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 $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ and $\text{LaCu}_3\text{Fe}_4\text{Mn}_x\text{O}_{12}$, as well as in Bi or Ni substituted $\text{BiNiO}_3$. The last compound shows a colossal dilatometric linear thermal expansion coefficient exceeding $-70 \times 10^{-6} \text{ K}^{-1}$ 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 $\alpha_L = (1/L)(\Delta L/\Delta T) = -1.16 \times 10^{-6} \text{ K}^{-1}$ leading to the 1.16 $\mu$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 $\beta$-$\text{LiAlSiO}_4$ [1, 2] $\text{ZrW}_2\text{O}_8$ [5], and $\text{Cd} (\text{CN})_2$ [6] can be categorized into the first generation of NTE materials. Indeed, crystallized glass, where $\beta$-$\text{LiAlSiO}_4$ 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 $\alpha_L = -30 \times 10^{-6} \text{ K}^{-1}$ coupled with a magnetic transition (mechanism 2) was discovered in an anti-perovskite manganese nitride [7–13]. $\text{PbTiO}_3$ 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 $\text{BiNiO}_3$ [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,
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 La3+ and Cu3+ as shown in figure 1(c). The formal valence state of this compound is La3+Cu3+3Fe3+4O12 at RT. Intermetallic charge transfer between Cu3+ and Fe3+ takes place on heating above 393 K resulting in La3+Cu2+3Fe3.75+4O12 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 \( \alpha_L = 22.6 \times 10^{-6} \text{ K}^{-1} \) 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 LaCu3Fe4−xMnxO12 as shown in figure 4 [23].

3. NTE in A- or B- site substituted perovskite compound BiNiO3

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 Bi3+0.5Bi5+0.5Ni2+O3 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.
The PND and XAS results have been used to construct the $P-T$ phase diagram for BiNiO$_3$ shown in figure 5. BiNiO$_3$ decomposes above 500 K at ambient pressure (AP), but is stabilized up to at least 565 K at 1.8 GPa (and to $\sim 1300$ K at 6 GPa under synthesis conditions). The boundary between the low pressure and temperature (LPT) and HPT phases has slope $dT_C/dp = -140$ K/GPa$^{-1}$. The 2.5–3.4% volume contraction occurs on both pressurizing and heating.

### 3.2. NTE in Bi$_{0.95}$La$_{0.05}$NiO$_3$

The large $\Delta T_{CT}$ of BiNiO$_3$ shows that colossal NTE is feasible but the transition is only observed above pressures of 1.5 GPa in pure BiNiO$_3$. Chemical substitutions for Bi is used to suppress the charge disproportionation in the Bi$_{3+}$Bi$_{5+}$Ni$_{2+}$O$_3$ phase and thereby shift the charge transfer transition to near ambient conditions. Partial substitution of La$^{3+}$ without charge degree of freedom for Bi destabilizes the characteristic Bi$^{3+}$/Bi$^{5+}$ disproportionation and shift the charge transfer transition to around 350 K at AP in Bi$_{0.95}$La$_{0.05}$NiO$_3$ [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)$^{3+}$Ni$^{3+}$O$_3$ valence distribution. The 2.9% volume shrinkage, which has a similar magnitude to that observed in undoped BiNiO$_3$ 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 ZrO$_2$ and HfO$_2$ [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 Bi$_{0.95}$La$_{0.05}$NiO$_3$ between 300 and 370 K is $\alpha_V = -413 \times 10^{-6}$ K$^{-1}$ and the linear coefficient is $\alpha_L = -137 \times 10^{-6}$ K$^{-1}$, showing that colossal NTE magnitudes are observable in Bi$_{1-x}$La$_x$NiO$_3$. Crystallography predicts the upper limit of the magnitude of thermal expansion as the formation of pores and other microstructural defects can lessens the effect in bulk ceramics.

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The figures included are references to experimental results and phase diagrams. The figures are not translated here, but they are meant to illustrate the phase transitions and NTE behavior observed in the studied materials.
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 $\Delta L/L$ increases with increasing temperature up to 270 K indicating the normal positive thermal expansion, but decreases above 270 K. The average observed $\alpha_L$ between 270 and 400 K is $-49 \times 10^{-6} \text{ K}^{-1}$ and the maximum negative slope between 320 and 380 K corresponds to a linear thermal expansion coefficient of $-82 \times 10^{-6} \text{ K}^{-1}$ [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$_x$NiO$_3$ (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$_x$NiO$_3$ (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 Ln$^{3+}$ content increases. Figure 8(a) summarizes the compositional dependence of the onset temperature of NTE ($T_{\text{NTE}}$) and the temperature hysteresis width. The $T_{\text{NTE}}$ 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$_{1-x}$Ln$_x$NiO$_3$ is in the orthorhombic (Bi, Ln)$^{3+}$Ni$^{3+}$O$_3$ state with an unique Bi/Ln site. The La$^{3+}$ ions are homogeneously distributed, because the ionic radius of La$^{3+}$ is close to that of Bi$^{3+}$. Suppose such a sample is in the HT (Bi, Ln)$^{3+}$Ni$^{3+}$O$_3$ state at AP. Charge disproportionation on cooling is suppressed by the presence of a La$^{3+}$ ion at the Bi$^{5+}$ site of the triclinic low-temperature phase. $T_{\text{NTE}}$ is therefore lowered by the La substitution, and the orthorhombic phase is dominant for Bi$_{0.90}$La$_{0.10}$NiO$_3$. On the other hand, a large difference in ionic radius between Bi$^{3+}$ and small Ln$^{3+}$ ions should lead to a partial Bi$^{5+}$/Ln$^{3+}$ ordering, as schematically illustrated in figure 8(b). The charge transfer transition is less affected by a small Ln$^{3+}$ because Bi$^{5+}$ 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$_x$NiO$_3$ 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 6](image-url) 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].
3.4. NTE in LaNi$_{1-x}$M$_x$O$_3$ (M: Al and Ga)

The above discussed NTE results from the temperature induced intermetallic charge transfer between Bi$^{5+}$ and Ni$^{2+}$. The presence of Ln$^{3+}$ in Bi$^{5+}$ site destabilizes the Bi$^{3+}$/Bi$^{5+}$ charge disproportionation in Bi$^{3+}$Ni$_3$O$_3$ and HP phase of Bi$^{3+}$Ni$_3$O$_3$ appears on heating at AP. In this context, substitution of Ni$^{2+}$ with a trivalent ion is also expected to stabilize Bi$^{3+}$(Ni, M)$_3$O$_3$ and thus leads to NTE. Figure 9 shows the XRD patterns of BiNi$_{1-x}$M$_x$O$_3$ (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$_x$NiO$_3$.

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

**Table 2.** The linear thermal expansion coefficient $\alpha_L$ of Bi$_{1-x}$Ln$_x$NiO$_3$ (Ln = La, Eu, Nd, Dy) estimated by the dilatometric measurement on heating [25].

| Ln  | $x$ in Bi$_{1-x}$Ln$_x$NiO$_3$ | $T$ (K) | $\alpha_L$ ($10^{-6}$ K$^{-1}$) |
|-----|--------------------------------|--------|-------------------------------|
| La  | 0.05                           | 330 → 380 | −71                           |
|     | 0.075                          | 220 → 280 | −36                           |
|     | 0.10                           | 210 → 300 | −5                            |
| Nd  | 0.05                           | 380 → 410 | −134                          |
|     | 0.075                          | 280 → 330 | −41                           |
|     | 0.10                           | 200 → 250 | −30                           |
| Eu  | 0.05                           | 430 → 460 | −70                           |
|     | 0.075                          | 330 → 390 | −41                           |
|     | 0.10                           | 250 → 310 | −44                           |
| Dy  | 0.05                           | 440 → 470 | −104                          |
|     | 0.075                          | 410 → 460 | −43                           |
|     | 0.10                           | 330 → 380 | −68                           |
samples partially decomposed after heating up to 550 K. These results indicate the presence of NTE, but $T_{\text{NTE}}$ is at around 500 K, well above RT and are almost independent of $x$. It is recently found that BiNi$_{1-x}$Fe$_x$O$_3$ also shows large NTE with $\alpha_L$ exceeding $-150 \times 10^{-6}$ K$^{-1}$ in the controlled temperature range near RT [26].

4. Conclusions

A brief overview of NTE induced by intermetallic charge transfer in A-site ordered double perovskites SrCu$_3$Fe$_4$O$_{12}$ and LaCu$_3$Fe$_{2-x}$Mn$_x$O$_{12}$ and A- or B-site substituted perovskite BiNiO$_3$ is provided. The distinct volume contraction in LaCu$_3$Fe$_4$O$_{12}$ is broadened by replacement of La$^{3+}$ by Sr$^{2+}$ or Mn substitution for Fe, leading to NTE. Substitution of Bi with Ln$^{3+}$ or Ni with Al$^{3+}$, Ga$^{3+}$ stabilized the (Bi, Ln)$^{3+}$(Ni, M)$^{3+}$O$_3$ phase which is present only in the HP condition for pure BiNiO$_3$ and suppress the intermetallic charge transfer transition accompanied by volume contraction to ambient condition. Colossal NTE with CTE over $-70 \times 10^{-6}$ K$^{-1}$ is observed by both diffraction and dilatometric measurements in the controlled temperature range for Bi$_{1-x}$Ln$_x$NiO$_3$ while $T_{\text{NTE}}$ is almost independent for BiNi$_{1-x}$Al$_x$O$_3$ and BiNi$_{1-x}$Ga$_x$O$_3$. These compounds are promising for the suppression of the thermal expansion of structure materials, but the presence of temperature hysteresis owing to the first-order transition is a problem for the practical applications. It is recently shown that the thermal hysteresis is suppressed in BiNi$_{1-x}$Fe$_x$O$_3$. Moreover, 18 vol. % addition of BiNi$_{0.85}$Fe$_{0.15}$O$_3$ with $\alpha_L = -187 \times 10^{-6}$ K$^{-1}$ compensates for the thermal expansion of epoxy resin [26].

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