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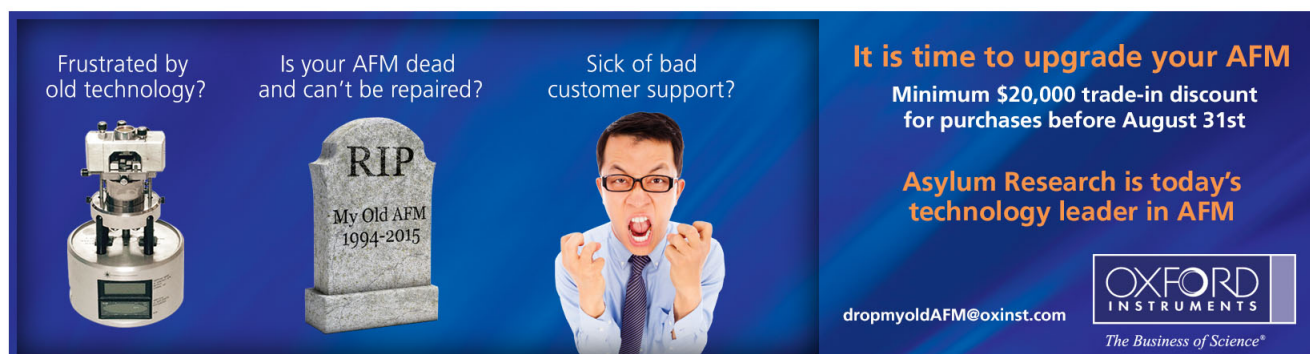Low-temperature negative thermal expansion of the antiperovskite manganese nitride Mn 3 CuN codoped with Ge and Si
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Giant negative thermal expansion in antiperovskite manganese nitrides

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Giant negative thermal expansion (NTE), over $\alpha = -30 \times 10^{-6} \, \text{K}^{-1}$ (α: coefficient of linear thermal expansion), at room temperature can be achieved in Mn_3ZnN-based antiperovskite manganese nitrides by simultaneous substitution of C and B for N as well as Sn for Zn. The developed NTE nitrides show larger negative α, although the width of the operating-temperature window is comparable to that of Mn_3CuN-based materials developed to date. Such a large, isotropic, and high-stiffness NTE material can compensate for the large positive thermal expansion of, for example, even aluminum or plastic materials. © 2011 American Institute of Physics. [doi:10.1063/1.3540604]

Control of thermal expansion is extremely important in various advanced industrial applications. Zero thermal expansion is ultimately required for use in many fields, such as high-precision optics and processing. There is a critical current need to be able to adjust the thermal expansion of a material to a particular value; for example, substrates and heat sinks that match the thermal expansion of Si are necessary to avoid possible damage caused by exfoliation of interfaces. However, it is generally difficult to control the thermal expansion of a material that is in a pure form. For this reason, materials that contract on heating—materials showing *negative* thermal expansion (NTE)—have considerable practical value.[1–5] We can adjust the overall thermal expansion of a material by forming a composite containing an NTE material as a thermal-expansion compensator, for instance.

Antiperovskite manganese nitride Mn_3AN ($A = Zn$, Ga, etc.)[6] is a candidate material exhibiting large NTE effects.[7–12] This class of nitrides is well known for a large magnetovolume effect, wherein a large volume expansion is triggered by magnetic transition from a high-temperature (high-T) paramagnetic (PM) phase to a low-T antiferromagnetic (AF) ordered phase. We have discovered that a discontinuous volume change in Mn_3AN becomes broad to an order of 100 K; giant NTE at room temperature is exhibited by partial substitution of Ge (Ref. 7) or Sn (Ref. 9) for A.

The development of NTE materials with larger volume change has been sought to expand applications of these materials. With respect to function and cost, Mn_3ZnN-based compounds[13,14] are anticipated as candidates for practical NTE materials, with better performance than their Mn_3CuN-based counterparts, which are currently available. Aiming to use Mn_3ZnN-based compounds as NTE materials operating at room temperatures, however, more precise control of the chemical composition is necessary because the magnetic transition temperature (operating temperature) of Mn_3ZnN-based compounds is higher than that of Mn_3CuN-based compounds. For Mn_3AN, the operating temperature and coefficient of linear thermal expansion α are difficult to control independently by changing the chemical composition.[7] We examined the effects of "codoping"—simultaneous sub-

stitution of C and B for N, as well as Sn for Zn—and verified the potential of the Mn_3ZnN-based compounds for use as commercial NTE materials.

All measurements were carried out using sintered polycrystalline samples.[7–9] First, we obtained Mn_3AN by a solid state reaction. Powders of Mn_2N and pure elemental Zn or Sn (99.9% or higher purity), a total of ~ 4 g, were mixed in a bag filled with nitrogen gas and then sealed in a quartz tube (8 mm diameter, 20 cm length) under vacuum ($<10^{-3}$ Torr). The sealed quartz tube was heated at 500–760 °C for 40–70 h. We adopted the same procedure for Mn_3SnC and Mn_3ZnB, for which powders of Mn, Zn, Sn, C, and B were used as starting materials; the reaction temperatures were 850 and 640 °C, respectively. The obtained Mn_3ZnB was not a pure-form antiperovskite but a precursor with a molar ratio of Mn:Zn:B = 3:1:1. To obtain a solid solution, we mixed powders of the stoichiometric compounds obtained above in an appropriate molar ratio, pressed into pellets, and sealed in a quartz tube under vacuum. Final sintering was conducted 800–850 °C for 60 h. The linear thermal expansion $\Delta L/L$ was measured using a strain gauge (KFL type; Kyowa Dengyo Co., Ltd.) in the low-temperature region (4–400 K). This simple method requires a material with known coefficient of thermal expansion. We used copper (99.99% purity) as such a known material and the corresponding thermal expansion data for pure copper.[15,16] Measurements of $\Delta L/L$ were partly conducted using a laser-interference dilatometer (LIX-2; Ulvac) in the high-temperature region (100–500 K). Magnetic susceptibility was measured at 5000 Oe using a superconducting quantum interference device magnetometer. The crystal structure was investigated using powder x-ray diffraction.

Figure 1 displays the linear thermal expansion $\Delta L/L$ of stoichiometric Mn_3AN ($A = Ni$, Zn, Ga, Pd, and In) and $Mn_3(Cu_{0.85}Ge_{0.15})N$ (stoichiometric Mn_3CuN exhibits no magnetovolume effect[17–19]). For all the compounds, the volume expands discontinuously at the magnetic transition from the high-T PM phase to the low-T AF ordered phase. The reentrant transition of Mn_3ZnN at 80 K is associated with another magnetic transition.[20] The absolute value of the volume change in Mn_3ZnN is about 1.5 times larger than that of $Mn_3(Cu_{0.85}Ge_{0.15})N$, showing its high potential for use as a thermal expansion compensator. Although Mn_3GaN shows a

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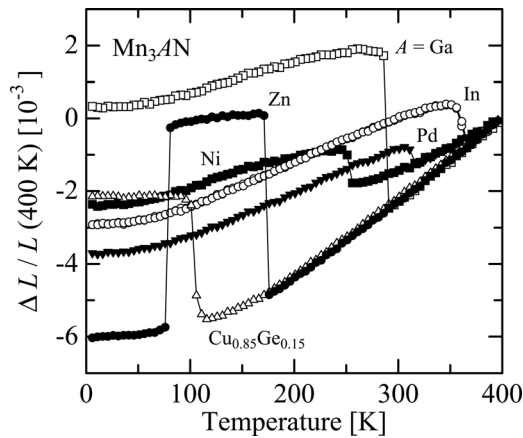
FIG. 1. Linear thermal expansion $\Delta L/L$ (400 K) of Mn$_3$AN.

large volume change as well, it is unfavorable in terms of cost because of the presence of Ga, which is an expensive element.

Figure 2 shows the linear thermal expansion $\Delta L/L$ of a solid-solution Mn$_3$(Zn$_{1-x}$Sn$_x$)N system. As the Sn substitution proceeds, the magnetic transition temperature becomes higher. It is known empirically that the transition temperature of Mn$_3$AN is scaled by the number of valence electrons on A, n_v.[6] The increased transition temperature with the Sn substitution is apparently consistent with this empirical rule: n_v is, respectively, 2 and 4 for Zn and Sn. For all the compounds, the $\Delta L/L$ data fall on the same line for each phase; the coefficient of linear thermal expansion α is commonly estimated to be 10×10^{-6} K^{-1} for the AF phase and 25×10^{-6} K^{-1} for the PM phase. The NTE behavior is realized when switching from the low-T universal line with $\alpha_{AF} = 10 \times 10^{-6}$ K^{-1} to the high-T universal line with $\alpha_{PM} = 25 \times 10^{-6}$ K^{-1}. This universality enables estimation of the best performance of this system that can be realized. For example, in principle, we can obtain an NTE of $\alpha = -25 \times 10^{-6}$ K^{-1} at $T = 280$–365 ($\Delta T = 85$ K) using Mn$_3$ZnN-based compounds. This value of α is twice as large as that of Mn$_3$(Cu$_{0.5}$Ge$_{0.5}$)N ($\alpha = -12 \times 10^{-6}$ K^{-1}), which has the same operating-temperature window. In the NTE manganese nitrides, the wider the operating-temperature window, the smaller is the absolute value of the negative α.
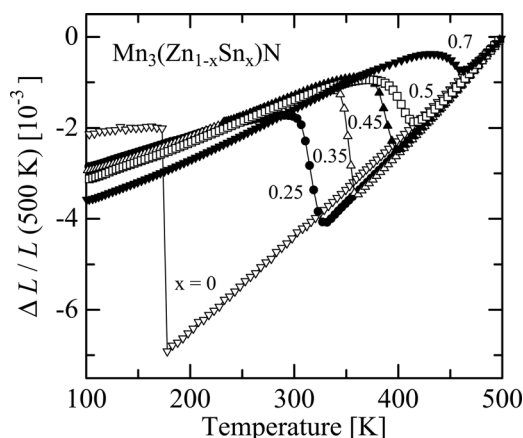
FIG. 2. Linear thermal expansion $\Delta L/L$ (500 K) of solid solution Mn$_3$(Zn$_{1-x}$Sn$_x$)N.
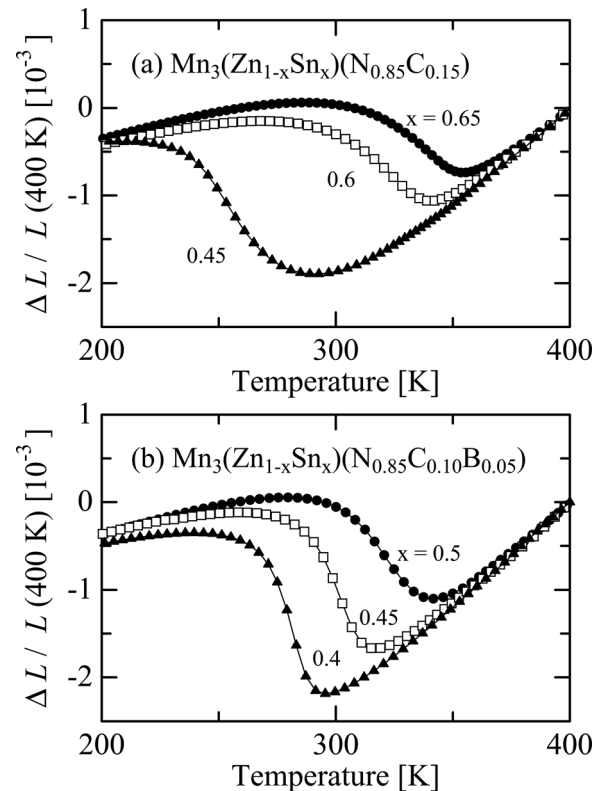
FIG. 3. Linear thermal expansion $\Delta L/L$ (400 K) of solid solution (a) Mn$_3$(Zn$_{1-x}$Sn$_x$)(N$_{0.85}$C$_{0.15}$) and (b) Mn$_3$(Zn$_{1-x}$Sn$_x$)(N$_{0.85}$C$_{0.10}$B$_{0.05}$).

However, such high performance has not yet been realized in the Mn$_3$(Zn$_{1-x}$Sn$_x$)N shown in Fig. 2. In particular, broadening of the operating-temperature window is indispensable for a wider range of applications. To improve performance, we adopted "codoping," which is simultaneous substitution of C and B for N, as well as Sn for Zn. Fig. 3(a) shows $\Delta L/L$ for Mn$_3$(Zn$_{1-x}$Sn$_x$)(N$_{0.85}$C$_{0.15}$). By carbon substitution, the operating temperature is lowered and its width is enlarged. For example, Mn$_3$(Zn$_{0.4}$Sn$_{0.6}$)(N$_{0.85}$C$_{0.15}$) and Mn$_3$(Zn$_{0.35}$Sn$_{0.65}$)(N$_{0.85}$C$_{0.15}$), respectively, yield NTE of $\alpha = -23 \times 10^{-6}$ K^{-1} at $T = 270$–336 ($\Delta T = 66$ K) and $\alpha = -21 \times 10^{-6}$ K^{-1} at $T = 284$–352 ($\Delta T = 68$ K). However, carbon doping seems to decrease the absolute value of the volume change. As a result, the value of α is comparable to or even smaller than that of the "ideal" performance estimated above, although the operating-temperature window is narrower than that of the ideal one.

The reduction in the volume change described above might be suppressed by boron doping. Fig. 3(b) shows $\Delta L/L$ for Mn$_3$(Zn$_{1-x}$Sn$_x$)(N$_{0.85}$C$_{0.10}$B$_{0.05}$). The simultaneous substitution of C and B for N achieved a larger NTE compared with Mn$_3$(Zn$_{1-x}$Sn$_x$)(N$_{0.85}$C$_{0.15}$). For example, Mn$_3$(Zn$_{0.55}$Sn$_{0.45}$)(N$_{0.85}$C$_{0.10}$B$_{0.05}$) and Mn$_3$(Zn$_{0.5}$Sn$_{0.5}$)(N$_{0.85}$C$_{0.10}$B$_{0.05}$), respectively, show an NTE of $\alpha = -37 \times 10^{-6}$ K^{-1} at $T = 270$–325 ($\Delta T = 55$ K) and $\alpha = -30 \times 10^{-6}$ K^{-1} at $T = 280$–340 ($\Delta T = 60$ K). Thus, using codoping of Sn at a 40–70% level plus C and B, we can manage to achieve NTE over a wide T range around room temperature.

Manganese nitride is a unique NTE material with numerous advantages over existing NTE materials. (1) The

operating temperature and coefficient of NTE are controllable in a pure form without forming composites. (2) The negative α is tunable across a wide range of values. Indeed, it can be greater than -30×10^{-6} K^{-1}, which is one order of magnitude larger than that for commercial NTE materials. [Typically, α is of the order of 10^{-6} K^{-1}, although for ZrW$_2$O$_8$, $\alpha = -9 \times 10^{-6}$ K^{-1} (Ref. 1).] (3) The negative thermal expansion is isotropic and shows no hysteresis, which is a great advantage. For example, microcracking during repeated thermal cycling can be avoided. Most existing NTE materials, with the exception of ZrW$_2$O$_8$, are anisotropic. (4) We can fabricate NTE antiperovskites using only ecologically favorable and economical elements such as Mn, Zn, and Sn. (5) The manganese nitrides are also stable in moist air and are mechanically hard. In particular, they exhibit an exceptionally large Young's modulus E of 211–320 GPa.[21] The Young's modulus of commercial NTE materials currently in use is typically 100 GPa or lower.[22]

The large negative α and large Young's modulus E of the manganese nitrides are essential for fabrication of composites. The absolute value of the large NTE over -30×10^{-6} K^{-1} is larger than that of the positive α of Fe (11.8×10^{-6} K^{-1}) and Al (23.1×10^{-6} K^{-1}). In addition, a high-stiffness (large Young's modulus) material can compensate for thermal expansion more effectively because the coefficient of linear thermal expansion α of a composite is defined as $\alpha = (\alpha_1 E_1 v_1 + \alpha_2 E_2 v_2)/(E_1 v_1 + E_2 v_2)$. Here, v is the volume fraction ($v_1 + v_2 = 1$), and suffixes 1 and 2 represent the component materials of a composite. Lightweight, stiff, and low-expansion materials can be fabricated by combining the manganese nitrides with plastics or lightweight metals such as aluminum, which, in spite of their light weight and high machinability, are considered unsuitable as matrices of low-expansion composites because of their small Young's modulus and large thermal expansion.

In summary, the simultaneous substitution of C and B for N as well as Sn for Zn enables us to obtain Mn$_3$ZnN-based NTE materials with a larger negative α (although the width of the operating-temperature window is comparable) than that of Mn$_3$CuN-based materials. The existence of giant, isotropic NTE compatible with the enhanced Young's modulus implies that extremely stiff, stable, and lightweight low-thermal-expansion composites can be designed based on antiperovskite manganese nitrides for use in various applications.

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