# High-Performance Co-Doped Photorefractive Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> Crystals

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## Introduction

The  $Sn_2P_2S_6$  crystals are known as efficient photorefractive materials, that can be efficiently modified by their doping [1,2]. Our recent works are directed to a search for the new efficient dopants and their combinations, which are provided by two methods: growth in the presence of two types of impurities, and by the indiffusion of the metals (Cu, Ag) into previously grown samples [3]. In the communication, we present the results of the investigations of the optical and photorefractive parameters of the co-doped  $Sn_2P_2S_6$ :(Sb,Cu) crystals which demonstrate the best parameters.

### Experiments

In course of our works, the various double-doped  $Sn_2P_2S_6$  samples were grown using a conventional vapor-transport technique. We checked different combinations of the Sb (or Te), which, as were shown before [1,2], are the most efficient photorefractive dopants, with one of two metals, Ag and Cu, that were used for modification of the  $Sn_2P_2S_6$  by the thermo-induced atom indiffusion [3]. It was founded that the most promising compound for photorefractive applications is the  $Sn_2P_2S_6$  sample co-doped by a combination of Cu and Sb, with the equal concentrations of about 1 mol.%. Other dopant combinations, like Te+Cu, Te+Ag, and Sb+Ag, did not led to the enhancements of the photorefractive parameters, and demonstrated increased DC conductivity. So, the main attention was applied to the Sb+Cu co-doped crystals.

The measurements of the optical transmission spectra in these co-doped samples show that they are similar to the case of the Sb-doped  $Sn_2P_2S_6$  crystals. The experiments on the photorefractive two-wave mixing were carried using He-Ne laser irradiation (633 nm). The measured max values of the two-wave mixing gain are  $\Gamma$ =15 cm<sup>-1</sup> (at 1 um grating period and 0.3 W·cm<sup>-2</sup> light beam intensity). The gain value depends on the light intensity and reduces down to 10 cm<sup>-1</sup> at 0.1 W·cm<sup>-2</sup>, that is less as compared with the case of the  $Sn_2P_2S_6$ :Sb1% crystal [1,2]. But, the main advantage of the photorefractive effect in the  $Sn_2P_2S_6$ :Sb.Cu composition is the single-exponential dynamics of the photorefractive response when the formation of the space-charge grating occurs practically without the compensation processes that are usually observed in other doped (and double-doped)  $Sn_2P_2S_6$  crystals. Also, the amplified signal demonstrates good stability, in comparison with the case of the Sb-doped  $Sn_2P_2S_6$ .

These Sb+Cu co-doped crystals, due to high enough two-wave mixing gain at 633 nm and temporal stability of the gain, allows realizing various photorefractive schemes on their base. This is illustrated by studying the performances of several optical schemes, namely: the dynamic interferometer based on the two-wave mixing, the ring-loop and the semi-linear oscillator scheme

with high efficiency and low generation threshold compared with other doped photorefractive  $Sn_2P_2S_6$  compounds.

# Modelling

The obtained experimental results well correlate with our modelling performed by means of the ab initio calculations of the electron spectra in the  $\mathrm{Sn_2P_2S_6}$  lattice with various defects. The calculations provide an information about the energy of the defect levels in the gap, and also the most probable positions of the dopant that can be determined by minimization of the total energy of the cell at various defect positions. Also this model allows estimating the variations of the physical parameters of the crystal induced by the impurity.

The model calculation of the electron spectra in the  $Sn_2P_2S_6$  lattice with two defects (Cu and Sb) in the same cell give an explanation of the absence of the compensations processes in the double-doped crystal. As it was shown by the photo-EPR studies [4], the  $Sb^{3+}$  impurity replaces the  $Sn^{2+}$  cations, and become charge-compensated due to appearance the Sn vacancies:  $(3Sn^{2+} + 2V_{Sn}^{2-})^0$ . This leads to formation the defects of two types, and can be a reason of the electron-hole compensation at the formation of the photorefractive holograms in the Sb-doped crystals. The  $Cu^{1+}$  impurity, located near  $Sb^{3+}$ , can compensate the appearance of the Sn vacancy. As it follows from the calculated electron spectra, the additional electron states originated from the Sb and Cu adatoms correspond to the same energy, and so are forming the single defect electron level in the gap. This correlates with the single-exponential dynamics of the space-charge grating formation, that is predicted by a single-level model of the photorefractive effect.

### Conclusions

Thus, the co-doping of the Sn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystals with Sb and Cu is a promising way to enhance their photorefractive parameters. This modification allows to obtain the photorefractive grating which is stable in time and does not demonstrate significant compensation processes.

### References

- [1] T. Bach, M. Jazbinšek, G. Montemezzani, P. Günter, A. Grabar, and Yu. Vysochanskii, J. Opt. Soc. Am. B 24, 1535 (2007).
- [2] A. A. Grabar, M. Jazbinšek, A. N. Shumelyuk, Yu. M. Vysochanskii, G. Montemezzani and P. Günter. Photorefractive effects in  $Sn_2P_2S_6$ . In: "Photorefractive Materials and Their Applications II". Springer, New York 327 (2007).
- [3] V. Shvalya, J. Zavašnik, V. Nasretdinova, H. Uršič, J. Kovač, A. Grabar, A. Kohutych, A. Molnar, D. R. Evans, D. D. Mihailović, U. Cvelbar, J. Mater. Chem. C 8, 9975 (2020).
- [4] B. E. Kananen, E. M. Golden, S. A. Basun, D. R. Evans, A. A. Grabar, I. M. Stoika, W. McClory, N. C. Giles, L. E. Halliburton, Optical Materials Express 6(12), 3992 (2016).