

# 第295回応用セラミックス研究所講演会

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## 演題：Structure and negative thermal expansion in $\text{PbTiO}_3$ -based ferroelectrics and $\text{ScF}_3$ -based fluorides

It is well known that most materials expand upon heating. However, there are some negative thermal expansion (NTE) materials, whose volume abnormally contracts upon heating, have been found in the past two decades. The appearance of NTE materials provides good possibility to effectively control thermal expansion of materials [1-3]. Most recently, a big family of NTE compounds has been found in functional materials of magnetic, valence state change, and ferroelectrics [1-3]. We call these materials as functionalized NTE materials [3]. We have systematically studied the NTE in  $\text{PbTiO}_3$  (PT)-based ferroelectrics which have been widely studied and applied as functional materials of piezoelectric, dielectric, non-volatile ferroelectric memory and so on. PT behaves a strong NTE over a wide temperature range of room temperature to its  $T_c$  (490 °C). The NTE control of PT-based ferroelectrics has been well established by various chemical modifications. Giant negative or zero thermal expansion (ZTE) has been found in PT-based perovskites. For example, the bulk coefficient of thermal expansion (CTE) of  $0.5\text{PbTiO}_3$ - $0.5(\text{Bi}_{1-x}\text{La}_x)\text{FeO}_3$  can be controlled from  $\alpha_v = -4.06 \times 10^{-5}/^\circ\text{C}$  for the  $x = 0.0$  to  $\alpha_v = -0.71 \times 10^{-5}/^\circ\text{C}$  for the  $x = 0.2$  by simply adjusting the composition of La [4b]. The adjustable CTE contains most NTE materials. A wide temperature zero thermal expansion has been found in some PT-based piezoelectrics (e.g.  $\text{PT-Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ) and multiferroic materials (e.g.  $\text{PT-Bi}(\text{Ni}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ). The NTE is highly associated with the temperature behavior of spontaneous polarization. It means the NTE nature is highly associated with ferroelectricity [4]. We proposed a new physical concept of spontaneous volume ferroelectrostriction (SVFS) for the possible nature of PT-based ferroelectrics [4b]. NTE of ferroelectrics could be controlled by adjusting the SVFS through the chemical substitutions or by decreasing particle size [4c]. Recently, we have realized the effective control of thermal expansion in  $\text{ScF}_3$ -based cubic compounds which exhibit  $\text{ReO}_3$ -type structure.  $\text{ScF}_3$  has a similar crystal structure to  $\text{ABO}_3$  perovskite in which A-site is vacant. The thermal expansion of  $\text{ScF}_3$  has been designed and well controlled using the introduction of local distortions in the macroscopic cubic lattice by heterogeneous cation substitution for the Sc site. For example,  $(\text{Sc}_{0.85}\text{Ga}_{0.05}\text{Fe}_{0.1})\text{F}_3$  exhibits a zero thermal expansion over a large temperature range (300-900K) which is almost broadest among ZTE materials. Even though the macroscopic crystallographic structure adheres to the cubic system; however, the local structure is slightly distorted to the rhombohedral one. The present work provides a new method to control the NTE of materials, which is the introduction of local distortion.

[1]T. A. Mary, et al, Science **272**, 90 (1996).[2] M. Azuma, et al, Nat. Commun. **2**, 347 (2011).

[3]J. Chen, et al, Chem. Soc. Rev. **44**, 3522 (2015).[4](a) J. Chen, et al, J. Am. Chem. Soc. **133**, 11114 (2011); (b) J. Chen, et al, Sci. Rep. **3**, 2458 (2013); (c) J. Chen, et al, Phys. Rev. Lett. **110**, 115901 (2013). [5]J. Chen, et al, J. Am. Chem. Soc. **136**, 13566 (2014).

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