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Magnetocaloric effect in Dy based chromium oxides

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Rare-earth based chromium oxides have attracted substantial research attention over the years because their unusual properties, such as magnetocaloric effect (MCE) [1-5]. An interesting member of these materials is RCrO$_4$, belonging to a family of ABO_4-type oxides, where A is a rare-earth and B = P, As, Cr, V. RCrO$_4$ compounds crystalize in zircon or monazite-type structure depending on the size of the trivalent rare-earth ion and the B element [1]. The RCrO$_4$ compounds are of significance because of the outer shell configuration ($3d^1 4s^0$) of the rare and unstable Cr^{5+} ion and the anomalous super-exchange formed by the zircon-type structure. RCrO$_4$ with R = La, Nd, Sm, Eu and Lu behave antiferromagnetically (AFM), while the remaining oxides in the RCrO$_4$ compound family are ferromagnetic (FM) [1-4]. The magnetic orders of RCrO$_4$ are dependent on the structure, based on the variation in the Cr–O–R bond angles and the interatomic distances [1]. In these materials, the R and Cr moments order simultaneously at the same temperature and the R^{3+} and Cr^{5+} ions, both influence the MCE [4]. In the present work, the magnetic and MCE properties of sol-gel synthesized DyCrO$_4$ rare-earth compound are studied. The as-synthesized sample was found to have an amorphous phase. Calcination of the amorphous powder at 500 ℃ for 2 h, transformed the hydroxide into DyCrO$_4$ oxide. Transmission electron microscopy (TEM) analysis of DyCrO$_4$, showed that the sample is agglomerated, and grain boundaries are indistinguishable. For both samples, the selected area electron diffraction (SAED) patterns confirmed the crystallinity, with the energy dispersive spectroscopy (EDS) verifying the pure elemental composition. The susceptibility as a function of temperature, χ(T), shows paramagnetic (PM) to FM transition for DyCrO$_4$ at 21.6 ± 0.1 K. The positive value of Curie-Weiss temperature, $_{CW}$, confirms the FM behaviour of DyCrO$_4$ sample below the Curie temperature, T_C. The maximum entropy change, ΔS_M (T, H), is observed at about 21.96 K, close to the FM transition of the sample. This observation shows that Dy^{3+} and Cr^{5+} ions both influence the MCE, as Dy and Cr moments order simultaneously at the same temperature, with T_C = 21.6 ± 0.1 K [4]. The transition temperatures observed in the (T) curves are further confirmed with M(μ_0, H) measurements. Further calcining the amorphous powder at 900 ℃ resulted in the formation of DyCrO$_3$ having orthorhombically distorted perovskite structures [5]. The MCE properties of the DyCrO$_3$ [5] and DyCrO$_4$ samples showed that both samples are good for MR application, with DyCrO$_4$ showing more efficiency than DyCrO$_3$ by have high maximum ΔS_M (T, H) and rate of cooling power (RCP) values. The cause of the observed anomaly in magnetic transition and MCE will be discussed.

References

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