heaters at a pressure of 5×10^{-4} Pa. After vacuum sintering, annealing in air was carried out to remove oxygen vacancies and change the oxidation state of chromium ions from +3 to +4. Annealing in air was carried out at 1000–1400°C for 10 h.

Thermogravimetric (TGA) and differential thermogravimetric (DTGA) analyses were carried out on a combined SDT Q600 TGA/DSC/DTA analyzer. Shrinkage curves were measured on a NETZSCH DIL 402C dilatometer and a specific surface area was determined on a Micromeritics ASAP 2020 specific surface area analyzer. Transmittance spectra were recorded on an Agilent Cary 5000 spectrophotometer.

2. RESULTS AND DISCUSSION

The TGA results are shown in Fig. 1a and the specific surface measurement data, in Fig. 1b. It follows from Fig. 1a that the minimum possible temperature of the synthesis of the reprecipitated Lu_2O_3 powder is $\sim 700^\circ\text{C}$. We chose temperatures in the range of 800–1100°C with a step of 100°C. The time of exposure at all the temperatures was 5 h. The synthesis was not carried out at temperatures below 800°C, since, around the minimum temperature, a powder with too fine particles is obtained. According to the results of the previous experiments, at synthesis temperatures above 1100°C, the powder is too coarse-grained. It can be seen in Fig. 1b that the specific surface area of the synthesized Lu_2O_3 powder depends almost linearly on the synthesis temperature. The optimum range of the specific surface area of the initial powder for use in optical ceramics is 7–15 m^2/g . Based on these data,

the precursor ($S_{sp} = 53.2 \text{ m}^2/\text{g}$) was synthesized at 1100°C for 5 h to obtain a powder specific surface area of about 10–12 m^2/g . For comparison, we note that the specific surface area of commercial Lu_2O_3 is 2.1 m^2/g . Figure 2 presents the shrinkage curves measured for the samples prepared from the commercial and reprecipitated Lu_2O_3 powders.

It can be noted that the reprecipitated powder yields pronounced shrinkage peaks at temperatures of 1227 and $\sim 1550^\circ\text{C}$. The first of these peaks is likely due to the formation of the LuAP and LuAM phases and, therefore, located at the same temperature for both powders. The second peak is related to the shrinkage itself and its temperature depends on the granulometric characteristics of the powder. For the commercial powder, the second peak corresponds to a temperature of $>1600^\circ\text{C}$. Consequently, the sintering temperature of the samples from the reprecipitated powder will be lower than the temperature of the samples from the commercial one. The lower sintering temperature suggests finer grains of the resulting ceramic and less equipment wear.

Figure 3 shows the transmittance spectra and appearance of the Cr:LuAG ceramic samples. The inset in Fig. 3a shows the samples synthesized from commercial Lu_2O_3 . Without measuring the transmittance spectra, it is clear that these samples are non-transparent. The ceramics made from the reprecipitated powder (insert in Fig. 3b) has a transmittance close to theoretical. The transmittance of the best (annealed at 1200°C) of the synthesized samples is 80% at a wavelength of 1300 nm, with a theoretical transmittance of 83.5%, which is a satisfactory result. The sample manufacturing technology requires further optimization.

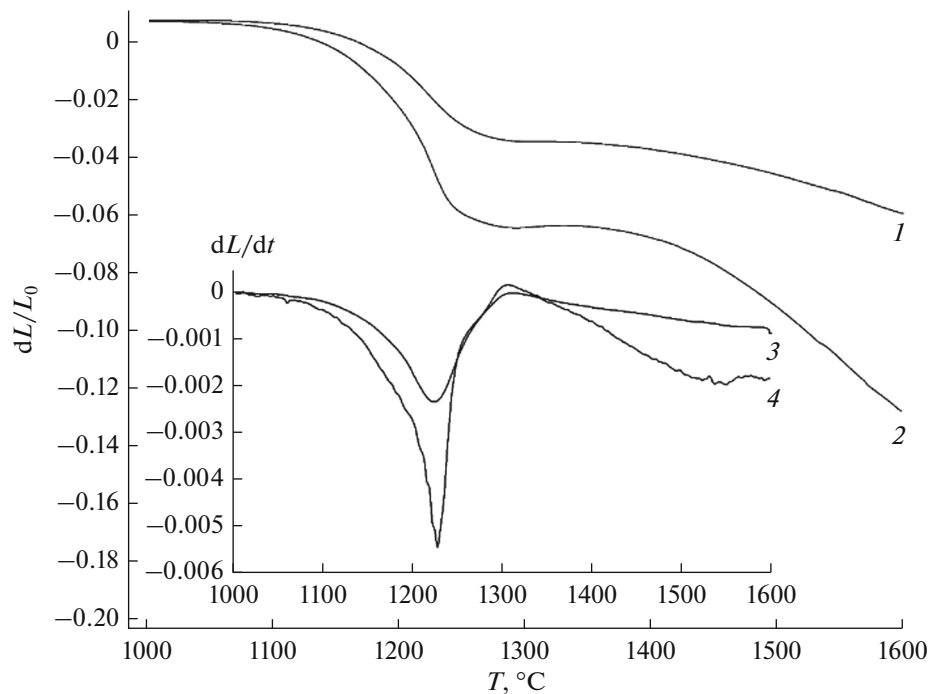


Fig. 2. Integral (1, 2) and differential (3, 4) shrinkage curves for the samples synthesized from (1 and 3) the commercial and (2 and 4) reprecipitated Lu_2O_3 powders.

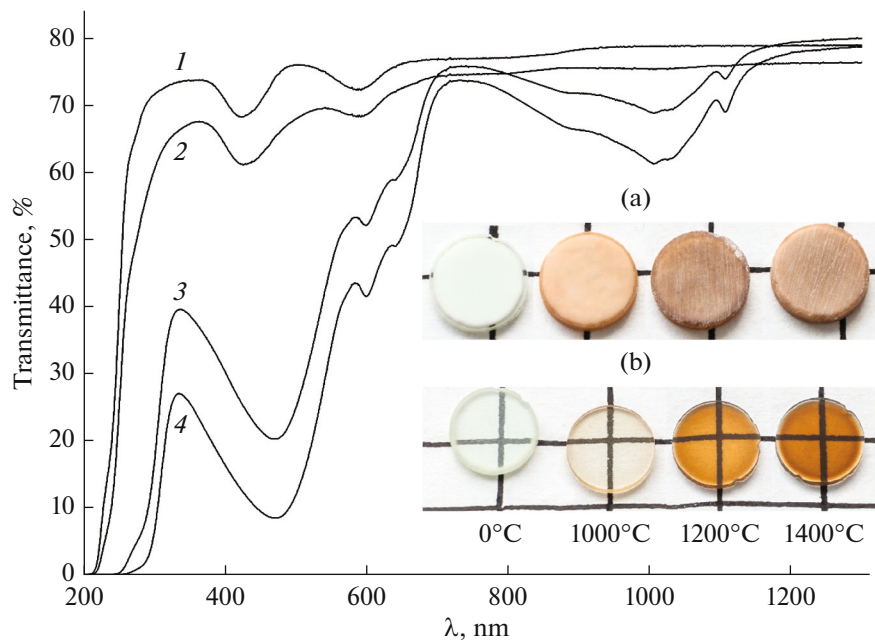


Fig. 3. Transmittance spectra of the samples from the reprecipitated Lu_2O_3 powder (curves 1–4) and appearance of all the samples synthesized from (a) the commercial powder and (b) reprecipitated powder. Annealing temperatures of the samples (from left to right): (1) unannealed, (2) 1000, (3) 1200, and (4) 1400°C. The annealing time is 10 h.

CONCLUSIONS

Thus, $\text{Cr}^{4+}:\text{LuAG}$ ceramic saturable absorber samples were obtained using commercial and reprecipitated Lu_2O_3 powders. The optimum conditions for the synthesis of the reprecipitated Lu_2O_3 powder were

determined. The shrinkage curves of the ceramics were measured and the effect of the initial Lu_2O_3 powder on the optical properties of the ceramics was examined. It was found that the commercial Lu_2O_3 powder is hardly suitable for the manufacturing of

Cr:LuAG ceramic samples using CaO/MgO sintering additives, which are necessary to compensate the Cr⁴⁺ charge.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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