Effect of Ce^{3+} Substitution at *B* site on Magnetic Phase Transitions in $CoCr_2O_4$ Nanoparticles

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$CoCr_2O_4$ belongs to the cubic spinel family where Co^{2+} occupies the tetrahedral *A* sites and Cr^{3+} populates the octahedral *B* sites [1]. Single crystals of $CoCr_2O_4$ undergo a paramagnetic to ferrimagnetic transition at $T_C = 93$ K, and subsequent lowering of the temperature leads to a conical spin state at 26 K (T_S) [1]. The appearance of ferroelectricity in $CoCr_2O_4$ has been ascribed to this spin modulation [1]. At 15 K, the compound shows the lock-in transition[1]. In polycrystalline $CoCr_2O_4$ spinel compounds, both ferrimagnetic and spiral magnetic orderings were observed at 94 K and 27 K, respectively, with missing lock-in transition [2]. The results of multiferroicity in $CoCr_2O_4$ were confirmed [3], where the conical-spiral ferroelectricity has been referred to as the interrelation of ferroelectric polarization, magnetization, and spiral wave vector [3]. The observed findings suggest that the nearest neighbor and isotropic antiferromagnetic *A*-*B* and *B*-*B* exchange interactions J_{AB} and J_{BB} compels the system to attain a "ferrimagnetic spiral", having spins located on the conical surfaces [3]. The occurrence of spiral ordering at 25 K has also been observed in $CoCr_2O_4$ nanoparticles (about 40 nm) without any lock-in transition [4]. The disappearance of T_S also occurred in undoped and Ni substituted $CoCr_2O_4$ thin films [5]. As a strong motivation of the importance of the spiral ordering and the exchange interaction, the present work aims at the substitution of rare-earth Ce^{3+} ion at Cr^{3+} site. A $Co(Cr_{0.95}Ce_{0.05})_2O_4$ compound was synthesized by the sol-gel technique. X-ray diffraction (XRD) studies of the sample calcined at 600 C, revealed pure phase. The crystallite size estimated from the XRD was approximately 9 nm. The average particle size calculated from the transmission electron microscopy (TEM), $D_{TEM} = 11 \pm 2$ nm. Electron diffraction patterns confirm the crystalline nature of the nanoparticles. Magnetization as a function applied field shows an increase in coercivity below T_C with subsequent lowering in temperature. Magnetization measured as a function of temperature indicated the ferrimagnetic $T_C = 86 \pm 1$ K which is lower and $T_L = 15 \pm 2$ K in agreement with the reported values for $CoCr_2O_4$. Interestingly the spiral ordering was smeared by the substitution of Ce at the Cr site. The present work envisages the impact of rare-earth ion substitution at the *B* site that can alter the exchange interaction in such a way that causes suppression of the spin modulation.

References:

[1] Y. Yamasaki *et al.*, Phys. Rev. Lett. **96** (2006) 207204.
[2] G. Lawes *et al.*, Phys. Rev. B **74** (2006) 024413.
[3] Y.J. Choi *et al.*, Phys. Rev. Lett. **102** (2009) 067601.
[4] D.P. Dutta *et al.*, J. Appl. Phys. **106** (2009) 043915.
[5] P. Mohanty *et al.*, Nanotechnology **31** (2020)285708.

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