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Synthesis and physico-chemical properties of spinel compounds with general formula $Zn_{1-x}Mn_xCr_2Se_4$

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The $ZnCr_2Se_4$ compound crystallizes in cubic spinel structure (space group *Fd*-3*m*), with lattice parameter $a = 10.4970$ Å. It is a semiconductor with magnetic helical structure below the Néel temperature $T_N \approx 20$ K [1, 2]. The normal cations distribution occurs in this spinel: zinc ions are located at the tetrahedral sites and chromium ions are in octahedral sites. It is known that elements substitution can strongly influence on the parent compound properties [3–6].

The compounds based on the $Zn_{1-x}Mn_xCr_2Se_4$ system, $x = 0.1$–0.5, were synthesized by ceramic method, according to the following reaction:

$$(1-x)ZnSe + xMnSe + Cr_2Se_3 = Zn_{1-x}Mn_xCr_2Se_4$$

Chemical compositions of the obtained samples were determined using ICP-AES method. XRD and Rietveld refinement analysis were used in order to obtain structural parameters (anion and lattice parameters).

Fig. 1 shows that the structural parameters increase with the growth of Mn amount, according to the assumption, because the ionic radius of Mn^{2+} (0.66Å) is larger than that of Zn^{2+} (0.60Å).

The magnetization of manganese doped compounds has been studied and magnetic isotherms were measured within a temperature range of 4.2÷300 K in high magnetic stationary fields (up to 14 T) using an induction magnetometer. The magnetic susceptibility was determined in the temperature range of 1.8−300 K using a Quantum Design SQUID-based MPMSXL−5-type magnetometer.

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The results of magnetic measurements showed that the compounds under consideration were antiferromagnets with the Néel temperature of 18–25 K and the Curie–Weiss temperature increased from $\theta = 84$ K for $x = 0.1$ to $\theta = 105$ K for $x = 0.5$. Below T_N the magnetic field dependence of magnetization showed two peaks at critical fields H_{c1} connected with metamagnetic threshold accompanied with transition from helical to conical phase and H_{c2} where the conical magnetic structure transformed into ferromagnetic phase. The values of H_{c1} remained almost constant while the values of H_{c2} shifted into higher magnetic fields as the Mn content increased.
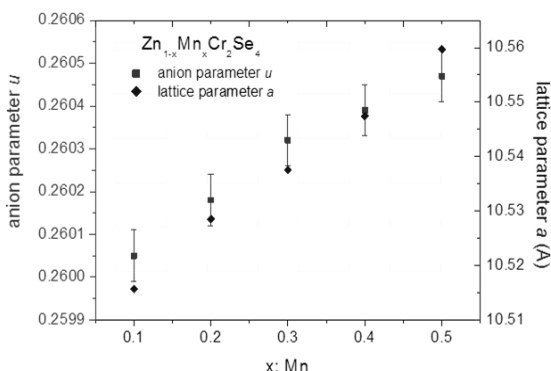

Fig. 1. The dependence of anion parameter and lattice parameter on the amount of manganese in $Zn_{1-x}Mn_xCr_2Se_4$
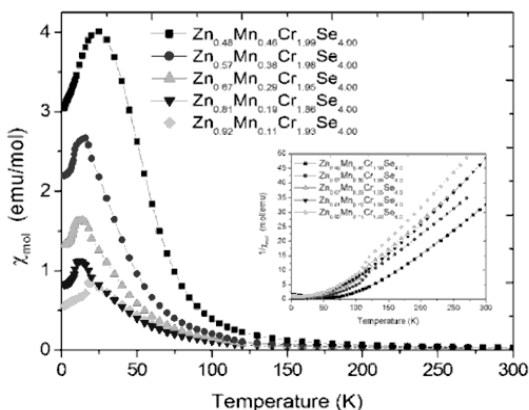

Fig. 2. The magnetic susceptibility χmol and inverse magnetic susceptibility $1/\chi$mol vs. temperature for $Zn_{1-x}Mn_xCr_2Se_4$ compounds

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New thermodynamic assessment of solid alloys in Au–Ni system from thermophysical properties of the end-members

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Electrodeposited Au–Ni alloys are used as contact materials for microelectromechanical systems switches due to their good hardness, wear resistance and low contact resistance [1]. Au–Ni alloys exhibit a large positive enthalpy of mixing originated from the significant size mismatch effect. Calphad method [2] is widely used for the optimization of existing thermodynamic information. However, this method cannot be applied when experimental data on phase equilibrium for systems are insufficient and/or mixing properties are lacking. The most desirable way is to assess thermodynamic properties of a binary system from the properties of pure components without the recourse to the experiments on mixtures. In this work we obtained the values of thermodynamic functions of mixing for Au–Ni system using the Hovi–Hietala–Urusov solid solutions theory [3], the Kaptay's equation for prediction of the excess entropy of mixing for binary alloys [4] and the equations for calculation of components activity coefficients [5]. The results of calculations are summarized in Table 1 and Table 2.The modified Hovi–Hietala–Urusov equation for the enthalpy of mixing,ΔH_m has the following form:

$$\Delta H_m = c X_{\text{Ni}} X_{\text{Au}} \delta^2, \qquad (1)$$

Where$X$ is the atomic fraction of a component, c (kJ mol^{-1}) is the constant equal numerically to 1420 for ionic compounds of NaCl type (Hovi–Hietala–Urusov) and 1379 kJ mol^{-1} in our case, δ is the improved Hovi–Hietala–Urusov size