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Large negative thermal expansion in $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($x \le 0.4$), compensating for the thermal expansion of cryogenic materials

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ABSTRACT

As the Mn doping level (x) increases in cubic $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($x \le 0.4$) compounds, the temperature window of negative thermal expansion (NTE) is shifted to lower temperatures and broadened due to the strengthening of ferromagnetism. Large coefficient of linear thermal expansion ($\alpha \sim -22.8$ ppm/K) is observed for $x = 0.25$ and 0.3 at cryogenic temperatures (<120 K). By adding the $x = 0.3$ powders, the thermal expansion of epoxy resin is effectively reduced. Nearly zero thermal expansion ($\alpha \sim 1$ ppm/K) and remarkably improved thermal conductivity are achieved at cryogenic temperatures in the composite with 50 vol.% addition of the NTE filler.

Most materials expand upon heating, which is referred to positive thermal expansion (PTE). The thermally induced change in dimension of a material can lead to thermal stress, which is proportional to temperature variation and the coefficient of thermal expansion (CTE) [1,2]. The accumulation of thermal stress during repeated thermal cycling will inevitably shorten the service life of devices [2]. In addition, thermally driven size change may lower the precision of optical and precise apparatuses [1,2]. If a device is constructed by different components, the thermally induced relative dimension change due to undesirable mismatched CTEs may degrade the performance [1,2]. The circumstances are extremely severe for materials employed in cryogenic engineering where a drastic change of environment temperature is very common [3]. Moreover, the heat capacity of materials decreases at low temperatures, and thus a slight thermal shock may yield a large temperature change. Therefore, effectively controlling the CTEs is a crucial issue for the applications of cryogenic materials [3,4].

Negative thermal expansion (NTE) materials, which contract upon heating, can be used to compensate and control the CTEs of materials by forming composites [1,5,6]. NTE has been observed in various materials due to different mechanisms, including flexible framework in crystal structure [7–9], ferroelectricity [10], charge transformation [11], and magnetovolume effect (MVE) [12–14]. Even so, NTE materials operating at cryogenic temperatures (<120 K) are still rare. Some materials with flexible framework in crystal structure (e.g., ZrW_2O_8 and ScF_3) show NTE over a wide temperature window (ΔT) up to 1000 K [7,8]. But their coefficients of linear thermal expansion (α) are small in magnitude (~ -10 ppm/K) [7,8]. $Sm_{2.75}C_{60}$ shows large NTE with $\alpha = -100$ ppm/K but a small ΔT (blow 32 K) [15]. Large NTE (-36 ppm/K) below the transition from antiferromagnetic (AFM) to paramagnetic (PM) ($T_N = 170$ K) has been reported in nano-sized CuO [16]. However, the thermal expansion of nanocrystal CuO seems to be sample dependent because either tiny NTE or even PTE was reported subsequently [17].

The antiperovskite manganese nitrides $ANMn_3$ (A: transition metal or semiconducting elements) have attracted increasing interest because of the large and tunable isotropic NTE, excellent mechanical properties (large Young's modulus and hardness) and metallicities (good thermal and electrical conductivities) [18–23]. In these compounds, NTE is originated from MVE accompanying with an abrupt contraction of lattice volume at T_N upon heating [14,18]. In order to expand the ΔT of MVE, non-magnetic elements (e.g., Ge, Sn) were most often used to substitute for A atoms in $ANMn_3$ [22]. However, the obtained NTE is usually shifted to higher temperatures as the doping level increases. So, NTE near room temperature or above rather than at cryogenic temperatures was often obtained [22]. In contrast, doping Mn at A sites can shift the NTE window to lower temperatures [24,25], and thus opening a new avenue for achieving cryogenic NTE window in $ANMn_3$ compounds.

Here, we report large low-temperature NTE in $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ compounds. The $x = 0$ sample exhibits a sharp MVE around 230 K [26]. By substituting Mn for Ga/Cu atoms, the ΔT of MVE is broadened and simultaneously shifted to lower temperatures. The samples with $x = 0.25$ and 0.3 show an average α of ~ -20 ppm/K at cryogenic

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temperatures. Furthermore, composites were prepared by dispersing $x = 0.3$ compound into epoxy resin. Compared with neat epoxy, the composites exhibit well-reduced and even nearly zero thermal expansion (ZTE), as well as remarkably enhanced thermal conductivity, which may have potential applications in cryogenic engineering.

Polycrystalline samples of $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($x \le 0.4$) were sintered by direct solid state reaction [24,25]. The samples were checked by X-ray diffraction (XRD) on a Bruker X-ray diffractometer (D8 Advance) with Cu K_α radiations at room temperature. For each sample, the XRD peaks can be indexed with the cubic antiperovskite structure (space group, *Pm-3m*), except for a small amount of MnO impurity (<3%) (Supplementary Fig. S1). The $(Ga_{0.7}Cu_{0.3})_{0.7}Mn_{0.3}NMn_3$ (GCNM) powders with various volume fraction (0, 30, 40 and 50 vol.%) were dispersed into commercially available bisphenol-A epoxy resin (type E51) with curing agent 4, 4′-diaminodiphenylsulfone (DDS). The above mixtures were then subjected to a magnetic stirring. The whole process was operated at 170 °C for half an hour. The final mixtures were poured into the preheated mold and then postcured to form composites. In order to prevent the fillers from sedimentation, the mold was rotating at the rotating speed of 20 rpm during the curing process.

The magnetization measurements were performed on a Superconducting Quantum Interference Device Magnetometer (Quantum Design). Linear thermal expansion $\Delta L/L$ was measured on a Physical Property Measurement System (Quantum Design) using a strain gauge [25]. On the same system, thermal conductivities of both neat epoxy and 50 vol.% GCNM/epoxy composite were measured as a function of temperature. The cross-section microstructures of composites were characterized by scanning electron microscope (SEM) (FEI Quanta 250FEG).

Fig. 1 displays the temperature dependent magnetization M (T) of $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($x \le 0.4$) measured at $H = 100$ Oe under both zero-field-cooling (ZFC) and field-cooling (FC) modes. For $x = 0$, a broad peak at $T_g = 36$ K was detected on ZFC $M(T)$ curve, which was attributed to a glass-like magnetic transition [25]. There is a kink at 245 K indicating an AFM to PM transition (T_N) as often observed in antiperovskite manganese nitrides [24,25]. As x increases, T_g moves to higher temperatures, while T_N is almost independent of x. At around $x = 0.2$, the two transitions are overlapping with each other at ~ 213 K. For $x = 0.25$ a ferromagnetic (FM) to PM transition appears at $T_C = 277$ K. Upon cooling, the ZFC M (T) curve begins to drop at T^* ~ 208 K, while the FC one continues increasing. With further cooling, another drop at $T^\#$ ~ 160 K can be found in both FC and ZFC M (T) curves. As x increases, $T^\#$ is decreased, T_C is increased, but T^* is nearly unaffected. T_C reaches 421 K at $x = 0.4$ (Supplementary Fig. S2). As reported previously, the FM order comes from the isotropic FM interactions between the dopant Mn atoms at the corner sites and the original ones at the face-center sites [27,28].

Fig. 2 shows the temperature dependence of the linear thermal expansion $\Delta L/L$ (360 K) for $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($x \le 0.4$). For the parent compound $Ga_{0.7}Cu_{0.3}NMn_3$, the lattice constant contracts sharply at T_N with a large change of 3620 ppm, which agrees well with the value recently reported by Takenaka et al. [26]. PTE was observed both below and above T_N, with a small and much larger α, respectively. ΔT is expanded to 20 K (210 K−230 K) with α ~ −145.4 ppm/K for $x = 0.15$, and further to 45 K (170 K–215 K) with α ~ −58.7 ppm/K for $x = 0.2$. Meanwhile, the PTE at low temperature is gradually suppressed and finally changes to NTE for $x \ge 0.25$. As a result, in $x = 0.25$ two NTE temperature windows were observed with α ~ −3.1 ppm/K at 10 K–120 K and ~ −51.1 ppm/K at 120 K–175 K. In the whole NTE window (10 K–175 K) the average α is ~ −19.1 ppm/K. Similarly, the α of $x = 0.3$ is ~ −9.3 ppm/K at 10 K–70 K, ~ −37.5 ppm/K at 70 K–125 K, and the average α is about −22.8 ppm/K at 10 K–125 K. For $x = 0.25$ and 0.3 samples, the NTE temperature window covers the cryogenic temperatures. As x increases to 0.31 and 0.32, there exists only one NTE window with α values of ~ −25.4 ppm/K (10 K–90 K) and ~ −25.7 ppm/K (10 K–80 K), respectively. In $x = 0.35$ and 0.40, the NTE window is further shifted to lower temperatures and only a small NTE tail was observed below 20 K.

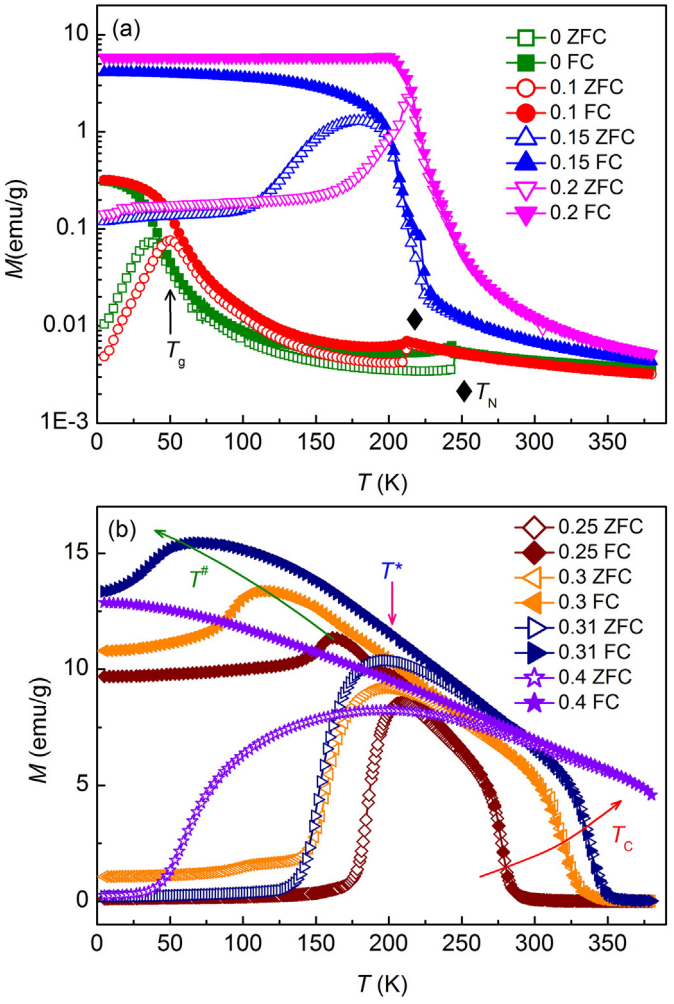

Fig. 1. The magnetization $M(T)$ measured at both zero-field-cooling (open symbols) and field-cooling (solid symbols) modes for $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($0 \le x \le 0.2$) in logarithmic scale (a) and $0.2 < x \le 0.4$ (b). The magnetic transitions at T_g, T_N, T_C, $T^\#$ and T^* are marked (see the main text for their definitions).

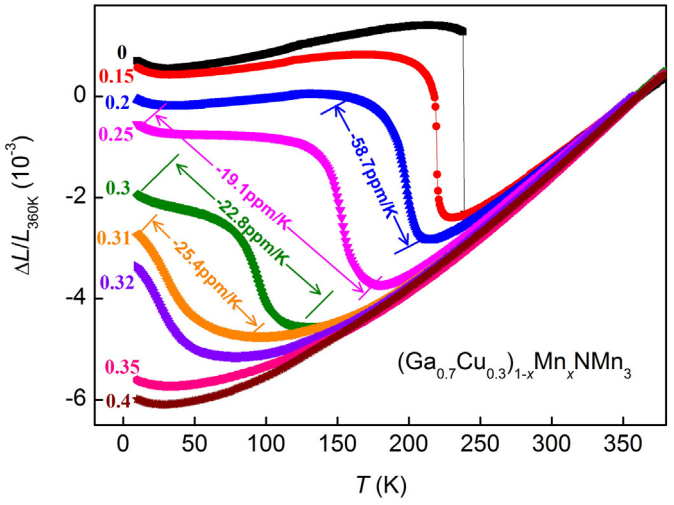

Fig. 2. Linear thermal expansion $\Delta L/L$ (360 K) for $(Ga_{0.7}Cu_{0.3})_{1-x}Mn_xNMn_3$ ($0 \le x \le 0.4$). Average linear coefficients of thermal expansion of selected temperature ranges were marked.