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Negative thermal expansion in Ge-free antiperovskite manganese nitrides: Tin-doping effect

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Giant negative thermal expansion (NTE) recently discovered in antiperovskite manganese nitrides Mn_3AN ($A=\text{Zn}, \text{Ga}$, etc.) is achieved by doping Ge on A as “relaxant” of the sharp volume change at the magnetic transition. To promote wider applications, we synthesized NTE antiperovskites without expensive Ge. We discovered that Sn broadens the volume change, though less effective than Ge. Simultaneous substitution of Sn for A and C for N expands the operation-temperature window of NTE almost as broad as that of the Ge-doped counterpart. We discuss relation between the broadening and the phase instability caused by Ge or Sn. © 2008 American Institute of Physics. [DOI: 10.1063/1.2831715]

Control of thermal expansion is of vital importance in highly advanced industries. Zero thermal expansion is ultimately required in many fields such as high-precision optics and processing. There is also a need to adjust thermal expansion of a material to some particular value: for example, substrates and heat sinks that match the thermal expansion of Si are necessary to avoid possible damages due to exfoliation of interfaces. However, it is difficult, in general, to control thermal expansion of a material in a pure form. This is a reason why materials showing a *negative* thermal expansion (NTE), i.e., materials that contract upon heating, have significant practical value.^{1–6} We can adjust the overall thermal expansion of materials by forming composites containing NTE materials as a thermal expansion compensator.

One of recent epochs is giant NTE around room temperature (T) discovered in Ge-doped antiperovskite manganese nitrides.^{7–9} The good performance of the Ge-doped manganese nitrides, a large, isotropic and nonhysteretic NTE up to $\alpha = -20 \times 10^{-6} \text{ K}^{-1}$ (α : coefficient of linear thermal expansion) as well as tunable α across a wide range of values, gives us prospect of future extensive applications. The origin of this NTE is magnetovolume effect (MVE), or Invar effect, of an itinerant-electron magnet.^{10–13} The technological essence is the discovery of Ge dopant that broadens the sharp volume contraction due to the first-order magnetic transition from low- T antiferromagnetic (AF) to high- T paramagnetic state of the stoichiometric antiperovskites Mn_3AN ($A=\text{Zn}, \text{Ga}$, etc.).¹⁴ Studies to date suggest that Ge may be an exceptional element for broadening the volume change and, without Ge, we have not yet successfully obtained volume contraction as broad as that seen in the Ge-doped compounds. This is one of the mysteries and, hence, the physical as well as chemical roles of this magic element Ge are now being studied from the various points of view.^{15,16} From the practical viewpoints, however, expensive Ge is unfavorable in cost. To promote a wider range of applications, it has been desired to discover low-cost substitutes for Ge. One of the promising candidates is Sn, which lies just under Ge in the

Periodic Table and, hence, is expected to have chemically similar properties.

We have systematically investigated effects of Sn doping on thermal expansion of the antiperovskite manganese nitrides. Tin also broadens the volume change at the magnetic transition. Although the sole doping of Sn is not sufficient for an enough wide operation-temperature window of NTE, the simultaneous substitution of Sn for A and C for N expands the operation-temperature window as broad as that of the Ge-doped compounds.

All of the measurements were performed using sintered polycrystalline samples.^{7–9,17,18} Firstly, we obtained Mn_3AN by solid state reaction. Powders of Mn_3N and pure element A (purity: 99.9% or higher), totally about 2 g, were mixed in a bag filled with nitrogen gas and then sealed in a quartz tube (9 mm in diameter and 20 cm in length) under vacuum ($<10^{-3}$ torr). The sealed quartz tube was heated at $500\text{--}760^\circ\text{C}$ for 40–70 h. We adopted the same procedure for Mn_3SnC , but the starting materials were powders of Mn, Sn, and C in a molar ratio of 3:1:1.05, and the reaction temperature was 850°C . The excess carbon was added in order to compensate possible deficiencies during the reaction. To obtain the solid solution, we mixed powders of the stoichiometric antiperovskites in an appropriate molar ratio, pressed into a pellet, and sealed it in a quartz tube under vacuum. The final sintering was carried out at 800°C for 60 h. [For example, we obtained about 0.4 g of $\text{Mn}_3(\text{Zn}_{1-x}\text{Sn}_x) \times (\text{N}_{1-y}\text{C}_y)$ in one procedure by using mixture of Mn_3ZnN , Mn_3SnN , and Mn_3SnC in a molar ratio of $1-x:x-y:y$.] Linear thermal expansion $\Delta L(T)/L$ was measured using a strain gage (KYOWA; types KFL and KFH). This method is simple but requires a material of known expansion. We used copper (purity: 99.99%) and the corresponding thermal expansion data of pure copper.^{19,20} Measurements of $\Delta L/L$ were partly carried out using a laser-interference dilatometer (ULVAC; LIX-2). The T dependence of lattice constant obtained from x-ray diffraction data was reported for $A=\text{Cu}$,²¹ Zn,²² and Ga.²³ Our $\Delta L/L$ data for stoichiometric Mn_3AN are in quantitative agreement with the above x-ray diffraction data, thus, validating our thermal expansion measurements. Magnetic

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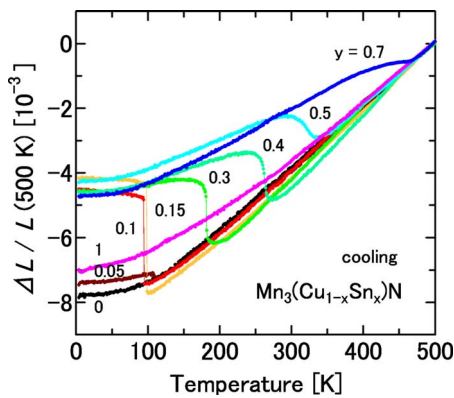


FIG. 1. (Color online) Linear thermal expansion of solid solution $\text{Mn}_3(\text{Cu}_{1-x}\text{Sn}_x)\text{N}$ in a cooling process.

susceptibility $\chi(T)$ was measured at 5000 Oe by a superconducting quantum interference device magnetometer. The crystal structure was investigated by means of x-ray powder diffraction.

Figure 1 displays $\Delta L/L$ data of $\text{Mn}_3(\text{Cu}_{1-x}\text{Sn}_x)\text{N}$. For small x , the thermal expansion at high temperatures is almost independent of Sn content x . The $\Delta L/L$ is linear in T at enough high temperatures and the slope decreases gradually with decreasing temperature, which appears to be consistent with the Grüneisen formula.²⁴ The slope α at room temperature or higher is about $21 \times 10^{-6} \text{ K}^{-1}$, that is larger than Fe ($11.8 \times 10^{-6} \text{ K}^{-1}$) and Cu ($16.5 \times 10^{-6} \text{ K}^{-1}$), comparable with Al ($23.1 \times 10^{-6} \text{ K}^{-1}$). Contrary, $\Delta L/L$ below the magnetic transition temperature is strikingly affected by Sn doping. Mn_3CuN does not show MVE, though it becomes ferromagnetic (FM) at the Curie temperature $T_C = 143 \text{ K}$. However, MVE is recovered by a small amount of Sn and drastically enhanced by a small increment of x from $x = 0.05$ to 0.10 (Fig. 1). The largest discontinuous jump in $\Delta L/L$ at the transition is estimated to be 3.3×10^{-3} for $x = 0.15$, which is next to that of Mn_3ZnN (4.6×10^{-3}) (Ref. 22) and Mn_3GaN (3.8×10^{-3}) (Ref. 23) among all of Mn_3AX ($X = \text{N, C}$) members, and comparable to that of $\text{Mn}_3(\text{Cu}_{0.85}\text{Ge}_{0.15})\text{N}$, the maximum in the Ge-doped series.⁷ It is noteworthy that at the same compositional region the cubic structure is restored. [The susceptibility $\chi(T)$ also changes from FM to AF around here, but it is rather continuous.] The present x-ray diffraction study revealed that the crystal structure changes from high- T cubic to low- T tetragonal T_1 ($c/a < 1$) at the anomaly temperature in $\Delta L/L$ (the magnetic-transition temperature) for $x \leq 0.05$, while it remains cubic over a whole T range for $0.10 \leq x \leq 0.7$.

As Sn substitution proceeds, the transition temperature increases and the volume change becomes gradual. It is known empirically that the transition temperature of Mn_3AN is scaled by the number of valence electrons on A, n_v .¹⁴ The drastic increase of transition temperature with Sn substitution is consistent with the empirical rule. (n_v is 1 and 4 for Cu and Sn, respectively.) It should be noticed that the gradual lattice change gives rise to a large negative slope (large NTE) over a wide T range around $x = 0.5$, similar to the Ge-doped counterpart.⁷⁻⁹ For example, $\text{Mn}_3(\text{Cu}_{0.5}\text{Sn}_{0.5})\text{N}$ (Fig. 1) shows NTE of $\alpha = -28 \times 10^{-6} \text{ K}^{-1}$ at $T = 296\text{--}332 \text{ K}$ ($\Delta T = 36 \text{ K}$). This NTE is isotropic because the cubic structure is maintained down to the lowest temperature. In addition, this NTE does not show any hysteresis. For further

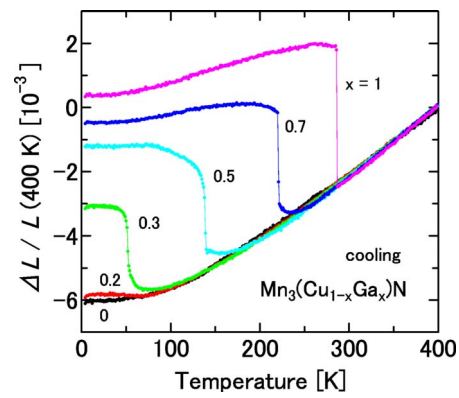


FIG. 2. (Color online) Linear thermal expansion of solid solution $\text{Mn}_3(\text{Cu}_{1-x}\text{Ga}_x)\text{N}$ in a cooling process.

Sn-doped compound $x = 0.7$, the transition temperature is about 470 K and the anomaly in $\Delta L/L$ appears around this temperature but the slope α does not become negative. Above 470 K , α is also about $21 \times 10^{-6} \text{ K}^{-1}$ indicating that the Sn doping does not affect $\Delta L/L$ above the transition temperature. Although the anomaly in $\Delta L/L$ appears, at first glance, to decrease as Sn doping proceeds, the spontaneous volume magnetostriction ω_s at the lowest- T ground state does not show remarkable change with Sn doping for $x > 0.1$. (Roughly speaking, ω_s is estimated as the difference in $\Delta L/L$ between Mn_3CuN and each Sn-doped compound.) Thus, the MVE itself does not become weak as Sn doping proceeds at least for $0.1 < x < 0.7$, although it becomes broad.

The present Sn-doping effects on the thermal expansion are essentially the same as the Ge-doping effects, except for the minimum x required for recovery of the cubic structure ($x = 0.15$ for Ge and $x = 0.1$ for Sn) and the width of the operation-temperature window of NTE ($\Delta T \sim 90 \text{ K}$ for Ge and $\Delta T \sim 40 \text{ K}$ for Sn). However, such a broad volume change is exceptionally achieved by Ge or Sn doping, and in many cases, the sharp volume change is not affected against the A-site substitution. Figure 2 displays $\Delta L/L$ of $\text{Mn}_3(\text{Cu}_{1-x}\text{Ga}_x)\text{N}$. Contrary to Ge- and Sn-doped series, the Ga-doped series exhibit the sharp volume change over all the concentration range. The difference is presumably ascribed to the difference in physical properties of the end materials.

Studies to date show that the Γ^{5g} triangular AF spin configuration as well as the cubic crystal structure are key ingredients for the pronounced MVE, typically for Mn_3ZnN and Mn_3GaN .¹⁴ The recent neutron-diffraction study¹⁵ indicates that also for solid solution $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$ the Γ^{5g} magnetic structure and the cubic crystal structure are simultaneously restored at $x = 0.15$ where MVE appears. For $\text{Mn}_3(\text{Cu}_{1-x}\text{Sn}_x)\text{N}$, the magnetic structure is yet to be confirmed but the present study shows that recovery of the cubic structure is associated with the appearance of MVE. On the contrary, both Mn_3GeN (Ref. 25) and Mn_3SnN ,²⁶ showing no MVE, do not have the cubic crystal or the Γ^{5g} magnetic structures. Therefore, as the doping proceeds, $\text{Mn}_3(\text{Cu}_{1-x}\text{M}_x)\text{N}$ ($M = \text{Ge, Sn}$) becomes unstable against the phase transition in crystal and magnetic structures that finally undergoes at Mn_3GeN or Mn_3SnN . The relaxed volume change is regarded as consequences of the above phase instability and/or phase competition. Indeed, the magnetic and structural phases of $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$ are very busy for

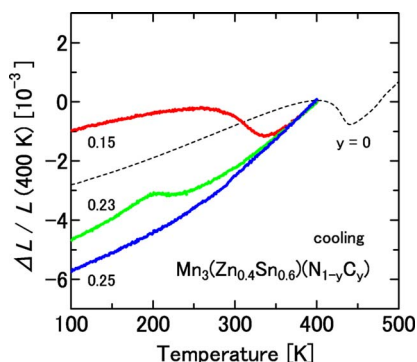


FIG. 3. (Color online) Linear thermal expansion of solid solution $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{1-y}\text{C}_y)$ in a cooling process. For $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})\text{N}$ (dashed line), data were collected by a laser-interference dilatometer in a warming process. The thermal expansion is nonhysteretic for the present system.

$x > 0.7$.¹⁴ Our preliminary experiments also suggest that the physical properties of $\text{Mn}_3(\text{Cu}_{1-x}\text{M}_x)\text{N}$ ($M = \text{Ge}, \text{Sn}$) are quite sensitive to the condition of thermal treatment in the neighborhood of $x \sim 1$.

The operation-temperature window of NTE is about half for the Sn-doped system compared with the Ge-doped one. Expansion of the temperature window was achieved by simultaneous substitution of Sn for A and C for N. Figure 3 displays $\Delta L/L$ of $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{1-y}\text{C}_y)$ showing effect of the “codoping.” The pure nitride $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})\text{N}$ shows NTE of $\alpha = -38 \times 10^{-6} \text{ K}^{-1}$ at $T = 410\text{--}440$ ($\Delta T = 30 \text{ K}$). With increasing C content y , the operation temperature decreases and its width becomes broader. Around $y = 0.1$, room-temperature NTE is realized. $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{0.85}\text{C}_{0.15})$ shows NTE of $\alpha = -23 \times 10^{-6} \text{ K}^{-1}$ at $T = 270\text{--}336$ ($\Delta T = 66 \text{ K}$). The decrease of the operation temperature is presumably due to the reduction in the number of valence electrons n_v . For further C doping, the anomaly in $\Delta L/L$ itself becomes weak and finally disappears for $y = 0.25$. By employing the codoping of Sn at 30%–60% level plus C, we did manage to achieve a NTE over a wide T range around room temperature using no expensive elements such as Ge.

In summary, we have successfully synthesized the anti-perovskite manganese nitrides showing negative thermal expansion without expensive Ge. Although the sole doping of Sn is not sufficient for an enough wide operation-temperature window, the simultaneous substitution of Sn for A and C for N can relax the sharp volume change in the almost same degree of the Ge-doped compounds. The low-

cost Ge-free manganese nitrides have been desired and accelerate research and development for commercial applications of this material.

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