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► **To cite this version:**

Sharvane Mauree, Kirill Ereemeev, Guillaume Durand, Pavel Loiko, Alexandre Le Coz, et al.. Fabrication and emission properties of Cr²⁺-doped ZnS hot-pressed transparent ceramics. Advanced Solid State Lasers Conference, Oct 2023, Tacoma, United States. 10.1364/asl.2023.sd1.2 . hal-04356009

HAL Id: hal-04356009

<https://hal.science/hal-04356009>

Submitted on 17 Sep 2024

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Fabrication and Emission Properties of Cr²⁺-Doped ZnS Hot-Pressed Transparent Ceramics

Sharvane Mauree¹, Kirill Ereemeev^{2,*}, Guillaume Durand¹, Pavel Loiko², Alexandre Le Coz¹, Marine Poitou¹, Florent Starecki¹, Virginie Nazabal¹, Patrice Camy², Alain Braud² and Odile Merdrignac-Conanec^{1,**}

¹Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes – UMR 6226, 35000 Rennes, France

²Centre de Recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252 CEA-CNRS-ENSICAEN, Université de Caen Normandie, 6 Boulevard Maréchal Juin, 14050 Caen Cedex 4, France

*kirill.eremeev@ensicaen.fr **odile.merdrignac@univ-rennes.fr

Abstract: Transparent Cr²⁺-doped zinc sulfide ceramics are fabricated by hot pressing at 950 °C / 120 MPa and their structure and emission properties are studied. The ceramics exhibit broadband emission and a long ⁵E(⁵D) lifetime (~6 μs). © 2023 The Author(s)

1. Introduction

Zinc chalcogenide (ZnS, ZnSe) crystals doped with transition-metal ions (e.g., Cr²⁺, Fe²⁺) attract attention as broadband gain media and efficient saturable absorbers of lasers operating in the near- and mid-infrared. Such wide bandgap II-IV semiconductors feature broadband transparency, tetrahedral coordination for the dopant ions and low phonon energies. The latter leads to a weak non-radiative path and increased quantum yield of luminescence at room temperature. Cr²⁺-doped zinc sulfide (ZnS) is a known material for broadly tunable and femtosecond mode-locked lasers emitting at 2.1–2.5 μm according to the ⁵E → ⁵T₂(⁵D) transition [1]. Cr²⁺:ZnS of high quality is commonly fabricated by chemical vapor deposition followed by hot isostatic pressing and chromium doping is ensured via thermal diffusion. This process is complex and costly, and the resulting elements suffer from moderate LIDT and non-uniform Cr²⁺ distribution.

Hot pressing (HP) presents a viable alternative to the above-mentioned process. Recently, we produced transparent ZnS ceramics from high purity nanopowders obtained via an original combustion method and further densified by hot pressing [2]. In the present work, we extend this work to Cr²⁺-doped ZnS transparent ceramics.

2. Synthesis and characterization of ceramics

Cr²⁺-doped ZnS precursor powders were prepared by solution combustion method from a homogeneous solution of zinc and chromium nitrates. A wide range of Cr concentrations was explored, from 50 to 3000 ppm. As-combusted powders were heat-treated in H₂S/N₂ (10/90) flow in a tubular furnace at 600 °C for 2 h [2]. The powders were subsequently densified by HP under vacuum (about 10⁻¹ mbar) at 950 °C in a 20 mm diameter graphite die. The heating rate was 10 °C/min and a pressure of 120 MPa was applied for 6 h. After HP, the samples were optically polished using 0.5 μm alumina powder. Figure 1(a) shows photographs of ZnS ceramics with different Cr doping levels. A typical SEM image of the ceramic with 250 ppm Cr is shown in Fig. 1(b). All the samples exhibited a dense and homogeneous microstructure made up of μm-sized polyhedral grains with some residual pores. An X-ray diffraction study showed that the ceramics could be readily indexed as cubic zincblende being as the major phase with a small content of the hexagonal wurtzite structure, Fig. 1(c). Traces of a secondary phase identified as ZnCr₂S₄ were observed for ≥ 1500 ppm Cr due to the solubility limit of Cr in the cubic ZnS structure.

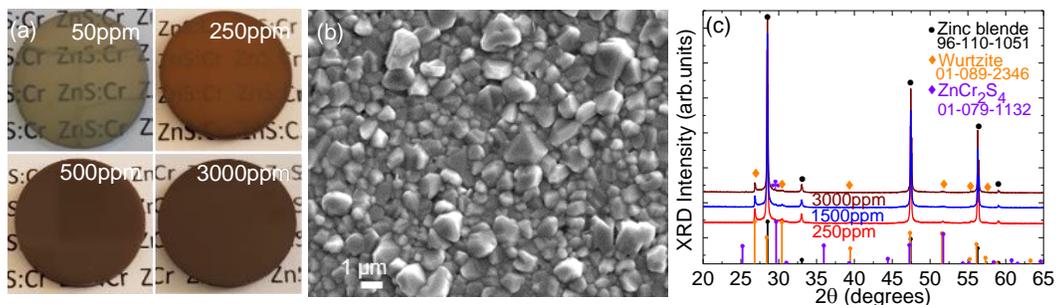


Fig. 1. Hot-pressed Cr²⁺:ZnS ceramics: (a) photographs of polished ceramic disks doped with 50, 250, 500 and 3000 ppm Cr; (b) a SEM image of a thermally etched surface of ceramic with 250 ppm Cr; (c) X-ray diffraction (XRD) patterns of ceramics.

The Raman spectra of Cr²⁺-doped ZnS ceramics are shown in Fig. 2(a). The observed Raman spectra are typical for zincblende-type ZnS. The latter belongs to the point group T_d with two atoms per primitive unit cell and three

optical phonons, which are doubly degenerate $T_2(\text{TO})$ phonons and a single $T_2(\text{LO})$ one. The most intense Raman peak at 349 cm^{-1} is due to the $T_2(\text{LO})$ phonon. The highest energy peak at 669 cm^{-1} is due to the $2(\text{LO})$ process at the Γ -point. The FTIR spectra of the undoped and Cr^{2+} -doped ceramics are shown in Fig. 2(b). ZnS characteristic phonon vibrations lead to the band at $15.2\text{ }\mu\text{m}$ while the weak band at $11\text{ }\mu\text{m}$ is the signature of the S – O vibration. The absorption at $1.7\text{ }\mu\text{m}$ changes nearly linearly with the Cr content and is assigned to the ${}^5T_2 \rightarrow {}^5E({}^5D)$ transition of Cr^{2+} ions in tetrahedral (T_d) sites in ZnS. The theoretical maximum transmission of zinc sulfide in the mid-infrared determined by Fresnel losses is about 75%. The transmission of undoped ceramic is close to this value. Upon Cr doping, the transmission of ceramics decreases while staying reasonably high for doping levels up to 1000 ppm.

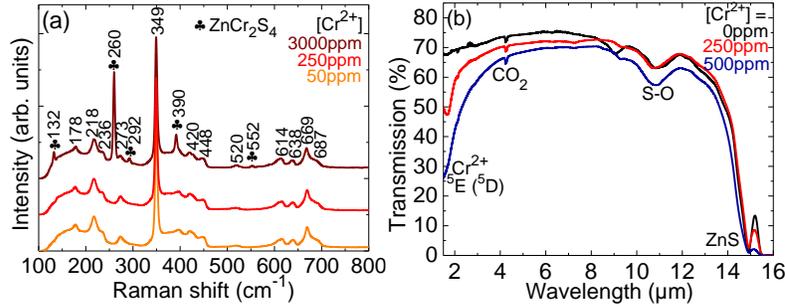


Fig. 2. Hot-pressed Cr^{2+} :ZnS ceramics: (a) Raman spectra, $\lambda_{\text{exc}} = 514\text{ nm}$; (b) IR transmission spectra.

3. Emission properties

Figure 3(a) shows the luminescence spectra of the zinc sulfide ceramic with 250 ppm Cr. They were measured under excitation at 1550 nm over a broad range of temperatures ($12 - 300\text{ K}$). The observed emission is assigned to the ${}^5E \rightarrow {}^5T_2({}^5D)$ transition of Cr^{2+} ions in T_d sites in zinc blende ZnS. At room temperature, the emission spectrum is very broad spanning from 1.6 to $3\text{ }\mu\text{m}$ with a maximum at $1.91\text{ }\mu\text{m}$ and a bandwidth of $\sim 400\text{ nm}$. The spectral broadening observed at 12 K is assigned to the disorder associated with random stacking faults in hot-pressed zinc sulfide. A typical luminescence decay curve for Cr^{2+} ions (measured for ceramic doped with 250 ppm Cr) is plotted in Fig. 3(b), revealing a single-exponential behavior. The luminescence lifetime τ_{lum} slightly decreased with Cr doping, from $6.2\text{ }\mu\text{s}$ (50 ppm) to $5.5\text{ }\mu\text{s}$ (3000 ppm). The temperature behavior of τ_{lum} for the 250 ppm Cr-doped ceramic is shown in Fig. 3(c), indicating a relatively weak non-radiative path.

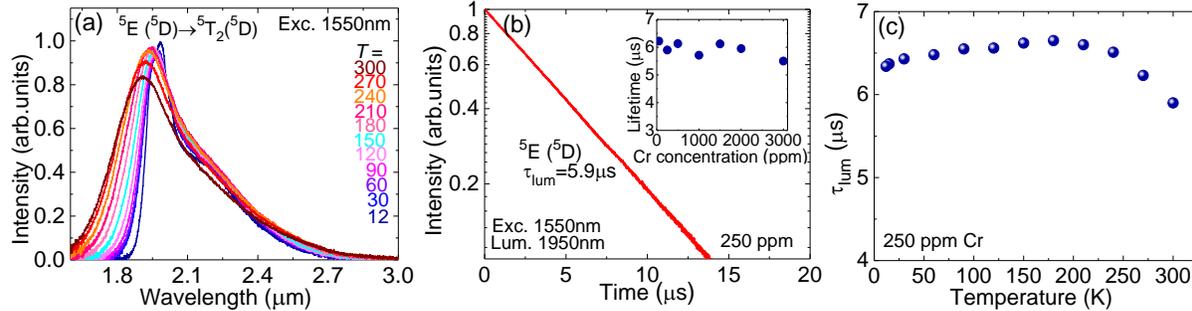


Fig. 3. Emission properties of Cr^{2+} ions (the ${}^5E \rightarrow {}^5T_2({}^5D)$ transition) in the hot-pressed zinc sulfide ceramic doped with 250 ppm Cr: (a) luminescence spectra for the range of temperatures of $12 - 300\text{ K}$, $\lambda_{\text{exc}} = 1550\text{ nm}$; (b) RT luminescence decay curve, $\lambda_{\text{exc}} = 1550\text{ nm}$, $\lambda_{\text{lum}} = 1950\text{ nm}$, *inset* – luminescence lifetime τ_{lum} as a function of Cr^{2+} concentration; (c) temperature dependence of τ_{lum} .

4. Conclusion

To conclude, we report on a viable route of fabrication of transparent zinc sulfide ceramics doped with Cr^{2+} ions by hot pressing of chromium-doped powders prepared by solution combustion method. The ceramics doped up to 1000 ppm Cr feature a dense and homogeneous microstructure made up of μm -sized polyhedral grains (densification: 99.7%), high transmission in the mid-infrared and a long lifetime of the ${}^5E({}^5D)$ level ($\sim 6\text{ }\mu\text{s}$).

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