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Focus Issue Review

Negative thermal expansion induced by intermetallic charge transfer

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Abstract

Suppression of thermal expansion is of great importance for industry. Negative thermal expansion (NTE) materials which shrink on heating and expand on cooling are therefore attracting keen attention. Here we provide a brief overview of NTE induced by intermetallic charge transfer in A-site ordered double perovskites SaCu₃Fe₄O₁₂ and LaCu₃Fe_{4-x}Mn_xO₁₂, as well as in Bi or Ni substituted BiNiO₃. The last compound shows a colossal dilatometric linear thermal expansion coefficient exceeding -70×10^{-6} K⁻¹ near room temperature, in the temperature range which can be controlled by substitution.

Keywords: negative thermal expansion, perovskite, charge transfer, x-ray diffraction

1. Introduction

Thermal expansion originating from anharmonic vibration of atoms is a common feature of matter in solid, liquid and gas states. For example, the coefficient of linear thermal expansion (CTE) of iron is $\alpha_L = (1/L)(\Delta L/\Delta T) = -11.6 \times 10^{-6} \text{ K}^{-1}$ leading to the 1.16 μ m expansion of a 10 cm long rod on heating by 1 K. Nanoscale production of electronic devices and optical communications requires precise positioning, and thus, even such small amounts of thermal expansion can be a problem. Negative thermal expansion (NTE) materials which shrink on heating and expand on cooling are attracting much interest because these are expected to compensate for the thermal expansion of structure materials by making composites [1–4]. Useful NTE materials for zero or controlled expansion composites should show a smooth contraction while heating through a wide temperature range. The

compounds with flexible frameworks in the crystal structures (mechanism 1) such as β -LiAlSiO₄ [1, 2] ZrW₂O₈ [5], and Cd $(CN)_2$ [6] can be categorized into the first generation of NTE materials. Indeed, crystallized glass, where β -LiAlSiO₄ crystallizes into a Li-Al-Si-O glass matrix, is widely used as a low thermal expansion material in cooktops and astronomical telescopes. The last decade has seen a remarkable development in materials with NTE resulting from phase transitions. In particular, a large NTE over $\alpha_{\rm I} = -30 \times 10^{-6} \, {\rm K}^{-1}$ coupled with a magnetic transition (mechanism 2) was discovered in an anti-perovskite manganese nitride [7-13]. PbTiO₃ based perovskites were found to show NTE originating from a ferroelectric-paraelectric transition (mechanism 3) [14-19]. An intermetallic charge transfer transition was shown to cause volume shrinkage (mechanism 4) in A-site ordered double perovskites upon heating [20-23]. Colossal dilatometric linear thermal expansion coefficient over $-70 \times 10^{-6} \text{ K}^{-1}$ is observed in the controlled temperature range near room temperature (RT) in Bi or Ni substituted perovskite compound BiNiO₃ [24–26]. The properties of these typical NTE materials are summarized in table 1, and the crystal structures of selected compounds are shown in figure 1. In this review,



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Figure 1. Crystal structures of NTE compounds. ZrW_2O_8 (a), anti-perovskite manganese nitride Mn_3XN (b), $ACu_3Fe_4O_{12}$ (c) and ambient-pressure and high-pressure phases of BiNiO₃ (d) and (e).

Table 1. Coefficients of linear thermal expansion and operating temperatures T_{oper} of typical negative thermal expansion materials.

Materials	$\alpha (\times 10^{-6} \mathrm{K}^{-1})$	T_{oper} (K)	Mechanism	Method ^a	References
β -LiAlSiO ₄	-1 to -6	300-900	1	D	[1, 2]
ZrW_2O_8	-6	425-1030	1	D/N	[5]
$Cd(CN)_2$	-33.5	170-375	1	D	[<mark>6</mark>]
Mn ₃ Cu _{0.53} Ge _{0.47} N	-16	265-340	2	D	[<mark>9</mark>]
Mn _{3.1} Zn _{0.5} Sn _{0.4} N	-36.4	335-375	2	D	[13]
PbTiO ₃	-6.6	298-367	3	Х	[14]
0.5PbTiO ₃ -0.5BiFeO ₃	-13.5	300-600	3	Х	[19]
SrCu ₃ Fe ₄ O ₁₂	-22.6	220-230	4	Х	[21]
Bi _{0.95} La _{0.05} NiO ₃	-82	320-380	4	D	[24]
$Bi_{0.95}Nd_{0.05}NiO_3$	-134	380-410	4	D	[25]

D: dilatometry, N: neutron diffraction, X: x-ray diffraction.

we focus on the NTE induced by intermetallic charge transition in A-site ordered double perovskites and modified BiNiO₃.

2. NTE induced by intermetallic charge transfer in A-site ordered double perovskites

LaCu₃Fe₄O₁₂ has so-called A-site ordered double perovskite structure where A-site of perovskite ABO3 is periodically occupied by La^{3+} and Cu^{3+} as shown in figure 1(c). The formal valence state of this compound is $La^{3+}Cu_3^{3+}Fe_4^{3+}O_{12}$ at RT. Intermetallic charge transfer between Cu³⁺ and Fe³⁺ takes place on heating above 393 K resulting in $La^{3+}Cu_3^{2+}Fe_4^{3.75+}O_{12}$ high-temperature (HT) phase. Because of the shrinkage of Fe-O bonds, the unit cell volume shrinks by 1% [20]. This transition is discontinuous first order one as shown in figure 2 and the thermal expansion coefficient cannot be defined. However, replacement of La³⁺ by Sr²⁺ changes the nature of transition to second order and NTE with $\alpha_{\rm L} = 22.6 \times 10^{-6} \,\mathrm{K}^{-1}$ is observed between 200 and 230 K as shown in figure 2 [21]. The NTE was confirmed by dilatometric measurements with thermal mechanical analysis (TMA) and strain gauge (figure 3) [22]. Similar NTE is also realized in LaCu₃Fe_{4-x}Mn_xO₁₂ as shown in figure 4 [23].

3. NTE in A- or B- site substituted perovskite compound BiNiO_3

3.1. Pressure induced intermetallic charge transfer in BiNiO₃

BiNiO₃ is a perovskite compound with a triclinically distorted crystal structure (space group P-1) stabilized by high-pressure (HP) synthesis at 6 GPa. Bi is a main group element, but it has Bi³⁺/Bi⁵⁺ charge degree of freedom depending on 6s² and 6s⁰ electronic configurations. These occupy distinct crystallographic sites in BiNiO₃ whose valence distribution is unusual $Bi_{0.5}^{3+}Bi_{0.5}^{5+}Ni^{2+}O_3$ as illustrated in figure 1(d) [27]. Powder neutron diffraction (PND) [28] and x-ray absorption spectroscopy (XAS) [29] studies revealed a pressure-induced melting of the Bi-charge disproportionation at 3-4 GPa and a simultaneous Ni to Bi charge transfer accompanied by a structural change to the orthorhombic GdFeO₃ type perovskite superstructure (figure 1(e)) with valence distribution Bi³⁺Ni³⁺O₃ and an insulator to metal transition. The structural transition is accompanied by a discrete shrinkage of lattice parameters and a 2.5% decrease in the unit cell volume [24]. This large change results from the dominant contraction of the Ni-O perovskite framework as Ni²⁺ is oxidized to the smaller Ni³⁺ at the transition, which outweighs the lattice expanding effects of reducing Bi⁵⁺ to Bi³⁺ and increases in the Ni-O-Ni angles.



Figures 2. Temperature dependence of lattice constants of $LaCu_3Fe_4O_{12}$ and $SrCu_3Fe_4O_{12}$ determined by XRD measurements. Reproduced with permission from [21], copyright 2011 John Wiley and Sons.



Figure 3. Thermal expansion of $SrCu_3Fe_4O_{12}$ evaluated by XRD, SXRD, TMA and strain gauge. Reproduced with permission from [22].

The PND and XAS results have been used to construct the *P*–*T* phase diagram for BiNiO₃ shown in figure 5. BiNiO₃ decomposes above 500 K at ambient pressure (AP), but is stabilized up to at least 565 K at 1.8 GPa (and to ~1300 K at 6 GPa under synthesis conditions). The boundary between the low pressure and temperature (LPT) and HPT phases has slope $dT_{CT}/dp = -140$ KGPa⁻¹. The 2.5–3.4% volume contraction occurs on both pressurizing and heating.

3.2. NTE in Bi_{0.95}La_{0.05}NiO₃

The large ΔT_{CT} of BiNiO₃ shows that colossal NTE is feasible but the transition is only observed above pressures of 1.5 GPa in pure BiNiO₃. Chemical substitutions for Bi is used to suppress the charge disproportionation in the Bi_{0.5}³⁺Bi_{0.5}⁵⁺Ni²⁺O₃ phase and thereby shift the charge transfer transition to near ambient conditions. Partial substitution of La³⁺ without charge degree of freedom for Bi destabilizes the characteristic Bi³⁺/Bi⁵⁺ disproportionation and shift the charge transfer transition to around 350 K at AP in Bi_{0.95}La_{0.05}NiO₃ [24, 30].

Synchrotron x-ray diffraction (SXRD) patterns on $Bi_{0.95}La_{0.05}NiO_3$ in figure 6(a) show merging of five main peaks characteristic for the triclinic phase with Bi^{3+}/Bi^{5+} charge disproportionation into three indicating the transition to the orthorhombic phase with (Bi, La)³⁺Ni³⁺O₃ valence distribution. The 2.9% volume shrinkage, which has a similar magnitude to



Figure 4. Temperature dependence of unit cell volumes of $LaCu_3Fe_{4-x}Mn_xO_{12}$ determined by XRD measurements. Reprinted with permission from [23], copyright 2014, AIP Publishing LLC.



Figure 5. Pressure–temperature phase diagram of $BiNiO_3$ determined by PND and XAS studies. Circles and squares show PND and XAS data, and blue and red symbols correspond to the low pressure and temperature (LPT) and high pressure and temperature (HPT) phases, respectively. Reproduced from [24].

that observed in undoped BiNiO₃ under a pressure of 1.8 GPa, was observed as shown in figure 6(b). Coexistence of the low and high temperature phases is observed at three points in the transition region and a linear fit to the weighted average volumes is used to obtain the transition width of $\Delta T_{CT} = 70$ K. Such a coexistence of two phases changing the fractions as functions of temperature appears to against the Gibbs phase rule, but is commonly observed in ZrO₂ and HfO₂ [31]. In these ceramics, low-temperature monoclinic and HT tetragonal phases coexist changing the phase fractions across the diffusionless (martensitic) phase transition. The deviation of the pressure from 1 atm at the domain boundary is thought to be the origin of such phenomena. The crystallographic volume thermal expansion coefficient of Bi0.95La0.05NiO3 between 300 and 370 K is $\alpha_{\rm V} = -413 \times 10^{-6} \text{ K}^{-1}$ and the linear coefficient is $\alpha_{\rm L} =$ $-137 \times 10^{-6} \text{ K}^{-1}$, showing that colossal NTE magnitudes are observable in Bi_{1-x}La_xNiO₃. Crystallography predicts the upper limit of the magnitude of thermal expansion as the formation of pores and other microstructural defects can lessen the effect in bulk ceramics.



Figure 6. Selected SXRD data of $Bi_{0.95}La_{0.05}NiO_3$ at various temperatures (a). Reproduced from [30]. Temperature dependence of the unit cell volume (b). The dilatometric linear thermal expansion of $Bi_{0.95}La_{0.05}NiO_3$ on heating and cooling (c) The inset shows the sample pasted on the strain gauge. Reproduced from [24].

Dilatometric measurements on a polycrystalline ceramic of $Bi_{0.95}La_{0.05}NiO_3$ prepared at HP were made during heating and cooling cycles as shown in figure 6(c). The strain $\Delta L/L$ (400 K) increases with increasing temperature up to 270 K indicating the normal positive thermal expansion, but decreases above 270 K. The average observed α_L between 270 and 400 K is -49×10^{-6} K⁻¹ and the maximum negative slope between 320 and 380 K corresponds to a linear thermal expansion coefficient of -82×10^{-6} K⁻¹ [24]. It was confirmed that the oxidation of Ni ion from 2+ to 3+ was the origin of this volume shrinkage by XAS measurement [32].

3.3. Tunable NTE in $Bi_{1-x}Ln_xNiO_3$ (Ln: Lanthanides)

The temperature range of NTE and the CTE can be controlled by tuning the composition, i.e., the element substituting Bi and the degree of substitution. Thermal expansion of Bi_{1-x} Ln_xNiO_3 (Ln:=La, Nd, Eu, Dy) were investigated [25]. Figure 7(a) shows the temperature dependence of the weighted average volume calculated from the unit cell volumes and the phase fractions refined by Rietveld analysis of laboratory XRD data. NTE with temperature hysteresis is present in all samples. The dilatometric curves measured by TMA (figure 7(b)) are consistent with the volume change. Table 2 summarizes the NTE parameters determined from the TMA data. For all systems, the temperature range of NTE upon heating shifts to the lower side and the volume shrinkage becomes more gradual as the Ln³⁺ content increases. Figure 8(a) summarizes the compositional dependence of the onset temperature of NTE (T_{NTE}) and the temperature hysteresis width. The $T_{\rm NTE}$ decreases almost linearly with the amount of substituted lanthanide, and this result shows that the temperature range can be controlled by chemical tuning. The transition temperature also depends on the ionic radius of Ln^{3+} . Substitution with a small Ln^{3+} stabilizes the triclinic phase and maintains it at a HT. This lanthanide dependence is explained as follows. Under HPT synthesis conditions, Bi_{1-r} Ln_xNiO_3 is in the orthorhombic (Bi, $Ln)^{3+}Ni^{3+}O_3$ state with an unique Bi/Ln site. The La3+ ions are homogeneously distributed, because the ionic radius of La³⁺ is close to that of Bi³⁺. Suppose such a sample is in the HT (Bi, Ln)³⁺Ni³⁺O₃ state at AP. Charge disproportionation on cooling is suppressed by the presence of a La³⁺ ion at the Bi⁵⁺ site of the triclinic low-temperature phase. $T_{\rm NTE}$ is therefore lowered by the La substitution, and the orthorhombic phase is dominant for Bi_{0.90}La_{0.10}NiO₃. On the other hand, a large difference in ionic radius between Bi3+ and small Ln3+ ions should lead to a partial Bi³⁺/Ln³⁺ ordering, as schematically illustrated in figure 8(b). The charge transfer transition is less affected by a small Ln³⁺ because Bi⁵⁺ can periodically exist owing to the Ln/Bi ordering. Since the amount of substitution is small, the partial ordering is not observed as a super structure. La substitution decreases not only the transition temperature, but also the sharpness of the transition, which is also a consequence of randomness. The unit cell volume and $\Delta L/L$ curves for $Bi_{1-x}Dy_xNiO_3$ in figure 7 show parallel shifts to a lower temperature with increasing x. Most importantly, the temperature hysteresis summarized in figure 8(a) is reduced by using smaller lanthanides.



Figure 7. Temperature dependence of the weighted average volume (a) and the dilatometric linear thermal expansion (b) of $Bi_{1-x}Ln_xNiO_3$ (Ln = La, Nd, Eu, Dy; x = 0.05, 0.075, 0.10) on heating and cooling. Reproduced from [25].

Table 2. The liner thermal expansion coefficient α_L of Bi_{1-x}Ln_xNiO₃ (Ln = La, Eu, Nd, Dy) estimated by the dilatometric measurement on heating [25].

Ln	x in $Bi_{1-x}Ln_xNiO_3$	<i>T</i> (K)	$\alpha_{\rm L} \ (10^{-6} \ {\rm K}^{-1})$
La	0.05	$330 \rightarrow 380$	-71
	0.075	$220 \rightarrow 280$	-36
	0.10	$210 \rightarrow 300$	-5
Nd	0.05	$380 \rightarrow 410$	-134
	0.075	$280 \rightarrow 330$	-41
	0.10	$200 \rightarrow 250$	-30
Eu	0.05	$430 \rightarrow 460$	-70
	0.075	$330 \rightarrow 390$	-41
	0.10	$250 \rightarrow 310$	-44
Dy	0.05	$440 \rightarrow 470$	-104
	0.075	$410 \rightarrow 460$	-43
	0.10	$330 \rightarrow 380$	-68

3.4. NTE in $LaNi_{1-x}M_xO_3$ (M: Al and Ga)

The above discussed NTE results from the temperature induced intermetallic charge transfer between Bi⁵⁺ and Ni²⁺. The presence of Ln³⁺ in Bi⁵⁺ site destabilizes the Bi³⁺/Bi⁵⁺ charge disproportionation in Bi³⁺_{0.5}Bi⁵⁺_{0.5}Ni²⁺O₃ and HP phase of Bi³⁺Ni³⁺O₃ appears on heating at AP. In this context, substitution of Ni²⁺ with a trivalent ion is also expected to stabilize Bi³⁺(Ni, M)³⁺O₃ and thus leads to NTE. Figure 9 shows the XRD patterns of BiNi_{1-x}M_xO₃ (M=Ga, Al) on heating. They reveal transitions from triclinic to orthorhombic phases via coexistence of two phases, essentially the same as those for Bi_{1-x}Ln_xNiO₃.

The weighted average unit cell volumes obtained by the Rietveld analysis of the XRD data are plotted in figure 10. Note that only the data on heating are plotted since the



Figure 8. (a) Composition dependence of $T_{\rm NTE}$ on heating and temperature hysteresis width determined by XRD. (b) Illustration of the Bi/Ln layer of BiNiO₃ (left) and Bi_{1-x}Ln_xNiO₃ (center and right) in the HT orthorhombic phase and low temperature triclinic phase (LT). Filled and open circles represent valence of 3+ and 5+, respectively. The large Ln³⁺ ions (red) are distributed homogeneously. On the other hand, the small Ln³⁺ ions (blue) have partial ordering. Reproduced from [25].



Figure 9. SXRD patterns of $BiNi_{0.925}Al_{0.025}O_3$ (a), $BiNi_{0.9}Al_{0.1}O_3$ (b), $BiNi_{0.95}Ga_{0.05}O_3$ (c) and $BiNi_{0.9}Ga_{0.01}O_3$ (d) at various temperatures revealing the transition from triclinic to orthorhombic phases on heating.

samples partially decomposed after heating up to 550 K. These results indicate the presence of NTE, but $T_{\rm NTE}$ is at around 500 K, well above RT and are almost independent of *x*. It is recently found that BiNi_{1-x}Fe_xO₃ also shows large NTE with $\alpha_{\rm L}$ exceeding $-150 \times 10^{-6} \,{\rm K}^{-1}$ in the controlled temperature range near RT [26].



Figure 10. Temperature dependence of the weighted average volume of $BiNi_{1-x}Al_xO_3$ (x=0.05, 0.075, 0.10) and $BiNi_{1-x}Ga_xO_3$ (x=0.05, 0.10) measured on heating.

4. Conclusions

A brief overview of NTE induced by intermetallic charge transfer in A-site ordered double perovskites SrCu₃Fe₄O₁₂ and LaCu₃Fe_{4-x}Mn_xO₁₂ and A- or B-site substituted perovskite BiNiO3 is provided. The distinct volume contraction in LaCu₃Fe₄O₁₂ is broadened by replacement of La³⁺ by Sr^{2+} or Mn substitution for Fe, leading to NTE. Substitution of Bi with Ln³⁺ or Ni with Al³⁺, Ga³⁺ stabilized the (Bi, Ln)³⁺(Ni, M)³⁺O₃ phase which is present only in the HP condition for pure BiNiO₃ and suppress the intermetallic charge transfer transition accompanied by volume contraction to ambient condition. Colossal NTE with CTE over $-70 \times 10^{-6} \text{ K}^{-1}$ is observed by both diffraction and dilatometric measurements in the controlled temperature range for Bi_{1-x}Ln_xNiO₃ while T_{NTE} is almost independent for $\text{BiNi}_{1-x}\text{Al}_x\text{O}_3$ and BiNi_{1-x} Ga_xO_3 . These compounds are promising for the suppression of the thermal expansion of structure materials, but the presence of emperature hysteresis owing to the first-order toransition is a problem for the practical applications. It is recently shown that the thermal hysteresis is suppressed in BiNi_{1-x}Fe_xO₃. Moreover, 18 vol. % addition of BiNi_{0.85}Fe_{0.15}O₃ with $\alpha_{\rm L} = -187 \times 10^{-6} \,\rm K^{-1}$ compensates for the thermal expansion of epoxy resin [26].

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