MATEC Web of Conferences **109**, 03002 (2017) DOI: 10.1051/matecconf/201710903002
ICMSNT 2017

Fabrication of Polycrystalline Transparent Co^{+2}: $MgAl_2O_4$ by a Combination of Spark Plasma Sintering (SPS) and Hot Isostatic Pressing (HIP) Processes

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Abstract. Transparent Co^{2+} doped $MgAl_2O_4$ spinel was fabricated by SPS consolidation followed by and HIP treatment. It was established that HIP treatment significantly improved transparency of the ceramic in a wide range of wavelengths, especially, in a range, which is relevant for Q-switching. Nonlinear absorption was demonstrated and the ground and excited state absorption cross sections were estimated. The positive effect of the HIP treatment on the optical properties is related to an elimination of extremely fine porosity and to the location of Co ions at Mg^{2+}sites in the spinel ionic structure. The experimental results indicate that the fabricated specimens can be used as a passive laser Q-switching material.

1 Introduction

Most types of passive laser Q-switching materials developed in the last two decades are based on transition metals cations like Co^{2+}, V^{3+}, or Cr^{4+} as an active dopant [1–4]. For infrared lasers in the 1.3–1.7 m range, especially for lasers exploiting the $^3I_{13/2} \rightarrow$ $^4I_{15/2}$ emission, passive Q-switches based on Co^{2+} doped $MgAl_2O_4$ spinel are an efficient solution [5–13]. Methods of the fabrication and optical properties of Co^{2+} doped $MgAl_2O_4$ single crystals [5, 7, 9] or glass-ceramics [14-15] have been widely studied and discussed in literature. Conventional methods are expensive and time consuming. Recently, SPS [16] and HIP [17] have been successfully applied to fabricate polycrystalline transparent Co doped $MgAl_2O_4$. The SPS process is very fast and may be carried out at relatively low sintering temperatures; however, it doesn't always provide a desired transmittance of ceramics. Prolonged treatments in the SPS apparatus lead to a massive interaction between graphite tooling and $MgAl_2O_4$. It was suggested that a combination of a short SPS process and additional HIP treatment may make available the fabrication of the transparent ceramic with improved optical properties.

2 Experimental Procedures

2.1 Powder synthesis and sintering

Co-doped spinel powder containing 0.09 at. % Co was used as starting material. The powder was synthesized at the Israeli Ceramic and Silicate Institute, Haifa, Israel by wet-chemistry, based on

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hydroxides co-precipitation as described in details by A. Goldstein et al. [17]. The Co-doped spinel powder was premixed with 0.7 wt.% LiF (99.98%, Alfa-Aesar, Heysham, Lancashire, UK). The mixing procedure was described in details in our previous contributions [18, 19]

The fabrication process was done in two steps. At the first step, consolidation experiments were performed using an SPS apparatus (FCT Systems, Rauensin, Germany). SPS parameters were as follows: the sintering temperature was 1550ºC, the heat rate was 20 ºC/min, the dwell time was one hour and the applied pressure was 60 MPa. After the SPS treatment the specimens were grinded and polished to an optical quality surface. Finally, the specimens were HIPed for 4 h at 1550ºC under 200 MPa Ar gas pressure.

2.2 Microstructure, mechanical and optical properties

Micro-structure of the SPS/HIP processed specimens was analysed by an inverted metallography light microscope (Axio, Zeiss, Oberkochen, Germany). Grain size distribution was determined from the micrographs using Thixomet image analysis software [20-22]. Optical in-line transmission measurements were performed using Bruker Vertex V70 FTIR in wavelength range between 0.8 and 7 μm. Bending strength was determined by a 3-point test using a LRXPlus tensile tester (Lloyd Instruments, Fareham, U.K.). Vickers hardness measurements were conducted applying 2000 g load by a Buehler Micromet 2010 apparatus. The elastic modulus was determined by the "pulse echo" method.

2.3 Nonlinear saturation properties

The transmission saturation measurements were performed by Nd: YAG laser with relatively high peak power as a pump laser for an optical parametric oscillator (OPO). A tuneable Potassium titanyl phosphate (KTP) crystal parametrically converts the laser wavelength from the 1065 nm pump to 1417 nm (tuneable OPO) signal. The signal was separated from the pump and idler beams by two filters and focused by a lens, allowing determining the beam waist by using the knife-edge technique. Finally, the transmitted radiation through the Co^{2+}: $MgAl_2O_4$ specimen was measured by a PbSe photo diode power meter.

3 Result and Discussion

The obtained specimens after SPS process were fully dense and translucent with dark tint between blue to black colours. An additional HIP treatment significantly improved the transparency. Figure 1 shows a photograph of the optically polished 2 mm thick Co^{2+} doped $MgAl_2O_4$ spinel sample after HIP treatment.

Figure 1. Co^{2+}: $MgAl_2O_4$ sample fabricated by SPS and HIP processes.

3.1 Microstructure and mechanical properties

Microstructure of the fully dense spacemen is presented in Figure 2. The average grain size was determined to be 8.2 microns.

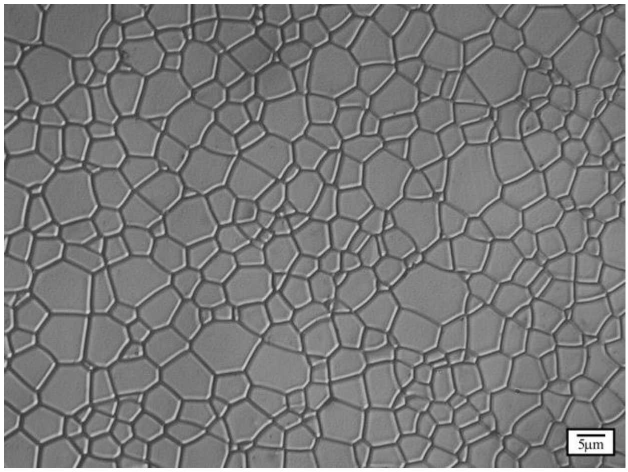

Figure 2. Microstructure of Co^{2+}: $MgAl_2O_4$ sample fabricated by SPS and HIP processes.

The values of hardness, bending strength and Young modulus for the cobalt doped ceramic are presented in Table 1. The obtained mechanical properties are in a good agreement with those previously reported for un-doped spinel of the same grain size [23, 24].

Table 1. Mechanical properties of polycrystalline Co^{2+}:$MgAl_2O_4$.

Vickers hardness, HV	Bending strength, MPa	Young modulus, MPa
1330±30	220±11	285±5

3.2 Optical properties

The optical transmittance from visible to the mid-IR and short-IR wavelength range is presented in Figure 3. In the visible range (at wavelength of 450 nm) a transmittance is about 70%, while at the mid-IR to short-IR spectra, which is the relevant rang for Q-switching the transmittance is higher than 80% and is closed to the theoretical value.

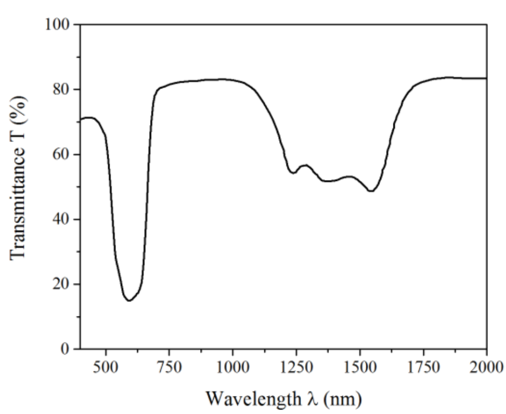

Figure 3. Transmission spectrum of a 2 mm thick Co^{2+}:$MgAl_2O_4$ sintered by SPS followed by HIP treatment.

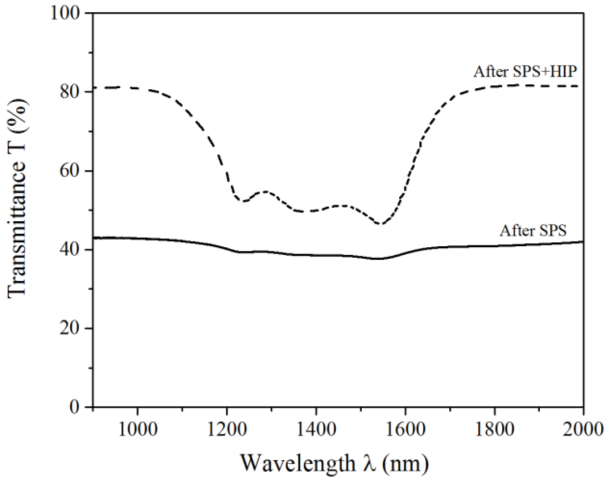

Figure 4. Transmission spectrum of a 2 mm thick Co^{2+}:$MgAl_2O_4$ of the SPS-processed and specimens after additional HIP treatment.

The effect of HIP treatment on the transparency is presented in Figure 4. For the SPS processed specimen the transmittance is relatively low for the entire range of wavelengths, for the HIPed specimen the transparency was significantly higher and a strong absorption related to the $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ transition [17] of the Co^{2+} ions was observed. The positive effect of HIP treatment on the spectra may be related to two factors: additional pore elimination by the high isostatic pressure and diffusion of Co ions to T_d symmetry sites of Mg^{2+} in the spinel structure [25] as a result of the additional dwell time at high temperatures.

3.3 Nonlinear saturation properties

The dependence of incident fluence on the transmission of Co^{2+}:$MgAl_2O_4$ at a wavelength of 1417nm is presented in Figure 5.

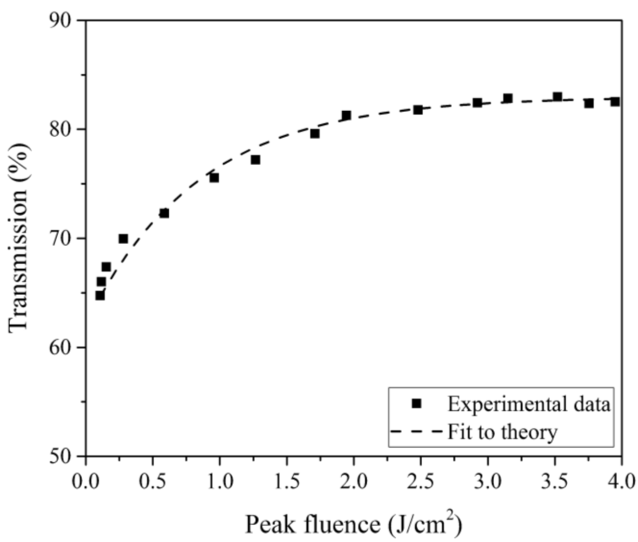

Figure 5. Transmission as a function of the incident fluence at 1417 nm for Co^{2+}:$MgAl_2O_4$ sintered by SPS followed by HIP treatment.

To measure the ground and excited state absorption cross sections through saturable absorption experiments, the energy fluence was increased until the excited state level was full with electrons. At this state the transmission curve becomes asymptotic. The results were fit to a slow saturable absorber model [11], when the pulse duration is much shorter than the excited state decay. The ground-state and the excited-state absorption (σ_{gsa} and σ_{esa}) cross-sections and the Co^{2+} ion density N were calculated from the fit. The estimated values are found to be $\sigma_{gsa} = 3.57 \cdot 10^{-19}\, cm^2$, $\sigma_{esa} = 2.49 \cdot 10^{-20}\, cm^2$ and $N = 1.05 \cdot 10^{19}\, cm^{-3}$, respectively. These values are in good agreement with previously reported results for single crystal [7], SPS processed [16] and HIP processed [17] Co-doped spinel.

4 Conclusions

The combination of SPS and HIP processes was applied for the fabrication of the Co^{2+} doped $MgAl_2O_4$ ceramic. The additional HIP treatment allowed significantly improving transmittance of the ceramic in a wide range of wavelengths. For the wavelengths range, which is the relevant, rang for Q-switching the transmittance is higher than 80% and is closed to the theoretical value. Nonlinear absorption was demonstrated. The ground and excited state absorption cross sections were estimated according to slow saturable absorber model. It was suggested that the positive effect of HIP treatment on the spectra is related to an elimination of extremely fine porosity and to the location of Co ions at sites of Mg^{2+} in the spinel ionic structure.

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