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ABSTRACT

Transparent ceramics of cobalt-doped zinc aluminium spinel (gahnite), Co$^{2+}$:ZnAl$_2$O$_4$, are synthesized by hot pressing at 1520 °C for 4 h in the presence of zinc fluoride, ZnF$_2$, as a sintering additive. The effect of the ZnF$_2$ content (3–10 wt%) on the microstructure, Raman spectra, optical absorption and luminescence of ceramics is studied. The ceramics feature clean grain boundaries, the absence of pores and a narrow grain size distribution (mean grain size: 70-100 μm) resulting in high in-line transparency close to the theoretical limit. The obtained ceramics are suitable for fabrication of saturable absorbers of erbium lasers.

Keywords: transparent ceramics, spinel, cobalt ions, microstructure, optical spectroscopy.

1. INTRODUCTION

Transition metal (TM) ions embedded in tetrahedral ($T_d$) sites in crystals are widely used for saturable absorbers (SAs) of lasers. Indeed, in addition to broad spectral bands inherent to TM ions, the $T_d$ local field symmetry provides high ground-state absorption (GSA) cross-sections making their saturation easier. A clear example is the cobalt ions (Co$^{2+}$). When doped into crystals in $T_d$ sites, Co$^{2+}$ ions feature intense and broad absorption at 1.3-1.6 μm corresponding to the $^4A_2 \rightarrow ^4T_1(4F)$ transition [1]. This absorption spectrally overlaps with the eye-safe emission of Erbium lasers [2,3]. The latter are used for range-finding, remote sensing, medicine, etc.

The state-of-the-art host materials for Co$^{2+}$ ions are the single-crystals of magnesium aluminium spinel, MgAl$_2$O$_4$. They provide low saturation fluence at ~1.54 μm, weak excited-state absorption (ESA) and, thus, low non-saturable losses, and high laser induced damage threshold (LIDT) [4]. Spinel crystals feature good thermal and thermo-mechanical properties. However, the growth of high optical quality spinel single-crystals is complicated. The transparent ceramic technology was proposed as an alternative, offering similar spectroscopic properties together with lower fabrication temperatures and size-scalable production. Transparent ceramics of Co$^{2+}$:MgAl$_2$O$_4$ were fabricated [5,6]. Other alternative materials are the Co$^{2+}$:MgAl$_2$O$_4$ based transparent glass-ceramics [7,8].

There is a great variety of spinel compounds. One example is zinc aluminium spinel (gahnite), ZnAl$_2$O$_4$ [9,10]. It features high thermal conductivity (~18 Wm$^{-1}$K$^{-1}$) being superior to MgAl$_2$O$_4$. However, single-crystals of ZnAl$_2$O$_4$ are extremely difficult to be grown due to dissociation of zinc aluminate at high temperatures close to the melting point (1930 °C).

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In contrast, transparent ceramics can be obtained at lower temperatures and their doping by the Co$^{2+}$ ions is easier. In the present work, we report on the synthesis and study of microstructure and spectroscopic properties of a series of novel Co$^{2+}$:ZnAl$_2$O$_4$ ceramics obtained in the presence of a sintering additive (ZnF$_2$).

2. SYNTHESIS OF CERAMICS

Co:ZnAl$_2$O$_4$ powders were prepared by hydrolysis of an alcohol solution of aluminium isopropoxide using joint aqueous solution of zinc formate and cobalt nitrate, as well as an aqueous solution of zinc fluoride. Zinc aluminate powders doped with 0.02 or 0.10 at.% Co and containing 3, 6 or 10 wt% of ZnF$_2$ used as a sintering additive were obtained.

The transparent Co:ZnAl$_2$O$_4$ ceramics were synthesized by hot pressing at 1520 °C for 4 h in home-made equipment. The initial powders were pressed under 50 MPa in a steel mold (diameter: 15 mm). The hot isostatic pressing was a multiple-step process: (i) heating up to 950 °C with a constant pressure of 3 MPa, (ii) first dwell for 10 min with a constant pressure, (iii) heating up to 1200 °C with a gradual pressure rise up to 40 MPa, (iv) second dwell for 20 min with a constant pressure, (v) heating up to 1520 °C, (vi) final dwell for 4 h, (vii) free cooling. Sintering of ceramics was carried out in vacuum. The ceramic disks (diameter: 15 mm, thickness: 2 mm) had a slight blue coloration due to the cobalt doping, Fig. 1. They were polished to laser quality from both sides for further optical studies.

![Figure 1. Photographs of the polished disks of Co$^{2+}$:ZnAl$_2$O$_4$ ceramics.](image)

3. RESULTS AND DISCUSSION

3.1 Structure and morphology

The phase purity and the structure (cubic, sp. gr. O$^{h}_h$ – Fd$3$–m) of Co:ZnAl$_2$O$_4$ ceramics were confirmed by X-ray powder diffraction (XRD), see Fig. 2. No significant structure alteration with respect to undoped ZnAl$_2$O$_4$ (ICSD card #009559) is observed. In the spinel structure, the Co$^{2+}$ ions are expected to replace the Zn$^{2+}$ ones in $T_d$ sites. The lattice constant $a$ for ceramics was weakly dependent on the ZnF$_2$ content. For the ceramic sample prepared from powders containing 0.1 at.% Co and 3 wt% ZnF$_2$, $a = 8.087$ Å.

![Figure 2. X-ray powder diffraction (XRD) pattern of ceramic sample prepared from powders containing 0.1 at.% Co and 3 wt% ZnF$_2$, numbers denote the Miller's indices (hkl), red peaks – theoretical pattern of undoped ZnAl$_2$O$_4$.](image)
distribution. There was a certain dependence of the grain size on the position in the ceramic disk: larger grains were found in the central part and smaller grains at the periphery of the disk. The mean grain size was determined by counting >100 crystallites for each sample. The grain size distribution for series of ceramic samples synthesized from powders containing 0.1 / 0.02 at.% Co and 3, 6 or 10 wt% ZnF$_2$ is shown in Fig. 4.

![Figure 3](https://photonicsforenergy.spiedigitallibrary.org/conference-proceedings-of-spie.org/storage/images/00113570E-3.png)

**Figure 3.** SEM image of the fracture surface of the Co:ZnAl$_2$O$_4$ ceramic sample prepared from powders containing 0.02 at.% Co and 10 wt% ZnF$_2$.

![Figure 4](https://photonicsforenergy.spiedigitallibrary.org/conference-proceedings-of-spie.org/storage/images/00113570E-3.png)

**Figure 4.** Grain size distribution for the series of Co:ZnAl$_2$O$_4$ ceramic samples synthesized from powders containing 0.1 / 0.02 at.% Co and 3, 6 or 10 wt% ZnF$_2$.

The effect of the ZnF$_2$ content on the mean grain size $D_{\text{grain}}$ is monitored. For 0.02 at.% Co doping, with increasing the amount of the sintering aid, first, $D_{\text{grain}}$ slightly increases (from 55 μm for 3 wt% ZnF$_2$ to 68 μm for 6 wt% ZnF$_2$) and then decreases to 60 μm for 10 wt% ZnF$_2$. More than 50% of total amount of grains are dispersed between 40 and 60 μm. A similar tendency is observed for 0.1 at.% Co doping. In general, the $D_{\text{grain}}$ values are larger than those observed for an undoped ZnAl$_2$O$_4$ ceramics ($D_{\text{grain}} = 40$ μm, using the same shape factor) produced by a similar method with 6 wt% ZnF$_2$ [11].

### 3.2 Raman spectra

The structure of ceramics was confirmed by Raman spectroscopy, Fig. 5. According to the group-theory analysis, the irreducible representations at the Γ point ($k = 0$) of the Brillouin zone are the following: Γ = $A_{1g} + E_g + T_{1u} + 3T_{2g} + 2A_{2u} + 2E_u + 5T_{1u} + 2T_{2u}$ [12]. Five modes ($A_{1g}$, $E_g$ and $3T_{2g}$) are Raman-active, five ($5T_{1u}$) are IR-active and other are acoustic or silent. In the Raman spectra of ceramics, all five modes are observed at 195 cm$^{-1}$ ($T_{2g}$), 417 cm$^{-1}$ ($E_g$), ~510 cm$^{-1}$ ($T_{2g}$), 657 cm$^{-1}$ ($T_{2g}$) and ~800 cm$^{-1}$ ($A_{1g}$). The spectra are weakly dependent on the starting composition. The two most intense modes are due to the motion of Al and O atoms [13].

![Figure 5](https://photonicsforenergy.spiedigitallibrary.org/conference-proceedings-of-spie.org/storage/images/00113570E-3.png)
A careful inspection of the Raman spectra did not reveal characteristic vibrations of possible fluoride phases (CoF$_2$ or ZnF$_2$). In particular, for CoF$_2$, these are 68, 246, 366 and 494 cm$^{-1}$ [14] and for and for ZnF$_2$ – 70, 253, 350 and 522 cm$^{-1}$ [15].

![Unpolarized Raman spectra of Co:ZnAl$_2$O$_4$ transparent ceramics (the spectra are shifted for the sake of comparison), $\lambda_{exc} = 514$ nm (Ar$^+$ ion laser line).](image)

### 3.3 Absorption spectra

The transmission spectra of the polished ceramic disks with the same thickness $t$ of 2.0 mm are shown in Fig. 6. The spectra contain two intense absorption bands attributed to Co$^{2+}$ ions in $T_d$ sites: at 0.5–0.7 μm (the $^4A_2$($^4F$) $\rightarrow$ $^4T_1$($^4P$) transition) and at 1.1–1.6 μm (the $^4A_2$ $\rightarrow$ $^4T_1$($^4F$) transition). For the fixed Co concentration in the precursor powders and with the increase of the content of the ZnF$_2$ sintering additive, the absorption in both bands gradually decreased indicating that the actual concentration of Co$^{2+}$ ions depends on the ZnF$_2$ content.

![In-line transmission spectra of Co:ZnAl$_2$O$_4$ polished ceramic disks (thickness: 2.0 mm).](image)

At the wavelength of ~2 μm (out of Co$^{2+}$ absorption), the measured in-line transmission of the ceramic disks $T$ is in the range of 83.2–84.0%, slightly depending on the initial composition. This is close to the theoretical value ($T = 84.8\%$, assuming a refractive index $n = 1.780$). The single-term Sellmeier equation for ZnAl$_2$O$_4$ is the following [16]:

$$\frac{1}{n(\lambda)^2} - 1 = \frac{A}{\lambda^2} + B,$$

where $A = 56 \times 10^{-16}$ m$^2$ and $B = 0.4628$ are the Sellmeier coefficients and the light wavelength ($\lambda$) is expressed in m. The dispersion of the refractive index of ZnAl$_2$O$_4$ and the theoretical transmission curve determined by the Fresnel losses at the uncoated surfaces are shown in Fig. 7.
3.4 Luminescence

The luminescence spectra of as-sintered Co:ZnAl$_2$O$_4$ ceramics are shown in Fig. 8. The spectra contain an intense band centered at ~645 nm (emission bandwidth: 43 nm) and a weak and broad band centered at ~860 nm both ascribed to Co$^{2+}$ ions in $T_d$ sites. The spin-allowed transitions in emission occur from the $^4T_1(^4P)$ state to the lower-lying $^4A_2(^4F)$ and $^4T_2(^4F)$ ones, respectively. The doublet states $^2E$ and $^2T_1(^2G)$ in Co:ZnAl$_2$O$_4$ are lying slightly below the $^4T_1(^4P)$ state and their populations are thermalized at room-temperature. Thus, $^2E(^2G)$ is the emitting state.

With the increase of the actual Co$^{2+}$ concentration in $T_d$ sites or, equivalently, with the decrease of the ZnF$_2$ content in the precursor powders, the luminescence intensity gradually increases while no significant change of the spectral shape is observed. No concentration-quenching is observed.

Other spectral features are the sharp emission lines at 676–723 nm and a weak and broad emission centered at ~740 nm, Fig. 8. Previously, we demonstrated [10] that gahnite ceramics and glass-ceramics contain chromium (Cr$^{3+}$) impurity ions that come with the ZnO raw material. The sharp emission lines at 676–723 nm are due to Cr$^{3+}$ ions substituting the Al$^{3+}$ cations in octahedral (O$_h$) sites in the spinel structure (the so-called N-lines) [17]. The broad emission centered at ~740 nm is assigned to the structure defects [18]. In particular, the transitions from the conduction band (CB) or shallow donor defect states (e.g., Al*$_{Zn}$ – aluminium antisite defects) to deep donor defect states (V*$_{O}$ – oxygen vacancies) may explain this emission.

To conclude, we systematically study the effect of the sintering additive (ZnF$_2$) on the microstructure, vibronic properties, optical absorption and luminescence of Co$^{2+}$:ZnAl$_2$O$_4$ transparent ceramics synthesized by the hot pressing method. We reveal a relation between the presence of ZnF$_2$ and the actual Co$^{2+}$ concentration in $T_d$ sites which is relevant for the development of saturable absorbers for the spectral range of ~1.5–1.6 μm, the wavelengths of interest for

![Figure 7. Dispersion of refractive index (after [16]) and the calculated theoretical transmission curve for ZnAl$_2$O$_4$.](image_url)
passive Q-switching of Erbium lasers. The ongoing studies focus on the measurements of LIDT of ceramics and their applications in pulsed lasers.

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