

論文 / 著書情報
Article / Book Information

題目(和文)	巨大負熱膨張物質における局所構造と電荷分布の解明
Title(English)	Clarification of local structures and charge distributions in giant negative thermal expansion materials
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
Doctoral Program

論文要旨

THESIS SUMMARY

系・コース： 材料 系
Department of Graduate major in 材料 コース
学生氏名： 西久保 匠
Student's Name

申請学位 (専攻分野)： 博士 (理学)
Academic Degree Requested Doctor of
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Academic Supervisor(main)
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要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

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 as shown in chapter 3. 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 $0.4 \leq x \leq 0.8$.

In chapter 4, I optimized the NTE of intermetallic charge transfer mechanism in BiNiO_3 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. Bi^{3+} and Bi^{5+} had a long-range ordering in the low temperature phase of $\text{Bi}_{0.95}\text{Sb}_{0.05}\text{NiO}_3$ while the ordering was short-ranged in $\text{Bi}_{0.9}\text{Sb}_{0.1}\text{NiO}_3$. 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, in chapter 5, I combined the NTE induced by simultaneous mechanisms of charge transfer between Bi and Ni in BiNiO_3 , and polar-nonpolar transitions in BiFeO_3 . The low-temperature phase has a polar rhombohedral structure (space group of $R\bar{3}c$) with a $\text{Bi}^{3+_{0.5(1+x)}\text{Bi}^{5+_{0.5(1-x)}\text{Ni}^{2+_{1-x}}\text{Fe}^{3+}_x\text{O}_3$ charge distribution with short-range ordered Bi^{3+} and Bi^{5+} . The volume shrinkage upon heating that was induced by intermetallic charge transfer between Bi^{5+} and Ni^{2+} decreased with increasing x because of the reduction in the amount of Ni^{2+} . Simultaneous polar-nonpolar transition also contributed to NTE, and a composition-independent volume reduction of $\sim 2\%$ 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 and these material should be investigated by local distribution of ion such as valence state or local structures. I focused on polar-nonpolar phase transition and charge transfer in this thesis, however there are a lot of mechanism result in NTE. Combining these mechanisms is expected in order to obtain new materials in the near future.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note：Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).

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