

Giant Negative Thermal Expansion in Antiperovskite Manganese Nitrides: Materials, Mechanism, and Applications

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Introduction

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 *negative* thermal expansion (NTE), materials that contract on heating, have significant practical value [1]. We can adjust the overall thermal expansion of materials by forming composites containing NTE materials as a thermal-expansion compensator.

The antiperovskite manganese nitride Mn_3AN ($A = Zn, Ga, \text{etc}$) [2] is a potential candidate for exhibiting large NTE effects. These nitrides are well known for their large magnetovolume effect (MVE) [3]: the lattice volume shows a sudden and pronounced increase with decreasing temperature T , as large as a few %, at the antiferromagnetic transition temperature. Recently, we discovered that the discontinuous volume change of Mn_3AN becomes broad to an order of 100 K and giant NTE at room temperature is exhibited by partial substitution of Ge or Sn for A [4-6]. Here, we briefly review this discovery and discuss a prospect of the future applications.

Experimental

All of the measurements were performed using sintered polycrystalline samples made by solid-state reaction. Powders of Mn_2N , Fe_4N , C, and pure elemental A (purity: 99.9% or higher) were used as the starting materials. $\Delta L/L$ (400 K) was measured using a strain gauge (KYOWA; type KFL). Magnetic susceptibility was measured at 5000 Oe by a SQUID magnetometer. The crystal structure was investigated by means of powder x-ray diffraction. The details of the experiments were described in our previous papers [4-6].

Results and Discussion

Figure 1 displays linear thermal expansion $\Delta L/L$ data for $Mn_3(Cu_{1-x}Ge_x)N$. Although Mn_3CuN does not show MVE, it is recovered by a small amount of Ge and drastically enhanced by a small increment of x from $x = 0.1$ to 0.15. The discontinuous jump in $\Delta L/L$ at the

transition is estimated to be 3.3×10^{-3} for $x = 0.15$, which is comparable to those of Mn_3ZnN (4.6×10^{-3}) and Mn_3GaN (3.8×10^{-3}), and one of the largest among Mn_3AX ($X = N, C$) members [2,4,7]. At the same compositional region, the cubic structure is recovered. The present x-ray diffraction study revealed that the crystal structure changes from high- T cubic to low- T tetragonal at the magnetic transition (or the anomaly temperature in $\Delta L/L$) for $x = 0-0.1$, while it remains cubic over a whole temperature range for $x = 0.15-0.7$.

As Ge 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 [2]. The drastic increase of transition temperature with Ge substitution is consistent with the empirical rule. (n_v is 1, 2, 3, and 4 for Cu, Zn, Ga, and Ge, respectively.) It should be noticed that the gradual lattice change gives rise to a large negative slope (large NTE) over a wide T range for $x = 0.4-0.6$. $Mn_3(Cu_{0.5}Ge_{0.5})N$, for example, shows NTE of $\alpha = -12 \times 10^{-6} K^{-1}$ (α : coefficient of linear thermal expansion) at $T = 280-365$ ($\Delta T = 85$ K). This NTE is isotropic because the cubic structure is maintained down to low temperatures. In addition, this NTE does not show any hysteresis. With further Ge substitution, the transition temperature exceeds 400 K and the anomaly in $\Delta L/L$ could not be identified within the covered T range.

Other members such as Mn_3ZnN and Mn_3GaN also show a broadened MVE and resultant NTE behavior upon Ge substitution. In order to achieve better performances, we adopted “co-doping”, simultaneous doping of Ge and another dopants. By employing the co-doping, we did

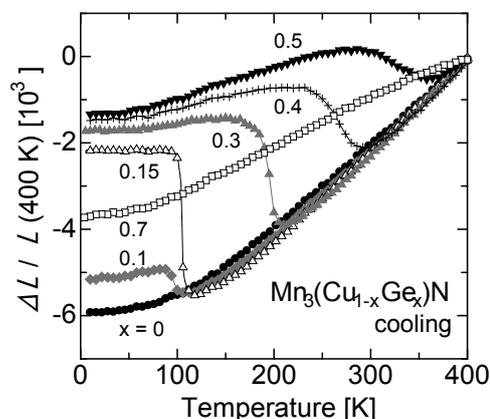


Fig. 1 Linear thermal expansion $\Delta L/L$ (400 K) of solid solution $Mn_3(Cu_{1-x}Ge_x)N$.

manage to achieve a NTE over a wide T range around room temperature. $\text{Mn}_3(\text{Ga}_{0.7}\text{Ge}_{0.3})(\text{N}_{0.88}\text{C}_{0.12})$ shows $\alpha = -18 \times 10^{-6} \text{ K}^{-1}$ at $T = 197\text{-}319 \text{ K}$ ($\Delta T = 122 \text{ K}$) and $\text{Mn}_3(\text{Zn}_{0.4}\text{Ge}_{0.55}\text{Mn}_{0.05})(\text{N}_{0.8}\text{C}_{0.2})$ shows $\alpha = -3 \times 10^{-6} \text{ K}^{-1}$ at $T = 150\text{-}305 \text{ K}$ ($\Delta T = 155 \text{ K}$). We also found that partial replacement of Mn by Fe lowers the operative temperature. $(\text{Mn}_{0.96}\text{Fe}_{0.04})_3(\text{Zn}_{0.5}\text{Ge}_{0.5})\text{N}$ shows NTE of $\alpha = -25 \times 10^{-6} \text{ K}^{-1}$ at $T = 316\text{-}386$ ($\Delta T = 70 \text{ K}$). Note that the T window for NTE is comparable to the criterion for practical use ($\Delta T \sim 100 \text{ K}$).

From the practical viewpoints, however, expensive elements such as Ga and Ge are unfavorable in cost. To promote a wider range of applications, it has been desired to discover low-cost substitutes. We have synthesized low-cost NTE compounds without Ga or Ge by co-doping of Sn and C. $\text{Mn}_3(\text{Zn}_{0.4}\text{Sn}_{0.6})(\text{N}_{0.85}\text{C}_{0.15})$, for example, shows $\alpha = -23 \times 10^{-6} \text{ K}^{-1}$ at $T = 270\text{-}336 \text{ K}$ ($\Delta T = 66 \text{ K}$).

Manganese nitride is a unique NTE material with a number of advantages over existing NTE materials. (1) The operation temperature and the coefficient of NTE can be controllable in a pure form without forming composites. (2) The negative α is tunable across a wide range of values. Indeed, at its largest, it can be $-25 \times 10^{-6} \text{ K}^{-1}$, one order of magnitude larger than commercial NTE materials. (Typically, α is of order 10^{-6} K^{-1} , though for ZrW_2O_8 , $\alpha = -9 \times 10^{-6} \text{ K}^{-1}$ [1].) This impacts on practical applications. The present NTE materials can compensate even high thermal expansion of plastics by forming composites. (3) The negative thermal expansion is isotropic and does not show any hysteresis. This can be a great advantage. For example, micro-cracking during repeated thermal cycling may be avoided. Most of the existing NTE materials, with the exception of ZrW_2O_8 , are anisotropic. (4) We can fabricate the NTE antiperovskites using only ecological and economical elements such as Mn, Cu, Zn, and Sn. (5) The manganese nitrides are also stable in moist air and mechanically hard. (6) Finally, the manganese nitrides

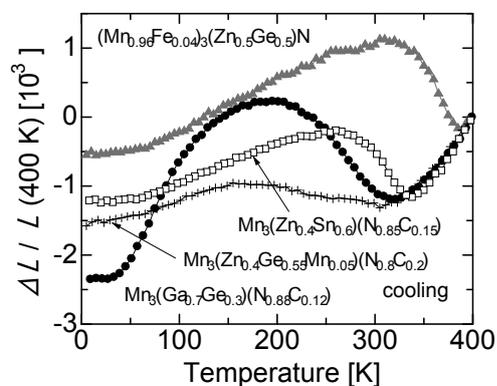


Fig. 2 Linear thermal expansion $\Delta L/L$ (400 K) of "co-doped" antiperovskite manganese nitrides showing negative thermal expansion.

are metallic. For many applications, NTE materials that have high electrical or thermal conductivity would be desirable.

In addition to substitution of the constituent elements, we have explored effects of nitrogen deficiencies on the thermal expansion properties of the manganese nitrides. The nitrogen deficiencies are introduced by increasing the temperature of heat treatment. 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 [8]. The obtained materials exhibits a low expansion of $|\alpha| < 0.5 \times 10^{-6} \text{ K}^{-1}$ over a broad temperature range, which includes room temperature. They have a wide range of applications, including zero-expansion structural parts, because they are reliable, mechanically hard, and low cost.

Conclusion

We successfully controlled thermal expansion properties of antiperovskite manganese nitrides. The gigantic negative thermal expansion (NTE) is several and ten times higher than that of commercially available NTE materials. Such a large, isotropic and nonhysteretic NTE is desirable for wide practical applications.

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References

1. Sleight, A. W. Compounds that contract on heating. *Inorg. Chem.*, **37** (1998) 2854-2860.
2. Fruchart, D. and Bertaut, E. F. Magnetic studies of the metallic perovskite-type compounds of manganese. *J. Phys. Soc. Jpn.*, **44** (1978) 781-791.
3. Wasserman, E. F., in *Ferromagnetic Materials Vol. 5*, edited by Buschow, K. H. J. and Wohlfarth, E. P. (Elsevier Science Publishing, 1990), 237-322.
4. Takenaka, K. and Takagi, H. Giant negative thermal expansion in Ge-doped anti-perovskite manganese nitrides. *Appl. Phys. Lett.*, **87** (2005) 261902.
5. Takenaka, K. and Takagi, H. Magnetovolume effect and negative thermal expansion in $\text{Mn}_3(\text{Cu}_{1-x}\text{Ge}_x)\text{N}$. *Mater. Trans.*, **47** (2006) 471-474.
6. Takenaka, K., Asano, K., Misawa, M. and Takagi, H. Negative thermal expansion in Ge-free antiperovskite manganese nitrides: Tin-doping effect. *Appl. Phys. Lett.*, **92** (2008) 011927.
7. Fruchart, R., Madar, R., Barberon, M., Fruchart, E. and Lorthioir, M. G. Transitions magnetiques et deformations cristallographiques associees dans les nitrides du type perovskite ZnMn_3N et SnMn_3N . *J. Phys. (Paris)*, **32 C1** (1971) 982-984.
8. Takenaka, K. and Takagi, H. Zero thermal expansion in a pure-form antiperovskite manganese nitride. *Appl. Phys. Lett.*, **94** (2009) 131904.