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# The Mössbauer Spectroscopy and Analytical Investigations of the Polycrystalline Compounds with General Formula $Zn_xSn_yCr_zSe_4$

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We present combined X-ray powder diffraction and Mössbauer  $^{119}\text{Sn}$  studies of polycrystalline compounds with a general formula  $Zn_xSn_yCr_zSe_4$  (where  $x + y + z \approx 3$ ). The obtained single-phase compounds crystallize in the spinel cubic structure —  $Fd\bar{3}m$ . Tin ions are found to occupy both tetrahedral and octahedral sublattices. On the contrary to the strong tetrahedral site preference energy of Sn, the presented data strongly suggest that the increase in lattice parameters with Sn doping is caused by Sn ions that incorporated into octahedral positions. A quadrupole and isomer shifts of  $^{119}\text{Sn}$  in  $(\text{SnSe}_4)^{6-}$  and  $(\text{SnSe}_6)^{4-}$  are also reported.

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## 1. Introduction

The parent compound of the studied solid solutions of  $ZnCr_2Se_4$  crystallizes in the  $MgAl_2O_4$ -type normal spinel cubic structure (space group  $Fd\bar{3}m$ ). Zinc and chromium, respectively, are tetrahedrally and octahedrally coordinated in the cubic close packing of selenium atoms, and the lattice parameter has a value  $a_0 = 10.4891 \text{ \AA}$  [1]. The expected formal valence states in the family of compounds with the general formula  $AB_2X_4$ , are 2+ for “A” atoms and 3+ for “B” atoms.

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Therefore substituting site “A” with another divalent atom (i.e. Sn for Zn) should not change the charge distribution in the system.

However, it is worth investigating how the various ionic radii of the dopant and the chemical disorder induced in solid solution will influence the magnetic properties of the basic material. First of the effects will change the effective Cr–Cr distance and therefore modify the magnetic interaction between the magnetic ions, the second one will create a random distribution of magnetic interactions and both can lead to a spin glass state.

At room temperature,  $\text{ZnCr}_2\text{Se}_4$  is a *p*-type semiconductor with a magnetic spiral structure (spiral angle  $\phi = 42 \pm 1^\circ$ ) [2]. Its Néel temperature is 20 K and the paramagnetic Curie–Weiss temperature is 115 K [3–5]. The magnetic properties result from the near-neighbor ferromagnetic Cr–Cr and the more distant neighbor antiferromagnetic Cr–Se–Cr interactions, and it has already been shown that the system can be easily substituted at various sites [6, 7]. Polycrystalline quaternary compounds with spinel structure containing zinc, tin, and selenium are not known in the literature. In this paper, we report the synthesis of polycrystalline samples from their binary constituents  $\text{ZnSe}$ – $\text{SnSe}$ – $\text{Cr}_2\text{Se}_3$ , and the results of their analytical and magnetic studies with an aim to show the effect of tin substitution on the cation distribution and magnetic properties of these spinels.

## 2. Experimental procedure

### 2.1. Samples preparation

The polycrystalline compounds of the general formula  $\text{Zn}_x\text{Sn}_y\text{Cr}_z\text{Se}_4$  (where  $x = 0.2, 0.3$ ) were obtained by ceramic technology in two steps. At first, the binary selenides were obtained by annealing the stoichiometric mixtures prepared of elements: Zn, Sn, Cr, and Se. All elements were of 5N purity. Secondly, the  $\text{Zn}_{1-x}\text{Sn}_x\text{Cr}_2\text{Se}_4$  compounds were synthesized from stoichiometric amounts of binary selenides:  $\text{ZnSe}$ ,  $\text{SnSe}$  and  $\text{Cr}_2\text{Se}_3$ . The mixtures were pulverized in an agate mortar and sealed in fused silica ampoules, which were evacuated to  $10^{-5}$  Torr. The samples were then sintered twice at 1073 K for 7 days. The compounds were again crushed into a powder, which was used for later studies. All measurements were carried out at room temperature.

### 2.2. Chemical composition

Chemical compositions of the obtained samples were determined using inductively coupled plasma — atomic emission spectrometry (ICP-AES) method. A sequential spectrometer with an excitation in the ICP plasma made by Spectro Analytical Instruments (Germany) was used with the following parameters: frequency — 27.12 MHz, power — 1.1 kW, quartz demountable torch — Ar/Ar/Ar, nebulizer gas —  $1.0 \text{ l min}^{-1}$ , nebulizer — concentric Meinhard, nebulizer pressure — 2.4 bar, sample rate —  $1.0 \text{ ml min}^{-1}$ , observation height 11 mm, holographic grating —  $2400 \text{ grooves mm}^{-1}$ , dispersion of grating in 1st reciprocal order —

0.55 nm mm<sup>-1</sup>, analytical lines (integration time) — Cr 286.511 nm (3 s); Sn 235.484 nm (5 s); Se 196.026 nm (3 s); Zn 334.502 nm (3 s).

In the preparation of the calibration curves, four standards were used. They contained the elements at the following concentration ranges: Zn and Cr 6.0 ÷ 60.0 μg ml<sup>-1</sup>, Sn 1.0 ÷ 10.0 μg ml<sup>-1</sup>, Se 20.0 ÷ 200.0 μg ml<sup>-1</sup>. Standard samples contained concentrated HNO<sub>3</sub> similarly as the samples analyzed after mineralization. The two-point recalibration was applied in the case of the spectrometrically. 65% HNO<sub>3</sub> (Merck) and deionized water were used for the experiment. The standard solutions of Cr, Sn, Zn and Se were of 1 mg ml<sup>-1</sup> concentration, made by Merck.

A spinel sample of 10 mg was put in ampoules and 1 ml of concentrated HNO<sub>3</sub> was added and heated. The mineralized samples were introduced into 25 ml volumetric flasks and diluted to the volume with distilled water.

TABLE I  
Structural parameters obtained from the Rietveld refinement for Zn<sub>x</sub>Sn<sub>y</sub>Cr<sub>z</sub>Se<sub>4</sub> series.

$x$	$R_F$ [%]	$R_{Brag}$ [%]	$R_{wp}$ [%]	$\chi^2$	Zn <sub>1-x</sub> Sn <sub>x</sub> Cr <sub>2</sub> Se <sub>4</sub>	
					$a_0$ [Å]	Coord. $u$ of Se
Nominal Zn <sub>0.8</sub> Sn <sub>0.2</sub> Cr <sub>2</sub> Se <sub>4</sub>	7.96	11.1	14.4	1.85	10.5039(2)	0.2584(2)
Zn <sub>0.87</sub> Sn <sub>0.063</sub> Cr <sub>1.98</sub> Se <sub>4.00</sub>	7.51	8.99	13.8	1.70	10.5040(2)	0.2585(2)
Nominal Zn <sub>0.7</sub> Sn <sub>0.3</sub> Cr <sub>2</sub> Se <sub>4</sub>	8.34	12.6	15.9	2.11	10.5066(3)	0.2591(3)
Zn <sub>0.71</sub> Sn <sub>0.061</sub> Cr <sub>1.88</sub> Se <sub>4.00</sub>	7.73	11.7	15.5	2.02	10.5067(3)	0.2594(3)

The molar fractions of constituent elements obtained with this procedure were finally normalized to the selenium nominal stoichiometry. The resulting compositions were found to be Zn<sub>0.87</sub>Sn<sub>0.063</sub>Cr<sub>1.98</sub>Se<sub>4.00</sub> for nominal Zn<sub>0.8</sub>Sn<sub>0.2</sub>Cr<sub>2</sub>Se<sub>4</sub> and Zn<sub>0.71</sub>Sn<sub>0.061</sub>Cr<sub>1.88</sub>Se<sub>4.00</sub> for nominal Zn<sub>0.7</sub>Sn<sub>0.3</sub>Cr<sub>2</sub>Se<sub>4</sub>. They are shown in Table I with results of the Rietveld refinement.

### 2.3. X-ray powder diffraction

X-ray powder diffraction data of polycrystalline samples were collected using a Philips X-Pert (PW3050) diffractometer (Cu K<sub>α</sub> radiation ( $\lambda_1 = 1.54056$  and  $\lambda_2 = 1.54443$  Å) over an angular range of  $2\theta$ : 10 ÷ 135°) in order to make phase analysis and to determine phase composition and lattice parameters (see Table I). First, the qualitative phase analysis was carried out. Generally, in all studied sintered compounds the presence of the spinel phase was evidenced (Fig. 1).

The Rietveld refinement was performed with the FullProf program v. 3.40 Windows [8], using at first the nominal composition for site occupancies. When the chemical analysis results became available, the procedure was repeated using the measured ratio of the elements. The comparison of these two approaches is shown in Table I and a clear improvement in the quality of the fit in the second

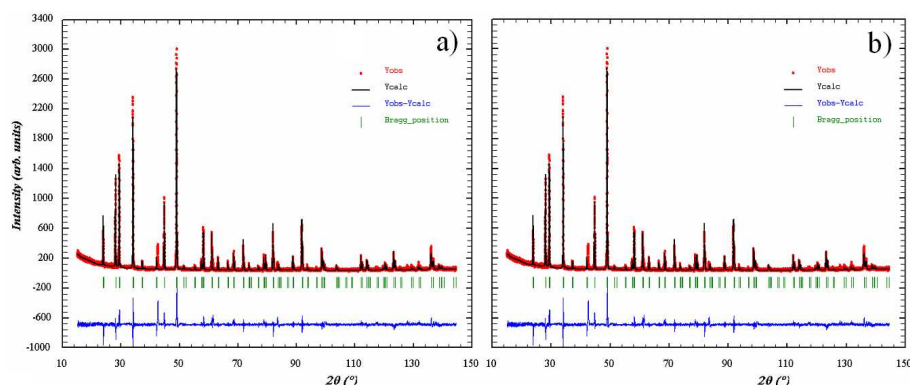


Fig. 1. Results of the Rietveld refinement obtained for:  $\text{Zn}_{0.87}\text{Sn}_{0.063}\text{Cr}_{1.98}\text{Se}_{4.00}$  (a),  $\text{Zn}_{0.71}\text{Sn}_{0.061}\text{Cr}_{1.88}\text{Se}_{4.00}$  (b).

case. The obtained lattice parameters and the anion free parameters are consistent between the models.

#### 2.4. The Mössbauer spectroscopy

The  $^{119}\text{Sn}$  Mössbauer spectra were recorded at room temperature using a constant-acceleration spectrometer. The investigated materials were pelletized using  $\text{Li}_2\text{CO}_3$  as a binder and the uniformity of the samples was confirmed by microscopic methods. The experimental spectrum shape was described with a transmission integral calculated according to the numerical Gauss-Legendre procedure.

### 3. Results and discussion

The applied preparative method allowed to obtain quaternary compounds of  $\text{ZnCr}_2\text{Se}_4$  doped with tin and X-ray phase analysis revealed only the presence of spinel phase. The actual composition showed a lower quantity of the built-in tin than the nominal composition, which was caused by tin release from the system during the sintering process.

The Mössbauer spectra were analyzed using two component associated with the two inequivalent tin ions positions in the sublattices to the spinel cubic structure. The first component was a quadrupole doublet (Q-1) connected with the share of tin in the tetrahedral sublattice, and second component was also a quadrupole doublet (Q-2) (which approximates an unresolved Zeeman sextet) connected with the share of tin in the octahedral sublattice. In Table II, we present the evolution of the values of the isomer shift (IS) and quadrupole splitting (QS) of the spectra components.

The best fit Mössbauer spectrum of the sample  $\text{Zn}_{0.87}\text{Sn}_{0.063}\text{Cr}_{1.98}\text{Se}_{4.00}$  shows that the Q-1 component associated probably with the  $(\text{Zn}_{1-\delta}\text{Sn}_\delta)\text{Cr}_2\text{Se}_4$  ( $\delta$ -parameter connected with the share of tin in the tetrahedral sublattice) phase,

TABLE II

Hyperfine parameters: isomer shift (IS) and quadrupole splitting (QS) and  $A$  — subspectral area of the investigated samples.

	Component	IS [mm/s]	QS [mm/s]	$A$ [%]
		$\pm 0.005$ [mm/s]	$\pm 0.005$ [mm/s]	$\pm 2$ [%]
$Zn_{0.87}Sn_{0.063}Cr_{1.98}Se_{4.00}$	$\delta$ -(Q-1)	1.45	2.45	68
	$\eta$ -(Q-2)	1.26	2.61	32
$Zn_{0.71}Sn_{0.061}Cr_{1.88}Se_{4.00}$	$\delta$ -(Q-1)	1.36	2.25	63
	$\eta$ -(Q-2)	1.13	2.75	37

and a Q-2 quadrupole doublet (which approximates an unresolved Zeeman sextet) that can be attributed to  $Zn_xSn_\delta Cr_ySn_\eta Se_4$  phase ( $\eta$ -parameter connected with the share of tin in the octahedral sublattice). We presented the Mössbauer spectrum in Fig. 2. This analysis clearly reveals the presence of tin in two non-

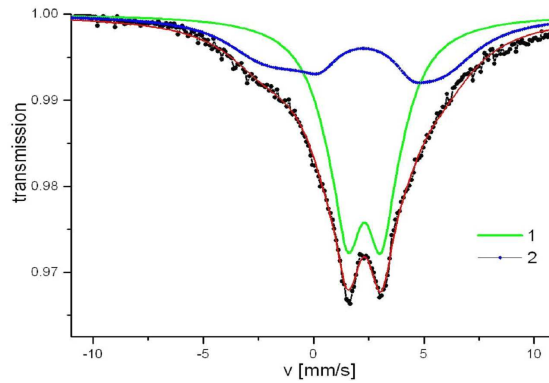


Fig. 2. The  $^{119}Sn$  Mössbauer transmission spectra for  $Zn_{0.87}Sn_{0.063}Cr_{1.98}Se_{4.00}$  sample.

-equivalent environments — namely the tetrahedral and octahedral positions. Unfortunately, in our case the Mössbauer spectroscopy is unable to distinguish between sites in the spinel structure that are nominally occupied (Wyckoff positions 8(a) and 16(d)) and unoccupied (Wyckoff positions 8(b) and 16(c)) sites. The data on isomer shift [9–11] for  $Sn(IV)Se_4$  (1.7 mm/s) and  $Sn(IV)Se_6$  (1.5 mm/s) are scarce, and usually they concern binary systems  $SnSe$  — IS = 3.40 mm/s and QS = 1.02 mm/s [12] we will only compare the results obtained for our compounds with different nominal tin concentration. Basing on the Mössbauer spectra, the percentages of the components connected with occupation of non-equivalent crystallographic positions by tin ions were defined. A significantly higher share of the  $\delta$  component indicates an occupational preference for tetrahedral lattice.

The Mössbauer spectrum of  $Zn_{0.71}Sn_{0.061}Cr_{1.88}Se_{4.00}$  sample can be also based on two components — the subspectra connected with Sn in tetrahedral

and octahedral environments. The determined change of hyperfine parameters is connected with a decrease in chromium ions and an occurrence of lattice defects. Similarly as in the case of the previous sample, a significantly higher percentage of the component connected with the share of tin in the tetrahedral sublattice was observed comparing to the component connected with the share of tin in the octahedral sublattice. However, the share of the component connected with the share of tin in the octahedral sublattice is significantly higher than in the case of the sample with higher chromium concentration.

The observation of the presence of tin in the octahedral sites is of primary importance, since it allows to explain the increase in the lattice parameters obtained from the X-ray diffraction. On the basis of the nominal compositions only, one may falsely conclude that the increase in lattice parameters is connected with the difference between ionic radii of tin and zinc ( $\text{Zn}^{2+}$  — 74 pm,  $\text{Sn}^{2+}$  — 118 pm [13]) because tin is present only in the tetrahedral position. The falseness of this interpretation is clear when one checks the result against the measured composition, where the tin concentration is almost the same in both cases. Additionally, the decrease in zinc content should introduce the vacancies, which additionally decrease the parameter.

On the other hand, if we assume that some tin is present in almost fully occupied chromium network, the increase in the unit cell size would be a simple result of the difference between the ionic radii of Cr and Sn ( $\text{Cr}^{3+}$  — 75.5 pm,  $\text{Sn}^{2+}$  — 118 pm).

The results of the Mössbauer investigations indicate a significantly higher share of the component connected with location of tin in the tetrahedral sublattice. However, in the case of  $\text{Zn}_{0.71}\text{Sn}_{0.061}\text{Cr}_{1.88}\text{Se}_{4.00}$  sample, the share of the component connected with the location of tin in the octahedral sublattice is higher. The fact is probably connected with lower Cr concentration in the sample.

Unfortunately, the re-analysis of our X-ray data using the tin distribution between tetrahedral and octahedral sites is insensitive to the distribution ratio and the refinement cannot be improved.

#### 4. Conclusions

The combined analysis using the Mössbauer spectroscopy and the X-ray powder diffraction revealed that the increase in lattice parameters caused by Sn doping in  $\text{ZnCr}_2\text{Se}_4$  is caused by a fraction of Sn ions located in the octahedral sites. Although the multiple sintering and quenching led to the incorporation of tin ions into  $\text{ZnCr}_2\text{Se}_4$ , they were redistributed between the octahedral and tetrahedral sites of spinel lattice.

The results of the Mössbauer investigations indicate a significantly higher share of the component connected with location of tin in the tetrahedral sublattice. However, in the case of  $\text{Zn}_{0.71}\text{Sn}_{0.061}\text{Cr}_{1.88}\text{Se}_{4.00}$  sample, the share of the component connected with the location of tin in the octahedral sublattice is higher. The fact is probably connected with lower Cr concentration in the sample.

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