

Beta-Zirconium Oxide Monophosphate: Structural Keys for an Ultralow Expansion Material

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Rietveld analyses performed on high-temperature X-ray (HTXRD) and neutron (HTND) powder patterns of β -(Zr₂O)(PO₄)₂ have allowed us to follow accurately the thermal variations of the cell parameters and to explain its strong dilatometric anisotropy in terms of structural distortions. It appeared that the anomaly resulted from two simultaneous mechanical effects: libration movements of the bridging oxygen atoms related to a rocking of the ZrO₇ and PO₄ polyhedra and a rotation effect resulting from electrostatic repulsions between Zr^{IV} cations of neighbor polyhedra. Both effects lead to a strong shrinkage of the *b* parameter and contribute to the ultralow overall expansion that has made β -(Zr₂O)(PO₄)₂ famous as a thermal-shock resistant material.

Introduction

Zirconyl phosphate sustains an irreversible phase transition from α - to β -form around 1100 °C upon heating.¹ The β -form is known to be a low thermal-expansion material with a stability range that extends up to 1600 °C,² that is, 200 °C higher than the usual thermal-shock resistant ceramic materials, as cordierite.³ Since the mid-1980s, many works have been devoted to this compound to elaborate compact ceramics by adding small amounts of various oxides (MnO₂, Fe₂O₃, ZnO, Nb₂O₅, La₂O₃) to favor sintering,^{4,5} and thermal-shock resistant Nicalon-reinforced composites.⁶ A high-temperature X-ray diffraction study showed that the thermal evolution of the crystal cell was very anisotropic, with a negative effect along the *b* axis explaining the low overall expansion coefficient.⁴

From a crystallographic point of view, the (ZrO₂)₂(PO₄) compound has long been formulated (ZrO)₂P₂O₇, and it is not before 1975 that Gebert et al. demonstrated that the crystal structure of the β -form (space group *Cmca*, *a* = 6.624(1), *b* = 8.637(2), *c* = 11.872(2), *Z* = 4) was made up of independent PO₄ tetrahedra, and therefore had to be written (Zr₂O)(PO₄)₂ (Figure 1).⁷ The ZrO₇ polyhedron shares oxygens O(2) and O(4) with neighbor PO₄ tetrahedra, shares O(3) with neighbor

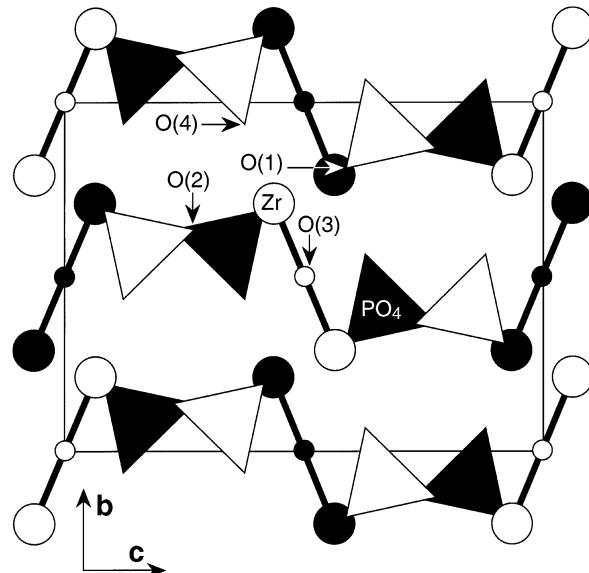


Figure 1. [100] projection of the β -(Zr₂O)(PO₄)₂ structure. The atoms at *x* = 1/2 are drawn in white and those at *x* = 0 are in black.

ZrO₇ via outstandingly short bonds (1.92 Å), two O(1)–O(1) edges with other ZrO₇ polyhedra and another O(1)–O(1) edge with a PO₄ tetrahedron (Figure 2). Therefore, all oxygen anions are in 2-fold coordination, except for O(1) which has three (2 Zr + 1P) neighbors.

Although intensively investigated, this promising material has never sustained high-temperature structural studies likely to clear up the underlying atomic mechanism of its anomalous expansion and its remarkable properties. This is the aim of the present work.

Experimental Procedures

Synthesis. Aqueous solutions of ZrOCl₂·8H₂O and NH₄H₂PO₄ were prepared, then mixed in stoichiometric proportions. The obtained gel was washed with water, dried, and annealed

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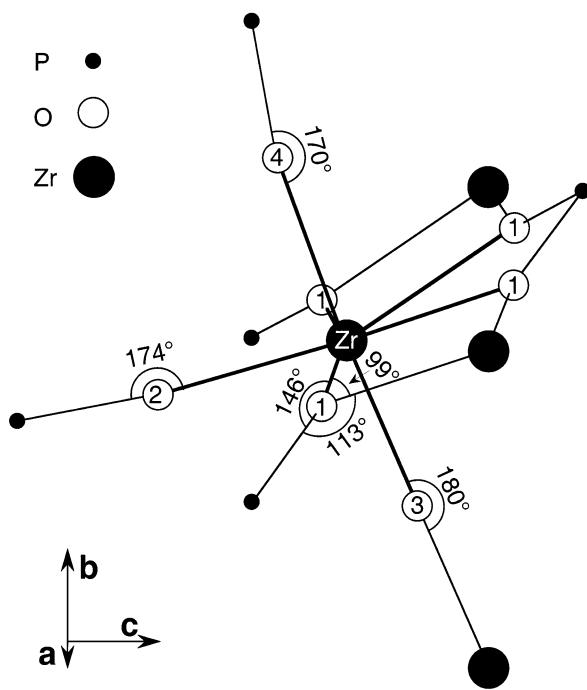
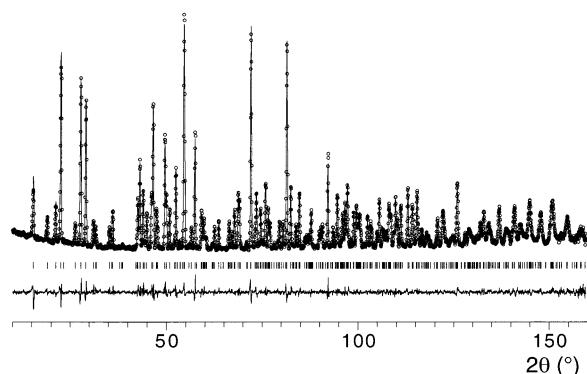
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Table 1. Zr–O and P–O Distances (Å) for the ZrO_7 and PO_4 Polyhedra from Single Crystal,⁷ Powder Neutron Diffraction Data at 20, 400, and 800 °C, and Bond Thermal Expansion Coefficient (This Work)

	single crystal ⁷	powder 20 °C, neut. / diff. (%)	powder 400 °C, neut.	powder 800 °C, neut.	thermal expansion of bond (10^{-6} K^{-1})
Zr–O(1) (2×)	2.167	2.172(2)/0.2	2.176(2)	2.182(2)	+6(1)
Zr–O(1) (2×)	2.287	2.293(2)/0.3	2.307(2)	2.329(3)	+20(2)
Zr–O(2)	2.056	2.068(3)/0.6	2.066(3)	2.059(3)	-6(2)
Zr–O(3)	1.927	1.922(2)/0.3	1.918(2)	1.917(2)	-3(1)
Zr–O(4)	2.114	2.125(3)/0.5	2.124(3)	2.117(3)	-5(2)
shortest Zr–Zr	3.710	3.717(1)/0.2	3.729(1)	3.752(1)	+12(1)
P–O(1) (2×)	1.558	1.554(2)/0.2	1.553(2)	1.548(3)	-5(2)
P–O(2)	1.500	1.502(3)/0.1	1.499(3)	1.494(4)	-7(3)
P–O(4)	1.500	1.509(3)/0.6	1.504(3)	1.505(4)	-3(3)

**Figure 2.** Tilted [100] view showing environment of the zirconium atom, including second-neighbor zirconium and phosphorus atoms.**Figure 3.** Rietveld plot of neutron diffraction pattern for $\beta\text{-Zr}_2\text{O}(\text{PO}_4)_2$ at 20 °C: observed (circles), calculated (solid, upper plot), difference (solid, lower plot) and angular positions of Bragg reflections (bars).

12 h at 1200 °C. The final powder diffraction pattern revealed no impurities.

High-Temperature X-ray Diffraction. Six powder patterns were recorded from 20 to 1000 °C on a 17-cm vertical Philips PW1050/25 goniometer fitted with a heating platinum–rhodium 40% holder, using Ni-filtered $\text{Cu K}\alpha$ radiation. 132 independent reflections were measured over the $14^\circ < 2\theta < 84^\circ$ range. This work was designed to follow the thermal variations of the cell parameters.

High-Temperature Neutron Diffraction. Three powder patterns of a vanadium-encapsulated sample were recorded at 20, 400, and 800 °C on the D2B beamline of the Institut Laue-Langevin (Grenoble, France) at $\lambda = 1.5938 \text{ \AA}$ (Ge monochromator). 380 independent reflections were measured over the $10^\circ < 2\theta < 160^\circ$ range. This work was designed to accurately determine the atomic positions and thermal anisotropic factors at various temperatures.

Rietveld Refinements. The Fullprof.2k program⁸ was run in Le Bail's (profile matching) mode for X-ray data and structure refinement mode for neutron ones (Figure 3), using the single-crystal data as starting values.⁷ The background intensities were interpolated from selected points. The refined data set included three cell parameters, the zero point, the Gaussian–Lorentzian shape factor, three coefficients of the $fwhm$ Cagliotti's polynomial, two asymmetry parameters, and, concerning neutron data, the overall scale factor, 11 atomic coordinates and the 26 anisotropic displacement parameters. No distance or angle constraint was applied.

The refinements led to the following reliability factors for neutron (respectively X-ray):

$$0.042 (0.024) \leq R_p = \sum |y_o^i - y_c^i| / \sum y_o^i \leq 0.046 (0.027)$$

$$0.056 (0.034) \leq R_{wp} (\text{id., weighted}) \leq 0.059 (0.038)$$

$$0.028 (0.029) \leq R_{\text{Bragg}} = \sum |I_o^i - I_c^i| / \sum I_o^i \leq 0.042 (0.035)$$

$$0.019 (0.017) \leq R_F = \sum |(I_o^i)^{1/2} - (I_c^i)^{1/2}| / \sum (I_o^i)^{1/2} \leq 0.032 (0.021)$$

The Zr–O and P–O distances obtained by neutron diffraction at 20 °C are in good agreement with those calculated from the single-crystal data (Table 1).

Results

The X-ray and neutron thermal expansion plots of the cell parameters (Figure 4) are in good agreement with each other and corroborate the previous HTXRD results,⁴ although the curves are clearly smoother and account for a continuous expansion phenomenon, consistent with the metastability of the β -form over the studied temperature range. The thermal expansion coefficients between 20 and 1000 °C are given in Table 2, along with those found by Yamai et al. (calculated from the extreme points) and those recalculated by linear fit from the thermal plots of these authors.⁴ Note the strong negative effect along the b -axis which reduces the mean linear expansion coefficient. This new value, which is significantly lower than that of the former diffraction study (1.5 instead of $2.4 \times 10^{-6} \text{ K}^{-1}$),⁴

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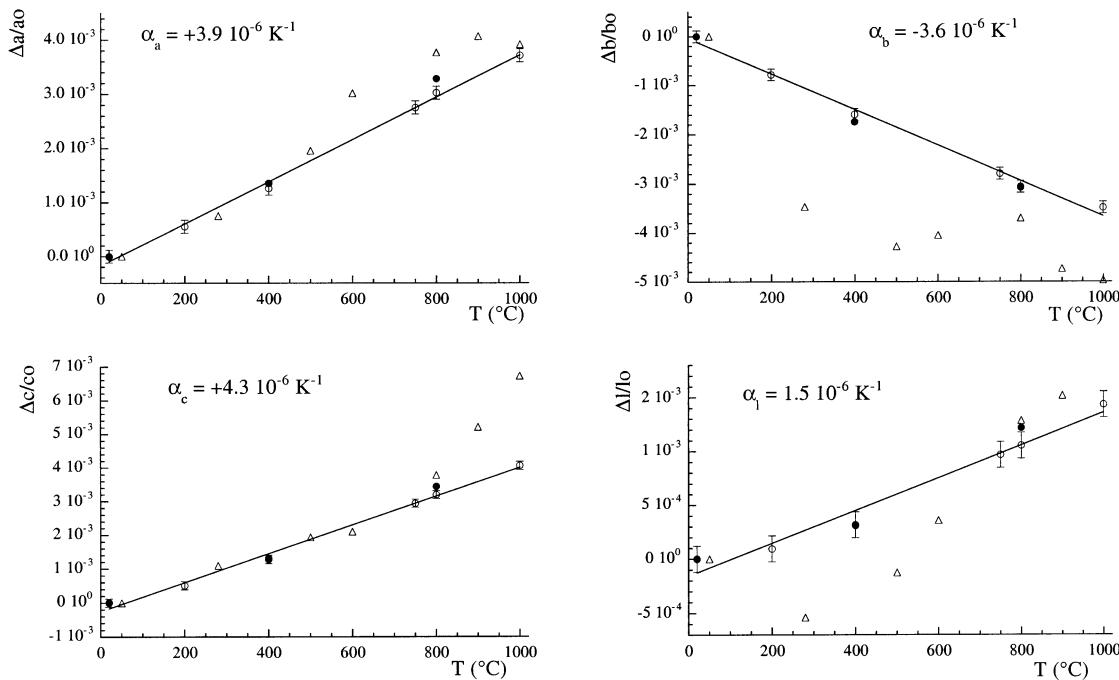


Figure 4. Relative thermal linear expansion of β -(Zr₂O)(PO₄)₂ along the *a*, *b*, and *c* axes; mean linear expansion of the cell (*l*). Experimental points of this work: white circles with error bars for HTXRD; black circles are for HTND; and formerly published data are shown in white triangles.⁴

Table 2. Thermal Linear Expansion Coefficients (10^{-6} K⁻¹) for β -(Zr₂O)(PO₄)₂ over the 20–1000 °C Range

	α_a	α_b	α_c	$\alpha_l = (\alpha_a + \alpha_b + \alpha_c)/3$
from ref 4	3.6	-5.0	6.4	1.7
recalculated from ref 4	4.7	-4.1	6.6	2.4
this work (X-ray)	3.9	-3.6	4.3	1.5

supports definitely the classification of β -(Zr₂O)(PO₄)₂ among the rare “ultralow expansion” oxides, according to the usual criterion ($\alpha_l < 2 \times 10^{-6}$ K⁻¹).⁹ This new value is in good agreement with the linear expansion coefficients measured by classical dilatometry on sintered ceramics of β -(Zr₂O)(PO₄)₂ ($1.5 < \alpha_l < 1.7 \times 10^{-6}$ K⁻¹).^{2,4,5}

Discussion

Comparison of the atomic positions from 20 to 800 °C shows that the anomalous thermal expansion stems from two simultaneous structural mechanisms.

Oxygen Libration. The transverse movements of bridging oxygen anions are well-known ways to achieve negative or ultralow expansion in refractory oxides¹⁰ made up of monodentate frameworks of covalent and regular polyhedra, as ZrP₂O₇,¹¹ ZrW₂O₈,¹² or NbZr-(PO₄)₃.¹³ In these compounds, the oxygen libration is part of a rocking effect involving rigid and covalent corner-sharing polyhedra (i.e., ZrO₆, PO₄, and WO₄). The case of β -(Zr₂O)(PO₄)₂ appears more complex. On one hand, it seems that the PO₄ tetrahedron could be

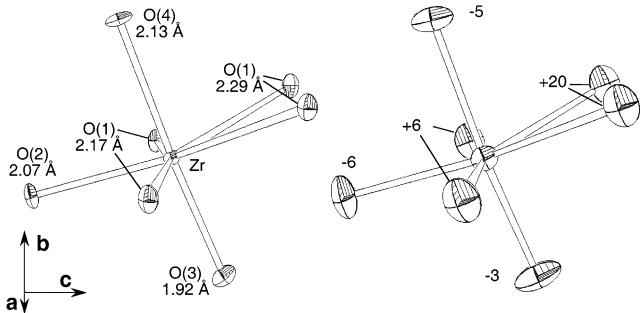


Figure 5. Tilted [100] view of the ZrO₇ polyhedron from HTND data: left, at 20 °C (with Zr–O distances); right, at 800 °C (with thermal expansion coefficients of bonds in 10^{-6} K⁻¹). 50% probability thermal ellipsoids by ORTEP.¹⁴

considered as rigid insofar as the thermal variations of the O–P–O angles do not exceed 0.4(2)° over the 20–800 °C range, while all P–O distances contract roughly at the same rate (Table 1). On the other hand, ZrO₇ is far from being so regular and therefore shows a very anisotropic expansion. This is due to differences in the oxygen atoms' environments as follows. (a) The 2-fold coordinated O(2), O(3), and O(4) atoms are involved in nearly linear and covalent Zr–O(2)–P, Zr–O(4)–P, and Zr–O(3)–Zr bondings (Figure 2), a highly favorable geometry for transverse movement; indeed, they show flat transverse thermal ellipsoids and allow negative bond expansion (Figure 5) but so far, we cannot ascertain that these movements are correlated as for the rocking of a rigid and regular polyhedron. (b) The 3-fold coordination of atom O(1) (Figure 2) keeps it from contracting simultaneously all of its bonds. While the P–O(1) bond expands negatively, the mean-length *a*-

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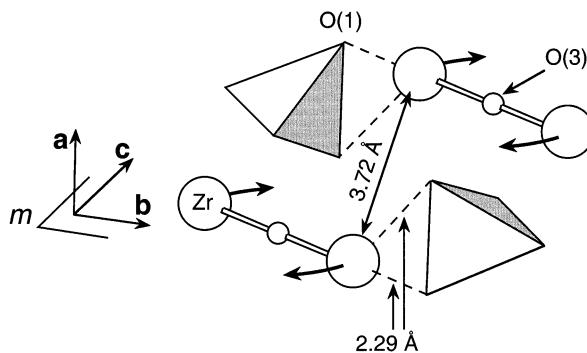


Figure 6. Repulsion effect between zirconium cations. Note the fixed O(3) atoms on inversion centers acting as pivots and the stretching of the long Zr–O(1) bonds.

directed Zr–O(1) ones (2.17 Å) have “normal” positive expansion and the long Zr–O(1) ones (2.29 Å) on both sides of the mirror stretch at an outstandingly high rate; this is made possible by their weakness, but another mechanism arising from polyhedra displacements takes an important part in the expansion. This will be discussed below.

ZrO₇ Rotation around O(3). In β -(Zr₂O)(PO₄)₂, the Zr cations of successive (100) layers form zigzag chains following the *a* axis, with short cation–cation distances (3.717(1) Å at 20 °C) because of the absence of intermediate oxygen anions (neighbor ZrO₇ polyhedra share an O(1)–O(1) edge). As shown in Table 1, this distance increases with temperature at a surprisingly high rate (12×10^{-6} K⁻¹), compared to the linear expansion of the cell itself (1.5×10^{-6} K⁻¹). Indeed, the zirconium cation follows a rotation movement around the bridging oxygen anion (Figure 6), with a 0.91° angular amplitude from 20 to 800 °C. In so doing, the zirconium cation also moves away from the other O(1)–O(1) edge shared with the PO₄ tetrahedron, contributing to the fast expansion of the long Zr–O(1) bonds observed previously. As the bridging oxygen atom lies on an inversion center, it results that the two O(3)-connected ZrO₇ polyhedra will rotate in the (*b*, *c*) plane, either clockwise or counter-clockwise depending on the generating symmetry operation. Obviously, the reason for this behavior is to be found in the outstanding closeness of the zirconium cations of neighbor units and their high electric charge that cause strong Coulombic repulsions and a dramatic “fleeing” movement as temperature increases and the structure softens.

Furthermore, the polyhedra rotation exerts mechanical strains on the neighborhood via the short Zr–O(2) and Zr–O(4) bonds extending in the (*b*, *c*) plane (Figure 7). Let us consider the labeled PO₄ tetrahedron, connected to the Zr and Zr' neighbor cations by the Zr–O(2) and Zr'–O(4) bonds (the four Zr–O(1) bonds can be ignored, either because they are nearly perpendicular to the plane, or because of their weakness). Under the mechanical action of the ZrO₇ rotation, the PO₄ tetrahedron will be simultaneously pushed along the Zr–O(2) bond and obliquely pulled by the Zr'–O(4) one, explaining the observed shift of the central phosphorus atom between 20 and 800 °C: 0.010 Å following *b* and 0.011(2) Å following *c*, taking central O(3) as reference. A faint rotation of the whole tetrahedron is also observed (0.20° ccw).

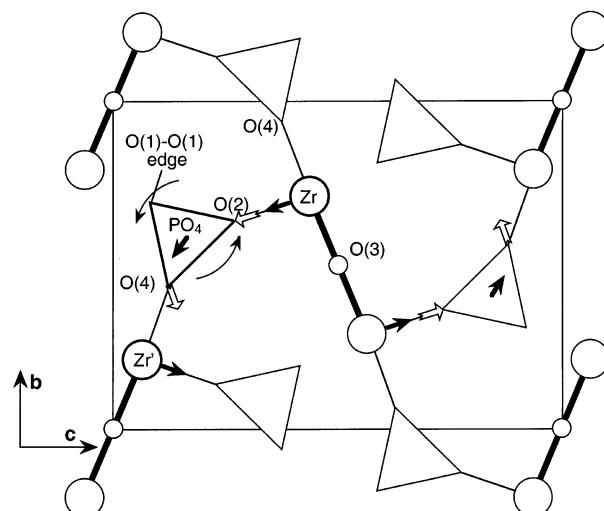


Figure 7. [100] projection of a layer (half cell) showing the push–pull effect of the zirconium atoms on a phosphate tetrahedron. The Zr–O(1) bonds have been omitted. Black arrows represent the movements of the cations, white arrows represent the pushing and pulling effects on the tetrahedron.

To summarize, the dilatometric behavior of β -(Zr₂O)(PO₄)₂ along each axis can be considered as the combined effect of the two mechanisms previously described.

a Axis. The expansion of the Zr–O(1) bonds is somewhat offset by a slight contraction of the P–O(1) bonds that lead to a positive definite, but moderate expansion of the axis, in the range of the refractory oxides ($(2\text{--}8) \times 10^{-6}$ K⁻¹).⁹

b Axis. By “contracting” the P–O(4), Zr–O(4), and Zr–O(3) bonds, roughly directed following the *b*-axis, the libration of the oxygen atoms takes an obvious part in the negative thermal expansion along this direction. Another contraction effect results from the rotation around O(3) due to cations repulsions, the net effect of which is difficult to measure precisely, insofar as the poor rigidity of the ZrO₇ polyhedron allows simultaneous distortions. However, an estimation can be given by taking into account the 0.91° rotation between 20 and 800 °C of the linear Zr–O(3)–Zr unit (considered of constant length for the calculation): the projection on the *b*-axis reduces by 0.024(2) Å, to be compared with the reduction of the cell edge itself of 0.027 Å. So, we can assume that this mechanism takes also a nonnegligible part to the negative expansion along the *b*-axis.

c Axis. Following this direction, the effect of the oxygen libration is strongly reduced by the fast expansion of the long Zr–O(1) bonds. One might also expect that the rotation of the ZrO₇ polyhedra would lead to a strong positive effect, but actually, the push–pull mechanism reduces it considerably: while the zirconium cation moves by 0.028(2) Å following *c*, the PO₄ tetrahedra shifts by 0.011(2) Å only.

At variance with the shrinkage due to the oxygen libration, the ZrO₇ rotations around O(3) result in a structural “folding”. Such a mechanism is made possible by the noncompactness of the structure in the (*b*, *c*) plane (Figure 7), the cavities of which provide free space for atomic displacements.

To our knowledge, the fact that cations repulsions may be the driving force of a negative expansion phenomenon has been observed only once, in Th₄(PO₄)₄

(P₂O₇).¹⁵ Although different, these structures show the following common features that can explain their similar properties: (a) the presence of high-charge (tetravalent) cations, (b) the extreme closeness of these cations, located in edge-sharing polyhedra, (c) a noncompact structure, and (d) a folding mode, that is, an atomic mechanism likely to convert the positive expansion of the cation–cation distance into a structural negative expansion along one or more directions.

Conclusion

The remarkable low expansion of β -(Zr₂O)(PO₄)₂ appears as a dual phenomenon, involving librations of the

bridging oxygen atoms, this mechanism being related to the classical polyhedra rocking effect, as well as Zr–Zr repulsions that result in a push–pull effect on the tetrahedra. After the discovery of a similar phenomenon in Th₄(PO₄)₄(P₂O₇),¹⁵ one can suggest that the Coulombic interactions, coupled with a structural folding mechanism, could be a new way to achieve very low or negative thermal expansion. The structural features observed in these compounds may become useful selection criteria for new or existing materials in the frame of further research on low or negative thermal expansion.

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