Magnetocaloric Effect in Multiferroic $GdMn_{1-x}Ti_xO_3$ Single Crystals

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$GdMnO_3$ has attracted significant attention due to the discovery of multiferroicity in this compound. It crystallizes in the orthorhombically distorted perovskite structure (space group *Pnma*), with Gd ions occupying the 4*c* site, Mn ions on the 4*b* site, and oxygen anions on 4*c* and other crystallographic sites. The compound orders into an antiferromagnetic phase below $T_N \sim 40$ K [1] and then undergoes an order-to-order magnetic phase transition into a low-temperature canted magnetic phase at $T_{\text{lock}} \sim 20$ K. In our previous paper, we reported on Mn–Fe substitution [2], and the present study focuses on Mn–Ti substitution. $GdMn_{1-x}Ti_xO_3$ ($0 \leq x \leq 0.1$) samples were synthesized via the solid-state reaction method to investigate the effect of Ti substitution on structural, magnetic, and magnetocaloric properties. It was found that samples up to $x = 0.1$ are single-phase with a crystal structure similar to the $GdMnO_3$ parent compound. Magnetic measurements reveal that Ti substitution progressively lowers the Néel temperature (T_N) from 42 K ($x = 0$) to 30 K ($x = 0.1$) and suppresses the magnetic locking temperature (T_{lock}) from 20 K to 2 K, indicating weakening of Mn–Mn exchange interactions. In the temperature interval $T_{\text{lock}} < T < T_N$, $M(B)$ curves show simple antiferromagnetic behavior; however, below T_{lock} the $M(B)$ curves change from a complicated butterfly-type profile ($x = 0$) to a simple ferromagnetic one ($x = 0.1$). The system exhibits pronounced magnetic anisotropy in both ferromagnetic and paramagnetic states, resulting in a direction-dependent magnetocaloric effect (MCE). Ordering of Gd^{3+} ions induces an inverse MCE (positive ΔS_M) along the *b* and *c* axes, while along the *a* axis only a normal MCE is observed. The magnetic entropy change displays a broad peak at $T_1 \approx 13$ K with $-\Delta S_M = 11.35$, 8.05, and 7.77 $\text{J kg}^{-1}\text{K}^{-1}$ and corresponding relative cooling power (RCP) = 197.72, 164.70, and 166.78 J kg^{-1} for $x = 0.0$, 0.05, and 0.1 under 5 T. A sharp $-\Delta S_M = 0.55$ $\text{J kg}^{-1}\text{K}^{-1}$ (0.5 T) appears at $T_{\text{lock}} = 20$ K ($x = 0.0$), which shifts to higher temperatures with an applied magnetic field. The large MCE at cryogenic temperatures in these compounds is promising for low-temperature magnetic refrigeration applications.

References:

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