Crossover of Thermal Expansion from Positive to Negative by Removing the Excess Fluorines in Cubic ReO3-type TiZrF7-x

Journal:	*Journal of Materials Chemistry C*
Manuscript ID	TC-ART-10-2017-004875.R2
Article Type:	Paper
Date Submitted by the Author:	18-Mar-2018
Complete List of Authors:	Yang, Cheng; Key Laboratory of Materials Physics, Institute of Solid State Physics Zhang, Yugang; Brookhaven National Laboratory Bai, Jianming; Brookhaven National Lab, Qu, Bingyan; Hefei University of Technology, Tong, Peng; Institute of Solid State Physics, CAS, Wang, Meng; Key Laboratory of Materials Physics, Institute of Solid State Physics Lin, Jianchao; Key Laboratory of Materials Physics, Institute of Solid State Physics Zhang, Ranran; High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China, Tong, Haiyun; Institute of Solid State Physics Chinese Academy of Sciences Wu, Ying; Institute of Solid State Physics Chinese Academy of Sciences Song, Wenhai; Key Laboratory of Materials Physics, Institute of Solid State Physics Sun, Yuping; High Magnetic Field Laboratory, Chinese Academy of Sciences

Crossover of Thermal Expansion from Positive to Negative by Removing the Excess Fluorines in Cubic ReO_3-type $TiZrF_{7-x}$

Cheng Yang,[a,b] Yugang Zhang,[c] Jianming Bai,[c] Bingyan Qu,[d] Peng Tong,[*,a,b] Meng Wang,[a] Jianchao Lin,[a] Ranran Zhang,[e] Haiyun Tong,[a,b] Ying Wu,[a] Wenhai Song,[a] and Yuping Sun[*,a,e]

[a] Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China

[b] University of Science and Technology of China, Hefei 230026, China

[c] National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, United States

[d] Laboratory of Amorphous Materials, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China

[e] High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China

***Corresponding Authors** [*]Email: tongpeng@issp.ac.cn (Peng Tong), [*]Email: ypsun@issp.ac.cn (Yuping Sun)

Electronic supplementary information (ESI) available.

Abstract: We report the crossover of the coefficient of thermal expansion (CTE) from positive to negative with withdrawing the excess fluorines in ReO_3-type $TiZrF_{7-x}$ (x = 0, 0.5 and 1) compounds. The average volumetric CTE between 300 K and 623 K changes from 8.07 ppm/K for x = 0, to 0.66 ppm/K for x = 0.5 and finally to -6.09 ppm/K for x = 1. After withdrawing the excess fluorines, the lattice expands and the edge-sharing polyhedra partially transform to corner-sharing ones, which enhances the transverse vibrations of fluorines and thus accounts for the crossover of CTE. Moreover, those compounds are narrow-gap semiconductors with the energy gap decreasing with x. NTE may also be achievable in other fluorine-excess cubic fluorides by removing the excess fluorines, which opens a new avenue of exploring the NTE in fluorides.

1. Introduction

In the past decade, materials showing negative thermal expansion (NTE) have attracted much attention from the viewpoints of both fundamental physics and technological applications.[1-12] In terms of applications, NTE materials can be used as thermal expansion compensator for precisely controlling of the coefficient of thermal expansion (CTE) of engineering materials. The reported NTE is either attributed to the flexible frameworks[1-3] in the crystal structures or intimately bounded with a magnetic or electronic ordering.[4-8] Metal fluorides, as a prototype of open-framework structured materials, have received increasing interest since the observation of wide-temperature-window NTE in cubic ReO_3-type ScF_3.[9] However, ScF_3 is so far the only ReO_3-type metal trifluoride that exhibits wide temperature range NTE.[9] More recently, NTE was widely observed in double-ReO_3-type metal fluorides (e.g., $M^{II}B^{IV}F_6$, M=Ca, Mn, Mg, Fe; B=Zr, Hf, Nb) where the two cations are ordered, forming the face-centered cubic crystal structure (space group, *Fm-3m*).[10-12] In these (double) ReO_3-type metal fluorides, cubic crystal symmetry is always indispensable to NTE or zero thermal expansion (ZTE) emerging.[10-12] The transverse vibrations of fluorines perpendicular to the cation-fluorine-cation chain are proposed to contribute negatively to the CTE (the Guitar-string model).[13,14] Crossover from NTE to ZTE and finally to positive thermal expansion (PTE) was widely observed, for example by chemical substitution in $(Sc_{1-x}M_x)F_3$ (M=Al, Ti, Fe and Ga),[15-17] or by redox intercalation in $(Sc_{0.9}Fe_{0.1})F_3$.[18] However, none improvement of NTE in ScF_3 has yet been reported in literatures.

Due to the open-framework feature of the ReO_3-type structure, excess fluorines can be adopted, forming the so-called anion-excess ReO_3-type compounds, such as γ-ZrF_4,[19] $MZrF_7$,[20] MZr_2F_{11},[21] and MZr_3F_{15}.[22] When excess fluorines are inserted, they will be chemically bonded with the metal cations (Zr^{4+}) due to the high electronegativity of fluorine. As a result, the coordination number of the related cations is expected to change since the original fluorines at the ideal (0.5 0 0) position are replaced by fluorine-fluorine pairs.[23] Also, the metal cations are slightly displaced.[23] Consequently, original corner-linked polyhedra will partially transform to edge-linked polyhedra, so that many anion-excess fluorides take a lower crystal symmetry than the cubic ReO_3-type.[19-22] Only very few of the F-excess ReO_3-type metal fluorides were reported to maintain a cubic structure at ambient conditions, such as $YbZrF_7$,[23,24] $SmZrF_7$[25] and recently reported $(Sc_{1-x}Zr_x)F_{3+\delta}$.[26] In addition, nonstoichiometric $LnZrF_{6+x}$ (Ln= Sm, Eu, Yb) compounds prepared by heating LnF_3-(Ln, Zr)-ZrF_4 systems were also reported to have a cubic structure by N. M. Kompanichenko et al.[27]

Herein, we report the realization of NTE by taking away the excess fluorines from cubic F-excess ReO_3-type $TiZrF_{7-x}$. The samples with $x = 0$, 0.5 and 1 are defined as TZF7, TZF6.5 and TZF6, respectively. The chemical analysis indicates the actual fluorine contents are very close to their nominal compositions. (Table S1 and Fig. S1). These compounds are narrow-gap semiconductors with the gap of ~ 1 eV. The TZF7 compound displays PTE with an average volumetric CTE, α_V = 8.07 ppm/K between 300 K and 623 K. α_V is reduced to 0.66 ppm/K for TZF6.5, and eventually to -6.09 ppm/K for TZF6 over the same temperature range. When the excess fluorines are removed, the lattice is expanded, which softens the frame-work structure, and the polyhedra are easier to rotate.[11] Hence, the transverse vibrations of fluorine atoms are favored, resulting in the CTE crossover.

2. Results and discussion

As shown in Fig. 1, all the three samples maintain cubic structure at room temperature. Bragg reflections can be well indexed with the space group *Pm-3m* (Fig. S2), which is consistent with the previous report on ZrF_4-TiF_3 solutions.[28] If the fluorine is stoichiometric, the samples might take the ScF_3-like structure, which means the cations are disordered (defined as regular ReO_3-type). However, if fluorine is excess, some fluorines at the ideal (0.5 0 0) positions will be partially replaced by the pairs of fluorines. In such case, the macroscopical crystal structure can still maintain cubic, though excess fluorines inserted, as have been observed in $YbZrF_7$ (defined as F-excess ReO_3-type).[23,24] As plotted in the inset of Fig. 1, the refined lattice constant (Table S2) is increased with reducing the F content. In an earlier literature, the $TiZrF_6$ single crystal was suggested to have the cation-ordered cubic structure (space group, *Fm-3m*).[29] The distinction in crystal structure of our present sample might probably originate from the different synthesis methods.[29] Besides, the samples are quite stable in air (Fig. S3).

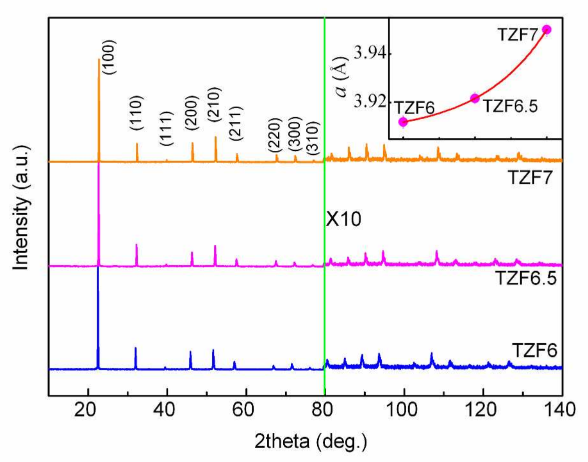

Fig. 1. Room temperature XRD patterns of three $TiZrF_{7-x}$ samples. Inset shows variation of lattice constant with the fluorine content.

Fig. 2 shows the thermal expansion behaviors derived from temperature dependent XRDs for the $TiZrF_{7-x}$ samples (see Fig. S4). It is shown that TZF7 displays PTE with $\alpha_V \sim 8.07$ ppm/K between 300 K and 623 K. TZF6.5 exhibits ZTE over the same temperature range investigated ($\alpha_V \sim 0.66$ ppm/K). Finally, a moderate NTE with α_V of -6.09 ppm/K from 300 K to 623 K was observed in TZF6.

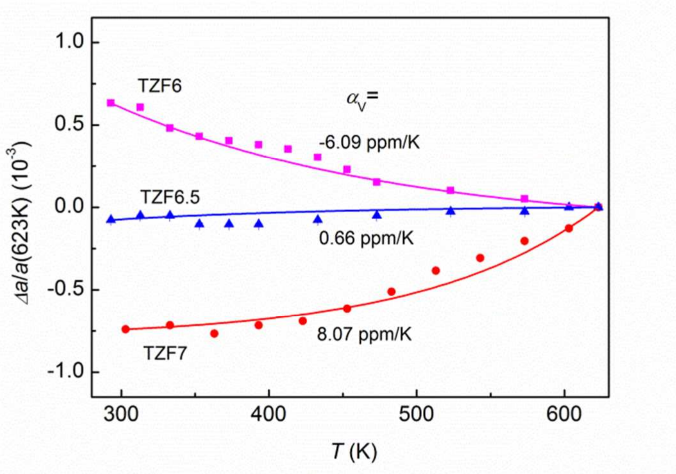

Fig. **2**. The relative change in the lattice constant for $TiZrF_{7-x}$. The average volumetric coefficient of thermal expansion is indicated for each sample.

X-ray photoelectron spectra (XPS) measurements were conducted for all $TiZrF_{7-x}$ samples and the starting materials ZrF_4 and TiF_3. As shown in Fig. 3(a)-(d), the Zr *3d* spectra of TZF7 is shifted to lower energy by ~ 0.45 eV compared with the case of ZrF_4, which could be attributed to the structure difference. From TZF7 to TZF6, the Zr 3*d* spectra are obviously broadened to the low binding energy side. In contrast, the F*1s* XPS peaks are almost unchangeable with F content (Fig. S5). So the broadening of Zr 3*d* spectra unambiguously indicates the appearance of lower valence Zr cations as the F concentration is decreased. The partial reduction of Zr^{4+} makes the valences of the two kinds of cations (Ti and Zr) closer, which is conductive to the formation of cation-disordered cubic structure. As shown in Fig. 3(e)-(f), the Ti *2p* XPS patterns for all $TiZrF_{7-x}$ samples are almost the same as that of raw material TiF_3, which suggests the valence of Ti changes very little with the variation of F content.

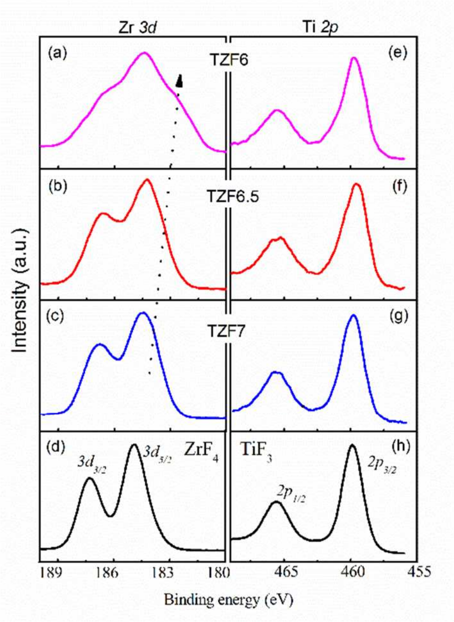

Fig. 3. The left column shows the Zr *3d* XPS spectra of TZF6 (a), TZrF6.5 (b), TZF7 (c) and ZrF_4 (d). The right column shows the Ti 2p spectra of TZF6 (e), TZrF6.5 (f), TZF7 (g) and TiF_3 (h). The dotted line with arrow guides the broadening of the Zr 3d spectra with reducing F content.

The Pair Distribution Function (PDF) measures the local crystal structure of a certain material without assumption of lattice periodicity, which gives a deeper insight into the “real” crystal structure.[30-32] The *G*(r)s for TZF6 and TZF7 were calculated from the synchrotron X-ray total scattering data (Fig. S6) which was terminated at 25 $Å^{-1}$.[30,31] Unlike the XRD result, the local PDF ($r < 6$ Å) for TZF7 is clearly distinguishable from that for TZF6, as shown in Fig. 4(a). Particularly, the PDF peak at 3.5 Å is strengthened in TZF7 compared with that in TZF6, while the peak at 4.5 Å changes in an opposite way. The regular cubic model was tested to fit the PDF data up to 15 Å for both samples. As shown in Fig. S7, for both compounds the model fails to fit the local PDF with $r < 6$ Å but describes the data well at longer distances. Moreover, the fitting is worse for TZF7 than for TZF6, indicating the local structure of TZF7 is more deviated from the regular cubic model relative to that of TZF6.

In the typical F-excess ReO_3-type compound $YbZrF_7$, the Yb and Zr take 3+ and 4+ valences, respectively. The excess fluorines and the original ones form the F-F pairs which are chemically bonded with Zr^{4+}.[23,24] Consequently, in $TiZrF_{7-x}$ the Zr^{4+} cations should adopt more fluorines than the other lower-valence cations. Since there is no cation ordering in those compounds, the random distribution of Zr^{4+} cations would lead to local fluctuation of fluorines in $TiZrF_{7-x}$. A local structure model combining both F-excess and regular cubic phases was tentatively tested to fit the local PDF up to 7.5 Å. As shown in Fig. S8 and Fig. S9, this model gives a better fitting than any single phase model does. The volume fraction of the F-excess cubic phase is found to decrease from 52.9% in TZF7 to 31.9% in TZF6. Such a trend basically agrees with the result of pyrohydrolysis analysis of fluorine content as shown in Table S1.

In the F-excess cubic lattice, the fluorines deviate from the ideal positions as in the regular cubic case. So the cation-fluorine bond lengths are scattered.[23] Accordingly, the PDF peak at ~ 2.1 Å originating from the shortest Zr/Ti-F bonds is wider in TZF7 than in TZF6 (see the left inset in Fig. 4(a)). This effect is more visible for the next nearest Zr/Ti-F distance at ~ 4.5 Å. As a result of adopting excess flruoines, shorter next nearest Zr/Ti-F bond shows up at ~ 3.5 Å at the expense of the original ones (Fig.4(b)). Hence, an intensity switch between the PDF peaks at 3.5 Å and 4.5 Å with removing the excess fluorines was observed as shown in Fig. 4(a). Usually, the Zr cations in TZF6 with lower charge valences are bigger in size than the Zr^{4+}, which may lead to longer bond length. However, after removing the excess fluorines, the left fluorines will move back to the ideal positions, which will lead to a shorter nearest Zr/Ti-F distance [see Fig. 4(b)]. It counteracts the bond elongation due to transformation, so that the PDF peak at ~ 2.1 Å doesn't show a significant shift to higher *r* values in TZF6 compared with in TZF7. The inserted excess fluorines tend to bring the nearby cations closer.[19] Hence, when the excess fluorines are removed, the nearest Zr/Ti-Zr/Ti distance (~ 3.95Å) is expanded as shown in the right inset of Fig. 4(a) and 4(b). This effect is accumulated at longer distances. That is the reason why the PDF peaks above 6 Å in TZF6 shift clearly towards higher values in comparison to those in TZF7 (Fig. 4(a)). Consistently, the lattice constant derived by XRD is larger in TZF6 than in TZF7 (inset of Fig. 1).

The transverse vibrations of fluorine atoms perpendicular to the cation-fluorine-cation chain (in other words, the rotation of polyhedra) are responsible for the negative contribution to the CTE in cubic metal fluorides.[13,14] If excess fluorines exist, as sketched in Fig. 4(b), the corner-linked polyhedra will be transformed to edge-linked ones, and thus the twisting of polyhedra is blocked.[19,24] When some excess fluorines are removed, the polyhedra are more free to rotate, which in turn favors the NTE. Besides, the expanded lattice as result of withdrawing the excess fluorines will soften the structural frame-work structure.[13] Therefore, the transverse thermal vibrations of fluorines are enhanced, which is beneficial to the NTE.[11] As a combined effect, the NTE is enhanced as the fluorine concentration is reduced in $TiZrF_{7-x}$. When the NTE is strengthened to be comparable to that of normal PTE due to the unharmonic lattice vibrations, the nearly ZTE was observed in TZF6.5. For TZF6, the further strengthened NTE overcomes the normal PTE, leading to an overall NTE behavior in a large temperature range. Adjusting the CTE by removing some excess fluorines might also be applicable to other cubic $MZrF_7$ compounds.

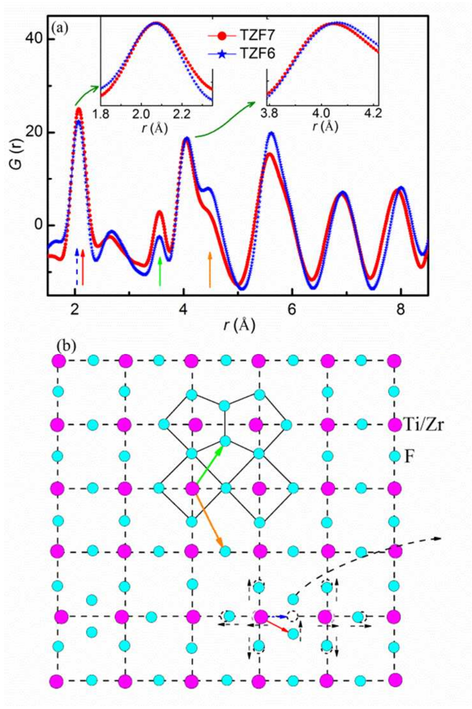

Fig. 4. (a) The Pair Distribution Function (PDF), *G*(r), for TZF6 and TZF7 calculated from total X-ray scattering data. Inset shows the normalized PDF peaks at 2.1Å and 4.0 Å for both compounds. (b) A sketch shows how the local structure is distorted with inserting a fluorine atom in $TiZrF_{7-x}$ and how the atoms are locally rearranged when an excess fluorine atom is removed. The colorful arrows in (a) and (b) mark the nearest (blue and red) and next nearest (green, orange) Zi/Ti-F distances.

UV-vis absorption deduced from the corresponding UV-Vis-NIR diffuse reflection spectra measurement was carried out for all samples. It can be clearly seen from Fig. 5(a) that all the $TiZrF_{7-x}$ samples show a notable visible-light absorption (400-700 nm). The band gaps (E_g) of TZF6.5 and TZF7 are estimated to be 0.93 eV and 1.04 eV, respectively (Fig. 5b), at the intercept of the linear part of the curve with $(Ahv)^{1/2}=0$. The E_g values are smaller than that observed in Fe-doped scandium fluoride (Sc, Fe)F_3 (E_g= 1.87 eV for $Sc_{0.9}Fe_{0.1}F_3$),[33] but are very close to that of typical semiconductor silicon (E_g= 1.12 eV).[34] For TZF6, the absorption slope is not covered within the wavelength range from 200 to 2000 nm, so the related E_g of TZF6 could not be estimated. It is reasonable to expect that E_g of TZF6 is smaller than that of TZF6.5 since the absorption slope is proposed to occur in the range beyond 2000 nm. When the fluorine content decreases, the valence electrons of the cations become greater in number. The valence electrons will form more impurity states around the Fermi level, thus narrowing the band gap of $TiZrF_{7-x}$ as x increases.[33]

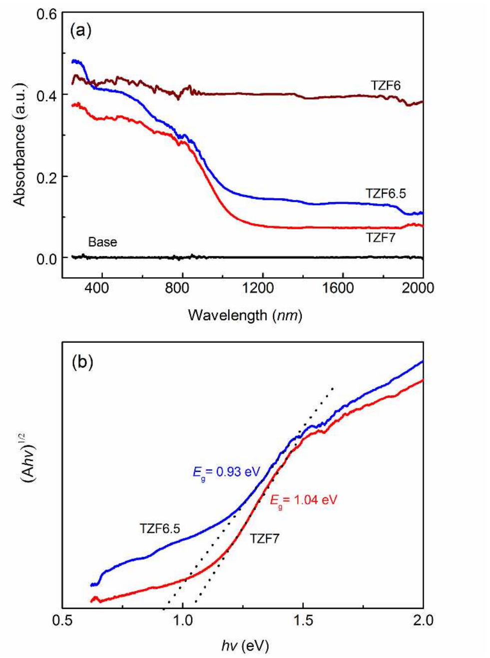

Fig. 5. (a) The UV-vis absorption of $TiZrF_{7-x}$ from wavelength of 250 nm to 2000 nm. (b) The plot of $(Ah\nu)^{1/2}$ against photon energy ($h\nu$) for TZF6.5 and TZF7, indicating the band gap (E_g) of 0.93 eV and 1.04 eV, respectively.

The values of E_g of $TiZrF_{7-x}$ locate in the region of narrow band-gap semiconductors, suggesting they are potentially useful as infrared detectors[35] or thermoelectrics.[36] Their low-CTE will preserve the optical performances during thermal cycling. Moreover, the values of CTE (e.g., for TZF7) show good compatibility with that of silicon (α_V ~ 8.1 ppm/K at room temperature)[37] widely used as substrate in micro-devices, which will minimum the thermal stress on the devices during temperature variation. So, further investigation on the optical properties of $TiZrF_{7-x}$ single crystals or thin films is strongly desired.

3. Conclusion

By reducing the fluorine concentration x, the crossover of CTE from positive to negative was observed in F-excess $TiZrF_{7-x}$ compounds with the cubic structure (space group, *Pm-3m*). These compounds exhibit narrow band gap of ~ 1 meV, which is decreased with decreasing x. PDF analysis indicates the local structure is modified by removing the excess fluorines. The excess fluorines locally change the regular cubic symmetry to the F-excess *Pm-3m* type. After withdrawing the excess fluorines, the lattice is expanded and thus the polyhedra are more free to rock. Both effects work cooperatively, which was proposed to be responsible for the crossover of CTE as x is decreased. The present study suggests an alternative way of tuning the CTE of cubic ReO_3-type fluorides.

4. Experimental

4.1. Syntheses. There polycrystalline samples with nominal compositions $TiZrF_{7-x}$ with x = 0 (TZF6), 0.5 (TZF6.5) and 1 (TZF7) were prepared via solid state reactions. For a typical procedure to prepare TZF7, powders of 0.03 mol TiF_3 (3N, Alfa aesar) and 0.03 mol ZrF_4 (3N, Alfa aesar). The same procedure was employed for all samples. First, the raw powders were mixed and thoroughly ground for at least 1 hour in a glove box. Then the mixture was pressed into a small pellet and sealed in a nickel tube in argon atmosphere. The nickel tube was transferred into an evacuated quartz ampule and heated at 850 °C for 10 hours, before rapid quench to room temperature. For the syntheses of TZrF6.5, the starting materials were 0.025 mol TiF_3, 0.005 mol Ti (3N, Alfa aesar) and 0.03 mol ZrF_4. While for TZF_6, precursors were 0.02 mol TiF_3, 0.01 mol Ti and 0.03 mol ZrF_4. The other procedures were the same as those of TZF7.

4.2. Measurements. X-ray diffractions (XRDs) were performed on a Philips X' pert PRO X-ray diffractometer, operating at 40 kV and 40 mA with Cu K_α radiations ($K_{\alpha1}$ = 1.5406 Å, $K_{\alpha2}$ = 1.5418 Å). Temperature-dependent lattice parameters were obtained from the standard Rietveld refinement. High-energy X-ray scattering was carried out for TZF6 and TZF7 samples on the beamline 28-ID-2 at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. The incident wavelength of the monochromatic synchrotron radiation was 0.1827 Å.

The XPS data were obtained from an X-Ray Photoelectron Spectrometer with an Al K_α X-ray source. All the peaks were corrected by assigning a value of 284.80 eV to the C_{1s} reference line of residual hydrocarbons. UV-vis-NIR spectra were recorded by a diffused reflection method with a spectrometer (UV-3600, Shimadzu Ltd.) using $BaSO_4$ as the standard background.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Key Research Program of Frontier Sciences, CAS (QYZDB-SSW-SLH015), and National Natural Science Foundation of China (NSFC) under Contract Nos. 51322105 and U1632158. The work conducted at the beamline (28ID) at National Synchrotron Light Source II (NSLS-II) of Brookhaven National Laboratory were supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contracts No. DE-SC0012704.

Notes and references

1 T. A. Mary, J. O. S. Evans, T. Vogt and A. W. Sleight, *Science*, 1996, **272**, 90.

2 A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. Evans, D. A. Keen, L. Peters and M. G. Tucker, *Science*, 2008, **319**, 794.

3 X. H. Ge, Y. H. Mao, X. S. Liu, Y. G. Cheng, B. H. Yuan, M. J. Chao and E. J. Liang, *Sci. Rep.*, 2016, **6**, 24832.

4 P. Mohn, *Nature*, 1999, **400**, 18.

5 S. H. Deng, Y. Sun, H. Wu, Q. Z. Huang, J. Yan, K. W. Shi, M. I. Malik, H. Q. Lu, L. Wang, R. J. Huang, L. F. Li and C. Wang, *Chem. Mater.*, 2015, **27**, 2495.

6 J. Chen, K. Nittala, J. S. Forrester, J. L. Jones, J. X. Deng, R. B. Yu and X. R. Xing, *J. Am. Chem. Soc.*, 2011, **133**, 11114.

7 M. Azuma, W. T. Chen, H. Seki, M. Czapski, K. Oka, M. Mizumaki, T. Watanuki, N. Ishimatsu, N. Kawamura and S. Ishiwata, *Nat. Commun.*, 2011, **2**, 347.

8 K. Takenaka, Y. Okamoto, T. Shinoda, N. Katayama and Y. Sakai, *Nat. Commun.*, 2017, **8**, 14102.

9 B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K.W. Chapman and A. P. Wilkinson, *J. Am. Chem. Soc.*, 2010, **132**, 15496.

10 J. C. Hancock, K. W. Chapman, G. J. Halder, C. R. Morelock, B. S. Kaplan, L. C. Gallington, A. Bongiorno, C. Han, S. Zhou and A. P. Wilkinson, *Chem. Mater.*, 2015, **27**, 3912.

11 L. Hu, J. Chen, J. L. Xu, N. Wang, F. Han, Y. Ren, Z. Pan, Y. C. Rong, R. J. Huang, J. X. Deng, L. F. Li and X. R. Xing, *J. Am. Chem. Soc.*, **2016**, 138, 14530.

12 B. R. Hester, J. C. Hancock, S. H. Lapidus and A. P. Wilkinson, *Chem. Mater*., 2017, **29**, 823.

13 L. Hu, J. Chen, A. Sanson, H. Wu, C. G. Rodriguez, L. Olivi, Y. Ren, L. L. Fan, J. X. Deng and X. R. Xing, *J. Am. Chem. Soc.*, 2016, **138**, 8320.

14 Y. M. Liu, Z. H. Wang, M. Y. Wu, Q. Sun, M. J. Chao and Y. Jia, *Comp. Mater. Sci*., 2015, **107**, 157.

15 C. R. Morelock, L. C. Gallington and A. P.Wilkinson, *Chem. Mater*., 2014, **26**, 1936.

16 C. R. Morelock, L. C. Gallington and A. P. Wilkinson, *J. Solid State Chem*., 2015, **222**, 96.

17 L. Hu, J. Chen, L. L. Fan, Y. Ren, Y. C. Rong, Z. Pan, J. X. Deng, R. B. Yu and X. R. Xing, *J. Am. Chem. Soc*., 2014, **136**, 13566.

18 J. Chen, Q. L. Gao, A. Sanson, X. X. Jiang, Q. Z. Huang, A. Carnera, C. G. Rodriguez, L. Olivi, L. Wang, L. Hu, K. Lin, Y. Ren, Z. S. Lin, C. Wang, L. Gu, J. X. Deng, J. P. Attfield and X. R. Xing, *Nat. Commun*., 2017, **8**, 14441.

19 J. P. Laval, *Acta Cryst.*, 2014, **C70**, 742.

20 M. Poulain and J. Lucas, *Mater. Res. Bull.*, 1972, **7 (4)**, 319.

21 J. P. Laval and A. Abaouz, *J. Solid State Chem.*, 1992, **100**, 90.

22 J. P. Laval, J. F. Gervais, L. Fournes, J. Grannec, P. Gravereau, A. Abaouz and A. Yacoubi, *J. Solid State Chem.*, 1995**, 118**, 389.

23 M. Poulain and B. C. Tofield, *J. Solid State Chem.*, 1981, **39 (3)**, 314.

24 J. O. Ticknor, "Using defects in anion excess rhenium trioxides to control thermal expansion: ytterbium zirconium fluorides as case study", B. S. thesis, *Georgia Institute of Technology* (2017).

25 M. Poulain, M. Poulain and J. Lucas, *J. Solid State Chem.*, 1973, **8 (2)**, 132.

26 T. Wang, J. L. Xu, L. Hu, W. Wang, R. J. Huang, F. Han, Z. Pan, J. X. Deng, Y. Ren, L. F. Li, J. Chen and X. R. Xing, *Appl. Phys. Lett.*, 2016, **109**, 101901.

27 N. M. Kompanichenko, A. O. Omel'chuk, O. P. Ivanenko and V. F. Zinchenko, *J. Fluor. Chem.*, 2010, **131**, 282.

28 J. C. Champarnaud-Mesjard, J. P. Laval and B. Gaudreau, *Rev. Chim. Miné.* 1974, **11**, 735-741.

29 M. Kraus, M. Muller, R. Fischer, R. Schmidt, D. Koller and B.G. Muller, *J. Fluor. Chem*., 2000, **101**, 165.

30 P. J. Chupas, X. Qiu, J. C. Hanson, P. L. Lee, C. P. Grey and S. J. L. Billinge, *J. Appl. Crystallogr.*, 2003, **36**, 1342–1347.

31 P. Tong, D. Louca, G. King, A. Llobet, J. C. Lin and Y. P. Sun, *Appl. Phys. Lett*., 2013, **102**, 041908.

32 S. Iikubo, K. Kodama, K. Takenaka, H. Takagi, M. Takigawa and S. Shamoto, *Phys. Rev. Lett.*, 2008, **101**, 205901.

33 L. Hu, J. Chen, L. L. Fan, Y. Ren, Q. Z. Huang, A. Sanson, Z. Jiang, M. Zhou, Y. C. Rong, Y. Wang, J. X. Deng and X. R. Xing, *Adv. Mater.*, 2015, **27**, 4592.

34 W. Bludau, A. Onton and W. Heinke, *J. Appl. Phys.*, 1974**, 45**, 1846.

35 A. Rogalski, *Rep. Prog. Phys.*, 2005**, 68**, 2267.

36 A. I. Hochbaum, R. K. Chen , R. D. Delgado, W. J. Liang, E. C. Garnett, M. Najarian, A. Majumdar and P. D. Yang, *Nature.*, 2008, **451**, 163.

37 Y. Okada and Y. Tokumaru, *J. Appl. Phys.*, 1984, **56**, 314.

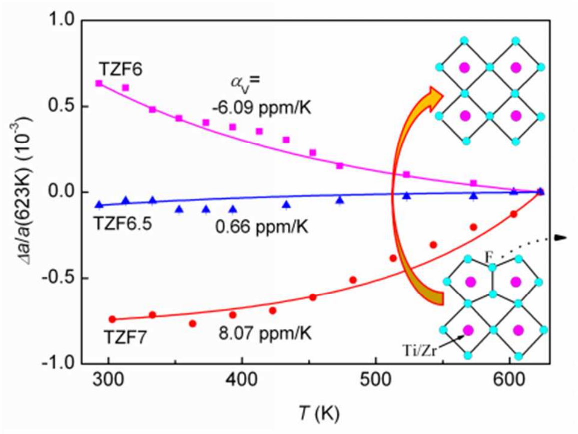

Table of contents entry: We realize crossover from PTE to NTE by removing excess fluorines in $TiZrF_{7-x}$.