

## In-, Au-, and Cu-bearing sphalerites studied by X-ray absorption spectroscopy

A.L. Trigub<sup>1,2</sup>, O.N. Filimonova<sup>2</sup>, D.E. Tonkacheev<sup>2</sup>, M.S. Nickolsky<sup>2,3</sup>, K.O. Kvashnina<sup>4,5</sup>,  
D.A. Chareev<sup>6,7</sup>, I.V. Chaplygin<sup>2</sup>, E.V. Kovalchuk<sup>2</sup>, S. Lafuerza<sup>4</sup>, B.R. Tagirov<sup>2</sup>

<sup>1</sup>National Research Centre 'Kurchatov Institute', 1 Akademika Kurchatova pl., Moscow, Russian Federation,

<sup>2</sup>Institute of Geology of Ore Deposits (IGEM RAS), Moscow, Russian Federation, <sup>3</sup>Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russian Federation, <sup>4</sup>ESRF-EFiguropian Synchrotron Radiation Facility, Grenoble, France, <sup>5</sup>Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, Dresden, Germany, <sup>6</sup>Institute of Experimental Mineralogy (IEM RAS), Chernogolovka, Moscow Region, Russian Federation, <sup>7</sup>Institute of Physics and Technology, Ural Federal University, Ekaterinburg, Russian Federation, [alexander.trigub@gmail.com](mailto:alexander.trigub@gmail.com)

Sphalerite is the main source of In- A 'critical' metal widely used in high-tech electronics. In this mineral the concentration of In is commonly correlated directly with Cu content. Here we use X-ray absorption spectroscopy of synthetic compounds and natural crystals in order to investigate the substitution mechanisms in sphalerites where In is present, together with the group 11 metals. All the admixtures (Au, Cu, In) are distributed homogeneously within the sphalerite matrix, but their structural and chemical states are different. Sphalerite with In, Au and Cu admixtures was studied by XANES/EXAFS spectroscopy techniques and by means of DFT calculations. Results of our work showed that in all the samples investigated In<sup>3+</sup> replaces Zn in the structure of sphalerite. Gold in synthetic sphalerites is coordinated with sulfur. Our EXAFS data suggest that at high Au concentrations (0.03-0.5 wt.%) the Au<sub>2</sub>S clusters predominate, with a small admixture of the Au<sup>+</sup> solid solution with an Au-S distance of 2.5 Å. In contrast to Au, the presence of Cu<sup>+</sup> with In exists only in the solid-solution state, where it is tetrahedrally coordinated with S atoms at a distance of 2.30 ± 0.03 Å. The distant coordination shells of Cu are disordered. These results demonstrate that the group 11 metals (Cu, Ag and Au) can exist in sphalerite in the metastable solid-solution state. The solid solution forms at high temperature via the charge compensation scheme 2Zn<sup>2+</sup> Me<sup>+</sup>+Me<sup>3+</sup>. The final state of the trace elements at ambient temperature is governed by the difference in ionic radii with the main component (Zn), and concentration of admixtures. This study was supported by the Russian Science Foundation grant No. 18-77-00078.