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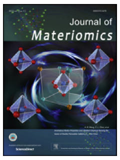

Metal fluorides, a new family of negative thermal expansion materials

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Abstract

In the past decades, the families of negative thermal expansion (NTE) materials have been in the uninterrupted growth with more new NTE materials reported; in particular, metal fluorides as the new members begin to draw attention. Herein, recent progress on the NTE properties of metal fluorides is reviewed, including compounds, mechanisms and the control of thermal expansion. Although some achievements have been made, there are still great development prospects. More in-depth investigations on metal fluorides with NTE behavior are expected.

Keywords: Metal fluorides; Negative thermal expansion

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1. Introduction

Most materials expand on heating owing to the anharmonicity of chemical bond. However, as a very exceptional phenomenon, negative thermal expansion (NTE), *i.e.*, volume shrinks on heating, can be observed in a small number of materials [1–4]. In fact, NTE phenomenon has been known for some time in several compounds such as ice, amorphous or crystalline forms of SiO_2, zeolites, perovskite ferroelectrics, tetrahedral semiconductors [5–8]. In these systems, NTE occurs over a limited temperature range and is often anisotropic. In 1996, the discovery of giant and isotropic NTE behavior over a board temperature range (from 0.5 to 1030 K) in ZrW_2O_8 triggers great research interest [1]. Over the past two decades, the field of NTE has rapidly expanded. Experimental and theoretical studies revolving around the NTE materials have been in full swing [9–15]. For example, the discovery of new NTE materials, the promotion in process technology, the development of composites using NTE materials as thermal-expansion compensators, the control of NTE properties by doping in single-phase material, and the exploration of NTE mechanisms, *etc*.

The NTE materials have emerged in both inorganic and organic fields. Presently, the NTE materials are mainly concentrated in the following several series: (1) metal oxide, including AM_2O_8 (A = Zr, Hf; M = W, Mo), AM_2O_7 (A = Zr, Hf; M = V, P), $A_2M_3O_{12}$ (A = Al, Y, Sc, Ga, *etc*; M = W, Mo), A_2O (A = Ag, Cu) [16–22]; (2) metal cyanide, including $M^{II}Pt^{IV}(CN)_6$ (M = Mn, Fe, Co, Ni, Cu, Zn, Cd), $M(CN)_2$ (M = Zn, Cd, Ni) [23,24]; (3) $PbTiO_3$ (PT)-based perovskite compounds [11,12]; (4) Mn_3AN/C-based (A = Cu, Ge, Zn, Sn, Ag, *etc*.) antiperovskite compounds [9,10,25–31]; (5) alloy system, such as Invar alloys ($Fe_{65}Ni_{35}$), FeCo, FePd, FePt, FeC and so on [32–34]; (6) low-dimensional materials, for example, zero-dimensional fullerene and clusters, one-dimensional carbon nanotubes, and two-dimensional thin film (graphite, grapheme, *etc*.) [35,36]; (7) metal-organic frameworks (MOFs), polymers, fibers, *etc*. [37,38]; (8) metal fluorides, AF_x (A = Sc, Zn, Ti, Mn, *etc*.) [39–49]. In recent years, metal fluorides as new NTE members begin to attract attention. Among them, ScF_3 with a cubic ReO_3-type structure behaves the most conspicuous NTE properties. The volumetric contraction can be observed in a wide temperature range from

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10 to 1100 K [39]. Compared with other NTE compounds, the strong NTE behavior in such a simple structure is really amazing. Additionally, some meaningful researches on NTE properties in metal fluorides have been reported in succession. In this article, we review the research progress on NTE properties of metal fluorides. Moreover, some views are put forward based on the existing achievements.

2. Metal fluorides with NTE behavior

Early in 2004, an unusual NTE behavior in the simple perovskite MnF_3 was experimentally obtained below the Neel point where the spins were ordered in an A-type magnetic structure (see Fig. 1(a)) [47]. In 2010, Greve et al. observed a giant NTE behavior (linear coefficient of thermal expansion (CTE), $\alpha_L = -14 \times 10^{-6}\ K^{-1}$) of cubic ScF_3 [39], larger than that of ZrW_2O_8 ($\alpha_L = -9 \times 10^{-6}\ K^{-1}$) [1] (see Fig. 1(b)). Besides the cubic zirconium tungstate, ScF_3 is the best known example of large isotropic negative expansion persisting over a wide temperature range. Thereafter, Li et al. investigated the structural relationship between NTE and quartic anharmonicity in ScF_3 [40]. In 2011, Chatterji et al. discovered the NTE behavior at low temperatures (below 100 K) in rutile-type ZnF_2 [41] (see Fig. 1(c)). Then, Wang et al. have given the theoretical study on NTE mechanism of ZnF_2 by means of the first principle calculations [42]. The cubic-to-rhombohedral phase transition of TiF_3 was once investigated by powder X-ray diffraction [43]. By the way, a clue was supplied that below 100 K the volume appeared to be essentially constant although the volume at 20 K, in fact, slightly larger than that measured at 100 K and it remained to be determined if this was significant. Because of larger temperature interval measured in experiments, more detailed information about the thermal expansion of TiF_3 in the range 0−100 K was lacked. Very recently, Wang et al. put forward definitely the NTE behavior of rhombohedral TiF_3 at low temperature and discussed the NTE mechanisms within the framework of first principle calculations [44] (see Fig. 1(d)).

3. NTE mechanisms

To predict the new NTE materials and gain in-depth insight into NTE mechanisms, important tests of the ability of first principle theory in probing various macroscopic physical properties of NTE are necessary. Generally, the origin of NTE behavior can be classified into two aspects, one is vibrational mode effects, and the other is non-vibrational mode effects. Lattice vibration, *i.e.* phonon, plays a decisive role in the NTE materials with open-framework structures. Some NTE-contributing phonon modes have been identified. In certain materials (*e.g.* ZrW_2O_8), polyhedra can rotate through coupled librations without distortion, called a "rigid unit mode" (RUM), as shown in Fig. 2. While, in some others (*e.g.* ZrW_2O_7), there are many vibrations involving librations with only small distortions of the polyhedra. These are titled quasi-rigid unit modes (QRUM). The RUMs and QRUM can lead to a rotary coupling between two adjacent polyhedra, contributing to the NTE behavior [17]. Additionally, non-linear A-O-M bridge as another vital mode is applied in some NTE materials such as $A_2M_3O_{12}$ series, where the O atom vibrates perpendicular to the A-O-M linkage and shortens the distance between A and M atoms [50]. For metal cyanides, the

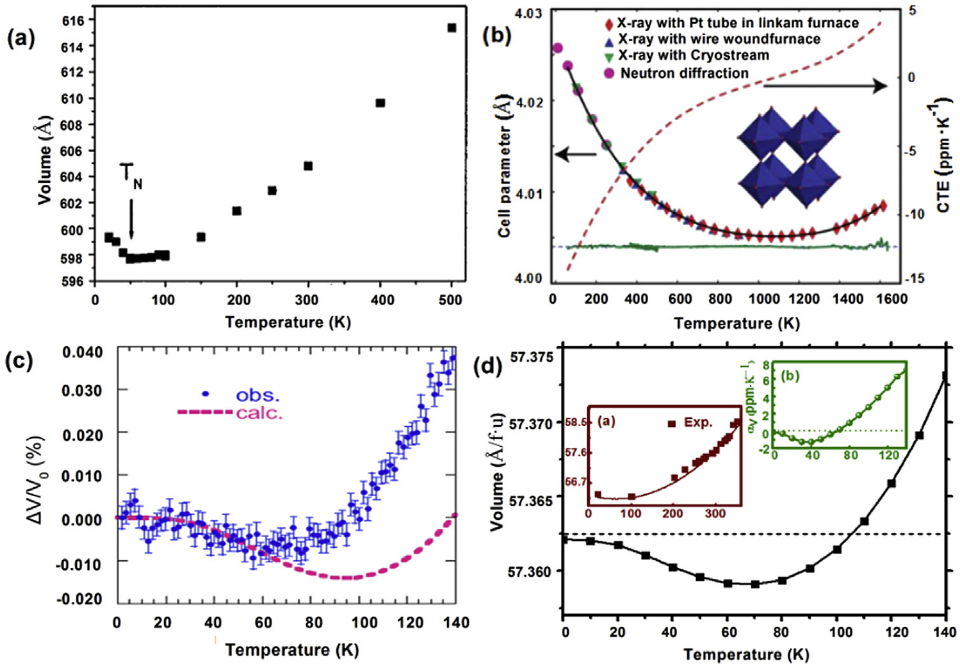

Fig. 1. (a) Temperature dependence of the unit-cell volume of MnF_3. The Neel point is shown [47]. (b) The temperature dependence of cell parameter and coefficient of thermal expansion (CTE) of ScF_3 [39]. (c) Temperature variation in $\Delta V/V_0$ of ZnF_2 [41]. (d) The calculated volume−temperature curve of rhombohedral TiF_3, insets show the experimental measurement and calculated CTE, respectively [44].