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X-RAY AND MAGNETIC INVESTIGATIONS OF THE POLYCRYSTALLINE COMPOUNDS WITH GENERAL FORMULA $Zn_xSn_yCr_zSe_4$

BADANIA STRUKTURALNE I MAGNETYCZNE POLIKRYSTALICZNYCH ZWIĄZKÓW O OGÓLNYM WZORZE $Zn_xSn_yCr_zSe_4$

Seleno-spinels with the general formula $Zn_xSn_yCr_zSe_4$ (where $x + y + z \approx 3$) were prepared as polycrystalline samples in the two nominal compositions: $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ and $ZnCr_{1.9}Sn_{0.1}Se_4$, using ceramic method. X-ray powder diffraction was used to analyse the obtained phases and to determine their crystal structure and lattice parameters. 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. Chemical compositions of the obtained samples were determined using JEOL-type Scanning Microscope which also revealed a variation in local distribution of cations and the porosity of the samples. The magnetisation data for $Zn_xSn_yCr_zSe_4$ system, shows that the saturation magnetic moments depend on location of tin ions in crystal lattice of $ZnCr_2Se_4$. It was found that the magnetic properties correspond well both with the chemical composition and with the crystal structure.
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Metodą ceramiczną otrzymano polikrystaliczne związki chemiczne o ogólnym wzorze $Zn_xSn_yCr_zSe_4$ (gdzie $x + y + z \approx 3$) dla dwóch założonych składów $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ i $ZnCr_{1.9}Sn_{0.1}Se_4$. Skład chemiczny określono przy użyciu mikroskopu skaningowego JEOL (SE 6480). Dla związku o nominalnym składzie $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ wyznaczono skład rzeczywisty jako $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$, natomiast dla związku o nominalnym składzie $ZnCr_{1.9}Sn_{0.1}Se_4$ wyznaczono skład rzeczywisty jako $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$. Za pomocą rentgenowskiej analizy strukturalnej oraz metody Rietvelda wyznaczono strukturę i parametry sieciowe otrzymanych związków. Badania magnetyczne wykonane w silnych polach magnetycznych wykazały, że momenty magnetyczne nasycenia zależą od obsadzenia jonów cyny Sn^{2+} w sieci krystalicznej $ZnCr_2Se_4$. Dla otrzymanych związków $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ i $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ zmierzone momenty magnetyczne nasycenia wynoszą odpowiednio $6.52\mu_B$/cz. i $5.56\mu_B$/cz. Wzrost nasycenia namagnesowania w $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$, gdzie jony cyny Sn^{2+} podstawiają się w miejsce niemagnetycznych jonów Zn^{2+}, świadczy o tym, że jony cyny Sn^{2+} mają wpływ na momenty magnetyczne w $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$. Badania magnetyczne wykonane przy użyciu magnetometru nadprzewodzącego SQUID potwierdziły obecność antyferromagnetycznego uporządkowania w sieci otrzymanych spineli oraz wykazały wpływ jonów cyny Sn^{2+} na oddziaływania antyferromagnetyczne w tym układzie.

1. Introduction

The parent compound of the studied solid solutions of $ZnCr_2Se_4$ crystallises in the $MgAl_2O_4$-type normal spinel cubic structure (space group $Fd\bar{3}m$). Zinc and chromium respectively are tetrahedrally and octahedrally co-ordinated in the cubic close packing of selenium atoms, and the lattice parameter has a value $a_0 = 10.4891 \overset{\circ}{A}$ [1-4]. $ZnCr_2Se_4$ spinel shows the p-type semiconducting properties and a helical antiferromagnetic spin structure below $T_N \approx 20$ K with a strong ferromagnetic component evidenced by a large positive Curie-Weiss temperature of 115 K [5].

The magnetic properties result from the near-neighbour ferromagnetic Cr-Cr and the more distant neighbour antiferromagnetic Cr-Se-Cr interactions, and it has already been shown that the system can be easily substituted at various sites [6, 7]. Polycrystalline quater-

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nary 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 $ZnSe$-$SnSe$-Cr_2Se_3, and the results of their X-ray 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

2.1. Samples preparation

Polycrystalline samples were obtained in the two nominal compositions: $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ and $ZnCr_{1.9}Sn_{0.1}Se_4$. The compounds with general formula $Zn_xSn_yCr_zSe_4$ (where $x + y + z \approx 3$) were prepared from the binary selenides ($ZnSe$, $SnSe$ and Cr_2Se_3). The binary selenides were prepared by annealing stoichiometric mixtures of the elements: Zn, Sn, Cr and Se (all elements were of 5N purity). The mixtures were pulverised in an agate mortar in stoichiometric quantities and sealed in fused silica ampoules evacuated to a pressure of about 10^{-5} Torr. The mixtures were pulverised in an agate mortar in stoichiometric quantities and sealed in fused silica ampoules evacuated to a pressure of about 10^{-5} Torr.

The samples were sintered three more times at 1073K for 198 hours. After the last sinter, the samples were quenched in water with ice.

2.2. Chemical composition

The chemical composition of $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ and $ZnCr_{1.9}Sn_{0.1}Se_4$ polycrystals was analysed with a JEOL-type Scanning Microscope (SE 6480). The results are presented in Table 1. Scattered electron images (SEI) (Fig. 1) and backscattered images (BEI) (Fig. 2) were collected at a room temperature. Also the chemical composition was determined using an energy-dispersive X-ray detector (EDX) attached to the Jeol microscope. The chemical composition was calculated as an average value using the data from measurements, which were done on individual 10 grains.

TABLE 1

Chemical composition of $Zn_xSn_yCr_zSe_4$ compounds using JEOL-type Scanning Microscope

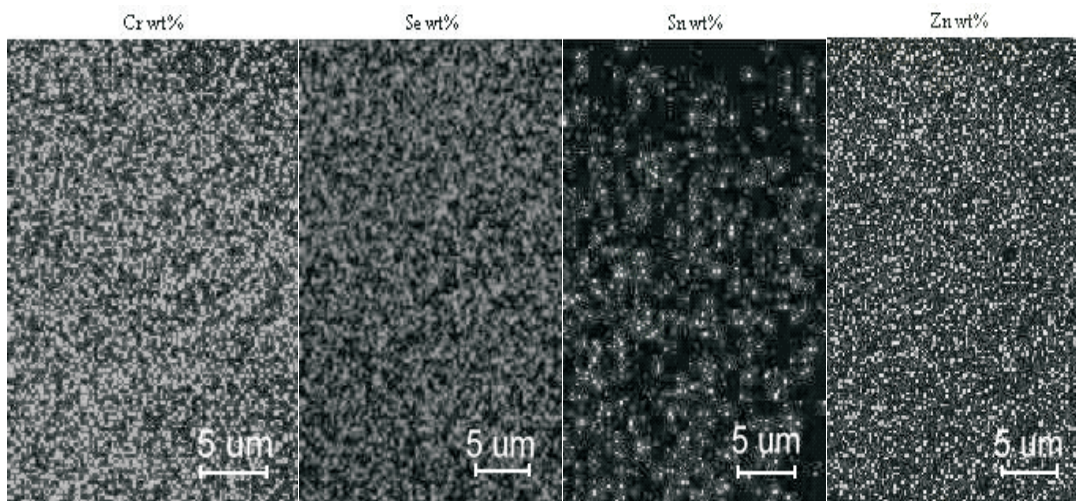| Nominal composition	%weight				Measured composition
	Zn	Sn	Cr	Se	
$Zn_{0.9}Sn_{0.1}Cr_2Se_4$	12.46	1.31	21.95	64.28	$(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_{4.00}$
$ZnCr_{1.9}Sn_{0.1}Se_4$	12.61	1.22	20.95	65.22	$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_{4.00}$

Fig. 1. A fracture surface by BEI COMPO showing distribution of elements for $(Zn_{0.87}Sn_{0.48})Cr_{2.02}Se_4$
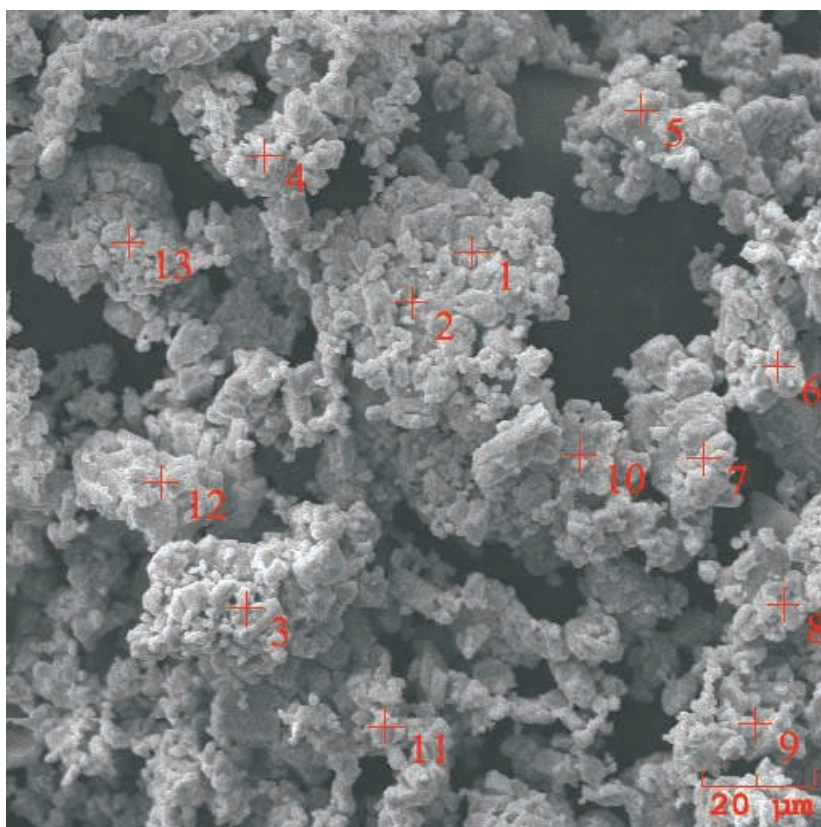
Fig. 2. A fracture surface by SEI for $(Zn_{0.87}Sn_{0.48})Cr_{2.02}Se_4$

2.3. X-ray Powder Diffraction

X-ray powder diffraction data of polycrystalline samples were collected using a Philips X-Pert (PW3050) diffractometer (CuK$_\alpha$ radiation (λ_1 =1.54056 and λ_2 =1.54443 $\mathring{A}$) over an angular range of 2θ : $10\div135°$) in order to make phase analysis and to determine phase composition and lattice parameters. All measurements were carried out at a room temperature. First, the qualitative phase analysis was carried out. Generally, in all studied sintered compounds the presence of the spinel phase was evidenced (Fig.5).
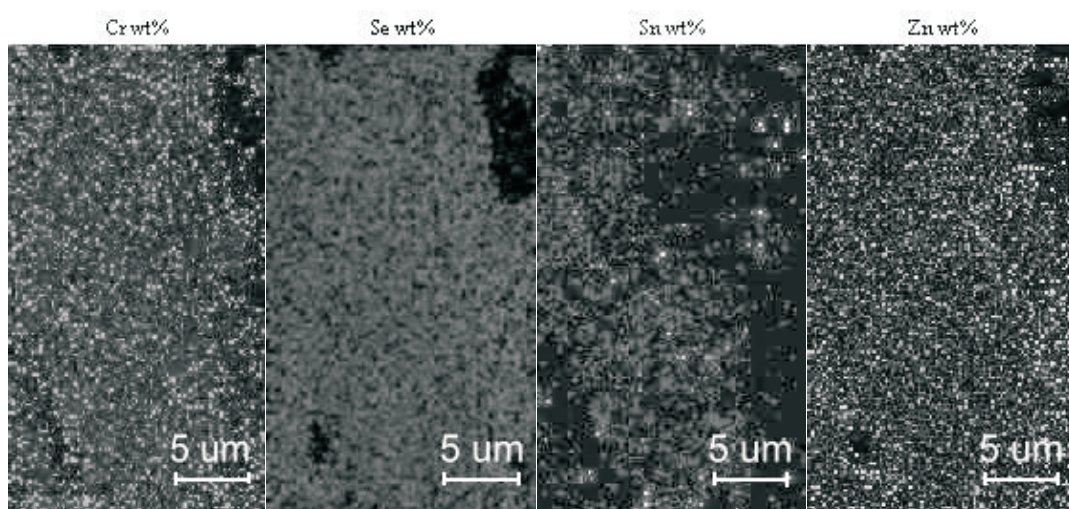

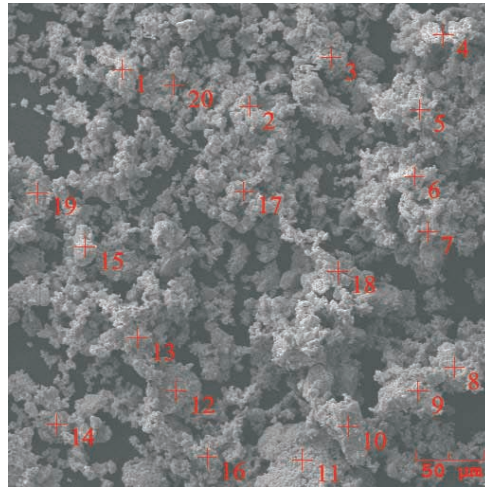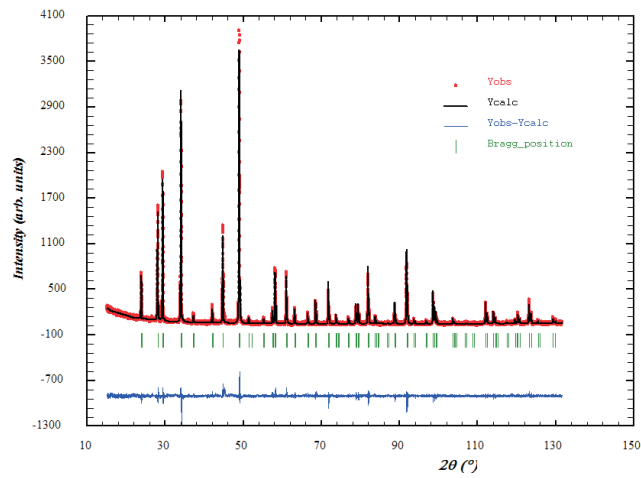Fig. 3. A fracture surface by BEI COMPO showing distribution of elements for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$

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Fig. 4. A fracture surface by SEI for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$

a)

b)
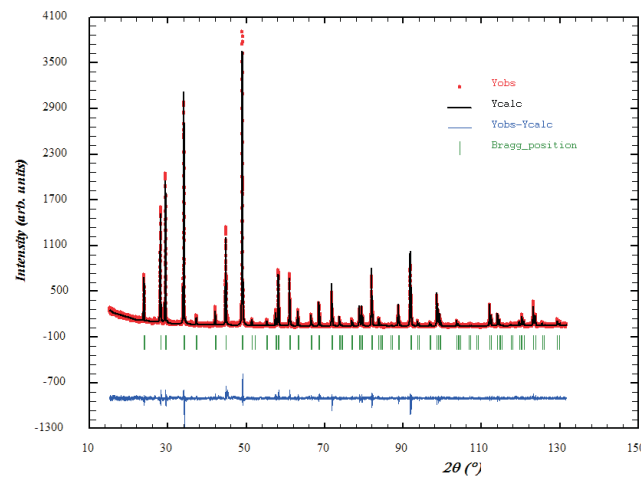
Fig. 5. Results of the Rietveld refinement obtained for: $(Zn_{0.87}Sn_{0.48})Cr_{2.02}Se_4$ (a); $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ (b)

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 2 and a clear improvement in the quality of the fit in the second case. The determined lattice parameters and the anion free parameters are consistent between the models.

Structural parameters obtained from the Rietveld refinement for $Zn_xSn_yCr_zSe_4$ series

x	R_F (%)	R_{Bragg} (%)	R_{wp} (%)	χ^2	$Zn_xSn_yCr_zSe_4$	
					a_0 (Å)	Coordinate u of Se
Nominal $Zn_{0.9}Sn_{0.1}Cr_2Se_4$	4.57	6.88	12.1	1.40	10.5042(1)	0.25923(16)
$(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_{4.00}$	3.90	5.36	11.6	1.28	10.5042(1)	0.25932(16)
Nominal $ZnCr_{1.9}Sn_{0.1}Se_4$	3.95	5.78	11.7	1.35	10.5068(2)	0.25945(16)
$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_{4.00}$	3.94	5.61	11.6	1.33	10.5067(3)	0.25944(16)

2.4. Magnetic measurements

Magnetization of the investigated compounds was studied in high magnetic stationary fields (up to 14T) within a temperature range of 4.2÷300K using an induction magnetometer. The temperature was measured with a thermocouple of chromel-Au+0.07%Fe with sensitivity 16μV/K. The measurements were performed using a Bitter-type magnet. The saturation magnetization for the polycrystalline compounds $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$, calculated per one molecule and per chromium atoms is given in Table 3. Magnetization isotherms for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ are given in Fig. 6.

Comparison of the most important parameters obtained from magnetic experiments for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ with the values for pure $ZnCr_2Se_4$

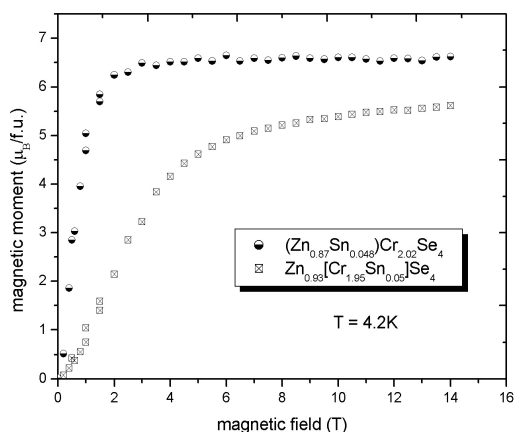| Chemical compound	μ_{eff}, T=300K		μ_{sat}, T=4.2K		Θ_{C-W} (K)	T_N (K)	c_M (K/mol)
	μ_B/mol	μ_B/Cr	μ_B/mol	μ_B/Cr			
$(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$	5.52	3.89	6.52	3.26	76	17	3.80
$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$	5.41	3.89	5.56	2.85	72	18	3.66
$ZnCr_2Se_4$ [1-4]	5.47	3.87	5.74	2.87	115	22	3.73

Fig. 6. Magnetization isotherms for $Zn_xSn_yCr_zSe_4$

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The magnetic measurements of the powdered samples $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]$ were carried out over the temperature range $1.8 \div 300$ K using a Quantum Design SQUID-based MPMSXL-5-type magnetometer (Fig. 7 and 8). The

superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements of the compounds samples were made at magnetic field of 0.5 T. The effective magnetic moment was calculated from the $\mu_{eff} = 2.83(\chi_M T)^{1/2}\mu_B$ equation.
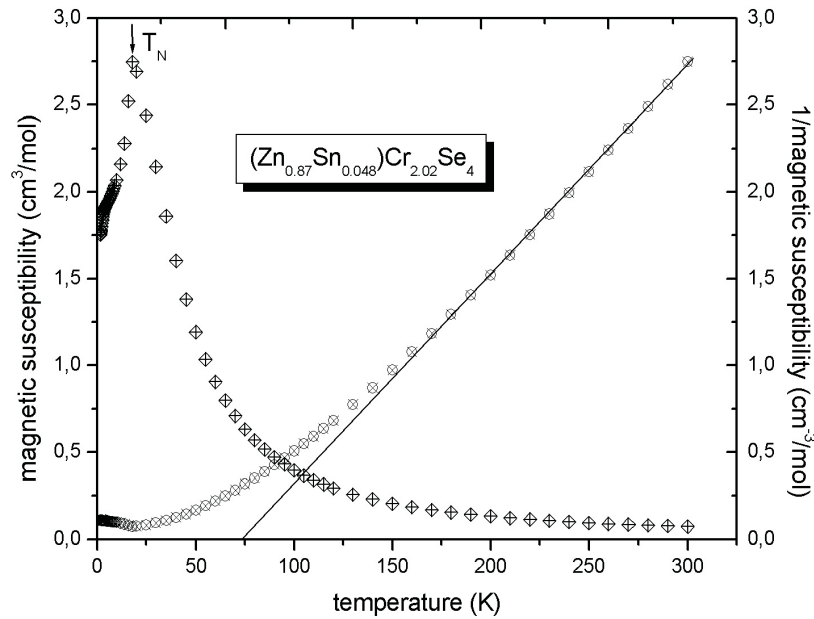

Fig. 7. Temperature dependence of the magnetic susceptibility and inverse magnetic susceptibility for $(Zn_{0.87}Sn_{0.48})Cr_{2.02}Se_4$
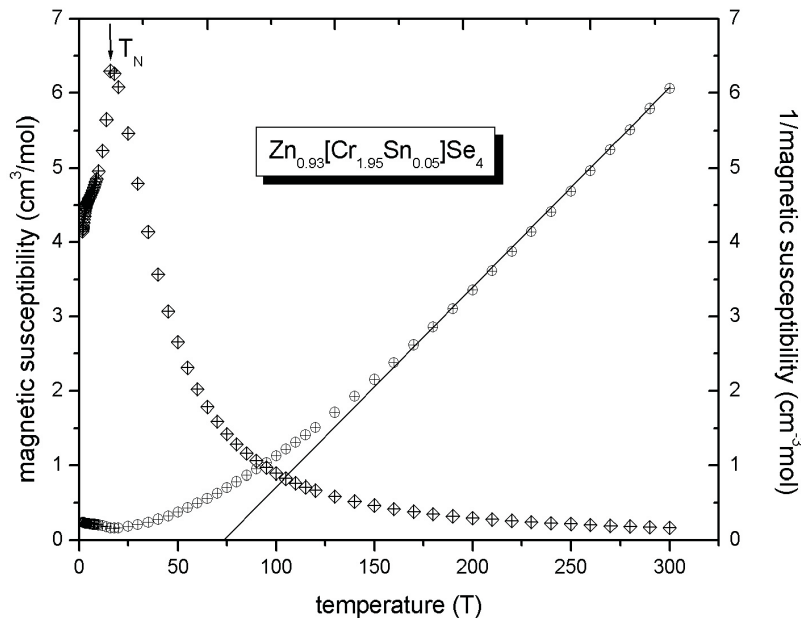

Fig. 8. Temperature dependence of the magnetic susceptibility and inverse magnetic susceptibility for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$

3. Results and discussion

The applied preparative method allowed to obtain quaternary compounds of $ZnCr_2Se_4$ 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 lattice parameters for spinel phase increase to 10.5042$\overset{\circ}{A}$ for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and to 10.5067$\overset{\circ}{A}$ for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ with doped Sn because ionic radius of Sn^{2+} (118pm) is bigger than ionic radius of Zn^{2+} (74pm) and Cr^{3+} (64pm) [9].

A scanning microstructure analysis confirmed the assumed chemical composition. For example, in the case of a sample with the nominal composition $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ the calculated average value was equal $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$, and for $ZnCr_{1.9}Sn_{0.1}Se_4$ sample, composition $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ was measured. This method also pointed out the variation in the local distribution of the elements (Fig. 1 and 3) and the porosity of samples (Fig. 2 and 4).

In the spinels with general formula ACr_2X_4 (where A = Cu, Zn, Cd; X = S, Se, Te) only the chromium ions, which occupy the octahedral sites, possess the magnetic moment. However, the value of this moment depends on the type of the A ions occupying the tetrahedral sites. When A = Zn^{2+}, Cd^{2+} or Cu^{2+}, chromium occurs as Cr^{3+} and possesses a magnetic moment of $3\mu_B$ per ion [10]. The local symmetry on this octahedral site leads to a non-degenerate orbital ground state with *S = 3/2*. The lattice built upon the B-site consist of tetrahedra of chromium ions. Each chromium ion is common to tetrahedra which are defined by the position of their six first-near neighbours.

The Cr^{3+} ion is known to have the largest octahedral site preference energy of all cations (69.5 kJ/molK) [11]. The spinel structure is stable only when the second cation can occupy a tetrahedral sites. These relations are clearly seen in the mixed crystals. However, the stability of the spinel structure decreases with an increase in anion polarizability (in the order: O, S, Se, Te) [12]. The atoms become too large to fit in the tetrahedral or octahedral sites of the spinel structure, and crystallization occurs in Cr_3S_4-type or related structure. This may be reason why $SnCr_2Se_4$ not exist.

For $ZnCr_2Se_4$, the saturation magnetic moment $5.74\mu_B$ lies very close to $6\mu_B$/f.u., which is a predicted value for spin only contribution of two Cr ions in high spin electron configuration $3d^3$ (S=3/2) [13-15]. The small decrease is attributed to the covalency effects and hybridisation of chromium 3d orbitals with anion 4p states.

Tin ions, built-in into the spinel crystal lattice, affect the values of the saturation magnetic moments. Fig. 6 presents the magnetization in saturation state at liquid helium temperature for various tin substitution for both investigated compounds.

For the $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$, the saturation effect is observed at a little lower fields (above 2T). For

$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ – compound, the saturation effect is observed at higher fields (above 6T). For the $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ compounds, the measured magnetic moments in saturation are $6.52\mu_B$/f.u. and $5.56\mu_B$/f.u., respectively. Since tin ions substitute here non-magnetic zinc, the increase in saturation magnetisation indicates that Sn2+ may influence on magnetic moment.

The magnetic properties of $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ as $\chi_M vs.$ T and $1/\chi_M vs.$ T (χ_M being the molar magnetic susceptibilities) dependencies are shown in Figures 7. The effective magnetic moment of $5.52\mu_B$ at 300K corresponding with presence of magnetic chromium ions. The susceptibility curve exhibits a maximum at 17K, indicating the presence of the antiferromagnetic ordering in the crystal lattice. The values of the Curie and Weiss constants determined from the $1/\chi_M = f$ (T) relation over temperature range 80÷300K are equal to 3.80 K · cm³mol^{-1} and 76K, respectively.

The magnetic properties of $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ as $\chi_M vs.$ T and $1/\chi_M vs.$ T dependencies are shown in Figures 8. A decrease of the effective magnetic moment of $5.41\mu_B$ at 300K corresponds with the decrease in the chromium amount. The susceptibility curve exhibits a maximum at 18K, indicating the presence of the antiferromagnetic ordering in the crystal lattice. Generally, the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ – compound shows linear $1/\chi_M = f$ (T) behavior in the 80÷300K range, with C = 3.66 K · cm³mol^{-1} and Θ = 72K. The decrease in case of both compounds of asymptotic Curie-Weiss temperature and a Neel temperature (Table 3.) indicates that tin in tetrahedral and octahedral site increases the antiferromagnetic interactions in the system.

4. Conclusions

Basing on the investigations carried out, we can draw the following conclusions:

- Multiple sintering and quenching led to incorporation of tin ions into $ZnCr_2Se_4$ crystal lattice, both in tetra- and octahedral sites of the spinel structure, and the obtained single-phase compounds crystallized in the spinel cubic structure.Multiple sintering and quenching led to incorporation of tin ions into $ZnCr_2Se_4$ crystal lattice (space group $Fd\bar{3}m$).

- The scanning electron microscopy test confirmed the chemical composition of the obtained compounds, but it also showed a variation in local distribution of the elements.

- Introduction of Sn to the spinel lattice of $ZnCr_2Se_4$ system changes the saturation magnetic moment per chromium atom. The saturation magnetic moments depends on location of tin ions in crystal lattice.

- A increase in values of magnetic moments for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ suggests that the tetrahedral sublattice contains Sn^{2+} and Zn^{2+} ions, the octahedral sublattice contain only Cr^{3+} ions.

Acknowledgements

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