On the Switching between Negative and Positive Thermal Expansion in Framework Materials

Andrea Sanson
Department of Physics and Astronomy - University of Padova, Padova (Italy)

ARTICLE HISTORY
Compiled May 20, 2019

Panel (a) of Fig. S1 shows the thermal expansion coefficient plotted against the cubic-to-rhombohedral phase-transition temperature for the the MZrF$_6$ series. For M=Ca, it has been assumed the transition temperature at 0 K since no transition was experimentally observed in CaZrF$_6$, at least down to 10 K [1]. The same relationship is present, for example, in Sc$_{1-x}$Ti$_x$F$_3$ compounds (blue circles in panel (a) of Fig. S1), where experimental data are available from Ref. [2]. Also here, for $x = 0$, we have set the transition temperature at 0 K since no transition was observed in ScF$_3$, at least down to 10 K [3]). Panel (b) of Fig. S1 shows a relationship between thermal expansion and lattice parameter in the cubic phase, while panel (c) shows a relationship between lattice parameter and phase-transition temperature: the NTE is progressively enhanced by increasing the lattice parameter, as well as the transition temperature increases as the lattice parameter decreases. These relationships between thermal expansion, phase-transition and lattice parameter cannot be generalized to all systems, but give clear evidence of their close correlation. This was the starting point which motivated the present study.

1. Computational details

The CRYSTAL-14 package was used in this calculation, a periodic ab initio program which uses a Gaussian-type basis set to represent the crystalline orbitals [7]. All-electron basis sets were employed, consisting of (9s)-(7631sp)-(621d) for zirconium atoms [8], (7s)-(311sp) for fluorine [9], (8s)-(6511sp)-(3d) for calcium [10], and (8s)-(6411sp)-(41d) for cobalt [11]. Pure density functional theory calculations have been performed using von Barth-Hedin [12] exchange and correlation functionals, which reproduce very well the experimental vibrational frequencies of the Raman active modes of CaZrF$_6$ [13]. The Brillouin zone was sampled with a 12×12×12 k-mesh of Monkhorst-Park scheme [14], while the truncation criteria for bi-electronic integrals (Coulomb and exchange series), controlled by five parameters, was set to default values (7 7 7 7 14). To ensure good convergence, the self-consistent-field convergence threshold on total energy was set to 10$^{-8}$ Hartree for initial geometry optimization, to 10$^{-10}$

Email: andrea.sanson@unipd.it
Figure S 1.: Thermal expansion coefficient of MZrF$_6$ series (red squares) and Sc$_{1-x}$Ti$_x$F$_3$ compounds (blue circles) plotted as a function of the cubic-to-rhombohedral phase-transition temperature (panel (a)) and as a function of the lattice parameter (panel (b)). Panel (c) shows the relationship between phase-transition temperature and lattice parameter. The dashed lines are a guide to the eyes. The experimental data were taken from average of Refs. [1,2,4–6]. For the lattice parameters, the values just before the cubic-to-rhombohedral transition are used.
Hartree for frequency calculation and subsequent energy scan. More details on the computational aspects can be found in Refs. [7,15].

References

[1] J.C. Hancock, K.W. Chapman, G.J. Halder, C.R. Morelock, B.S. Kaplan, L.C. Gallington, A. Bongiorno, C. Han, S. Zhou, A.P. Wilkinson, Large Negative Thermal Expansion and Anomalous Behavior on Compression in Cubic ReO$_3$-Type A$^{II}$B$^{IV}$F$_6$: CaZrF$_6$ and CaHfF$_6$, Chem. Mater. 27, 3912 (2015).

[2] C. R. Morelock, L. C. Gallington, and A. P. Wilkinson, Evolution of Negative Thermal Expansion and Phase Transitions in Sc$_{1-x}$Ti$_x$F$_3$, Chem. Mater. 26, 1936 (2014).

[3] B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman, and A. P. Wilkinson, Pronounced Negative Thermal Expansion from a Simple Structure: Cubic ScF$_3$, J. Am. Chem. Soc. 132, 15496 (2010).

[4] L. Hu, J. Chen, J. Xu, N. Wang, et al., Atomic Linkage Flexibility Tuned Isotropic Negative, Zero, and Positive Thermal Expansion in MZrF$_6$ (M = Ca, Mn, Fe, Co, Ni, and Zn), J. Am. Chem. Soc. 138, 14530 (2016).

[5] Von D. Reinen and F. Steffens, Struktur und Bindung in ubergangs metall-Fluoriden M$^{II}$Me$^{IV}$F$_6$, A. Phasenumbergange, Z. anorg. allg. Chem. 441, 63 (1978).

[6] V. Rodriguez, M. Couzi, A. Tressaud, J. Grannec, J. P. Chaminade, J. L. Soubeyroux, Structural phase transition in the ordered fluorides M$^{II}$ZrF$_6$, (M$^{II}$ = Co, Zn): I. Structural study, J. Phys.: Condens. Matter 2, 7373 (1990).

[7] R. Dovesi, R. Orlando, A. Erba, C.M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Mascio, M. Ferrabone, M. De La Pierre, P. DArco, Y. Noel, M. Causa, M. Rerat, B. Kirtman, CRYSTAL14: A program for the ab initio investigation of crystalline solids, Int. J. Quantum Chem. 114, 1287 (2014).

[8] L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. Nilsen, S. Jakobsen, K. P. Lillerud, and C. Lamberti, Disclosing the complex structure of UiO-66 MOF: a synergic combination of experiment and theory, Chem. Mater. 23, 1700 (2011).

[9] R. Nada, C.R.A. Catlow, C. Pisani, and R. Orlando, An ab-initio Hartree-Fock perturbed-cluster study of neutral defects in LiF, Model. Simul. Mater. Sci. Eng. 1, 165 (1993).

[10] M. Catti, R. Dovesi, A. Pavese, and V. R. Saunders, Elastic constants and electronic structure of fluorite (CaF$_2$): an ab initio Hartree-Fock study, J. Phys. Cond. Matter 3, 4151 (1991).

[11] E. Ruiz, M. Llunell, and P. Alemany, Calculation of exchange coupling constants in solid state transition metal compounds using localized atomic orbital basis sets, J. Solid State Chem. 176, 400 (2003).

[12] U. von Barth and L. Hedin, A local exchange-correlation potential for the spin polarized case. I, J. Phys. C: Solid State Phys. 5, 1629 (1972).

[13] A. Sanson, M. Girola, G. Mariotto, L. Hu, J. Chen, X. Xing, Lattice dynamics and anharmonicity of CaZrF$_6$ from Raman spectroscopy and ab initio calculations, Mater. Chem. Phys. 180, 213 (2016).

[14] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13, 5188 (1976).

[15] F. Pascale, C. M. Zicovich-Wilson, F. Lopez Gejo, B. Civalleri, R. Orlando, and R. Dovesi, The calculation of vibrational frequencies of crystalline compounds and its implementation in the CRYSTAL code, J. Comput. Chem. 25, 888 (2004).