

Structural model for thermal expansion in $MZr_2P_3O_{12}$ ($M=Li, Na, K, Rb, Cs$)

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A structural model is proposed to describe the highly anisotropic thermal expansion in the sodium zirconium phosphate $NaZr_2P_3O_{12}$ structure as a result of the thermal motion of the polyhedra in the structure. In the proposed model the rotations of the phosphate tetrahedra are coupled to the rotation of the zirconium octahedra. Of the two versions considered, the first one allows angular distortions to occur only in the ZrO_6 octahedra; the second one permits all polyhedra to be distorted.

1. Introduction

During the last few years, the sodium zirconium phosphate $NaZr_2P_3O_{12}$ (NZP), NASICON has become known as a fast ion conductor. There was a lot of interest shown in these properties in the mid-seventies by various workers [1, 2]. In the early eighties Alamo and Roy [3-5], at The Pennsylvania State University, started a general crystal chemistry study in the system $Na_2O-ZrO_2-P_2O_5-SiO_2$ in order to find new structural families of near-zero thermal expansion materials. Their attention was drawn by a paper by Boilot and Salanie [6], which claimed that in the series $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (known as NASICON), the thermal expansion could vary from strongly positive values to nearly zero. Alamo *et al.* [3-5] found that these low values could be attained because of the anisotropic behaviour of the unit cell parameters of the (NZP) structure. When the temperature increases, the a parameter of the hexagonal unit cell decreases and the c parameter increases (Fig. 1). We also reported the low thermal expansion properties of the alkali series [7, 8], namely $MZr_2P_3O_{12}$ ($M=Li, Na, K, Rb, Cs$). Therefore, it was of interest to study the atomic movements in the crystal network as a function of temperature for this series. In this paper a structural model is developed in order to illustrate the anisotropic character of the structure and to better understand its thermal expansion behaviour.

2. Structure

Hagman and Kierkegaard [9] found that the NZP unit cell is rhombohedral and the space group is $R\bar{3}c$ (#167) in which the oxygen atoms are in 36(f), the phosphorus atoms in 18(e), the zirconium atoms in 12(c), and the alkali atoms in 6(b) equipoint positions. The structure consists of PO_4 tetrahedra and ZrO_6 octahedra linked by the corners to form a three-dimensional network (Fig. 2). Each phosphate group is on a two-fold rotation axis and is linked to four ZrO_6 octahedra. Each zirconium octahedron lies on a three-fold rotation axis and is connected to six PO_4 tetra-

hedra. The alkali atoms are located in holes between the ZrO_6 octahedra. Sljukic *et al.* [10] synthesized all the alkali members of the family, and found that the unit cell parameters have an anisotropic behaviour: when the size of the alkali atom increases, the c parameter increases and the a parameter decreases (Fig. 3). A similar trend in general was observed by Alamo and Roy [11] in their recent publication.

3. Structural models

The structure of each member of the NZP family can be derived from the sodium zirconium phosphate structure by rotating the polyhedra in the network. Because each oxygen belongs to a tetrahedron and an octahedron, the rotations of these polyhedra will not be independent. A strictly rigid ion model is not compatible with the space group symmetry for big rotations of the polyhedra: hence, two models were developed:

1. The first model allows angular distortions only in the ZrO_6 octahedra. Fig. 4 exhibits a projection down the three-fold axis of a zirconium octahedron, within which the plane formed by the three $O(1)$ atoms will rotate faster than the $O(2)$ plane, causing the angle $O(1)-Zr-O(2)$ to deviate from 60° (shearing action).

2. The second model allows both PO_4 tetrahedra and ZrO_6 octahedra to be distorted. Fig. 5 exhibits a projection of a phosphate tetrahedron in the plane perpendicular to the two-fold axis where the line $O(1)-P-O(1)$ can rotate faster than the line $O(2)-P-O(2)$, causing the angle between them to deviate from 90° . For the ZrO_6 octahedron the distortion process is the same as in the first model.

The rotation of the PO_4 tetrahedron is constrained to rotate about a two-fold rotation axis and the ZrO_6 octahedron is constrained to rotate about a three-fold axis. Since a common oxygen couples the motion of the tetrahedron and the octahedron, the only way for these constraints to be satisfied simultaneously is for the atoms to have a translatory motion and as a result a change in the unit cell parameters (it was assumed

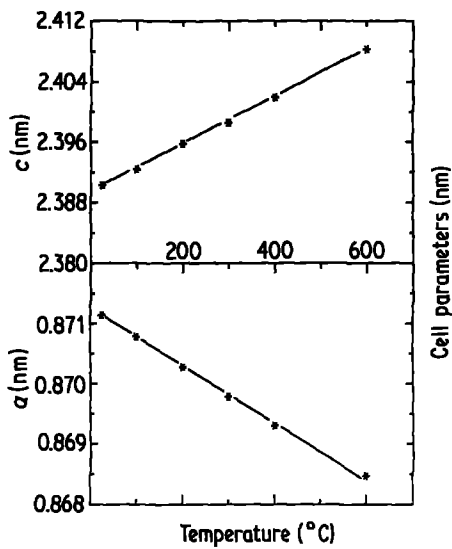


Figure 1 High temperature X-ray diffraction data showing anisotropy of axial thermal expansion in $\text{KZr}_2(\text{PO}_4)_3$. (a) $\bar{\alpha}_c = 13.13 \times 10^{-6}$, (b) $\bar{\alpha}_a = -5.655 \times 10^{-6}$.

that there is no variation of bond lengths during the rotation of the polyhedra). Each rotation generates a new set of atomic co-ordinates and new cell dimensions. (This method was used by Megaw in her work on phase transitions in quartz [12].)

The a parameter was derived by calculating the distance on the projection of the structure down the three-fold axis, between the zirconium atoms #7 and #13 (Fig. 6), which is $a(3)^{1/2}/3$ and is fixed by the space group symmetry. The c parameter was derived by calculating the distance of the projection of the structure along the two-fold axis, between the oxygen atoms #96 and #82, which is $c/3$, also constrained by the space group symmetry (Fig. 7). To calculate the cell parameters and to determine the position of the atoms in the space, four angles were used: ϕ_1 , ϕ_2 , θ_1 , and θ_2 , as defined in Figs 4 and 5. RP_1 , RP_2 , RZ_1 , and RZ_2 are respectively the projections of the P-O and the Zr-O bonds onto their respective symmetry axes and are assumed to be constants in our models.

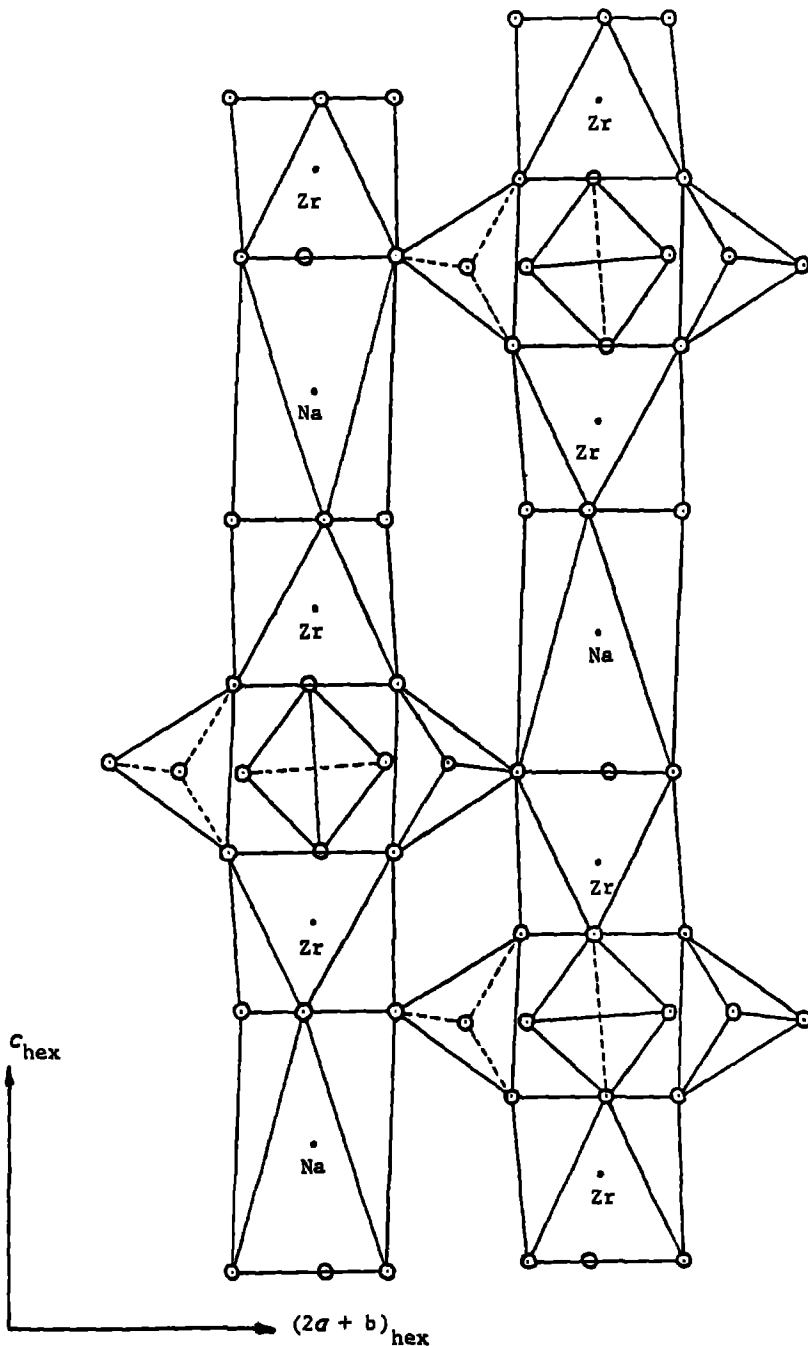


Figure 2 Schematic drawing of the (NzP) structure.

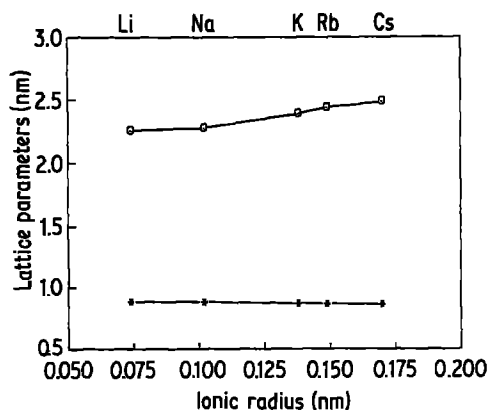


Figure 3 Lattice parameters of the various alkali members of the (NZP) family as a function of the ionic radius of the alkali atom. (○) *c*-axis, (*) *a*-axis.

3.1. Rigid tetrahedra model #1

From Figs 4 and 5 it can be seen that

$$RP_1 \sin \theta_1 = RZ_1 \sin \phi_1 \quad (1)$$

so θ_1 is easily derived from ϕ_1 . θ_2 is easily calculated since the difference $\Delta\theta = \theta_1 - \theta_2$, in this model is fixed and known.

$$\theta_2 = \theta_1 - \Delta\theta \quad (2)$$

To calculate ϕ_2 , one can make use of the fact that there is a centre of symmetry at (1/3, 1/6, 1/6). The oxygen atom #100 is the symmetric one from #73 and the expression of the angle ϕ'_2 , which is equal to ϕ_2 (symmetric), is

$$\phi'_2 = \pi/6 - \text{Arctan} \left\{ \frac{[RZ_1 \cos \phi_1 + DP - (3)^{1/2} RP_2 \cos \phi_2]}{2RZ_2} \right\} \quad (3)$$

where DP is the distance between the lines 0(1)–0(1) and 0(2)–0(2) on the *a*-axis. *a* and *c* are given by the expressions

$$a = (3)^{1/2} \left[2RP_2 \cos \theta_2 + 2RZ_2 \cos \left(\phi_2 + \frac{\pi}{6} \right) \right] \quad (4)$$

and

$$c = 6(RP_1 \cos \theta_1 + DC + RP_2 \sin \theta_2) \quad (5)$$

where DC is the height (in the *c* direction) of a ZrO_6 octahedron.

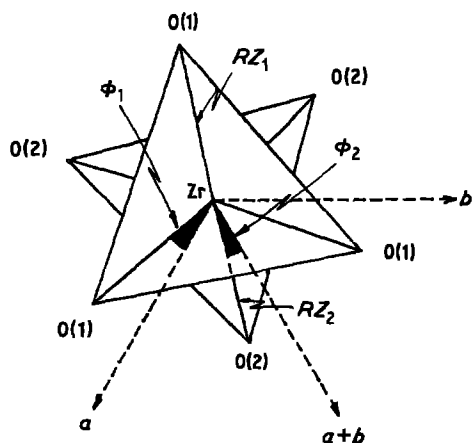


Figure 4 Projection of a ZrO_6 octahedron in the plane perpendicular to the three-fold axis (*c*-axis).

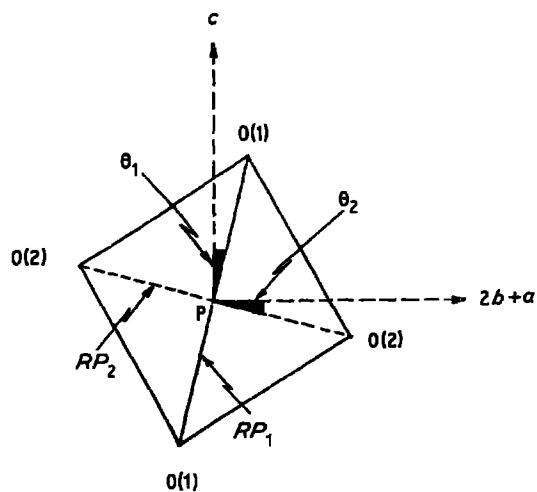


Figure 5 Projection of PO_4 tetrahedron in the plane perpendicular to the two-fold axis (*a*-axis).

3.2. Angular distortion model #2

In this model also θ_1 is calculated in the same way as in the rigid tetrahedra model. To calculate the other angles, it is assumed that there is a linear relationship between the angular distortions in the tetrahedra and the octahedra

$$\theta_1 - \theta_2 = U(\phi_2 - \phi_1 - T) \quad (6)$$

U and T can be calculated using the NZP and the KZP structural data [9, 13] as follows

$$U = \frac{[(\theta'_1 - \theta'_2) - (\theta''_1 - \theta''_2)] / [(\phi'_1 - \phi'_2) - (\phi''_1 - \phi''_2)]}{1} \quad (7)$$

and

$$T = \frac{[(\theta'_1 - \theta'_2) - (\theta''_1 - \theta''_2)] / [U + (\phi'_1 - \phi'_2) - (\phi''_1 - \phi''_2)]}{1} \quad (8)$$

where θ' and ϕ' are the angles for the KZP structure and θ'' and ϕ'' are the angles for the NZP structure. The observed distortions in the polyhedra are thus maintained in calculated structures with different rotation angles. So in a general case

$$\theta_1 - \theta_2 = \theta'_1 - \theta'_2 + U(\phi_1 - \phi_2 - \phi'_1 + \phi'_2) \quad (9)$$

ϕ_2 and θ_2 are calculated by successive iterations: the oxygen atom #73 is rotated from an arbitrary angle F_2 ; and the angle θ_2 for the oxygen #100 is given by the preceding expression.

Then the angle F_2 is calculated

$$F_2 = \pi/6 - \text{Arctan} \left\{ \frac{[RZ_1 \cos \phi_1 + DP - (3)^{1/2} RP_2 \cos \theta_2]}{2RZ_2} \right\} \quad (10)$$

ϕ_2 and F_2 are equal because of the centre of symmetry.

If $|\phi_2 - F_2| > 1 \times 10^{-9}$, then $\phi_2 = F_2$ and a new set of θ_2 and F_2 values is calculated using the preceding equations. These iterations are continued until $|\phi_2 - F_2| < 1 \times 10^{-9}$.

The *a* and *c* parameters are derived from the same expressions as in the first rigid ion model.

3.3. Principle of use

Starting from the NZP structure the polyhedra are

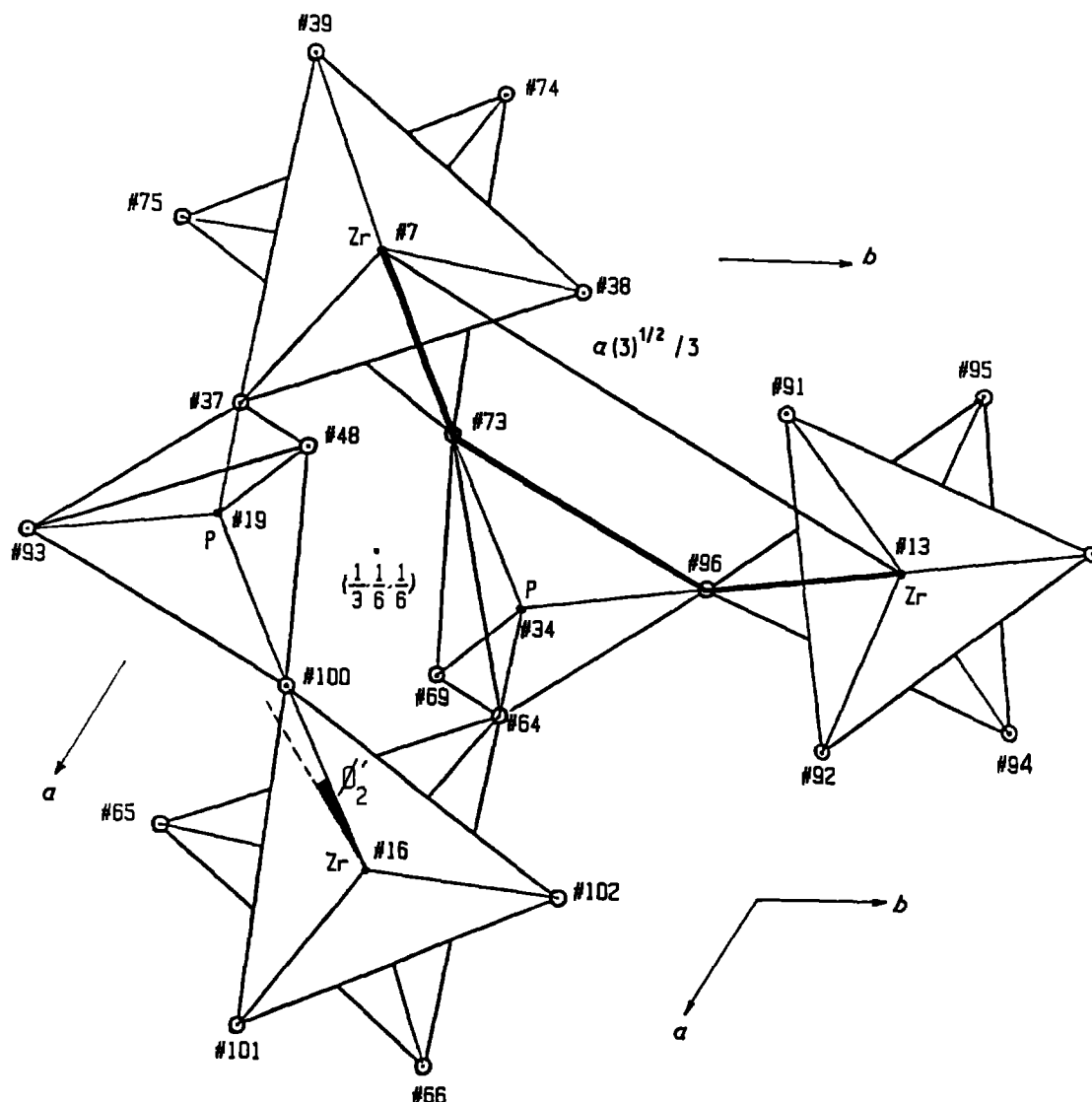


Figure 6 Detail of the projection of the (NZP) structure in the plane perpendicular to the three-fold axis.

rotated until the calculated lattice parameters are in good agreement with those of other family members. All the constants of the structure entered in the program are calculated from the NZP or the KZP structural data.

4. Results

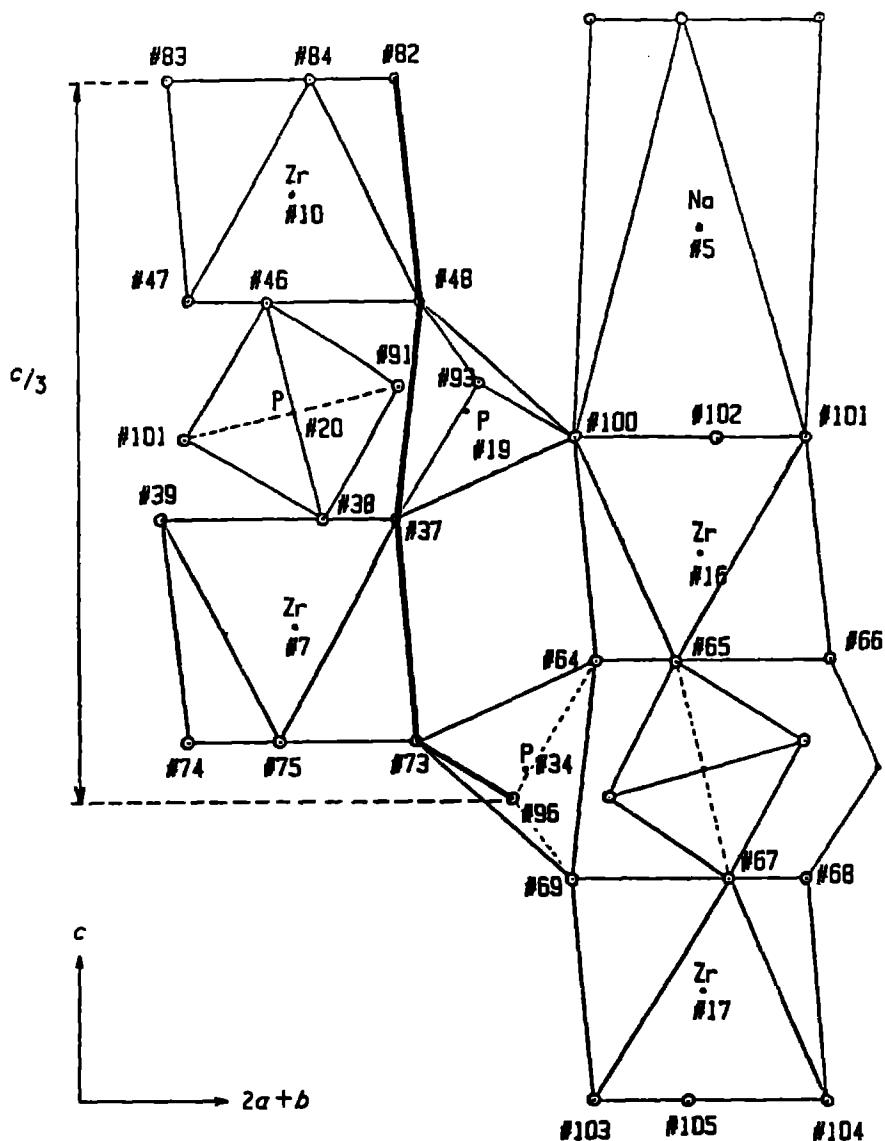
Fig. 8 shows the calculated lattice parameters given by the angular distortion model 2 as a function of the angle ϕ_1 . The observed trends are as expected since the behaviour is anisotropic: c increases and a decreases when ϕ_1 increases (in the range of ϕ_1 values studied). Both parameters go through an extremum for different values of the rotation. Therefore, there is a range of values for ϕ_1 where the unit cell dimension behaviour is isotropic but it can hardly be seen. The magnitude of the variation of the cell parameters is higher in the c direction than in the a direction. In Fig. 9 the angle ϕ_1 against the ionic radii of the alkali atoms is shown [14]. These values of the rotation of the polyhedra were calculated from the measured cell dimensions of the samples. The difference between the two models is small. However, the angular distortion model #2 seems to be closer to reality, since it describes the KZP structure better: the rotation angles of the polyhedra given by this model are very close to the values calculated from the structure (Table I). This

result was also checked using a program which can calculate X-ray powder diffraction patterns [15]. The structure available in the literature [13] for KZP was approached with the model with an R-factor of 10% for 80 powder diffraction peaks. This experiment was more an attempt to measure the reliability of the model rather than a true structure analysis. As far as intensities are concerned, the calculated X-ray powder patterns for the other samples (rubidium and caesium) were in good agreement with the observed ones, but a reliability factor could not be calculated for these materials because structures of NZP and KZP only have been fully determined so far. Fig. 9 can also be used to predict the rotation of the polyhedra or the values of the unit cell parameters from the ionic radius of the alkali atom present in the material; but more work needs to be done for a more accurate determination.

TABLE I Angles in the (KZP) structure given by the structure analysis and both models

Angle (deg)	Structure analysis	Model #1	Model #2
ϕ_1	11.16	11.57	11.01
ϕ_2	7.13	5.71	5.66
θ_1	15.09	15.76	14.99
θ_2	14.03	14.14	14.05

Figure 7 Detail of the projection of the (NZP) structure in the plane perpendicular to the two-fold axis (*b*-axis).



The distance between the alkali atom and its first and second oxygen neighbours as a function of ϕ_1 is shown in Fig. 10. The size of the hole where the alkali atom is located increases as a function of ϕ_1 . Note that there is an angle ϕ_1 (near 25°), where the first and second oxygen neighbours of the alkali atom are equidistant from it. In measurements of thermal expansion, the unit cell parameters are found to be anisotropic and behave in the same way, when the size of the alkali

ion increases. In fact, the oxygen atoms tend to move away from the alkali atoms when the temperature increases. Therefore, ϕ_1 will increase to enlarge the cavity for the alkali atom, the *c* parameter will increase, and the *a* parameter will decrease. Fig. 11 shows the angular distortions of the polyhedra as a function of the angle ϕ_1 . It is clear from these plots that the ZrO_6 octahedra are much more affected than

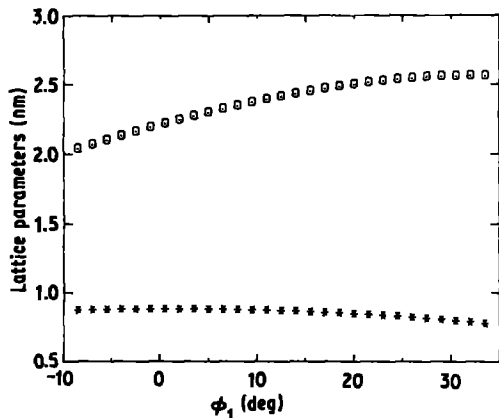


Figure 8 Calculated lattice parameters against the angle ϕ_1 (model #2). (○) *c*-axis, (*) *a*-axis.

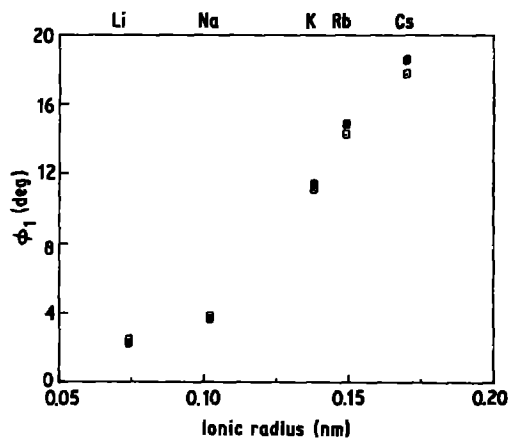


Figure 9 Angle of rotation ϕ_1 against the ionic radius of the alkali atom for the various members of the (NZP) family. (●) model #1, (○) model #2.

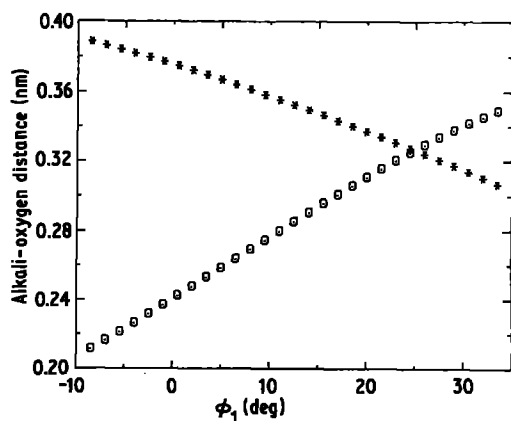


Figure 10 Distance between the alkali atom and its first and second oxygen neighbours as a function of ϕ_1 . \odot , octahedron; *, tetrahedron.

the PO_4 tetrahedra. This is one of the reasons why, in the rigid tetrahedron model #1, the phosphate groups were chosen to remain undistorted.

5. Conclusions

The proposed model can describe the structure of every member of the alkali zirconium phosphate family with a rather good reliability, and can be used to predict the unit cell dimensions and the position of the atoms in the structure from the ionic radius of the alkali atom present in the material. However, a complete structure analysis needs to be done in order to confirm all these predictions. In the near future it might be possible to predict thermal expansion coefficients with this model.

Acknowledgements

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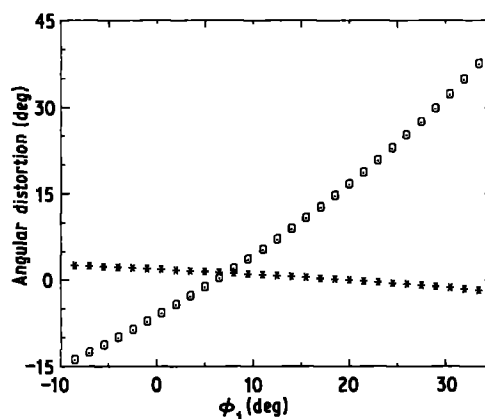


Figure 11 Angular distortions in the polyhedra as a function of ϕ_1 (model #2). \odot octahedron, (*) tetrahedron.

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