Mechanism of the low thermal expansion in α-Hf$_2$O(PO$_4$)$_2$ and its zirconium analog

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ABSTRACT

The thermal expansion of recently characterized α-Zr$_2$O(PO$_4$)$_2$ and α-Hf$_2$O(PO$_4$)$_2$ is found to be very low (respectively 2.6 and 2.9×10^{-6} K^{-1}, 20–900 °C). High-temperature X-ray diffraction and Rietveld analysis allowed to identify a dual contraction mechanism, involving a classical ring deformation and the rocking of bridging oxygens.

1. Introduction

The search for low-expansion oxides for relieving the vulnerability of ceramics to thermal shocks has been a constant challenge during the six past decades. Such compounds like zircon (ZrSiO$_4$), spodumene (LiAlSi$_2$O$_6$), eucryptite (LiAlSiO$_4$), cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$), NaZr$_2$(PO$_4$)$_3$ derivates (NZPs) are now well-known industrial materials, Supporting applications as refractories, catalyst supports, engine parts, lamps, brazing fixtures, induction heating liners, rocket nozzles, gauges, spark plugs and cookware. They are also appreciated for their dimensional stability in specific devices like large optical instruments and high precision thermometers.

Owing to the high strength of the Zr–O and P–O bonds, anhydrous zirconium phosphates exhibit a remarkable stability, both thermal and chemical, and also a negligible bond expansion rate, which made them a promising field of investigations for ceramists. However, the study of the ZrO$_2$–P$_2$O$_5$ binary system by Alamo and Roy [1] only revealed three intermediate compounds.

The thermal expansion of zirconium diphosphate ZrP$_2$O$_7$ has been under investigation since the works of Harrison et al. [2]. ZrP$_2$O$_7$ occurs under two cubic forms: α (low temperature) and β (high temperature), with cell parameters $a_\alpha = 3a_\beta$. Their structures are made of corner-connected ZrO$_6$ and PO$_4$ units that differ only by the ordering of the P$_2$O$_7$ groups in the former [3]. In the α-form, the strongly bent P–O–P linkages tend to stretch, inducing

a strong thermal expansion, whereas in the β-form, these linkages are roughly linear, thus allowing a polyhedra rocking effect that reduces considerably the expansion [4,5]. Because of the excessive expansion of the α-form, zirconium diphosphate cannot be used as a refractory.

Very little is known about zirconium monophosphate Zr$_3$(PO$_4$)$_4$. According to some authors [1,6], it is supposed to be isotypic with the low-expansion NZP, and should be likewise formulated Zr$_{0.25}$Zr$_2$(PO$_4$)$_3$. Its thermal expansion has never been studied.

The best refractory material in the ZrO$_2$–P$_2$O$_5$ binary is undoubtedly the zirconium oxide phosphate Zr$_2$O(PO$_4$)$_2$. Its β-form (orthorhombic *Cmca* [7]), made up of ZrO$_7$ polyhedra (Fig. 1), is obtained between 1120 and 1220 °C from the low-temperature α-form through a progressive and irreversible transition [8]. β-Zr$_2$O(PO$_4$)$_2$ is well known for its stability, both thermal (up to 1600 °C) and chemical, and also for its near-zero expansion ($\alpha_l = 1.5 \times 10^{-6}$ K^{-1}) [9], that stems from a somewhat complexe mechanism, involving polyhedra rocking and reduction of the structural cavities driven by inter-cations repulsions [10]. β-Zr$_2$O(PO$_4$)$_2$ can be sintered either as a compact ceramic [9] or a porous low-density material, nowadays a commercial product.

The newly resolved structures of α-Zr$_2$O(PO$_4$)$_2$ and α-Hf$_2$O(PO$_4$)$_2$ (monoclinic *I2/m*) are similar, thus allowing the existence of a continuous solid solution [8]. They consist in arrays of edge- and corner-connected polyhedra forming [100] ribbons (Fig. 1), connected to each other following [010] by M^{IV}–O–P bent linkages. The main difference with the β-form lies in the mixed 6/7-fold coordination of the M^{IV} cation. The strong distortion of the M^{IV}O$_6$ polyhedron may be the cause of the lower stability of

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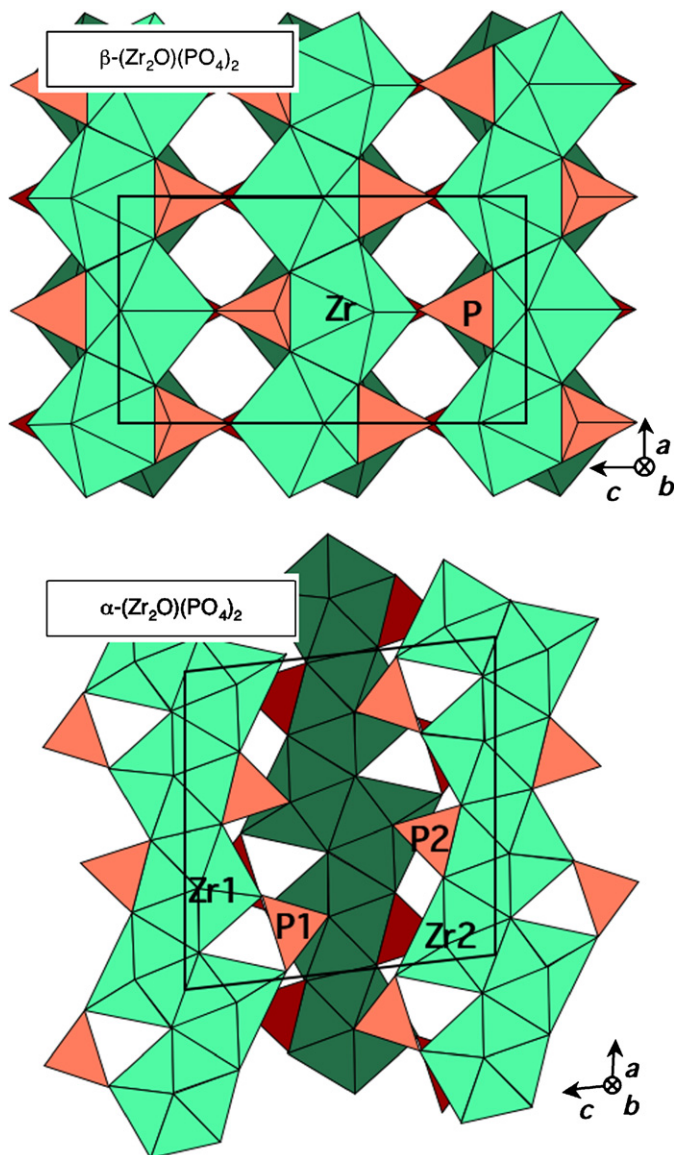 *E-mail address:* gw@ccr.jussieu.fr (G. Wallez).

Fig. 1. Crystal structures of the two forms of $Zr_2O(PO_4)_2$. α-form: Zr(1) and Zr(2) are respectively in seven- and six-fold coordination (green polyhedra); the structure is made of [100] ribbons of polyhedra connected together via the vertices of the vertical edges of the PO_4 tetrahedra (orange).

the α-form. However, the substitution of smaller Hf^{IV} ($r_i = 0.76$ Å in seven-fold coord. [11]) for Zr^{IV} ($r_i = 0.78$ Å) reduces the strain in the $M^{IV}O_6$ polyhedron and increases strongly the temperature domain, to the extent of forbidding the phase transition for the Hf-rich compositions [8]. This makes $Hf_2O(PO_4)_2$ fully stable under its α-form up to its decomposition, above 1500 °C.

In the present work, we will study the thermal expansion of α-$Zr_2O(PO_4)_2$ and α-$Hf_2O(PO_4)_2$.

2. Experimental and results

High-temperature X-ray powder diffraction (HTXRD) on α-$Zr_2O(PO_4)_2$ and α-$Hf_2O(PO_4)_2$ was performed on a Philips PW1050/25 17 cm vertical goniometer with a Ni-filtered copper anticathode (40 kV, 20 mA), fitted with a Pt–Rh (40%) heating sample holder. Patterns were recorded at 20, 150, then every 150–900 °C in the $14° \leqslant 2\theta \leqslant 80°$ range, 2θ step 0.02°, with a counting time of

24 s/step. The thermal expansion plots (Fig. 2) were drawn from the cell parameters obtained by Rietveld refinements using Fullprof [12]. The axial expansion coefficients (Table 1), calculated by linear fit over the 20–900 °C range, rank similarly for the two isotypes. They show a strongly anisotropic behavior, with an ultra-low expansion of the **a**-edge and a contraction of the **b**-edge that balance the strong expansion of the **c**-edge. As a result, the mean linear expansion is much lower than for ZrP_2O_7, but not as low as for β-$Zr_2O(PO_4)_2$ (Fig. 3).

In order to refine the atomic positions by the Rietveld method, we chose the Hf compound rather than the Zr one because of the higher weight of the tetravalent cation, which allows a more precise observation. The higher anisotropy of the α-$Hf_2O(PO_4)_2$ expansion also suggests that the atoms have stronger movements, therefore easier to observe in this compound. Otherwise, the expansion mechanism can be expected to be similar in both compounds.

Because of the limited 2θ range of the HTXRD patterns, the number of collected independent reflections (261) was not sufficient to refine accurately the atomic coordinates and thermal factors of all atoms (35 *I*-dependent parameters) without constraints. Therefore, soft constraints were applied on the P–O distances and O–P–O angles of the two phosphate tetrahedra and a common thermal displacement parameter was given to all oxygens and the two phosphorus at each temperature (thus reducing to 28 *I*-dependent parameters). These simplifications, commonly made for small and quasi-rigid polyhedra can also be legitimated by the fact that the discussion below is exclusively based upon the observation of the inter-cations distances, more reliable than the cation-oxygen ones. Final reliability factors R_{Bragg} were between 0.020 and 0.030, χ^2's between 4.3 and 7.1. The Rietveld plot at 20 °C is shown on Fig. 4. The thermal expansion rates of the shortest and most significant inter-cations distances in α-$Hf_2O(PO_4)_2$ are gathered in Table 2.

3. Discussion

Analyzing the thermal evolution of the shortest inter-cations distances is a convenient way to explain the low expansion of the α-form insofar as the contraction mechanisms always occur between neighbor or second-neighbor atoms. Three different kinds of cation pairs will be considered, depending on the number of the oxygen atoms shared (0, 1 or 2). Figs. 5 and 6 give a complete view of these interactions.

First, all but one distances between two edge-sharing cations (pairs *G–I*) exhibit an expansion higher than $10 \times 10^{-6} K^{-1}$, as a probable effect of the unscreened short-distance Coulombic interactions. We can also suggest that the Hf(1)–P(2) repulsions (*H*) mechanically contract the corresponding O(22)–O(23) edges, resulting in an expansion of the neighbor O(23)–O(23) edge and, likewise, a contraction of the Hf(1)–Hf(1) distance. This would oppose to the weak repulsion of the much distant Hf(1)–Hf(1) pair, and therefore explain the abnormally low-expansion rate of distance *F*.

Secondly, the distances between two cations linked by only one oxygen neighbor (mostly Hf–P pairs) tend to shorten or show a very faint positive expansion (pairs *A–E*, *M*, *N*), as a probable result of the libration of the bridging oxygen. One should keep in mind that the bond lengths themselves never contract on heating, but the mean positions of two atoms sustaining transverse thermal displacements are likely to get closer. Logically, the contraction is particularly strong in linkages *A* and *B*, which involve an oxygen in two-fold coordination. On the contrary, oxygens in three-fold coordination can oscillate only
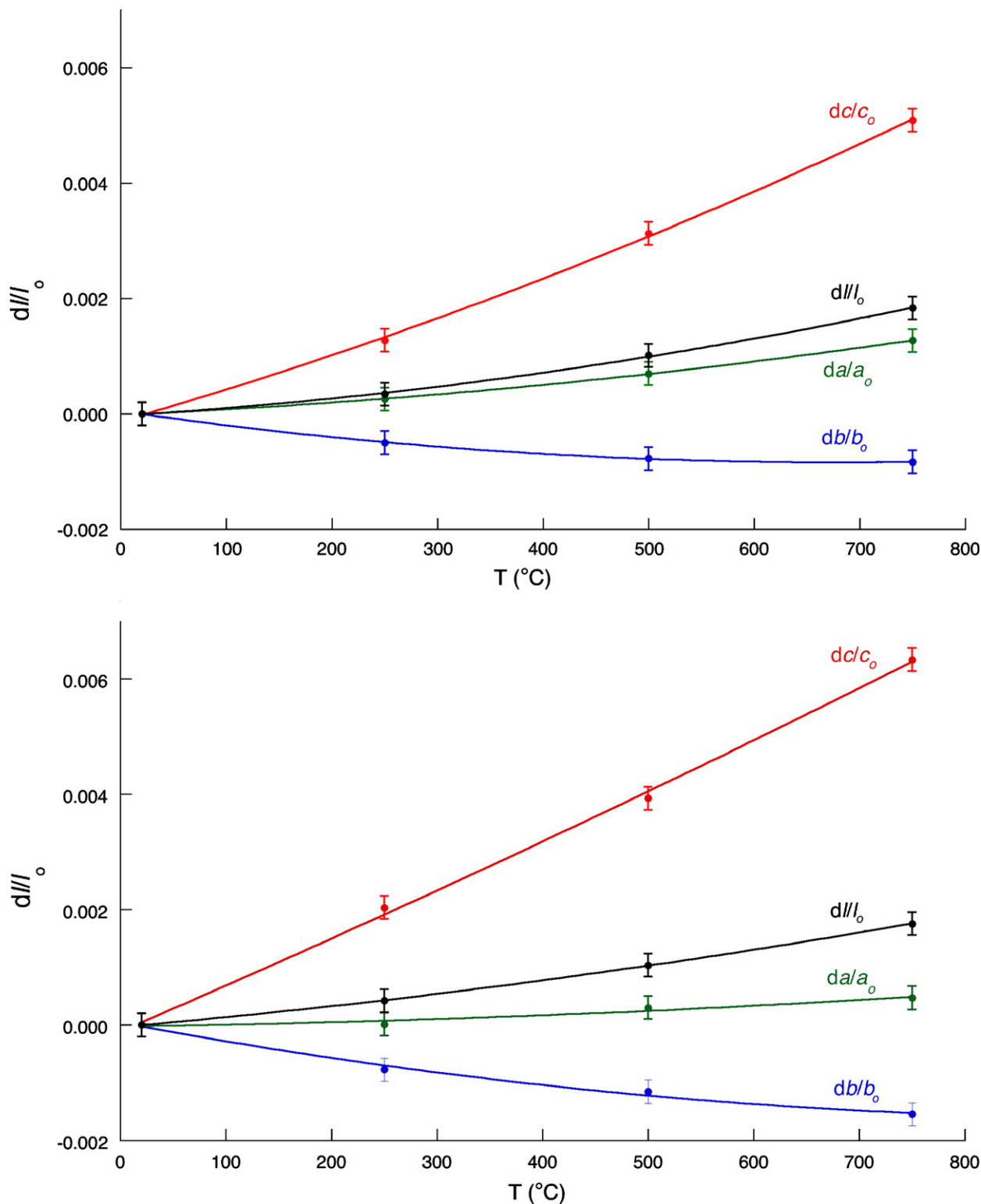
Fig. 2. Linear thermal expansion plots for α-Zr$_2$O(PO$_4$)$_2$ and α-Hf$_2$O(PO$_4$)$_2$. dl/l_o ($=$ d$V/3V_o$) is the mean linear expansion of the cell.

perpendicular to the plane of the three neighbor cations, thus reducing the contraction effect. Obviously, α-Hf$_2$O(PO$_4$)$_2$ does not obey to the classical model of rigid corner-connected polyhedra in which inter-cations distances contract under effect of a global rocking [13]. Should the polyhedra of the present compound behave as rigid bodies, such a phenomenon would be impossible. Indeed, the contraction of the linkages probably stems from

independent oscillations of the oxygens, in the same way as in β-Zr$_2$O(PO$_4$)$_2$ [10] and isotypic U$_2$O(PO$_4$)$_2$ [14].

Cations repulsions and oxygens oscillations affect oppositely the expansion of the ribbons. Except for the positive definite repulsion G, all the interactions contributing to their longitudinal expansion are near-zero or negative, thus resulting in a very low α_a coefficient.

Following the **b**-axis, the bent Hf(1)–O(11)–P(1) (M) and Hf(2)–O(21)–P(2) (N) linkages (respectively 142.4° and 148.6°) only allow limited oscillations of the oxygens, resulting in a faint but positive expansion of the inter-cations distances that cannot account for the negative α_b coefficient. Indeed, the real reason is to be found in a third mechanism that occurs between neighbor ribbons of the same (010) layer, despite the lack of direct linkages.

Table 1
Relative thermal linear expansion coefficients ($10^{-6}\,K^{-1}$) for α-(Zr$_2$O)(PO$_4$)$_2$ and α-(Hf$_2$O)(PO$_4$)$_2$ obtained by linear fit over the 20–900 °C range

	α_a	α_b	α_c	$\alpha_l = \alpha_V/3$
α-(Zr$_2$O)(PO$_4$)$_2$	1.7	−1.1	7.0	2.6
α-(Hf$_2$O)(PO$_4$)$_2$	1.0	−1.6	9.2	2.9
β-(Zr$_2$O)(PO$_4$)$_2$	3.9	−3.6	4.3	1.5

Values for β-(Zr$_2$O)(PO$_4$)$_2$ [10] are given for comparison.

It consists in Coulombic interactions between PO$_4$ tetrahedra of neighbor ribbons (pairs J–L), under effect of either O···O or P···P repulsions: the P–P distances expand at very high rates (up to $24 \times 10^{-6}\,K^{-1}$) thus giving a strong α_c coefficient. Because these interactions are stronger than those occuring between the Hf cations (pairs G and I), the polyhedra rings (Fig. 6) deform at heating by increasing the tilt of the Hf(1)–P(1) and Hf(2)–P(2) directions (respectively by 0.5(1)° and 0.9(2)° between 20 and 900 °C), thus contracting the **b**-axis. This kind of coupled expansion-contraction mechanism is known to occur in various compounds made up of polyhedra rings and sustaining a strong axial expansion, like the NZP [15–17].

Although very low, the thermal expansion of α-Zr$_2$O(PO$_4$)$_2$ is not as low as that of β-Zr$_2$O(PO$_4$)$_2$. From a practical point of view, the title compound also suffers of an irreversible phase transition to the β-form from 1120 °C on, which limitates strongly its application as a high-temperature material. This drawback could be relieved by substituting hafnium for zirconium, thus stabilizing
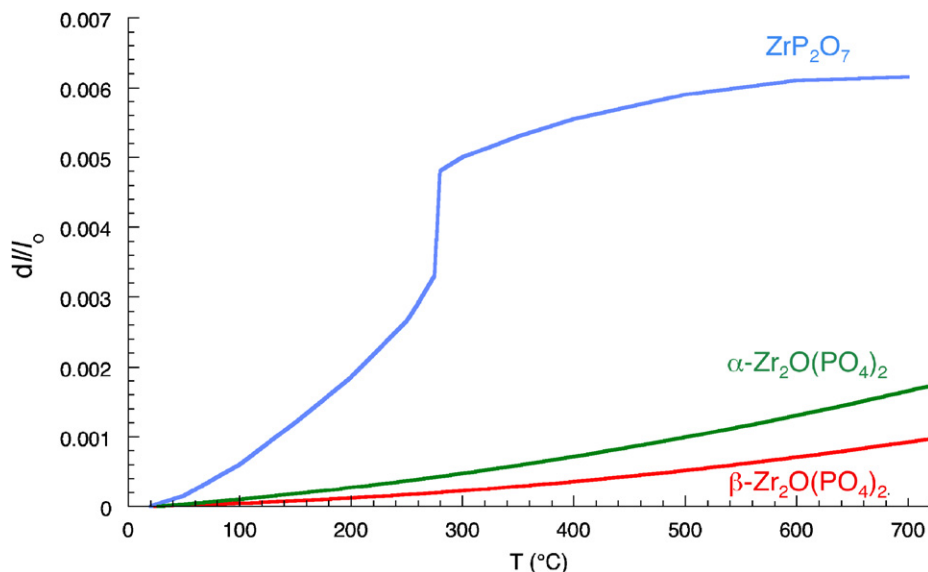

Fig. 3. A comparison of the mean linear expansions of β-Zr$_2$O(PO$_4$)$_2$ [10], α-Zr$_2$O(PO$_4$)$_2$ (this work) and ZrP$_2$O$_7$ [4].
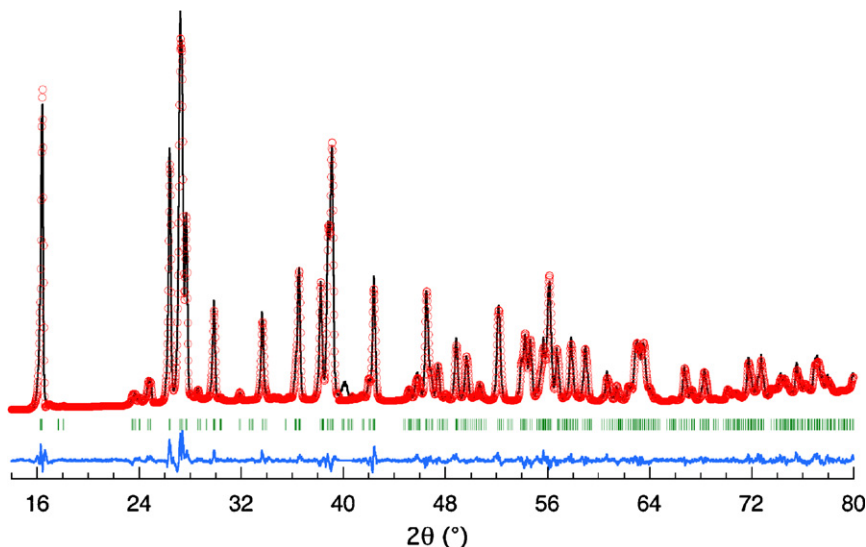

Fig. 4. Rietveld plot for α-Hf$_2$O(PO$_4$)$_2$ at 20 °C: observed (dots), calculated (solid) and angular positions of possible Bragg reflections (bars), lower plot: (I_c–I_o) difference curve.

Table 2
Thermal relative evolution of the shortest Hf–Hf, Hf–P and P–P distances in α-Hf$_2$O(PO$_4$)$_2$

M–O–M′ or M–[O–O]–M′ linkage	Pair/see fig. ♯	Oxygens' coordination(s)	M–M′ distance at 20 °C (Å)	M–O–M′ angle at 20 °C (deg)	M–M′ relative expansion (10^{-6} K^{-1}, $\pm 2 \times 10^{-6}$ K^{-1})
Hf(1)–O(12)–P(1)	A/5	2	3.45(1)	148(1)	−18
Hf(2)–O(13)–P(1)	B/5	2	3.350(7)	139.2(6)	−13
Hf(1)–O(23)–P(2)	C/5	3	3.575(3)	144.1(3)	−7
Hf(2)–O(22)–P(2)	D/5	3	3.589(5)	159.8(5)	0
Hf(1)–O(3)–Hf(2)	E/5	3	3.856(6)	143.8(6)	+2
Hf(1)–[O(23)–O(23)]–Hf(1)	F/5	3, 3	3.818(6)		+1
Hf(1)–[O(22)–O(3)]–Hf(2)	G/5	3, 3	3.504(4)		+14
Hf(1)–[O(22)–O(23)]–P(2)	H/5	3, 3	2.976(6)		+11
Hf(2)–[O(3)–O(3)]–Hf(2)	I/5	3, 3	3.225(5)		+15
P(1)···P(1)	J/5	No common O	4.098(7)		+22
P(1)···P(2)	K/5	No common O	4.717(7)		+24
P(2)···P(2)	L/5	No common O	5.363(5)		+16
Hf(1)–O(11)–P(1)	M/6	2	3.379(2)	142.4(3)	+2
Hf(2)–O(21)–P(2)	N/6	2	3.460(2)	148.6(2)	+0

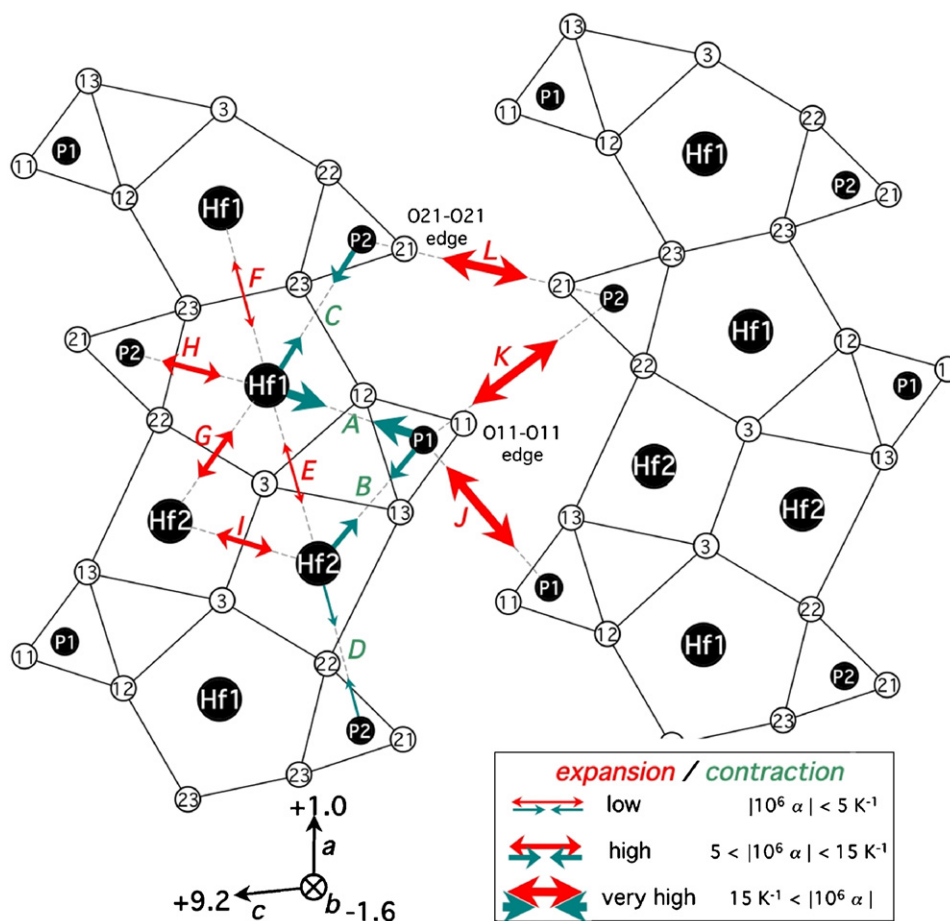Angles and distances are given at 20 °C [8]. Oxygens between brackets represent a shared edge.

Fig. 5. Thermal evolution of the inter-cations distances in the (010) plane of α-Hf$_2$O(PO$_4$)$_2$.

the material up to 1500 °C, at the price of an increase of cost and density. Indeed, the most interesting application of α-Zr$_2$O(PO$_4$)$_2$ may lie in the making of ceramic/fiber composites. β-Zr$_2$O(PO$_4$)$_2$, already tested successfully in this role, has shown an excellent chemical compatibility with the SiC fibers [18], but the expansion coefficient of the α-form matches better with that of SiC (about 4.0×10^{-6} K^{-1}). Further investigations in this scope are now in progress.

4. Conclusion

The remarkable low expansion of α-(Zr$_2$O)(PO$_4$)$_2$ appears based upon the combination of a strong ring-like deformation and the rocking of bridging oxygens. It is noteworthy that the latter effect operates independently on every oxygen in two-fold coordination. After evidencing a similar phenomenon in β-Zr$_2$O(PO$_4$)$_2$ and related compounds, we can suggest that low-expansion materials
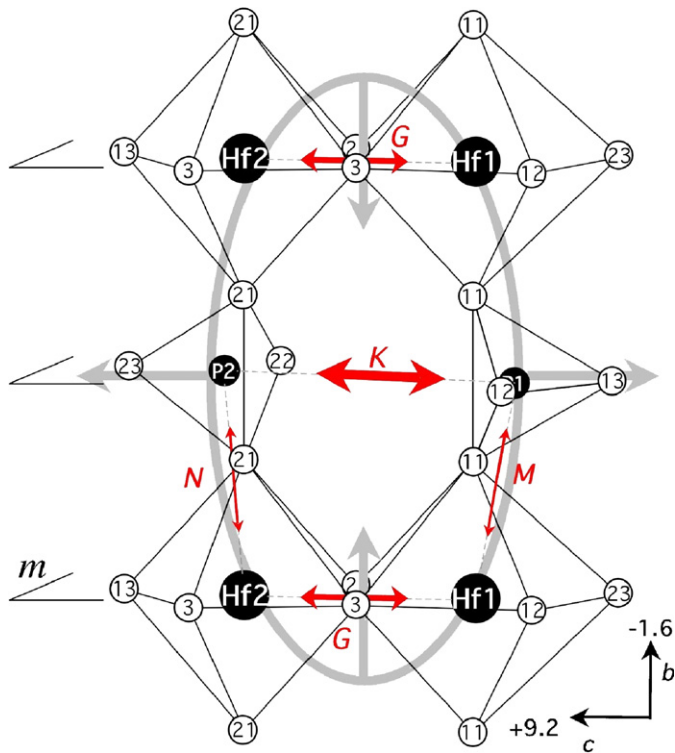
Fig. 6. Thermal evolution of the inter-cations distances perpendicular to the (010) plane of α-Hf$_2$O(PO$_4$)$_2$. The gray ring and arrows show the expansion-contraction coupling. Interactions *J* and *L* operate likewise on the P1–Hf1–Hf1–P1–Hf1–Hf1 and P2–Hf2–Hf2–P2–Hf2–Hf2 rings.

can be found also among the very wide family of compounds connected not only by corners, but also edges, thus widening considerably the field of research.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.02.032

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