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Zero thermal expansion in a pure-form antiperovskite manganese nitride

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A zero thermal expansion material in a pure form is fabricated using an antiperovskite manganese nitride. The isotropic zero thermal expansion is achieved by optimizing the heat treatment and the chemical composition. **The present study suggests that the heat treatment affects the thermal expansion mainly via the nitrogen content of the material.** The obtained materials exhibit a low expansion of $|\alpha| < 0.5 \times 10^{-6} \text{ K}^{-1}$ (α is the coefficient of linear thermal expansion) over a broad temperature range, which includes room temperature. They are desirable for many fields of industry as reliable, mechanically hard, and low-cost zero thermal expansion materials. © 2009 American Institute of Physics. [DOI: 10.1063/1.3110046]

Recent advances in technology require industrial materials capable of withstanding severe conditions. Although thermal expansion is typically from 10^{-5} to 10^{-6} in length, currently it is a fatal problem; for example, high-precision processing such as ULSI fabrication requires accuracy on the nanometer scale. Thus, zero thermal expansion (ZTE) materials are desired in many fields of precision engineering, including machining and processing, optics, and electronics.

One method to cancel thermal expansion is to form composites with an overall ZTE by combining normal materials displaying a positive thermal expansion with exceptional materials showing a *negative* thermal expansion (NTE). Therefore, NTE materials have significant practical value as thermal-expansion compensators.^{1,2} However, in such ZTE composites, one ingredient expands while the other contracts as the temperature T changes. Hence, the stress induced at interfaces or grain boundaries can cause microcracks, which degrade the mechanical properties. However, this microcracking problem can be overcome if the material is formed by one material without thermal expansion. Such an ideal pure-form ZTE material is highly desired.^{3–5}

One candidate for a pure-form ZTE material is antiperovskite manganese nitride Mn_3XN (X denotes transitional metals and semiconducting elements),⁶ which has recently received much attention due to its large NTE up to $\alpha = -30 \times 10^{-6} \text{ K}^{-1}$ (α is the coefficient of linear thermal expansion) at room temperature.^{7–12} For these manganese nitrides, partial substitution of the constituent elements can tune the negative value of α across a wide range of values. Herein we control the thermal expansion by optimizing the heat treatment conditions and chemical composition to achieve a single-phase manganese nitride with ZTE over a broad T range, which includes room temperature.

All of the measurements were performed using polycrystalline samples sintered in a sealed quartz tube.^{11,13–15} **Changing the temperature of the final sintering T_s between 800 and 980 °C tuned the thermal expansion.** Linear thermal expansion $\Delta L(T)/L$ was measured using a strain gage (KYOWA, type KFL) and a laser-interference dilatometer

(ULVAC, LIX-2). The accuracy of the length change measurement using the laser-interference dilatometer was 20 nm, which is equivalent to less than 10^{-7} K^{-1} in α .¹⁶ The data measured by the strain gage, shown by symbols here, agrees with the data measured by the laser-interference dilatometer, shown by lines (see Fig. 2). Comparing the data measured by both methods, the resolution of the strain gage measurements was estimated to be $\pm 0.5 \times 10^{-6} \text{ K}^{-1}$ in α . The x-ray powder diffraction measurements confirmed that all of the samples have the cubic structure in the T region of NTE and ZTE. **The nitrogen content of the sample was determined by using both a HORIBA EMGA-2800 and a YANACO MT-6 analysers.**¹⁵

The discovery that Ge doping onto the X sites modifies the sharp volume contraction into a continuous one has triggered recent studies designed to utilize Mn_3XN as a thermal-expansion compensator.⁷ Stoichiometric Mn_3XN , such as Mn_3GaN , exhibits a sharp volume contraction due to magnetovolume effects.^{6,14,17} As Ge doping proceeds, the volume contraction becomes gradual and a giant NTE appears in the doping range of about 50%. Further Ge doping weakens the anomaly of the thermal expansion and eventually restores a positive thermal expansion. Therefore, we envisaged that optimization of the chemical composition may realize ZTE in a pure-form Mn_3XN . Indeed $\text{Mn}_3(\text{Ga}_{0.5}\text{Ge}_{0.4}\text{Mn}_{0.1})\text{N}$ displays a low thermal expansion around $\alpha = -3 \times 10^{-6} \text{ K}^{-1}$.⁷ Thus, **we initially determined the optimal chemical composition exhibiting ZTE using simultaneous doping of Ge or Sn on X and of C on N.**

Figure 1 shows the linear thermal expansion $\Delta L(T)/L$ of $\text{Mn}_3(\text{Ga}_{0.5}\text{Ge}_{0.4}\text{Mn}_{0.1})(\text{N}_{1-x}\text{C}_x)$ measured by a strain gage. The pure nitride ($x=0$) displayed $\alpha = -3 \times 10^{-6} \text{ K}^{-1}$ above 334 K. **As the carbon concentration x increased, the operating temperature of NTE (magnetic transition temperature) decreased, the volume contraction became gradual, and the slope of $\Delta L(T)/L$ decreased.** $\text{Mn}_3(\text{Ga}_{0.5}\text{Ge}_{0.4}\text{Mn}_{0.1}) \times (\text{N}_{0.9}\text{C}_{0.1})$ showed a low expansion of $|\alpha| < 0.5 \times 10^{-6} \text{ K}^{-1}$ at $T = 190\text{--}272 \text{ K}$. Upon further carbon doping, the thermal expansion became positive over the entire T region and the anomaly became inconspicuous. The present results provide considerable evidence that a pure-form ZTE is possible in this class of nitride. However, due to the high

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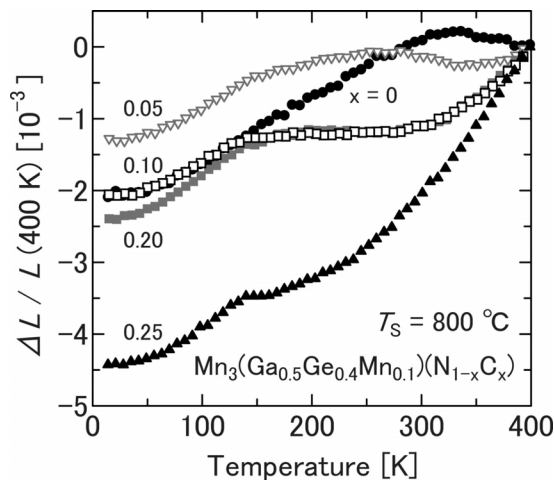


FIG. 1. Linear thermal expansion of a solid solution of $\text{Mn}_3(\text{Ga}_{0.5}\text{Ge}_{0.4}\text{Mn}_{0.1})(\text{N}_{1-x}\text{C}_x)$ measured by a strain gage. All of the samples were sintered at 800 °C. Nitrogen and carbon contents are nominal.

cost of Ga and Ge, economical substitutes are required for wider practical applications.

Zinc and copper are also effective for thermal contraction when they occupy the X sites. In addition, our recent study¹¹ suggests that Sn doping onto the X sites also modifies the sharp volume contraction into a gradual one with the help of simultaneous N-site doping. We tried to produce a low-cost ZTE in $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{1-x}\text{C}_x)$ by optimizing the chemical composition but reduction of the thermal expansion was insufficient under the limitation of a fixed sintering temperature $T_s = 800$ °C. This is probably because the compositional region exhibiting ZTE is too narrow under the adopted sintering condition. We then explored the relation between T_s and α . The slope of $\Delta L(T)/L$ was drastically reduced when T_s was above 800 °C (Fig. 2). $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{0.8}\text{C}_{0.2})$ sintered at 800 °C showed $\alpha = -20 \times 10^{-6} \text{ K}^{-1}$ at $T = 205\text{--}270$ K. As T_s increased, the operating temperature increased and the negative slope decreased. The sample sintered at 945 °C exhibited a low expansion of $|\alpha| < 1 \times 10^{-6} \text{ K}^{-1}$ at $T = 235\text{--}292$ K. Further optimization of the sintering conditions should realize a lower thermal expansion.

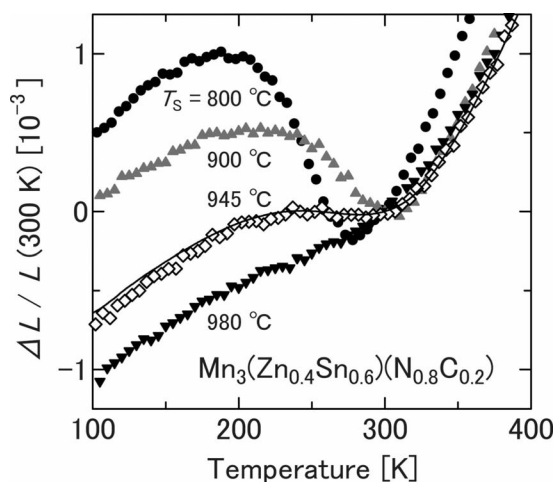


FIG. 2. Linear thermal expansion of $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{0.8}\text{C}_{0.2})$ measured by a strain gage (symbols) and by a laser-interference dilatometer (line). Sintering temperatures T_s change between 800 and 980 °C. Nitrogen and carbon contents are nominal.

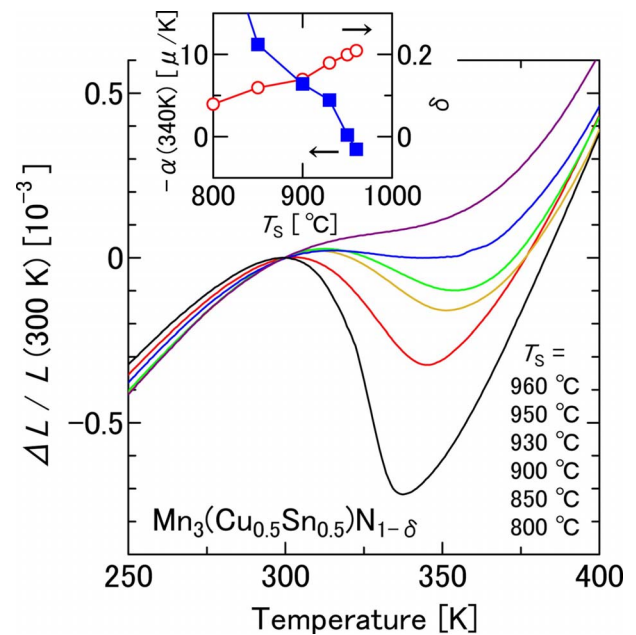


FIG. 3. (Color online) Linear thermal expansion of $\text{Mn}_3(\text{Cu}_{1-x}\text{Sn}_x)\text{N}_{1-\delta}$ measured by a laser-interference dilatometer. Sintering temperatures T_s , shown in the main panel, change between 800 and 960 °C. Inset: Coefficient of linear thermal expansion α at 340 K (solid squares) and amount of the nitrogen deficiency δ (open circles) vs T_s .

sion. The NTE behavior disappeared when the sample was sintered at a higher temperature.

Another candidate of a low-cost ZTE material is $\text{Mn}_3(\text{Cu}_{1-x}\text{Sn}_x)\text{N}$. $\text{Mn}_3(\text{Cu}_{0.5}\text{Sn}_{0.5})\text{N}$ sintered at 800 °C showed $\alpha = -28 \times 10^{-6} \text{ K}^{-1}$ at $T = 304\text{--}332$ K (Fig. 3). As the sintering temperature increased, the operating temperature increased and the negative slope decreased. The relationship between T_s and α is summarized in the inset (solid squares). The sample sintered at 950 °C showed a low expansion of $|\alpha| < 0.5 \times 10^{-6} \text{ K}^{-1}$ at $T = 307\text{--}355$ K, especially $|\alpha| < 0.1 \times 10^{-6} \text{ K}^{-1}$ at $T = 335\text{--}350$ K. The operating temperature can be easily controlled by changing the chemical composition. Figure 4 shows $\Delta L(T)/L$ for the slightly modified compositions, while a low expansion of $|\alpha| < 0.5$

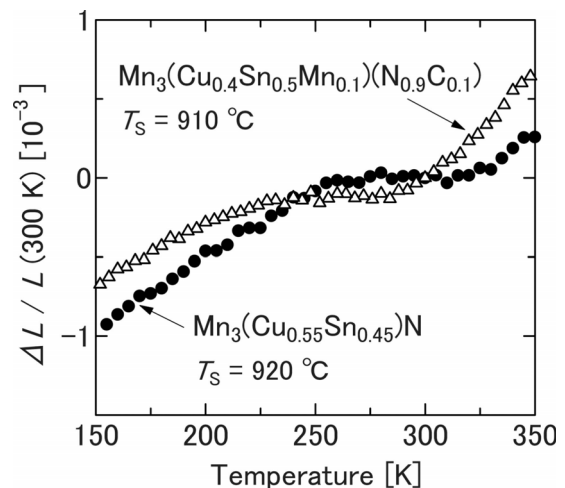


FIG. 4. Linear thermal expansion of $\text{Mn}_3(\text{Cu}_{0.55}\text{Sn}_{0.45})\text{N}$ sintered at 920 °C (solid circles) and $\text{Mn}_3(\text{Cu}_{0.4}\text{Sn}_{0.5}\text{Mn}_{0.1})(\text{N}_{0.9}\text{C}_{0.1})$ sintered at 910 °C (open triangles) measured by a strain gage. Nitrogen and carbon contents are nominal.

$\times 10^{-6} \text{ K}^{-1}$ is maintained. $\text{Mn}_3(\text{Cu}_{0.55}\text{Sn}_{0.45})\text{N}$ sintered at 920°C showed a low expansion of $|\alpha| < 0.5 \times 10^{-6} \text{ K}^{-1}$ at $T = 255\text{--}323 \text{ K}$, which includes room temperature.

Generally the amount of interstitial nitrogen in metals and compounds tends to decrease as the sintering temperature T_s increases. Indeed, the present analyses confirmed that the nitrogen deficiency of the sample, defined as δ in the formula $\text{Mn}_3(\text{Cu}_{0.5}\text{Sn}_{0.5})\text{N}_{1-\delta}$, increased with increasing T_s (inset of Fig. 3, open circles). Therefore, the nitrogen deficiency is one of main origins of decrease in the negative slope of $\Delta L(T)/L$. The present ZTE in a pure-form manganese nitride is a consequence of broadening the sharp volume contraction in Mn_3XN . It is known so far that such broadening can be caused by Ge or Sn doping onto the X sites and carbon doping onto the nitrogen sites. The present study suggests that the nitrogen deficiency effectively tunes the broadening, which has practical implications because the nitrogen deficiencies can be easily controlled by the sintering temperature T_s .

Recent experiments¹⁸ suggest that the local strain caused by Ge doping is relevant to the broadening of the volume contraction. Broadening of the volume contraction is accelerated by nitrogen deficiencies and/or carbon replacement on the nitrogen site because this type of local strain may be assisted by the randomness in the nitrogen site. However, the carbon dopants decreased the operating temperature, while the nitrogen deficiencies increased the operating temperature. The role of the nitrogen sites on the electronic states and physical properties of the antiperovskites should be further evaluated. In this regard, effects of the heat treatment other than nitrogen deficiency should be also explored because the physical properties of antiperovskites are sensitive not only to the amount of defects but also to the degree of their ordering in the interstitial-element (B, C, N, etc.) site.¹⁹ A detailed investigation on the effect of the heat treatment on the physical properties is currently under way.

The present ZTE material has the following advantages compared to ZTE composites currently in use. (1) *Reliable in performance*: Because the present material consists of a single-phase manganese nitride with isotropic crystal structure, the grain boundaries are stable against T variation and the microcracks are avoided. (2) *Economical*: All of the constituent elements (Mn, Zn, Cu, Sn, N, and C) are economical, and the fabrication process is simple due to the pure form. (3) *Mechanical hardness*: The pure-form materials demonstrate characteristic hardness, which is inherent to nitrides. Due to this improved performance, the present ZTE materials may be commonplace in future commercial applications. In particular, they may be employed even for structural components where current commercial ZTE composites are inappropriate. Because the sintering process of the manganese

nitrides is still crude, the intrinsic mechanical properties have yet to be estimated. Nevertheless, preliminary measurements suggest that they have an enhanced Vickers hardness of 400 Hv and an exceptionally large Young's modulus of 300 GPa.²⁰ As the sintering procedure is improved, stiffer and harder ZTE materials will be fabricated.

In summary, we have fabricated zero thermal expansion materials, which consist of only a pure-form antiperovskite manganese nitride by optimizing the chemical composition and heat treatment conditions. A low thermal expansion is achieved mainly by nitrogen deficiencies, which are controlled via the final sintering temperature. The present zero thermal expansion material may have a wide range of applications, including zero-expansion structural parts.

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¹A. W. Sleight, *Inorg. Chem.* **37**, 2854 (1998).

²A. E. Phillips, A. L. Goodwin, G. J. Halder, P. D. Southon, and C. J. Kepert, *Angew. Chem., Int. Ed.* **47**, 1396 (2008).

³A. W. Sleight, *Endeavour* **19**, 64 (1995).

⁴J. R. Salvador, F. Guo, T. Hogan, and M. G. Kanatzidis, *Nature (London)* **425**, 702 (2003).

⁵T. Suzuki and A. Omote, *J. Am. Ceram. Soc.* **89**, 691 (2006).

⁶For a review, see D. Fruchart and E. F. Bertaut, *J. Phys. Soc. Jpn.* **44**, 781 (1978).

⁷K. Takenaka and H. Takagi, *Appl. Phys. Lett.* **87**, 261902 (2005).

⁸K. Takenaka and H. Takagi, *Mater. Trans.* **47**, 471 (2006).

⁹Y. Sun, C. Wang, Y. Wen, K. Zhu, and J. Zhao, *Appl. Phys. Lett.* **91**, 231913 (2007).

¹⁰S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, and S. Shamoto, *Phys. Rev. B* **77**, 020409(R) (2008).

¹¹K. Takenaka, K. Asano, M. Misawa, and H. Takagi, *Appl. Phys. Lett.* **92**, 011927 (2008).

¹²R. Huang, L. Li, F. Cai, X. Xu, and L. Qian, *Appl. Phys. Lett.* **93**, 081902 (2008).

¹³T. Kaneko, T. Kanomata, and K. Shirakawa, *J. Phys. Soc. Jpn.* **56**, 4047 (1987).

¹⁴W. S. Kim, E. O. Chi, J. C. Kim, N. H. Hur, K. W. Lee, and Y. N. Choi, *Phys. Rev. B* **68**, 172402 (2003).

¹⁵K. Asano, K. Koyama, and K. Takenaka, *Appl. Phys. Lett.* **92**, 161909 (2008).

¹⁶H. Imai, M. Okaji, T. Kishii, H. Sagara, H. Aikawa, and R. Kato, *Int. J. Thermophys.* **11**, 937 (1990).

¹⁷Ph. l'Heritier, D. Boursier, R. Fruchart, and D. Fruchart, *Mater. Res. Bull.* **14**, 1203 (1979).

¹⁸S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, M. Takigawa, and S. Shamoto, *Phys. Rev. Lett.* **101**, 205901 (2008).

¹⁹Y. Kimura, K. Sakai, F.-G. Wei, and Y. Mishima, *Intermetallics* **14**, 1262 (2006).

²⁰Y. Nakamura, K. Takenaka, A. Kishimoto, and H. Takagi (unpublished).