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Effect of structural phase transition of GdCrO4 to GdCrO3 on magnetism

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Rare-earth orthochromites (RCrO3) with orthorhombically distorted perovskite (ABO3) structure exhibit a wealth of magnetic phenomena such as temperature-induced magnetization reversal (TMR), spin-reorientation (SR), spin-flipping (SF), and exchange-bias (EB). These occur as a result of magnetic interactions among the cations such as Cr3+−Cr3+, Cr3+−R3+ and R3+−R3+, where R is the rare earth element, such as Gd, Sm, Tm [1]. Rare-earth orthochromites also form a class of magnetoelectric multiferroics which exhibit the coexistence of ferroelectric and magnetic orders [1]. Some of these materials, such as single crystalline GdCrO3, exhibit a giant magnetic entropy change (ΔSm) at a reasonable magnetic field, making it a potential candidate for the application in magnetic refrigeration [2]. TMR and EB have been reported in several RCrO3 compounds due to the competition between the R3+ moment and the canted weak ferromagnetic (FM) component of Cr3+ ions [3]. In the present work, GdCrO4 samples were obtained using sol-gel technique [4]. X-ray diffraction technique was used to identify the phase of the samples. The as synthesized samples were amorphous in nature showing a broad hump. Calcination of the samples at 630 ℃ led to GdCrO4 phase formation [5]. Further calcination of the samples at 1030 ℃ for 1 hour led to the decomposition of GdCrO4 into GdCrO3. Upon heat treatment, the Cr5+ oxidation state in the GdCrO4-zircon phase reduces to the relatively stable Cr3+ together with oxygen loss to stabilize the GdCrO3 perovskite-structure [5]. The role of thermal decomposition of GdCrO4 to GdCrO3 on crystal structure and magnetic transitions, studied using XRD and vibrating sample magnetometer (VSM), will be discussed. Magnetization measurements as a function of temperature (M-T) with different probing magnetic fields were carried out to locate the various magnetic transitions in the samples under different measurement protocols such as zero field cooled (ZFC), field cool cooling (FCC) and field cool warming (FCW). Anomalies in the M-T curves observed at T ≈ 10 K and T ≈ 170 K correspond to spin - flip and Néel transitions, respectively. This is in agreement with previously reported values [1]. The hysteresis loops measured across the transition temperatures validate the magnetic transitions as observed in the M-T curves.

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