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Zero thermal expansion in metal–organic framework with imidazole dicarboxylate ligands

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Exploring new abnormal thermal expansion materials is important to understand the nature of thermal expansion. Metal–organic framework (MOF) with unique structure flexibility is an ideal material to study the thermal expansion. This work adopts the high-resolution variable-temperature powder x-ray diffraction to investigate the structure and intrinsic thermal expansion in Sr-MOF ($[Sr(DMPhH_2IDC)_2]_n$). It has the unique honeycomb structure with one-dimensional (1D) channels along the *c*-axis direction, the *a*–*b* plane displays layer structure. The thermal expansion behavior has strong relationship with the structure, ZTE appears in the *a*–*b* plane and large PTE along the *c*-axis direction. The possible mechanism is that the a/b layers have enough space for the transverse thermal vibration of polydentate ligands, while along the *c*-axis direction is not. This work not only reports one interesting zero thermal expansion material, but also provides new understanding for thermal expansion mechanism from the perspective of the structural model.

Keywords: negative thermal expansion, metal–organic framework, zero thermal expansion, transverse thermal vibration, structure flexibility

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1. Introduction

Most materials will expand when heated called as positive thermal expansion (PTE), one of which is attributed to the anharmonic lattice vibrations.[1] However, there also have very few compounds with abnormal thermal expansion, such as negative thermal expansion (NTE) or zero thermal expansion (ZTE) in a particular temperature zone.[2–4] Albeit rare, this phenomenon has increasing importance in thermal expansion controllable for highly sophisticated equipment and technology field such as telescopes and integrated circuit engineering.[5,6] So far, for the NTE mechanism, it is very complex. For example, phonon-related materials are found in many open-framework materials such as oxides,[7–10] fluorides,[13–17] and MOF.[18,19] Others are the electronic and magnetic transitions-related ones like charge-transfer[20,21] ($LaCu_3Fe_4O_{12}$ and V_2OPO_4) and magneto-volume effect materials[22,23] ($ANMn_3$ and $Er_2(Fe,Co)_{14}B$). Based on these NTE mechanisms, one can achieve the ZTE materials through chemical modification in single phase compounds, such as guest insertion,[24] nanometer effect,[25] and element substitution.[26] In fact, for the 1D or two-dimensional (2D) ZTE materials, it is also important to understand thermal expansion mechanism, while it has few reported. It is well known that the phonon-related mechanism has much larger NTE temperature range.[15,27] Hence, it is very worth exploring ZTE mechanism in the framework of material physics.

In recent years, metal–organic frameworks (MOFs) have attracted considerable interest, due to the unique pore structure and flexible framework, which focus on many applications such as catalysis, gas separation, and storage, sensing, drug delivery, energy, environment.[18,19,28] The net framework structure of MOFs is composed of metal ions or clusters through the bridging of organic ligands. Most MOFs have large flexibility, which depends on the presence of much weaker interactions (coordination bonds, hydrogen bonds or π–π stacking).[18] There have reported many classical NTE materials in MOFs. For example, MOF-5 displays large isotropic NTE behavior,[19,29] other like Cu_3BTC_2,[30] UiO-66(Hf),[31] Cu-TDPAT,[32] and so on. The NTE-driven force in these MOFs is often attributed to transverse "skipping rope type" vibrations of the bridging organic ligands.[30–32]

In this work, we have found an interesting ZTE behavior in MOF-Sr ($[Sr(DMPhH2IDC)_2]_n$). The high-resolution variable-temperature powder x-ray diffraction (XRD) was conducted to investigate the structure and intrinsic thermal expansion and attempted ZTE mechanism from the the perspective of structural model.

2. Experimental methods

The sample of Sr-MOF has the same preparation method as reported in Ref. [33]. Thermal expansion behavior was characterized based on the high-resolution synchrotron XRD (SXRD), which was performed at the 11-BM-B beamline of Advanced Photon Source ($\lambda = 0.412634$ Å). The lattice con-

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stants were extracted by using FULLPROF program[34] based on the Le Bail method. Thermal gravimetric analyses (TGA) were conducted on an NETZSCH STA 409PC synchronous thermal analyzer (heating rate of 10 °C/min; in air).

3. Results and discussion

Recently, Xie *et al.*[34] reported one interesting substituted imidazoledicarboxylate based MOFs, $[Sr(DMPhH2IDC)_2]_n$ [DMPhH3IDC=2-(3,4-dimethylphenyl)-1H-imidazole-4,5-dicarboxylic acid], possessing high proton conductivity (0.92×10^3 S·cm^1). Figure 1(a) shows the structure of Sr-MOF with the tetragonal phase ($I41/a$), of which constitutes with the Sr ion (eight-coordinated) and six H2DMPhIDC anions. To understand the framework better, one can use one atom to replace the organic ligands (Fig. 1(b)) and retain the Sr atoms to achieve one topological consideration of the three-dimensional (3D) network, as shown in Fig. 1(c). It clearly observes that the structure like one honeycomb with 1D channels.

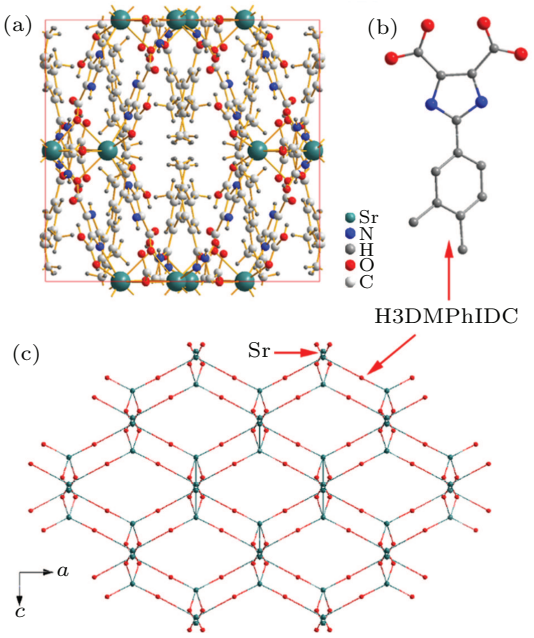


Fig. 1. (a) Crystal structure of Sr-MOF ($[Sr(DMPhH_2IDC)_2]_n$). (b) Chemical structure of HDMPhIDC ligand, where the H atoms is omitted. (c) A structural unit diagram of Sr-MOF, where the ligands are simplified to one atom and the metal atom of Sr is retained.

In order to investigate the intrinsic thermal expansion of Sr-MOF, the variable temperature synchrotron x-ray diffraction was conducted from 100 K to 475 K at APS. Figure 2(a) shows the high resolution SXRD data of Sr-MOF with Le Bail fitted at 300 K. The fitted results indicated that the lattice parameter $a = 16.79599(8)$ Å and $c = 17.57654(10)$ Å, which is consistent with the previous report.[33] Obviously, from the temperature dependence of the diffraction, the (100) diffraction peak shows essentially no shift from 100 K to 475 K, which indicates that the dimensions of a–b plane is nearly ZTE as a function of temperatures. However, the (110) diffraction peak has much larger shift from 100 K to 475 K. In combination with the behavior of (100) diffraction peak, it suggests that the Sr-MOF has large thermal expansion along c axial direction. In order to exclude the factor of mass loss in the heating process for x-ray diffraction measurement, the TG-DSC measurement was conducted. As shown in Fig. 2(b), the results indicated that the Sr-MOF could keep stable up to 600 K. Hence, in the heating process of XRD measurement, no water molecules and ligands get out.

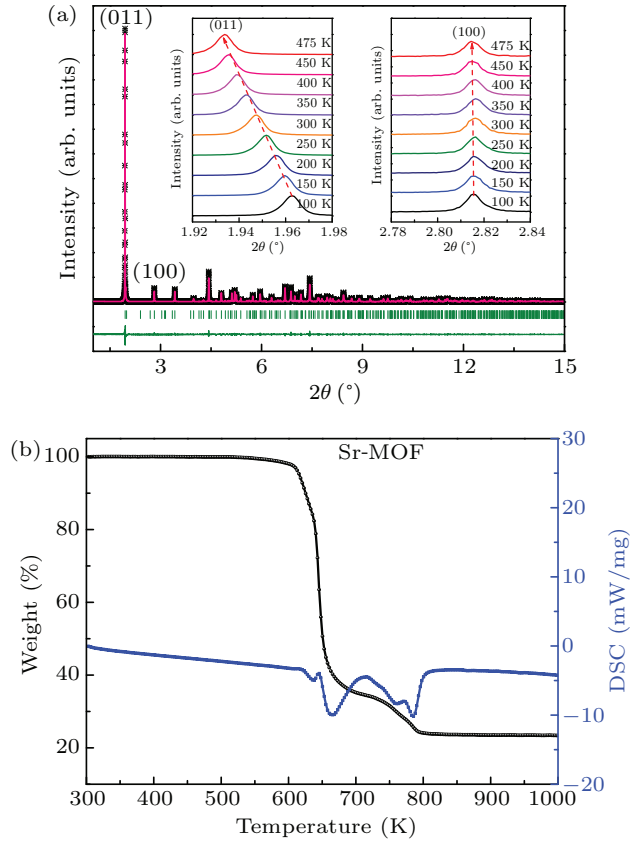


Fig. 2. (a) The high resolution SXRD data of Sr-MOF with Le Bail fitted at 300 K. The inset shows the diffraction peak for (011) and (100) plane as a function of temperature. (b) The TG-DSC curve of Sr-MOF.

Here, the lattice constants were extracted with the LeBail pattern decomposition technique. The space group of structural model is $I41/a$ from 100 K to 475 K. Figure 3 shows the temperature-dependent lattice parameter change of Sr-MOF. The coefficient of thermal expansion (CTE) of the a axis displays near ZTE (average value $-1.07(3)$ ppm/K) throughout the temperature range. While the CTE along the c-axis direction is quite large to $+84.01(4)$ ppm/K. The volume CTE of Sr-MOF is calculated to be $+81.97(3)$ ppm/K, which closes proximity to the c axis. It is indicated that the material of Sr-MOF has large PTE along c axial and zero area thermal expansion behavior in the a–b plane.

It is well known that the MOFs as one kind of compounds have phonon-driven NTE behavior. Different from the traditional inorganic porous materials such as ZrW_2O_8[35] and ScF_3,[36] whose NTE come from the transverse thermal vibration of O or F atoms. Here, the bridging parts are replaced to

the polydentate ligands in MOFs, so the flexibility of polydentate ligands is the key for the thermal expansion. As shown in the structural unit diagram of Sr-MOF (Fig. 1(c)), one can see that the *a*–*b* plane displays a square layer. Similar to the DABCO-based MOFs structure,[37] it exhibits near ZTE in their layered direction over a temperature range of 100 K–475 K. Due to the fact that the space steric in *a*–*b* layer is the largest, thus it could ensure the transverse thermal vibration of ligands. However, along the *c* axis the angles of Sr–ligands–Sr linkage is much lower than 180°, it will cause the lengths of Sr–ligands–Sr linkage increasing with the temperature, thus lead to lager PTE in the *c* axis.

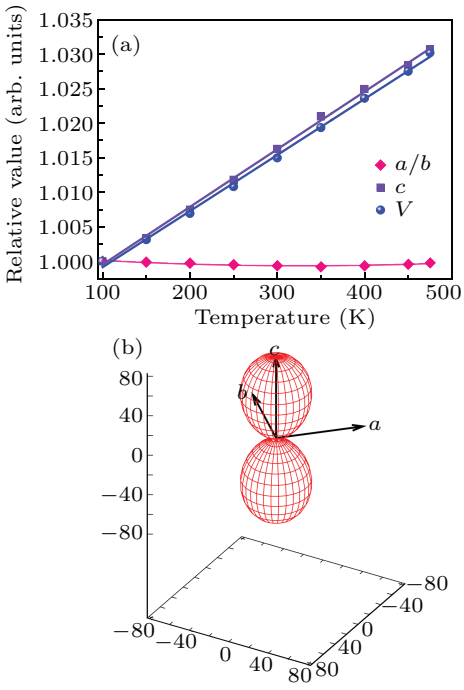


Fig. 3. (a) Temperature-dependent lattice parameter change of Sr-MOF, (b) the spatial distribution of CTE plotted by PASCal software.

4. Conclusion

In conclusion, we have investigated the intrinsic thermal expansion of Sr-MOFs through the high-resolution variable-temperature powder x-ray diffraction. We observed the ZTE behavior along the *a*–*b* plane and large PTE in *c*-axis direction. Such interesting results could attribute to the unique honeycomb structure, it could provide enough space for the transverse thermal vibration of polydentate ligands in a/b-axis direction, not for the *c*-axis direction. This work not only reports one 2D ZTE materials, but also provides some insight into exploring new abnormal thermal expansion materials.

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