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On the switching between negative and positive thermal expansion in framework materials

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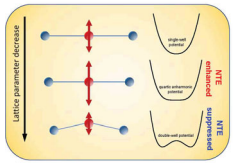
ABSTRACT
The control of thermal expansion represents a challenge in materials design. This work shows that the length of the lattice parameter is a key element for controlling thermal expansion. By varying the lattice parameter through external pressure, chemical or other methods, the single-well potential energy of the polyhedra rotations (or of the atomic transverse vibrations) responsible for negative thermal expansion (NTE), can be turned into a quartic anharmonic potential or into a double-well potential, thus enhancing or suppressing the NTE, respectively. This result applied to framework materials should be taken into account to overcome the challenge of controlling thermal expansion.



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Controlling thermal expansion; negative thermal expansion; framework structures

IMPACT STATEMENT
This research reveals that the thermal expansion of framework-type materials can be tuned by acting on the length of the lattice parameter.

1. Introduction

The vast majority of materials expand on heating, while rare exceptions contract with increasing temperature. This fascinating property, known as negative thermal expansion (NTE), is very interesting both from a scientific and technological perspective. As a matter of fact, thermal expansion represents a problem for many materials and engineering applications, because when two coupled-materials expand differently when heated, this can lead to thermal shock breakage and failures of the system. For this reason, controlling thermal expansion represents a challenge for material design, and NTE is the starting point to develop materials with controlled thermal expansion [1,2].

Different methods are under investigation to control the thermal expansion. The application of external pressure is one of these. Indeed, on the basis of thermodynamics considerations, it is expected that the positive thermal expansion is diminished under pressure, while the negative thermal expansion is enhanced [3]. This behavior was observed, for example, in zinc cyanide [4], but a few years ago a reverse behavior was discovered in ferroelectric $PbTiO_3$ [5] and in other compounds [6,7]. Other promising routes to control the thermal expansion are represented by chemical intercalation [8] and chemical modification [2,9]. Very interesting is the case of metal fluorides with ReO_3-type structure, where the thermal expansion can be tuned from negative to zero to positive [8,10]. Specifically, in the cubic $MZrF_6$ series (M = Ca, Mn, Fe, Co, Ni, Zn) the thermal expansion coefficient changes from about -6.7 to $+18.2 \times 10^{-6}$ K^{-1} [11], with $CaZrF_6$ that displays a large NTE over a wide temperature range, much stronger than the most famous ZrW_2O_8 and other corner-sharing framework structures [12]. Other interesting examples are given by $Sc_{1-x}M_xF_3$ (M = Y, Ti, Al, Ga, Fe) solid solutions [6,13–15], where

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the precursor is scandium fluoride (ScF_3), another popular NTE material [16]. Recently, nano-size effects have also been exploited to suppress the NTE of ScF_3 [17].

The aim of this work is to understand how the application of external pressure, chemical modifications or other methods like nano-size effects, can create the conditions to tune the thermal expansion. We aim to shed light on the possible origin of the switching between negative and positive thermal expansion or vice versa.

2. Methods

The $MZrF_6$ series has been adopted as reference for this study. We recall that such series, with the exception of $CaZrF_6$, shows a cubic to rhombohedral structural phase transition which occurs with decreasing temperature [18,19]. The same behavior is displayed by other metal fluorides with ReO_3-type structure [20,21], including the $Sc_{1-x}M_xF_3$ solid solutions [6,13–15]. This transition, which leads to symmetry lowering and is frequently observed also under pressure [14,16], can be visualized as rotation of octahedra about the crystallographic 3-fold axis (Figure 1).

Figure S1(a) of the Supplemental Material shows the thermal expansion coefficient plotted against the cubic-to-rhombohedral phase-transition temperature for the $MZrF_6$ series. It is interesting to observe the strict relationship between thermal expansion behavior and phase-transition temperature. The same strict relationship is present, for example, in $Sc_{1-x}Ti_xF_3$ compounds (Supplemental Material). This relationship cannot be considered always true or cannot be generalized to other systems (for example $MgZrF_6$ does not fit the curves of Figure S1 [22]), but gives clear evidence of the existence of a close correlation between thermal expansion and phase-transition. On the other hand, it is well-known that Rigid Unit Modes (RUMs) softening in NTE framework structures is at the origin of structural phase transitions [23].

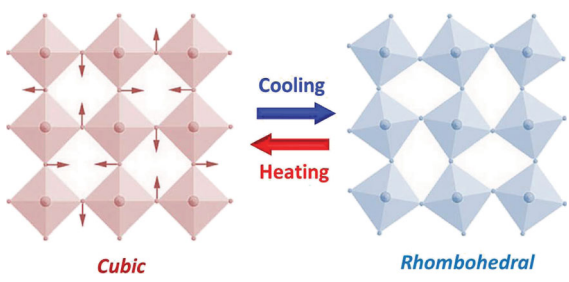

Figure 1. Sketch of the cubic-rhombohedral structural phase-transition, which involves rigid rotations of the octahedra, in their cubic (left) and rhombohedral (right) forms. From the vibrational point of view, the rigid rotations of octahedra correspond to the triple-degenerate vibrational mode with F_{1g} symmetry.

Another very interesting relationship can be found between thermal expansion and lattice parameter in the cubic phase (Figure S1(b)—Supplemental Material), as well as between lattice parameter and phase-transition temperature (Figure S1(c)—Supplemental Material): the NTE is progressively enhanced by increasing the lattice parameter, as well as the transition temperature increases as the lattice parameter decreases. Hence, thermal expansion, cubic-to-rhombohedral transition and lattice parameter have to be correlated to each other. Specifically, the lattice parameter seems to play a fundamental role in the thermal expansion and in the phase-transition behavior. This experimental observation gives input to start the present study in the manner described below.

Accordingly, first-principles calculations based on density functional theory have been performed, focusing the attention on the triple-degenerate vibrational mode with F_{1g} symmetry of the $MZrF_6$ series. This vibrational mode, corresponding to rigid rotation of MF_6 and ZrF_6 octahedra (Figure 1) around M and Zr [24], respectively, plays a key role. Indeed, it can be identified as a Rigid Unit Mode strongly contributing to NTE [24], as well as it can be connected to the cubic-to-rhombohedral phase transition, also involving rigid rotations of octahedra. For our purposes, we have chosen to study $CaZrF_6$, the one of $MZrF_6$ series with the largest NTE and which shows no transition, and $CoZrF_6$, which exhibits positive thermal expansion and cubic-to-rhombohedral transition at about room temperature (Figure S1—Supplemental Material). Other computational details are reported in the Supplemental Material.

3. Results and discussion

The geometry optimization for $CaZrF_6$ gives a lattice parameter of about 8.4260 Å with fluorine position $x = 0.23889$, while that for $CoZrF_6$ leads to a lattice parameter of about 7.8247 Å and fluorine position $x = 0.25695$. These lattice parameters are in good agreement with the experimental data (Figure S1—Supplemental Material), with a difference of about 1.0% and 2.4%, respectively. However, when we calculate the vibrational frequencies at the Γ-point of the Brillouin zone, we find that the vibrational mode with F_{1g} symmetry, corresponding to rigid rotation of MF_6 and ZrF_6 octahedra, has a negative frequency (about −1.09 THz) in the case of $CoZrF_6$. As expected, this means that $CoZrF_6$ at 0 K is instable in the cubic form, unlike instead of $CaZrF_6$.

By performing an energy scan of the F_{1g} mode, i.e. the energy study as a function of angular rotation θ of ZrF_6 (or MF_6) octahedra (Since the Zr-F and M-F bond

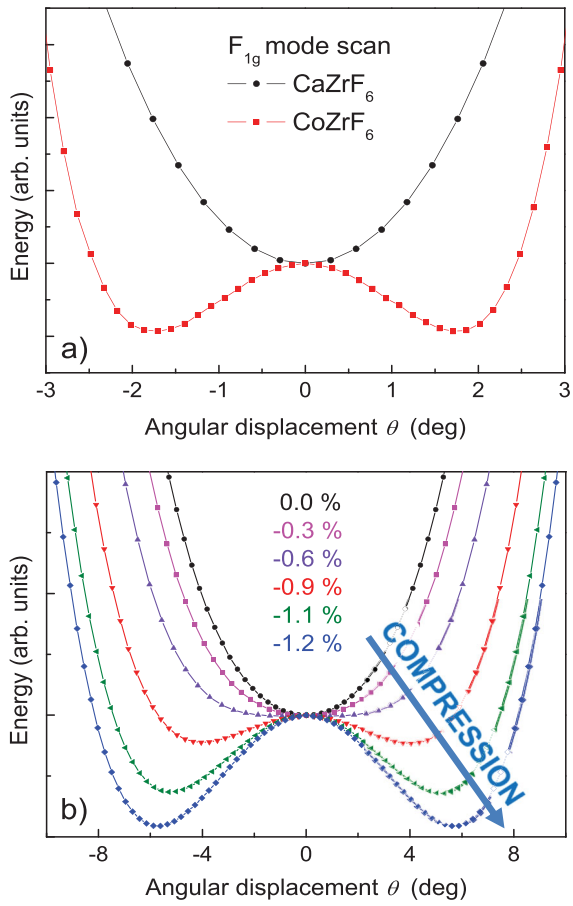

Figure 2. Energy scan of the F_{1g} vibrational mode, corresponding to rigid rotation of the ZrF_6 or MF_6 octahedra. Panel (a): in $CaZrF_6$ (black circles) and $CoZrF_6$ (red squares), where the double-well potential found in $CoZrF_6$ is consistent with the cubic-to-rhombohedral transition observed experimentally at low temperature. Panel (b): in $CaZrF_6$ under compression, corresponding to a gradual reduction of the lattice parameter up to −1.2%. Note that the single-well potential firstly turns into a quartic anharmonic potential, then it turns into a double-well potential, progressively deeper and with increasingly distant minima positions.

length are similar,the angular displacement θ of the ZrF_6 and MF_6 octahedra will be very similar to each other),[1] we can observe the existence of a double-well potential in the case of $CoZrF_6$ (Figure 2(a)), where the two minima correspond to equilibrium positions. Therefore, at low temperature, CoF_6 and ZrF_6 octahedra are rotated with respect to the cubic form, consistently with the rhombohedral form observed experimentally at low temperature (Figure 1). In contrast, $CaZrF_6$ displays a single-well potential energy (Figure 2(a)), in agreement with the experimental absence of the cubic-to-rhombohedral transition at low temperature.

Now, by applying an external pressure (here up to about 2.8 GPa), we have progressively reduced the lattice parameter of $CaZrF_6$ (up to −1.2 %) and performed an energy scan of the F_{1g} vibrational mode. The result is reported in Figure 2(b). It is very interesting to observe that reducing the lattice parameter, the single-well potential firstly turns into a quartic anharmonic potential, then it turns into a double-well potential, progressively deeper and with increasingly distant minima positions (Figure 2(b)). This indicates that by reducing the lattice parameter, we can create the conditions to have the cubic-to-rhombohedral transition (the smaller the lattice parameter, the higher the phase-transition temperature and the rhombohedral distortion), and, most importantly, we can tune the thermal expansion as will be described below.

We know that the NTE is strongly related to RUMs [3,25], hence to the rotations of ZrF_6 and MF_6 octahedra. At a given temperature T, the lattice parameter $a(T)$ can be written as

$$a(T) = a_0\langle\cos\theta\rangle_T \simeq a_0\left(1 - \langle\theta^2\rangle_T/2\right) \tag{1}$$

where a_0 is the lattice parameter with no rotation, $\langle\theta^2\rangle_T$ is the mean-square angular displacement of the ZrF_6 (or MF_6) octahedra at temperature T. According to Equation (1), the distribution of the angular displacement, $\rho(\theta, T)$, plays a key role in the thermal expansion behavior. This distribution can be connected to the one-dimensional energy potential, $V(\theta)$, through equation [26]

$$\rho(\theta, T) = \exp[-V(\theta)/k_BT] \times \left\{\int \exp[-V(\theta)/k_BT]\mathrm{d}\theta\right\}^{-1} \tag{2}$$

where k_B is the Boltzmann constant. Then using the energy potentials shown in Figure 2(b), the angular distribution $\rho(\theta, T)$ has been reconstructed as a function of temperature for the different levels of lattice compression, as reported in Figure 3. It can be observed that the angular distribution consists in one single distribution which gradually widens with increasing lattice compression, up to split into two peaks at high compressions (Figure 3). This behavior is very important to explain the change of thermal expansion, including the switching between negative and positive thermal expansion and vice versa. In fact, by Equation (1), the relative thermal expansion is

$$\frac{\Delta a}{a} \simeq -\Delta\langle\theta^2\rangle/2 \tag{3}$$

and depends on the 'temperature evolution' of the mean-square angular displacement $\langle\theta^2\rangle$, which can be calculated at any temperature and compression by equation

$$\langle\theta^2\rangle_T = \int \theta^2\rho(\theta, T)\mathrm{d}\theta \tag{4}$$

The panel (a) of Figure 4 shows the temperature evolution of the mean-square angular displacement $\langle\theta^2\rangle$ calculated

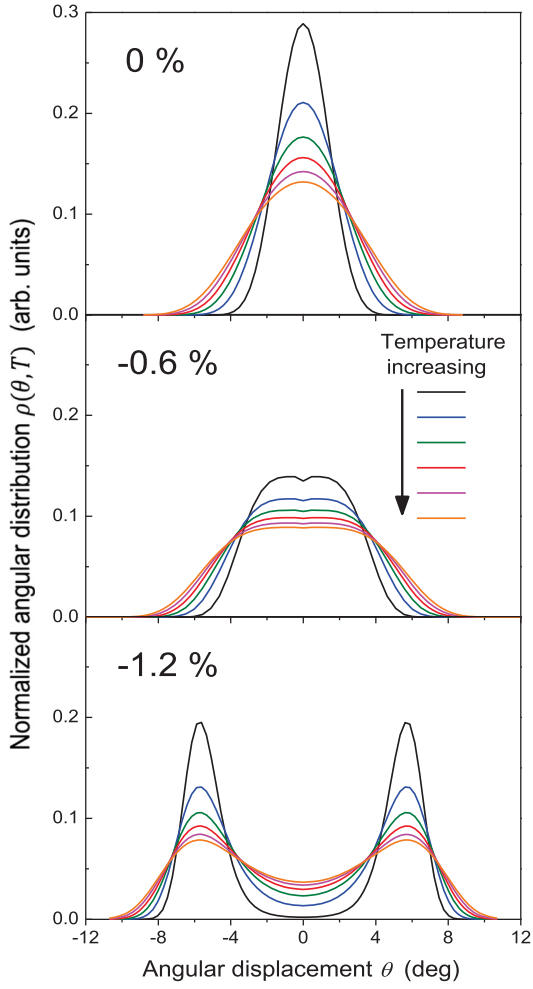

Figure 3. Temperature evolution of the angular distribution $\rho(\theta, T)$ at selected lattice compressions: no compression (top panel), −0.6% compression (middle panel) and −1.2% compression (bottom panel). The angular distribution gradually widens with increasing lattice compression, up to split into two peaks at high compressions.

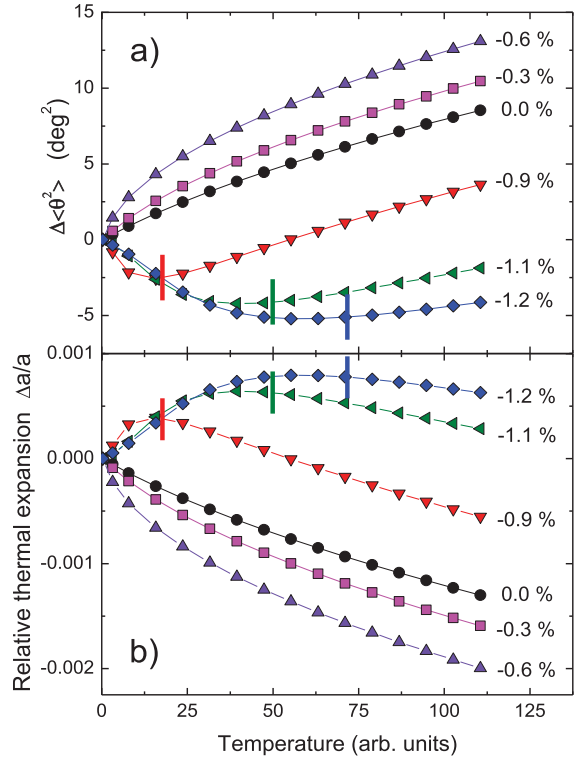

Figure 4. Thermal evolution of the mean-square angular displacement $\langle\theta^2\rangle$ (panel (a)) and corresponding thermal expansion behavior (panel (b)) at different lattice compressions. The NTE is enhanced for lattice compressions up to −0.6%, to then switch into positive thermal expansion for higher compressions. The vertical bold-lines indicate the phase-transition temperature evident for the lattice compressions −0.9%, −1.1% and −1.2%.

at different lattice compressions, while the panel (b) shows the corresponding thermal expansion resulted from Equation (3). This figure allows us to derive the following outcomes:

(i) at low lattice compressions (here up to −0.6 %) the NTE is enhanced. This because the single-well potential in which the octahedra rotate, turns into a quartic anharmonic potential (Figure 2(b)). The presence of a quartic potential increases the variation of $\langle\theta^2\rangle$ with temperature (Figure 4(a)) and thus enhances the NTE (Figure 4(b)). The origin of the strong NTE of ScF_3, explained in terms of quartic anharmonic potential [27], can be placed in this context. In other words, ScF_3, unlike other metallic MF_3 fluorides, has a proper lattice parameter so to have a quartic anharmonic potential in which the ZrF_6 octahedra can rotate more freely, thus resulting in a very strong NTE;

(ii) at higher lattice compressions (here starting from −0.9 %) the thermal expansion switches from negative to positive. This because the single-well potential in which the octahedra rotate, turns into a double-well potential (Figure 2(b)). The presence of a double-well potential reduces the variation of $\langle\theta^2\rangle$ with temperature (Figure 4(a)) and thus inhibits the NTE (Figure 4(b)). Note that above the phase-transition temperature, the thermal expansion returns negative but with lower magnitude. For example, the tuning of thermal expansion recently reached in ScF_3 nanoparticles and explained in terms of localized rhombohedral distortion [17], falls in this second case. By reducing the crystal size, from bulk to progressively smaller nanoparticles, the average lattice parameter becomes smaller and smaller [17], therefore, according to Figure 2(b), the rotational potential of the ScF_6 octahedra turns into a double-well potential. This explains the observed rhombohedral distortion of ScF_3 in nano-form and the subsequent suppression of NTE. Also, the low

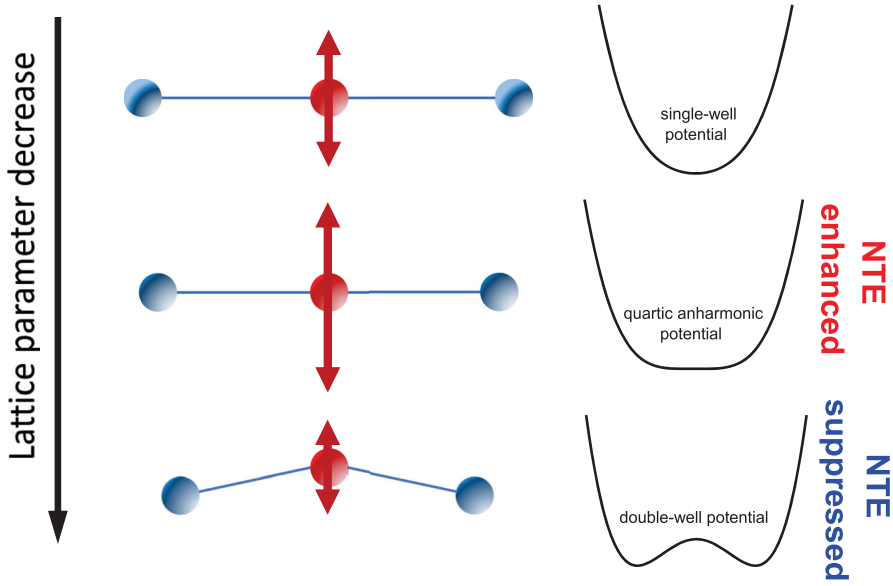

Figure 5. Effect of the lattice parameter magnitude on the thermal expansion behavior: by varying the lattice parameter, regardless of the method used, the single-well potential related to polyhedra rotations (or in general to transverse vibrations) can be turned into a quartic anharmonic potential or into a double-well potential. This enhances or inhibits, respectively, the variation with temperature of the transverse vibrations, thus enhancing or inhibiting, respectively, the NTE. As a result, we can tune the thermal expansion by changing the lattice parameter length among these three configurations.

NTE of ReO_3, one order of magnitude smaller than that of ScF_3 although sharing the same crystal structure, can be explained in this context. Shorter lattice parameter than that of ScF_3 gives hybridization of O-2p and Re-t2g states, formation of antibonding orbitals in conduction band and, consequently, structural distortion [28]. The structural distortion reduces the thermal variation of the ReO_6 octahedra rotation $\langle\theta^2\rangle$ and so NTE is suppressed.

4. Conclusions

In summary, in this work, it has been found out that the magnitude of the lattice parameter plays a key role in the control of thermal expansion. By varying the lattice parameter, regardless of the method used, the single-well potential in which the octahedra rotate (or atoms move transversely) can be turned into a quartic anharmonic potential or into a double-well potential, thus enhancing or inhibiting the NTE, respectively. This is depicted schematically in Figure 5. This result, applied to materials where NTE is due to rotational/transverse vibrational modes, should be kept in mind to overcome the challenge of controlling thermal expansion.

Disclosure statement

No potential conflict of interest was reported by the author.

Note

1. Since the Zr–F and M–F bond length are similar, the angular displacement θ of the ZrF_6 and MF_6 octahedra will be very similar to each other.

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