



**HAL**  
open science

## **Fabrication and emission properties of Cr<sup>2+</sup>-doped ZnS hot-pressed transparent ceramics**

Sharvane Mauree, Kirill Eremeev, Guillaume Durand, Pavel Loiko, Alexandre Le Coz, Marine Poitou, Florent Starecki, Virginie Nazabal, Patrice Camy, Alain Braud,  
et al.

### ► To cite this version:

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

**HAL Id: hal-04356009**

**<https://hal.science/hal-04356009v1>**

Submitted on 17 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

# Fabrication and Emission Properties of Cr<sup>2+</sup>-Doped ZnS Hot-Pressed Transparent Ceramics

Sharvane Mauree<sup>1</sup>, Kirill Ereemeev<sup>2,\*</sup>, Guillaume Durand<sup>1</sup>, Pavel Loiko<sup>2</sup>, Alexandre Le Coz<sup>1</sup>, Marine Poitou<sup>1</sup>, Florent Starecki<sup>1</sup>, Virginie Nazabal<sup>1</sup>, Patrice Camy<sup>2</sup>, Alain Braud<sup>2</sup> and Odile Merdrignac-Conanec<sup>1,\*\*</sup>

<sup>1</sup>Université de Rennes, CNRS, Institut des Sciences Chimiques de Rennes – UMR 6226, 35000 Rennes, France

<sup>2</sup>Centre 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 Cr<sup>2+</sup>-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 <sup>5</sup>E(<sup>5</sup>D) lifetime (~6 μs). © 2023 The Author(s)

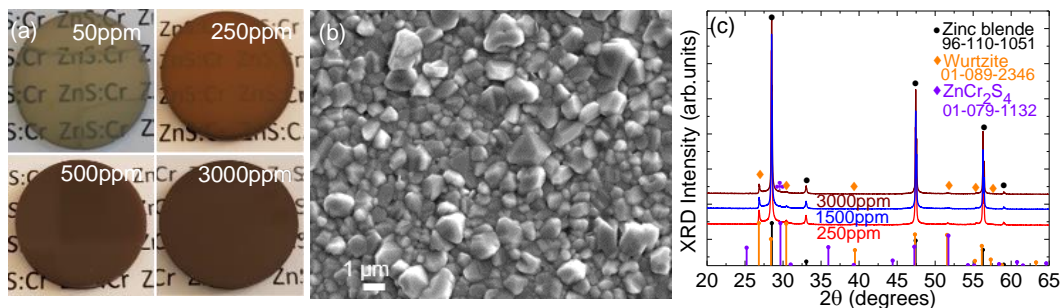
## 1. Introduction

Zinc chalcogenide (ZnS, ZnSe) crystals doped with transition-metal ions (e.g., Cr<sup>2+</sup>, Fe<sup>2+</sup>) 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. Cr<sup>2+</sup>-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 <sup>5</sup>E → <sup>5</sup>T<sub>2</sub>(<sup>5</sup>D) transition [1]. Cr<sup>2+</sup>: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 Cr<sup>2+</sup> 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 Cr<sup>2+</sup>-doped ZnS transparent ceramics.

## 2. Synthesis and characterization of ceramics

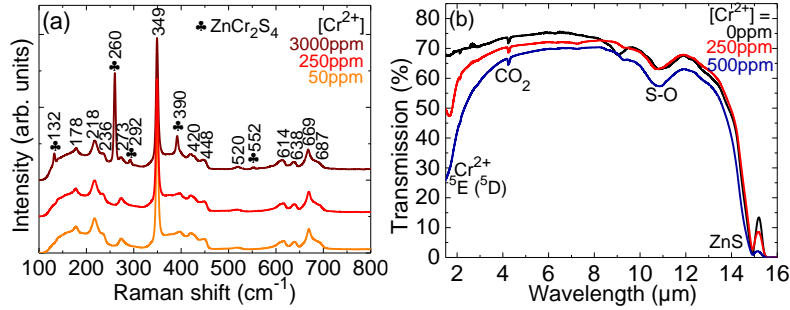
Cr<sup>2+</sup>-doped ZnS precursor powders were prepared by solution combustion method from a homogeneous solution of zinc and chromium nitrates. A wide range of Cr concentrations was explored, from 50 to 3000 ppm. As-combusted powders were heat-treated in H<sub>2</sub>S/N<sub>2</sub> (10/90) flow in a tubular furnace at 600 °C for 2 h [2]. The powders were subsequently densified by HP under vacuum (about 10<sup>-1</sup> 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 ZnCr<sub>2</sub>S<sub>4</sub> were observed for ≥ 1500 ppm Cr due to the solubility limit of Cr in the cubic ZnS structure.



**Fig. 1.** Hot-pressed Cr<sup>2+</sup>: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 Cr<sup>2+</sup>-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<sub>d</sub> with two atoms per primitive unit cell and three

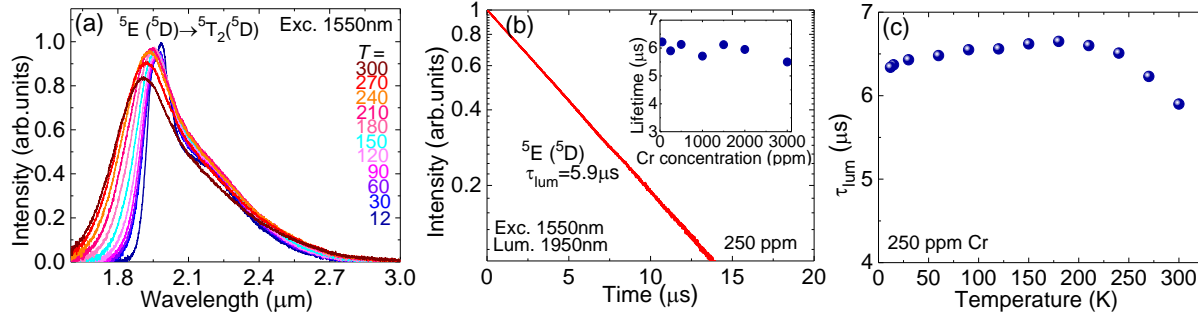
optical phonons, which are doubly degenerate  $T_2(\text{TO})$  phonons and a single  $T_2(\text{LO})$  one. The most intense Raman peak at  $349\text{ cm}^{-1}$  is due to the  $T_2(\text{LO})$  phonon. The highest energy peak at  $669\text{ cm}^{-1}$  is due to the  $2(\text{LO})$  process at the  $\Gamma$ -point. The FTIR spectra of the undoped and  $\text{Cr}^{2+}$ -doped ceramics are shown in Fig. 2(b).  $\text{ZnS}$  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  $\text{S}-\text{O}$  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  $\text{Cr}^{2+}$  ions in tetrahedral ( $T_d$ ) sites in  $\text{ZnS}$ . 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  $\text{Cr}^{2+}:\text{ZnS}$  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  $1550\text{ nm}$  over a broad range of temperatures ( $12 - 300\text{ K}$ ). The observed emission is assigned to the  ${}^5E \rightarrow {}^5T_2({}^5D)$  transition of  $\text{Cr}^{2+}$  ions in  $T_d$  sites in zinc blende  $\text{ZnS}$ . 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  $12\text{ K}$  is assigned to the disorder associated with random stacking faults in hot-pressed zinc sulfide. A typical luminescence decay curve for  $\text{Cr}^{2+}$  ions (measured for ceramic doped with 250 ppm Cr) is plotted in Fig. 3(b), revealing a single-exponential behavior. The luminescence lifetime  $\tau_{\text{lum}}$  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  $\tau_{\text{lum}}$  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  $\text{Cr}^{2+}$  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  $\tau_{\text{lum}}$  as a function of  $\text{Cr}^{2+}$  concentration; (c) temperature dependence of  $\tau_{\text{lum}}$ .

### 4. Conclusion

To conclude, we report on a viable route of fabrication of transparent zinc sulfide ceramics doped with  $\text{Cr}^{2+}$  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  $\mu\text{m}$ -sized polyhedral grains (densification: 99.7%), high transmission in the mid-infrared and a long lifetime of the  ${}^5E({}^5D)$  level ( $\sim 6\text{ }\mu\text{s}$ ).

### References

- [1] S. Mirov, V. Fedorov, I. Moskalev, D. Martyshkin, and C. Kim, "Progress in  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$  doped mid-IR laser materials," *Laser Photon. Rev.* **4**(1), 21-41 (2010).
- [2] G. R. Durand, N. Hakmeh, V. Dorcet, V. Demange, F. Chevire, and O. Merdrignac-Conanec, "New insights in structural characterization of transparent  $\text{ZnS}$  ceramics hot-pressed from nanocrystalline powders synthesized by combustion method," *J. Eur. Ceram. Soc.* **39**(10), 3094-3102 (2019).