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Outline of the thesis

Clarification of local structures and charge distributions in giant negative thermal expansion materials

(巨大負熱膨張物質における局所構造と電荷分布の解明)

Takumi Nishikubo

Thermal expansion is barely noticeable in daily life, but it has a great influence in industry and nanotechnology as seen above. Therefore, there is an increasing demand for technologies for reducing thermal expansion. One of the techniques for thermal expansion suppression is the usage of negative thermal expansion materials. In order to adjust the operation temperature of NTE or temperature hysteresis, atomic substitution for the parent materials were undertaken for most of phase transition type NTE materials. In the case of the phase transition type NTE, the transition temperature width and the negative CTE are in the trade-off relationship so, large volume reduction of the parent compound is essential. Attempts to reduce ferroelectric distortion and dope with an ion which not participate in charge transfer lead to achievement of negative thermal expansion, but this sometimes leads to volume reduction of the low temperature phase. To keep a volume reduction large, merging multiple mechanisms might be effective.

In this thesis, Bi-containing perovskites as candidates of NTE materials are focused. In particular, polar-nonpolar transition in BiInO_3 , $\text{BiZn}_{1/2}\text{Ti}_{1/2}\text{O}_3$ and BiFeO_3 , and intermetallic charge transfer between Bi and Ni in BiNiO_3 are investigated by structural analysis including local structure and valence distribution analysis.

First, I investigate the NTE behaviors in polar-nonpolar phase transition in BiInO_3 based compounds. NTE from polar orthorhombic to nonpolar orthorhombic phases was observed in $(1-x)\text{BiInO}_3$ - $x\text{BiZn}_{1/2}\text{Ti}_{1/2}\text{O}_3$. I confirmed the polar environment in BiInO_3 in the view of local structure. The structure of BiInO_3 was definitely polar $Pna2_1$ and polar-nonpolar phase transition was found in high temperature. The contribution of Bi displacement to the electric polarization in pure BiInO_3 was redistributed to the B-site off-center shift keeping the net polarization almost constant. The reduction of the large local polar distortion leads to realization of negative thermal expansion with wide operation temperature and suppressed temperature hysteresis. In addition, new LiNbO_3 -type oxide was obtained in $\text{BiIn}_{1-x}\text{Zn}_{x/2}\text{Ti}_{x/2}\text{O}_3$ with $0.4 \leq x \leq 0.8$.

Next, I optimized the NTE of intermetallic charge transfer mechanism in BiNiO₃ by Sb substitution. This randomness of the A-site ion might realize the multiple charge transfer such as Ni to Sb to Bi because Sb ion is also valence skipper ion that only has 3+ and 5+ as same as Bi ion. Bi³⁺ and Bi⁵⁺ had a long-range ordering in the low temperature phase of Bi_{0.95}Sb_{0.05}NiO₃ while the ordering was short-ranged in Bi_{0.9}Sb_{0.1}NiO₃. The latter composition exhibited a second-order like phase transition and this behavior brought continuous NTE with a linear coefficient of thermal expansion of -106 ppm K⁻¹ without temperature hysteresis in a wide temperature range of 200–320 K.

Finally, I combined the NTE induced by simultaneous mechanisms of charge transfer between Bi and Ni in BiNiO₃, and polar-nonpolar transitions in BiFeO₃. The low-temperature phase has a polar rhombohedral structure (space group of *R3c*) with a Bi³⁺_{0.5(1+x)}Bi⁵⁺_{0.5(1-x)}Ni²⁺_{1-x}Fe³⁺_xO₃ charge distribution with short-range ordered Bi³⁺ and Bi⁵⁺. The volume shrinkage upon heating that was induced by intermetallic charge transfer between Bi⁵⁺ and Ni²⁺ decreased with increasing *x* because of the reduction in the amount of Ni²⁺. Simultaneous polar-nonpolar transition also contributed to NTE, and a composition-independent volume reduction of ~2% was observed. The magnitude of the volume shrinkage was larger than that expected only by charge transfer, indicating that the polar-nonpolar transition enhanced the NTE. This combination of multiple mechanism might stimulate further material design of negative thermal expansion.

The conclusion of whole results in this thesis is that combining various mechanism is one of the best way to explore new useful NTE materials. In the case of phase transition type NTE materials, NTE might be realized by element substitution even if it is not observed in the end members. However, it may lead to decrease in the volume change. I found that it is possible to realize negative thermal expansion and tune the properties such as a temperature range without deterioration of NTE properties by combination of various mechanism. These materials should be investigated by local distribution of ions such as valence state or local structures. In this thesis, I focused on polar-nonpolar phase transition and charge transfer transition accompanied by volume collapse at high pressure. However, there are various other mechanisms for NTE. Combining these mechanisms is expected to be examined in order to obtain new materials in the near future.