Colossal negative thermal expansion in $BiNiO_3$ induced by intermetallic charge transfer

Useful negative thermal expansion (NTE) materials for zero or controlled expansion composites should show a smooth contraction while heating through a wide temperature range. Volume shrinkages in framework type materials can extend over very wide ranges, for example, ZrW_2O_8 shows a near-continuous volume decrease of $\Delta V/V = -2.0\%$ over 0.3–1050 K, equivalent to an average linear expansion of $\alpha_L = (1/L)(\Delta L/\Delta T) = -7\times10^{-6}$ K^{-1} where the linear dimension L is the cubic unit cell parameter. NTE can also result from transitions between different electronic or magnetic states strongly coupled to the lattice, giving large negative expansions down to a previous record dilatometric value of -25×10^{-6} K^{-1} for $(Mn_{0.96}Fe_{0.04})_3(Zn_{0.5}Ge_{0.5})N$ at 316-386 K.

Perovskite $BiNiO_3$ has a triclinically distorted crystal structure with the unusual valence distribution $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ and shows the charge ordering of the Bi valences, as illustrated in the inset of Fig. 1(a) [1]. Powder neutron diffraction and X-ray absorption spectroscopy (XAS) studies revealed the 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 $GdFeO_3$ type perovskite superstructure with valence distribution $Bi^{3+}Ni^{3+}O_3$ [2]. Figure 1(a) shows the pressure dependence of the unit cell volume derived by fitting the neutron diffraction data [3]. It shows that the unit cell volume decreases by 2.5% across the transition. This large change results from the dominant contraction of the Ni-O perovskite framework as Ni^{2+} is oxidized to the smaller Ni^{3+} at the transition, which outweighs the lattice expanding effects of reducing Bi^{5+} to Bi^{3+} and increases in the Ni-O-Ni angles.

The charge transfer transition in $BiNiO_3$ has a negative dT/dp slope, which enables the same structural change accompanying the volume reduction to be observed by heating at a moderate pressure. Figure 1(b) shows the temperature dependence of the lattice parameters and unit cell volume of $BiNiO_3$ on heating at a pressure of 1.8 GPa, with the transition occurring at around 500 K. Structure refinements from neutron data and XAS and resistivity measurements confirm that the high pressure and temperature state is the same orthorhombic, metallic $Bi^{3+}Ni^{3+}O_3$ phase generated by pressurization at ambient temperature. Figure 1(c) shows the Ni-K edge XAS spectra for $BiNiO_3$ measured at beamline **BL39XU** at various temperatures and 2.3 GPa. The edge energy E_0^K shifts to a higher value between 414 and 463 K indicating the Ni^{2+} to Ni^{3+} valence state change. The volume drop of 3.4% observed by heating in Fig. 1(b) has a similar value to the pressure-induced change in Fig. 1(a).

Our neutron diffraction and XAS results have been used to construct the P-T phase diagram for $BiNiO_3$ shown in Fig. 2. $BiNiO_3$ decomposes above 500 K at ambient pressure, 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 high pressure and temperature (HPT) phases has the slope $dT_{CT}/dp = -140$ $KGPa^{-1}$. The 2.5–3.4% volume contraction occurs on both pressurization and heating.

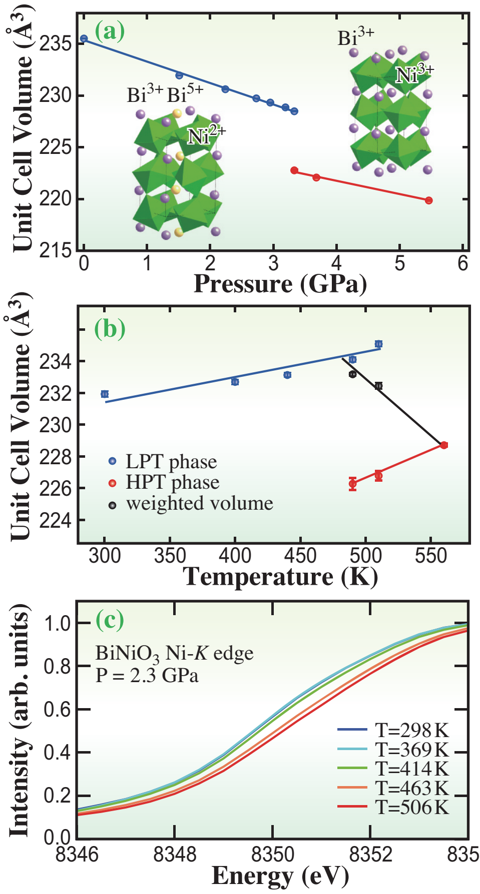

Fig. 1. Structural and spectroscopic data indicating the intermetallic charge transfer and the volume shrinkage. **(a)** Pressure dependence of the unit cell volume of $BiNiO_3$. **(b)** Temperature dependence of the unit cell volume at 1.8 GPa. Both show the $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ to $Bi^{3+}Ni^{3+}O_3$ phase transition accompanied by volume shrinkage at around 3.5 GPa and 500 K. **(c)** Ni-K edge XAS spectra for $BiNiO_3$ at various temperatures and 2.3 GPa indicating the Ni^{2+} to Ni^{3+} valence state change between 414 and 463 K.

The large ΔT_{CT} of $BiNiO_3$ shows that colossal NTE is feasible but the transition is only observed above the pressure of 1.5 GPa in pure $BiNiO_3$. However, chemical substitutions for Bi may be used to suppress the charge disproportionation in the $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ phase and thereby shift the charge transfer transition to near ambient conditions. This is conveniently achieved by a partial substitution of La for Bi, which suppresses the characteristic insulator to metal transition accompanying charge transfer to around 350 K at ambient pressure in $Bi_{0.95}La_{0.05}NiO_3$.

X-ray diffraction measurements at beamline **BL02B2** on $Bi_{0.95}La_{0.05}NiO_3$ in Fig. 3(a) show the 2.9% volume shrinkage, which has a similar magnitude to that observed in undoped $BiNiO_3$ under a pressure of 1.8 GPa. 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 ΔT_{CT} = 70 K. The crystallographic volume thermal expansion coefficient between 300 and 370 K is $\alpha_V = -413\times10^{-6}$ K^{-1} and the linear coefficient is $\alpha_L = -137\times10^{-6}$ K^{-1}, showing that CNTE magnitudes are also observable in $Bi_{1-x}La_xNiO_3$. 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. Dilatometric measurements on a polycrystalline ceramic of $Bi_{0.95}La_{0.05}NiO_3$ prepared at high pressures were performed during heating and cooling cycles, as shown in Fig. 3(b). The strain $\Delta L/L$ (400 K) increases with increasing temperature up to 270 K, indicating a 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} [3]. This is more than three times larger than the previous maximum NTE value of -25×10^{-6} K^{-1} by dilatometry, reported for the linear expansion of an anti-perovskite manganese nitride $(Mn_{0.96}Fe_{0.04})_3(Zn_{0.5}Ge_{0.5})N$ ceramic over a similar temperature range.

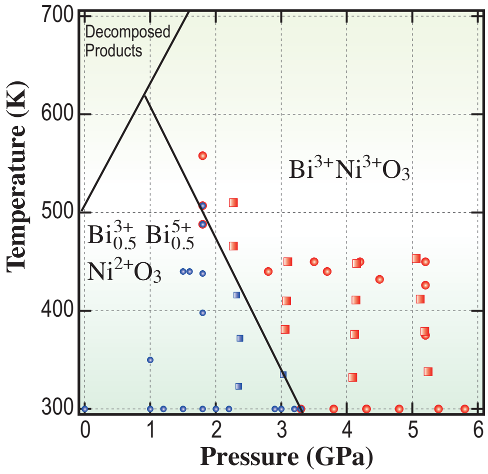

Fig. 2. Pressure-temperature phase diagram of $BiNiO_3$ determined by powder neutron diffraction (PND) and XAS studies. Circles and squares show PND and XAS data, and blue and red symbols correspond to the LPT and HPT phases, respectively [3].

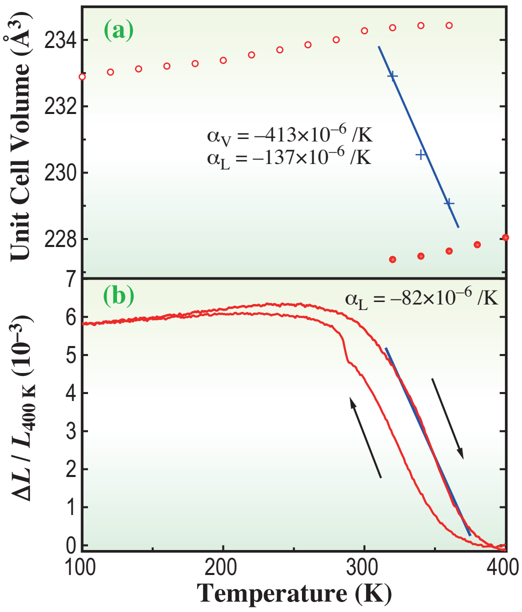

Fig. 3. Thermal measurements for $Bi_{0.95}La_{0.05}NiO_3$ at ambient pressure showing thermal expansion coefficient values over the linear regions indicated. **(a)** Temperature dependence of the unit cell volume on heating with LPT and HPT data denoted by open and closed circles, and crosses showing the weighted average volume in the transition region. **(b)** Dilatometric linear thermal expansion of $Bi_{0.95}La_{0.05}NiO_3$ on heating and cooling showing a 20 K hysteresis [3].

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