Giant Negative Thermal Expansions Induced by Electronic Phase Transitions

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Abstract

Negative thermal expansion (NTE) materials which shrink on heating attracts the keen attention because these can compensate for the thermal expansion of structural materials by making composites and solve the critical problems caused by the thermal expansion. We utilize $6s^2$ lone pair activity of Pb^{2+} and Bi^{3+} and valence skipping nature of these ions for exploration of NTE materials [1]. $PbVO_3$ is a $PbTiO_3$-type compound with an enhanced polar tetragonal structure (c/a = 1.23) owing to d_{xy} orbital ordering of V^{4+} (d^1). Hole doping by Bi^{3+} substitution for Pb^{2+} decreases the polar distortion and enables temperature induced polar-nonpolar transition accompanied by ~ 9 % volume shrinkage [2, 3]. Similarly ferroelectric transition temperature of $BiFeO_3$ can be reduced by A- and B-site substitutions and NTE has been achieved [4]. $BiNiO_3$ is a perovskite compound stabilized by high-pressure (HP) synthesis at 6 GPa. It has a characteristic valence distribution of $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ and undergoes a pressure induced intermetallic charge transfer transition resulting in $Bi^{3+}Ni^{3+}O_3$ HP phase above 4 GPa. This transfer causes Ni's valence to change from Ni^{2+} to Ni^{3+}, leading to the Ni–O bond contracting and unit cell volume de-creasing by 2.5% [5]. In the case of $BiNi_{1-x}Fe_xO_3$, the charge transfer transition between Bi^{5+} and Ni^{2+} can be induced by heating at ambient pressure (AP), leading to an NTE [6, 7]. Similarly, $PbCrO_3$ exists in a $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$ valence distribution at AP and exhibits a 9.8% pressure-induced volume collapse [8]. We investigated the phase relation of $PbCrO_3$ in the pressure-temperature space and found that, contrary to $BiNiO_3$, $PbCrO_3$ returns to the ambient pressure phase when the temperature is increased under pressure. The slope of the phase boundary in the P-T phase diagram of $BiNiO_3$ is negative because the metallic $Bi^{3+}Ni^{3+}O_3$ HP-LT phase has higher entropy than $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$. On the other hand, glassy distribution of Pb^{2+} and Pb^{4+} enhances the entropy of the $Pb^{2+}_{0.5}Pb^{4+}_{0.5}Cr^{3+}O_3$ phase and the phase boundary has a positive slope [9]. Large thermal expansion rather than NTE is expected in $PbCrO_3$ if the high-pressure phase is stabilized by chemical substitutions and indeed, $Pb_{0.7}Ca_{0.3}CrO_3$ exhibits approximately 12% unit cell volume expansion on heating between 300 – 400 K [9].

References

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Biography

Professor Masaki Azuma obtained his Ph.D. from Kyoto University, Japan in 1995. From 2004 to 2010, he served as an associate professor at the Institute for Chemical Research, Kyoto University. Currently, he is a professor at Institute of Science Tokyo, Japan. He is the chairman of the World Research Hub Initiative at Institute of Science Tokyo, and a council member of the High Pressure Science and Technology Advanced Research Institute (HPSTAR) in Japan. He is a senior researcher in the field of solid-state physics and chemistry. He has discovered various functional new materials such as spin ladder compounds, ferromagnetic ferroelectrics, lead-free piezoelectric materials, and negative thermal expansion materials by high-pressure synthesis, and clarified their functional manifestation mechanisms by synchrotron radiation X-ray diffraction and spectroscopy.

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