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Growth, structure and characterization of physico-chemical and magnetic properties of $CdCr_2Se_4$:Mn single crystals

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ABSTRACT

Crystal structure, magnetic and specific heat measurements, electrical conductivity, as well as DSC/TG measurements for single-crystalline $Cd_xMn_yCr_zSe_4$ (where $x + y + z \approx 3$) spinels are presented. The electrical conductivity and dc magnetic susceptibility measurements exhibit thermally activated semiconducting properties and ferromagnetic (FM) order for all compositions below the Curie temperature T_C = 130 K, respectively. The long-range FM interactions, defined by the Curie temperature, do not substantially depend on the manganese content, and the nearest neighbour FM interactions, represented by the positive value of the Curie-Weiss temperature, decrease from 183 K to 156 K. Hysteresis loops of all crystals have a very small coercive field (~18 Oe) and remanence (~0.09 μ_B/f.u.) with full saturation above 10 kOe. These effects are interpreted in terms of the superexchange integrals for the first two coordination spheres including spin defects.

1. Introduction

The ternary spinel-type compounds with a general formula ACr_2Se_4 (A = Cd, Cu, Hg) form a special group of ferromagnetic semiconductors with Curie temperatures up to 460 K. They have particular perspectives in spintronics due to the coexistence of semiconducting and ferromagnetic properties. Electrical injection, transport and manipulation of spin polarized carriers in a semiconductor are essential requirements for utilizing the spin degree of freedom in a future semiconductor spintronics technology. Ferromagnetic semiconductors are promising chemical compounds in this area – their exchange split band edges offer both spin injection and spin-selective transport in heterostructures. The strong coupling between the 3*d* spins of the magnetic ions and the *sp* electrons taking advantage of a large effect of magnetoresistivity, as well as numerous unusual physical characteristics renewed the interest in semiconducting and ferromagnetic Cr-based chalcogenide spinels [1–3]. Chromite selenides are considered a prospective alternative for creating thermoelectric materials. The thermoelectric effect is based on three different effects. This group of compounds can be used for creating thermoelectric materials based on two of them. Such thermoelectric generators need two type of materials, n- and p-type. $CdCr_2Se_4$ is one of prospective substances for thermoelectric generators. It is not very expensive, easy to synthesize as n- or p-type material, its value of Seebeck coefficient is +60 μV/K [4].

$CdCr_2Se_4$ crystallizes in a spinel structure, which is described by the $Fd\bar{3}m$ space group (No. 227). The cation Cd^{2+} is located in tetrahedral sites, and the trivalent cation Cr^{3+} is located in octahedral sites; the Se^{2-} anion is located in a 32*e* special position, which has one free parameter *u*, called an anion parameter. In case of an ideal spinel structure, the anion parameter has a value of 0.25 [5]. The pure $CdCr_2Se_4$ spinel, with a lattice parameter of 10.721–10.750 Å, combines the *p*-type semiconducting and ferromagnetic properties with a Curie temperature of T_C = 126.2÷142 K and a paramagnetic Curie-Weiss temperature of θ = 172÷204 K [3,6–10]. Magnetization of $CdCr_2Se_4$ reaches a full saturation of 5.4÷5.98 μ_B per molecule and the ferromagnetic properties are the result of a prevalence of large and positive nearest-neighbour Cr–Se–Cr interactions and a weaker superexchange couplings

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between the more distant chromium ions [11]. The Cr 2*p* XPS spectra of $CdCr_2Se_4$ showed the spin-orbit splitting between the final Cr $2p_{3/2}$ and Cr $2p_{1/2}$ states of 9.5 eV. The Cr $2p_{3/2}$ states are split into two peaks at 574.2 and 575.2 eV. The peak separation with the binding energy difference ΔE of 1 eV is typical of the $3d^3$ elements with localized magnetic moment of 3 μ_B [2]. The magnetic investigations, which were carried out on the polycrystalline $Cd_{0.85}Mn_{0.01}Cr_{1.97}Se_4$ spinel, showed that it was an *n*-type semiconductor and a ferromagnet with $T_C = 135$ K and $\theta = 145$ K. The Mn doping is boosting the ferromagnetism, which is evidenced by a higher value of the Curie-Weiss temperature [12]. In order to improve the ferromagnetic and semiconducting properties of $CdCr_2Se_4$, Mn^{2+} ions were introduced into crystal lattice of $CdCr_2Se_4$.

In this paper, we present details of single crystal synthesis together with the thermodynamic computations of thermodynamic parameters for the chemical transport reactions, results of structural, magnetic and electrical studies, as well as specific heat and DSC/TG measurements, in order to show the influence of magnetic manganese ions on structural and physico-chemical properties of $CdCr_2Se_4$.

2. Experimental procedure

2.1. Sample preparation and thermodynamic calculations

The correct reaction of chemical transport depends on the following conditions: the change of Gibbs energy ΔG° or equilibrium constant K_a, the value of enthalpy ΔH° and the choice of the proper transporting substance.

The change of the equilibrium constant K_a should be close to 1 (i.e. $\log K_a$ should be close to zero). This is a guarantee for the reversibility of the process and sureness that there are significant quantities of reactants and reaction products in the equilibrium state. The value of enthalpy ΔH° should be different from zero. The sign of ΔH° indicates the direction of the reaction. For $\Delta H^\circ > 0$ (endothermic reaction), dissolution of the substance will occur at a higher temperature and crystallization will occur at a lower temperature. For $\Delta H^\circ < 0$ (exothermic reaction), the reaction course will be opposite.

The choice of the transporting substance consists in finding such substances, with which a big difference in the partial pressure at possibly the slightest low temperature difference can be obtained [13].

The equilibrium state of a system can be described by the following relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\, lnK_{P,T} \quad (1)$$

where ΔG° is standard free energy of reaction at temperature *T*; ΔH° is standard enthalpy of reaction at temperature *T*; ΔS° is standard entropy of reaction at temperature T; $K_{P,T}$ is the equilibrium constant at temperature T; *R* is universal gas constant; and *T* is temperature.

For this reason, the thermodynamic model of synthesis of $CdCr_2Se_4$ single crystals doped with manganese was created based on the following reaction scheme:

$4(1-x)CdSe + 4xMnSe + 2CrCl_3 = Cd_{1-x}Mn_xCr_xSe_4 + 3(1-x)CdCl_2 + 3xMnCl_2$ for x = 0.1÷0.4.

In order to estimate the transport reaction ability properly, accompanying reactions that may affect the qualitative and quantitative composition of the gaseous solution or change the direction of the reaction should be included in the calculation. Usually, these are reactions of dissociation of solvent or reaction products.

Considering the above, and because of the fact that the transporting agent $CrCl_3$ dissociates into $CrCl_2$, $CrCl_4$ and Cl_2 above 773 K [14], chemical transport reactions may be realized by several independent reactions, which may occur in the CdSe–MnSe–$CrCl_3$ system:

1) $2CdSe + 2CrCl_{3(g)} = 2CdCl_{(g)} + 2CrCl_{2(g)} + Se_{2(g)}$
2) $2CdSe + 4CrCl_{3(g)} = 2CdCl_{2(g)} + 4CrCl_{2(g)} + Se_{2(g)}$
3) $2MnSe + 2CrCl_{3(g)} = 2MnCl_{(g)} + 2CrCl_{2(g)} + Se_{2(g)}$
4) $2MnSe + 4CrCl_{3(g)} = 2MnCl_{2(g)} + 4CrCl_{2(g)} + Se_{2(g)}$
5) $2CdSe + CrCl_{4(g)} = 2CdCl_{(g)} + CrCl_{2(g)} + Se_{2(g)}$
6) $2CdSe + 2CrCl_{4(g)} = 2CdCl_{2(g)} + 2CrCl_{2(g)} + Se_{2(g)}$
7) $2MnSe + CrCl_{4(g)} = 2MnCl_{(g)} + CrCl_{2(g)} + Se_{2(g)}$
8) $2MnSe + 2CrCl_{4(g)} = 2MnCl_{2(g)} + 2CrCl_{2(g)} + Se_{2(g)}$
9) $2CdSe + Cl_{2(g)} = 2CdCl_{(g)} + Se_{2(g)}$
10) $2CdSe + 2Cl_{2(g)} = 2CdCl_{2(g)} + Se_{2(g)}$
11) $2MnSe + Cl_{2(g)} = 2MnCl_{(g)} + Se_{2(g)}$
12) $2MnSe + 2Cl_{2(g)} = 2MnCl_{2(g)} + Se_{2(g)}$

In the CdSe–MnSe–$CrCl_3$ system, the conditions for the simultaneous transport of CdSe and MnSe (the same sign of enthalpy and the same value of volatility) and for the crystallization of the $Cd_{1-x}Mn_xCr_2Se_4$ single crystals should be met. The calculations of the equilibrium constant values ($\log K_a$) and enthalpy ΔH°, in the temperature range of 200–1473 K were carried out. These calculations were done using FactSage program (Figs. 1 and 2).

The binary selenides (CdSe and MnSe) were synthesized from elements (5N purity) by ceramic method. The selenides were

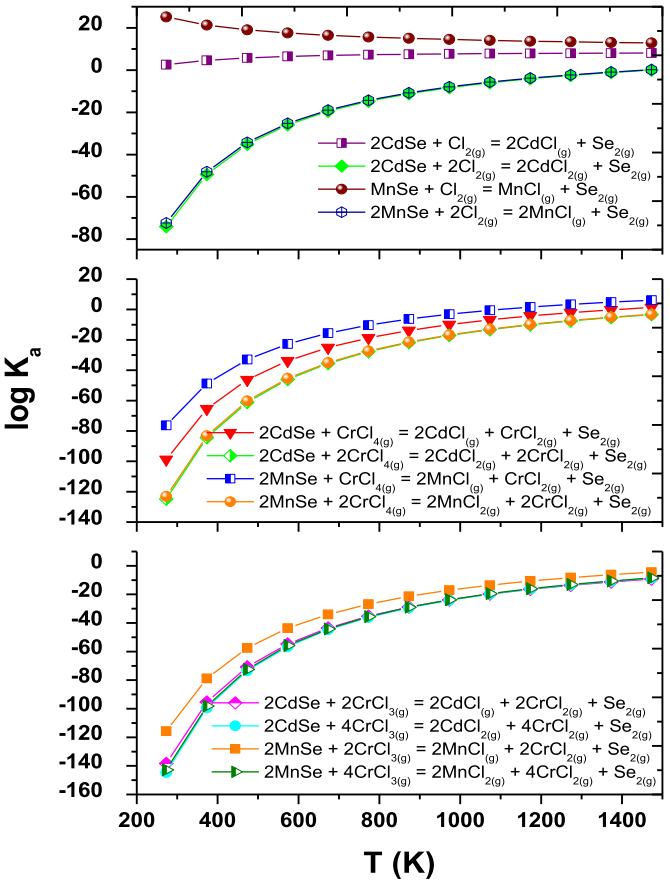

Fig. 1. The dependence of the $\log K_a$ *vs.* temperature *T* for the transporting reactions 1–12.