Influence of the milling time on the magnetic order of the $ZnCr_2Se_4$ nanoparticles

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Seleno-spinels are promising compounds in the commercial use of thermoelectric devices [1-3] due to the rather large unit of a cubic cell (approximately 10 Å) and a strong covalent bond. Pure $ZnCr_2Se_4$ combines *p*-type semiconducting behaviour and a helical antiferromagnetism (AFM) below the Néel temperature $T_N \approx 20$ K associated with a structural transition from cubic to tetragonal as well as a strong ferromagnetic (FM) component evidenced by a large positive Curie–Weiss temperature (θ) of 115 K [4,5]. The helical structure has a FM arrangement in the (0 0 1) planes with a turning angle of 42° between the spins in adjacent (0 0 1) planes. Therefore, one can expect that the nano-sized crystallites of $ZnCr_2Se_4$ will also have unique properties and new potential applications, similar to the $CuCr_2S_4$ nanospinel [6].

$ZnCr_2Se_4$ nanocrystals were synthesized by High – Energy Ball-Milling of the single crystals this compound at ambient temperature with the milling time of 1, 3 and 5h. Dynamic (ac) magnetic susceptibility was measured at an internal oscillating magnetic field H_{ac} = 10 Oe with an internal frequency f = 120 Hz in the temperature range of 2–300 K. Specific heat was measured using heat capacity option for Quantum Design Physical Properties Measurement System (QD PPMS) which uses a pulse technique with two-tau model fitting.

Magnetic measurements of $ZnCr_2Se_4$ nanoparticles showed that with increasing the milling time from 1 to 5h: 1) the long-range superexchange interactions changed from AFM to ferrimagnetic (FIM) and the ordering temperature increased from 19.4 K to 21.5 K, 2) the short-range superexchange interactions changed from FM to AFM visible in the paramagnetic Curie-Weiss temperature changing from positive (θ = 38.4 K) to negative (θ = -260 K), 3) the effective magnetic moment increased from 6.428 μ_B/f.u. to 12.707 μ_B/f.u., suggesting superparamagnetic-like behaviour. Magnetic susceptibility χ measured as a function of frequency at 100 Hz, 300 Hz, 1 kHz and 10 kHz showed the shift of the χ maximum towards higher temperatures which is characteristic of spin glasses (Vogel-Fulcher law). The amount of atoms in the formula unit n_D = 8.2, Debye temperature θ_D = 160 K and the entropy with a significantly lower value in relation to the expected one of 2Rln4 (~22 J/molK) were estimated from the measurements of specific heat using Debye's function. It was also found that there was no structural phase transition at the ordering temperature. The above results suggest that the milling time strongly affect the magnetic order of the spinel under study.

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