International Journal of Thermophysics, Vol. 12, No. 4, 1991

NZP: A New Family of Low-Thermal Expansion Materials[1]

D. K. Agrawal,[2] C.-Y. Huang,[2] and H. A. McKinstry[2]

A new structural family of low-expansion materials known as NZP has been recently discovered and has generated great interest for wide-ranging applications such as fast ionic conductors, devices requiring good thermal shock resistance, hosts for nuclear wastes, catalyst supports in automobiles, etc. This family is derived from the prototype composition $NaZr_2P_2O_{12}$ in which various ionic substitutions can be made leading to numerous new compositions. The bulk thermal expansion of these materials varies from low negative to low positive values and can be controlled and tailored to suit the needs for specific applications. In general, most of the NZP members demonstrate an anisotropy in their lattice thermal expansions, which is the main cause of the low-thermal expansion behavior of these materials. In $CaZr_4P_6O_{24}$ and $SrZr_4P_6O_{24}$ an opposite anisotropy has been observed which has led to the development of near-zero expansion crystalline solution composition. On the basis of the coupled rotations of the polyhedral network formed by ZrO_6 octahedra and PO_4 tetrahedra, a crystal structure model to interpret and explain the thermal expansion behavior has been discussed.

KEY WORDS: ceramics; sodium zirconium phosphate; structure model; thermal expansion.

1. INTRODUCTION

Ceramic materials can be arbitrarily divided into three classes depending upon their coefficients of thermal expansion [1]:

High-expansion group, $\alpha > 8 \times 10^{-6}\ {}^{\circ}C^{-1}$;
intermediate group, $2 < \alpha < 8 \times 10^{-6}\ {}^{\circ}C^{-1}$; and
very low-expansion group, $0 \leqslant \alpha < 2 \times 10^{-6}\ {}^{\circ}C^{-1}$.

---

[1] Paper presented at the Tenth International Thermal Expansion Symposium, June 6–7, 1989, Boulder, Colorado, U.S.A.

[2] Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

For several decades prior to World War II the ceramic community utilized three families of low-thermal expansion materials, namely, cordierite, zircon, and silica glass. In 1948, Hummel [2] discovered a family of lithium aluminum silicates, β-eucryptite and β-spodumene, which had very low and even negative thermal expansion. Since then this one family has dominated the science and technology of low-expanding ceramics, being used in many applications from household dinnerware to 6-m mirror blanks for the largest telescopes. In the early 1980s, requirements such as a new "zero" expansion material which could be processed easily for mirror substrate applications in space satellites caused a few researchers to look for new materials. For this task of finding new low-α structural families, one could fall back only on earlier guidelines of an open structure with a relatively rigid framework make up of strongly bonded small polyhedra. A little-used idea of Fairbairn [3] based upon the packing density (total volume of atoms in a unit cell/volume of the unit cell) for a crystalline material can give a quantitative measure of the open structure.

In 1979, Boilot et al. [4], while studying the ionic conductivity and phase transformations in the $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ system, a subsystem of NZP family, also reported that the thermal expansion of this system changed from strongly positive to nearly zero and even negative. This led to the discovery of an entirely new and very large structural family of totally controllable ultra low-α materials [5–9]. $NaZr_2P_3O_{12}$ is a prototype composition from which numerous new compositions can be derived by ionic substitutions. In the last few years several compositions with near-zero expansion in different temperature ranges have been developed. These materials have now attracted wide attention in academia and in industry for their strong potential as future candidates for devices requiring good thermal shock resistance, catalyst supports in the automobile industry, hosts for nuclear waste [10], fast ionic conductors in sulfur batteries [11–13], etc.

In this presentation we review and discuss the progress made in the past few years on the development of this new NZP family, focusing on the low-expansion behavior of the materials.

2. NZP STRUCTURE

Most of the important properties of NZP materials are essentially attributed to the unique crystal structure of $NaZr_2P_3O_{12}$, which has rhombohedral symmetry and belongs to the $R\bar{3}c$ (No. 167) space group. The basic crystal structure consists of a three-dimensional network of PO_4 tetrahedra and ZrO_6 octahedra which are connected by corner sharing in such a manner that a stable and flexible framework structure is built up

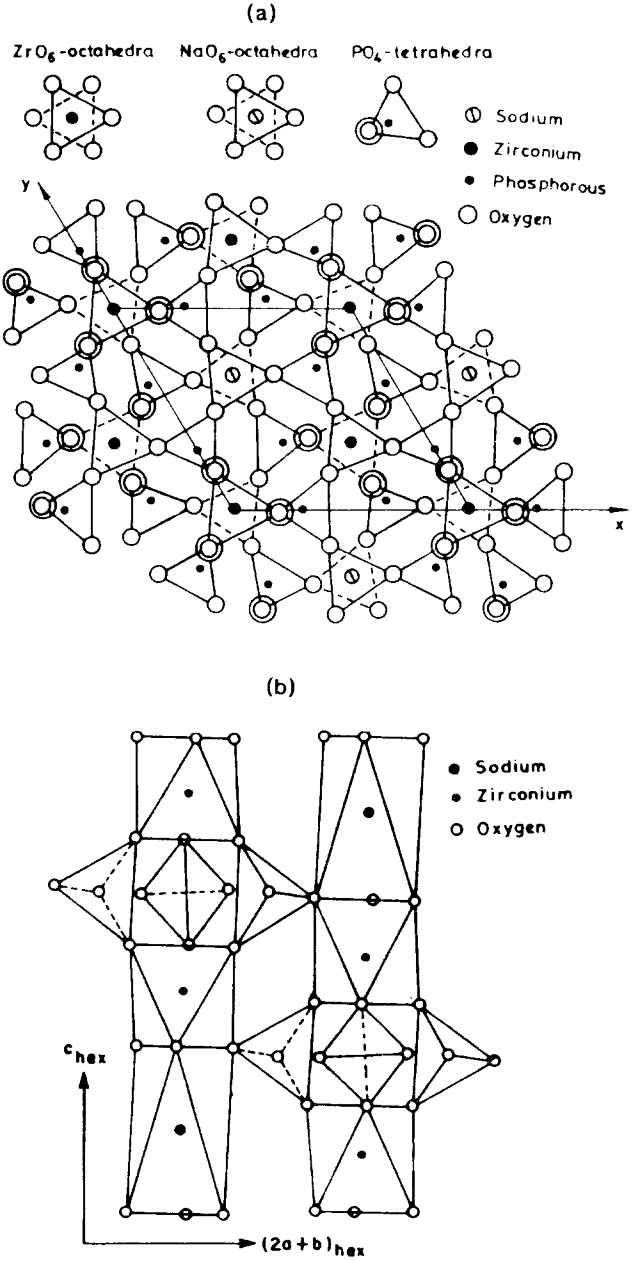

Fig. 1. Crystal structure of $NaZr_2P_3O_{12}$; NZP viewing (a) along the *c* axis and (b) perpendicular to the *c* axis.

Table I. Atomic Positions of $NaZr_2P_3O_{12}$

Atom (number of positions)	Wyckoff notations	Point symmetry	Numbering
Na (6)	b	$\bar{3}$	1–6
Zr (12)	c	3	7–18
P (18)	e	2	19–36
O_1 (36)	f	1	37–72
O_2 (36)	f	1	73–108

from the rigid but deformable polyhedcra. Each ZrO_6 octahedron is connected to six PO_4 tetrahedra, and each PO_4 tetrahedron is connected to four ZeO_6 octahedra by sharing oxygens. A schematic diagram of the NZP structure is shown in Fig. 1. There are six formula units of $NaZr_2P_3O_{12}$ or 108 atoms in one unit cell, and Na goes to the crystallographic position b as listed in Table I.

2.1. Ionic Substitution

An interesting aspect of the crystal chemistry of the NZP structure is its flexibility toward ionic substitutions at different lattice sites leading to

Table II. Various Ionic Substitution Schemes in NZP Structure at Different Lattice Sites

	Structural formula $[M'_1][M''_3]\,Zr^{VI}_2P^{IV}_3O_{12}$				
Substitution scheme	M'_1	M''_3	Zr_2	P_3	O_{12}
Isovalent substitution at M′ site	H, NH_4, Li, K, Rb, Cs, Cu	□	—	—	—
Hetrovalent substitution at M′ site	1/2(Mg, Ca, Sr, Ba, Cu)	□	—	—	—
Isovalent substitution at Zr site	—	□	Ge, Ti, Sn, Hf	—	—
Balanced substitution at Zr and M″ sites	—	Na	Cr, Fe, Al, Sc, Y, Gd	—	—
Balanced substitution at P and M″ sites	—	Na	—	SiP_2	—
Balanced substitution at M′ and Zr sites	□	□	NbZr	—	—
Balanced substitution at M′ and P sites	□	□	—	P_2S	—

numerous chemical compositions [14]. For example, Na can be replaced by H, NH_4, Li, K, Rb, Cs, Mg, Ca, Sr, Ba, and Cu; Zr by Ti, Ge, Cr, Al, Fe, Hf, Th, Sn, and rare earths; and P, by Si and S. The flexibility is demonstrated by the fact that H (smallest ion), Li, and Cs (one of the largest ions) can exist in the same crystallographic site, a condition not known in any other structure. Table II shows some important ionic substitution schemes in the NZP structure. Partial as well as complete ionic substitutions are possible; this makes it possible to tailor a desired property by modifying the composition. For example, in the $Ca_{1-x}Sr_xZr_4P_6O_{24}$ system, compositions of zero thermal expansion in certain temperature ranges have been produced [15]. Due to its flexibility to accommodate almost the whole periodic table, NZP structure has proved to be an excellent host to immobilize almost all 42 elements present in commercial nuclear waste and still maintains its structural integrity [10].

3. SYNTHESIS

NZP materials can be synthesized by the solid-state method (or powder mixing), solution–solgel method, or hydrothermal method. Normally, Ti-based compositions are prepared by solid-state methods because no suitable water-soluble Ti salt is available. The sol-gel method is found to be better in most cases because the mixing of the components is achieved at a molecular level, thus ensuring a high degree of reactivity [16]. The hydrothermal method provides a low-temperature route for synthesis of ultrafine powers of NZP family of materials.

3.1. Solid-State Method

In this method dry powders of carbonates of alkali or alkaline earths, ZrO_2, and $NH_4H_2PO_4$ are used as precursors. Stoichiometric amounts of the powders are mixed in acetone with hand grinding, air-dried, sometimes ball-milled, heat-treated at 175°C, and then calcined to remove the volatiles such as CO_2, NH_3, and 600°C for 4 h and 900°C for 16 h. Final calcination temperature varies for different compositions due to different carbonate decomposition temperatures. Intermediate grinding and mixing are required before final calcination to ensure complete homogenization of the powder. The calcined powder is consolidated into disks which are subjected to final sintering at 1000–1400°C for 48 h to obtain single-phase NZP material. In this method the ceramic body has a low density and often free ZrO_2 and ZrP_2O_7 as minor secondary phases persist.

3.2. Sol-Gel Method

In this method aqueous solutions of alkali earth nitrates, $ZrOCl_2 \cdot 8H_2O$, and $NH_4H_2PO_4$ or H_3PO_4 are used as precursors. Stoichiometric amounts of nitrate and Zr solutions are mixed first under constant-stirring conditions at room temperature, and then the P solution is added slowly. This order of mixing is very important to obtain a homogeneous gel and single-phase material. The gel is dried at 90°C for 24 h and then calcined at 700°C for 16 h. The calcined product is consolidated into disks which are heat-treated at 1200°C for 24 h to produce highly dense ceramics of single-phase NZP material.

3.3. Hydrothermal Method

Recently, $M^{+}Zr_2P_3O_{12}$ (M^{+} = Li, Na, K, Rb, Cs) and $M^{+2}Zr_4P_6O_{24}$ (M^{+2} = Mg, Ca, Sr, Ba) have been prepared by the hydrothermal method at 200°C [17]. In this method stoichiometric amounts of metal chloride or nitrate were dissolved in 0.5 *M* $ZrOCl_2$ solution and then H_3PO_4 was added drop by drop under constant-stirring conditions. The obtained gel was dried at 70°C, then ground, rehydrated, and redried. The dried gel and water are loaded in Teflon-lined Parr acid-digestion bombs and then heated between 170 and 230°C for 1 to 3 days. After this treatment, the solid and solution phases are separated by centrifugation, the solid phase of fine NZP powder is washed and dried.

In addition to ceramics and powders of NZP compounds, single crystals can also be grown either by the hydrothermal method or by a flux technique using B_2O_3 as a flux [18].

4. THERMAL EXPANSION

An important property of the NZP family of materials is the low thermal expansion, which can be controlled and tailored by ionic substitutions. The measurements for bulk thermal expansion were made on a Harrop Dilatometric Analyzer using a sintered sample. A computer-controlled high-temperature X-ray diffractometer was used to determine axial thermal expansions. Data collected by step-scanning around each peak (up to 160° 2θ) were analyzed using a curve-fitting program and precise peak positions (better than 0.01° 2θ) were thus determined. These peaks were then indexed and used to calculate cell dimensions using a program based on the least-squares method [19]. Normally, 30–50 peaks were used for each set of cell parameter calculations and the standard deviation is less than 2 parts per 100,000.

Figure 2 illustrates the bulk thermal expansion behavior of some selected NZP compositions. α varies from low negative values to low positive values, and some compositions have near-zero or ultralow expansion over wide temperature ranges. Partial substitution schemes in some NZP subsystems provide potential to tailor the thermal expansion to a desired value in a specific temperature range.

In general, NZP materials are characterized by an anisotropy in their

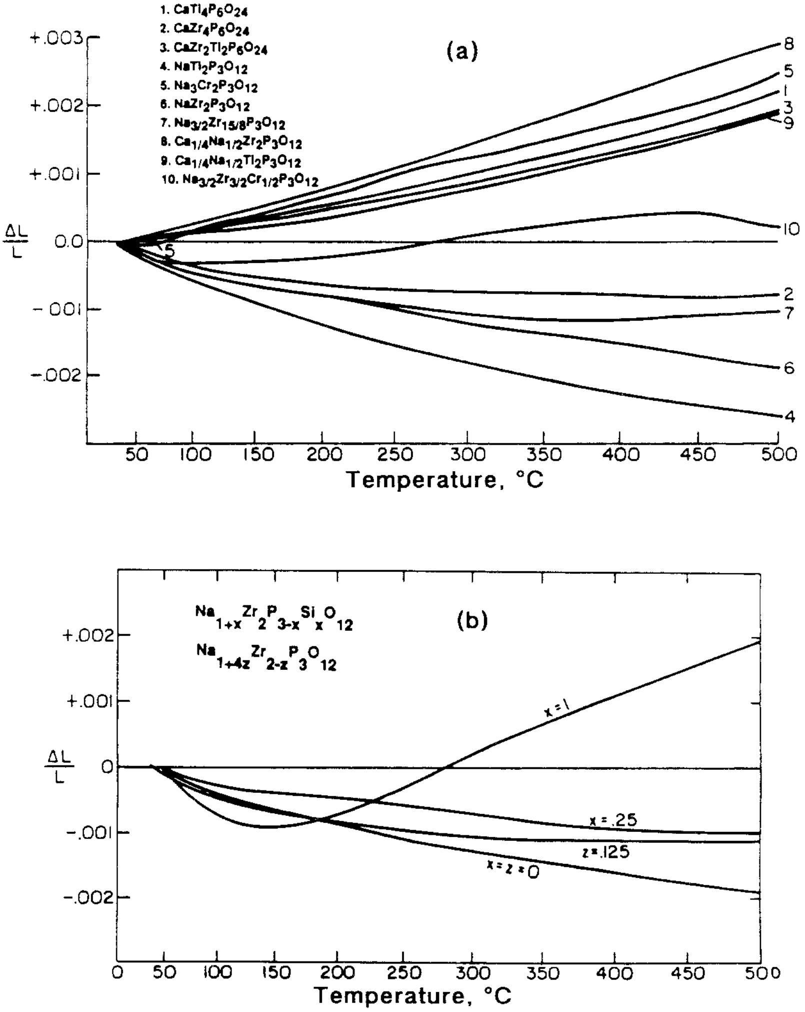

Fig. 2. Bulk thermal expansion behavior of some NZP compounds: (a) complete substitutions; (b) crystalline solutions.

lattice thermal expansions, i.e., in the hexagonal lattice of NZP in most cases the α is positive along the c axis (expansion) and negative along the a axis (contraction), and as a result the overall bulk expansion is averaged out to be low. This fact is demonstrated in Figs. 3 and 4, in which the lattice parameters-versus-temperature plots for $M^{+}Zr_2P_3O_{12}$ (M^{+} = Li, Na, K, Rb, Cs) and $M^{+2}Zr_4P_6O_{24}$ (M^{+2} = Mg, Ca, Sr, Ba) are shown. Strikingly, $SrZr_4P_6O_{24}$ demonstrates an opposite anisotropy to that of $CaZr_4P_6O_{24}$, i.e., in SrZP α_a is positive and α_c is negative; this is quite interesting and may be related to an order–disorder phenomenon proposed

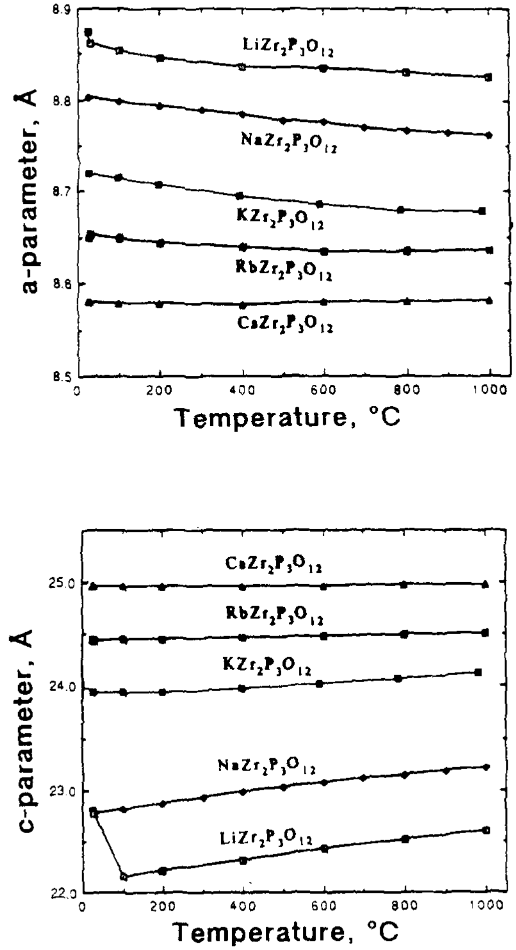

Fig. 3. Lattice thermal expansion of $M^{+}Zr_2P_2O_{12}$ (M^{+} = Li, Na, K, Rb, Cs).

by Ohashi and Matsuhiro [20], however, further study of this relationship is needed. The low thermal expansion of NZP materials is essentially attributed to the presence of a strongly bonded polyhedral network which rotates in a coupled fashion. The anisotropic thermal expansion of these compounds could be thought of in terms of the effect that is produced by changing the size of the octahedron at the Na position. When a substitution of Na by a larger atom is made, the unit cell contracts in the *a* direction and expands in the *c* direction. When the Na–O bond length increases with temperature, the P tetrahedra and Zr octahedra in their

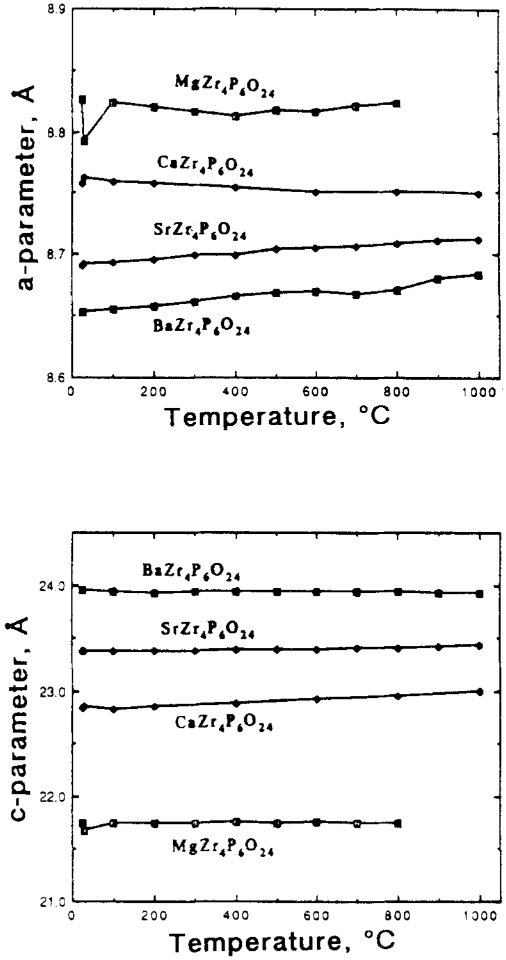

Fig. 4. Lattice thermal expansion of $M^{+2}Zr_4P_6O_{24}$ (M^{+2} = Mg, Ca, Sr, Ba).

coupled motion transform that expansion into an expansion and contradiction along different crystallographic directions. The difference in thermal expansion depends on where the rotation angle of the polyhedra starts due to the size of the particular ionic substitution.

5. STRUCTURE–THERMAL EXPANSION MODEL

The essential structure of NZP is described in a rigid ion model in which the rotation of the polyhedra can account for the negative and positive thermal expansions of the lattice and, also, lend credence to the wide range of ionic substitutions possible in the structure. The idea of the coupled rotation is based on the previous work of Taylor [21], who studied several minerals including quartz, and Megaw [22], who made detailed analysis of the X-ray diffraction data that Young [23] had obtained as a function of temperature. Megaw showed that the tetrahedra rotate with temperature so that one of the primary alterations of the α-quartz on its way to β-quartz is that the polyhedra rotate about the twofold electric vector in the quartz structure. Alamo developed a model as described by Lenain et al. [24] in which the mechanism of the coupled rotations of the phosphorus tetrahedra and zirconium octahedra explains the anisotropic and low-expansion nature of the NZP materials. Due to symmetry restrictions, the PO_4 tetrahedron is constrained to rotate about a twofold axis and the ZrO_6 octahedron about a threefold axis. Since a common oxygen is shared by both polyhedra, resulting in a coupling of the motion of the octahedron and tetrahedron, 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 lattice parameters. The following description is an updated version of our earlier model [24], with few modifications; only the main pertinent points are presented here.

The principle used here is that the lattice parameters are a function of the orientation of the polyhedra within the structure, assuming that the polyhedra act as units. The determination of the a and c parameters is illustrated in Fig. 5, in which the thick solid paths represent three-dimensional bonds between atoms. For the a parameter (Fig. 5a) in NZP, a path is traced following rigid P–O bond to the place in the structure where the tetrahedron surrounding the P 34 must join with Zr octahedron. The projection of the Zr atoms 7 and 16 are located at the fixed position (0, 0) and (2/3, 1/3), respectively, in the a–b plane of the hexagonal structure, and the projected distance is equal to $a/\sqrt{3}$. To obtain the relationship for the c parameter, the pathway is more convoluted (Fig. 5b) and goes from atom 82 to atom 96, the projected distance of this circuitous path gives one-third of the c parameter.

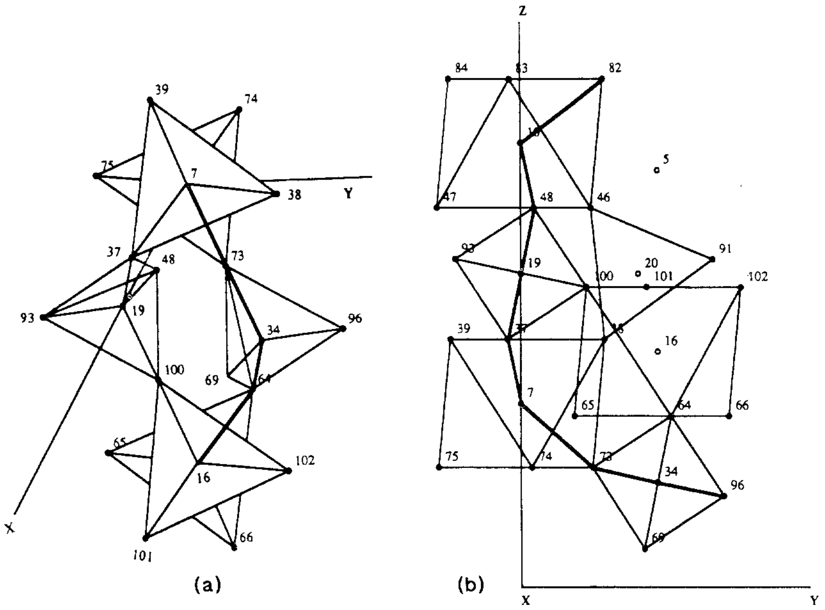

Fig. 5. Determination of lattice parameters based on the proposed model: (a) *a* parameter; (b) *c* parameter.

The model is sensitive to the starting "shape" of the polyhedra. In the present discussion, the room-temperature crystal structure as proposed by Hong [12] is used. If the positional structure parameters (total of eight) taken from the data of Hagman and Kierkegaard [25], Hazen et al. [26], and Sljukic [27], for example, are used, the curve in Fig. 6a between the *a* and the *c* parameters as a function of rotation angle is altered slightly. Superimposed on the curves in Fig. 6 are cell parameters obtained in this work [28] in zirconium and titanium system from room temperature to 1000°C, the arrows point to the increasing temperature. The behavior of the less examined $Na_4Zr_2Si_3O_{12}$ system is also predicted.

In the case of the $MZr_2P_3O_{12}$ family (Fig. 6a), Li data approach the curve from top to bottom and Na data deviate progressively inside the curve as the temperature increases, K lies nicely on the curve, Rb lies outside the curve, and Cs lies still further outside the curve—it is fascinating that this occurs when the angle of rotation is $-20°$ away from the angle for $NaZr_2P_3O_{12}$ from which the model is derived. The position where the Na is placed in the structure is surrounded by six oxygens in $NaZr_2P_3O_{12}$. As the rotation angles is increased to that for Cs, six other oxygens move in closer while the six close ones have moved out. Consequently, it is likely

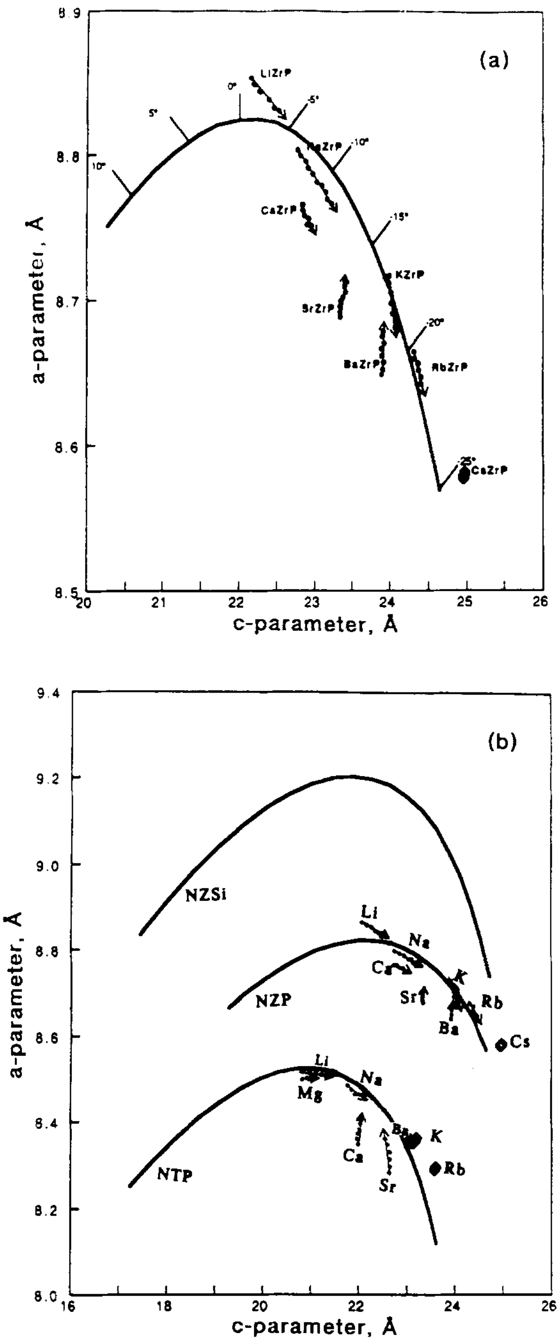

Fig. 6. Plots of the *a* and *c* parameters as a function of rotation angle for NZP, NTP, and $Na_4Zr_2Si_3O_{12}$ (NZSi) compounds. References for starting crystal structures: NZP [12], NTP [29], and NZSi [30].

that Cs has a coordination number of 12 in $CsZr_2P_3O_{12}$. A structure analysis would be required to confirm this hypothesis.

The alkaline earth substitutions do not fall on the curves as predicted by the model, and all data points lie inside the curve in both Zr and Ti cases except BaTiP, which is on the curve and is superimposed on the K data (Fig. 6b). BaTiP exists only in a disordered form, and no ordered phase was observed at low temperatures. A recent study [27] suggests that an order–disorder transformation which exists in these analogues may be responsible for the observed deviation. In the case of BaZP the high-temperature disordered phase has been quenched from 1000°C to room temperature. It is understood that CaZP and SrZP would require higher temperatures to transform to disordered phases. Ca data (Fig. 6a) lie inside the curve from top to bottom as the temperature is increased. Sr and Ba analogues show the opposite temperature dependence from CaZP and the alkali analogues, the plotted values go from bottom to top as the temperature is increased. This is consistent with our earlier observation regarding the opposite anisotropy behavior of CaZP and SrZP [15].

In an effort to extend this mechanism of coupled rotations in order to explain the thermal expansion of other ceramic materials, the crystal structures of Al_2TiO_5, $ZrSiO_4$, and cordierite were examined. The preliminary calculations reveal that for Al_2TiO_5 and $ZrSiO_4$ the arrangement of the atoms with respect to the symmetry elements precludes any polyhedral rotation linkages. In cordierite, key characteristics of the NZP structure do exist, i.e., a tetrahedron on a twofold axis and an octahedron on a threefold axis. However, the situation is by no means analogous since the polyhedra in cordierite share edges and not corners as in the NZP structure, so that no coupled rotations of the polyhedra are possible in the cordierite structure.

6. SUMMARY

A new structural NZP family of large number of low-expanding materials has been shown to have great potential for various applications for devices requiring high-thermal shock resistance. These materials can be easily synthesized by traditional ceramic methods into various shapes and to high densities. Most compositions exhibit low bulk thermal expansions and an anisotropy in the lattice thermal expansion which can be lowered by changing the composition of the starting material. A structural model based on the coupled rotations of the polyhedra explained anisotropic behavior of the thermal expansion of the NZP materials. Disagreements in the data of alkaline earth analogues of NZP may be attributed to the reported order–disorder phenomenon occurring in these compounds.

REFERENCES

1. F. A. Hummel, *Electronic and Newer Ceramics* (Industrial Publications, Chicago, 1958), Chaps. V, VI, VII.
2. F. A. Hummel, *Foote Prints* **20**:3 (1948).
3. H. W. Fairbairn, *Bull. Geol. Soc. Am.* **54**:1305 (1943).
4. J. P. Boilot, J. P. Salanic, G. Desplancher, and D. L. Potier, *Mat. Res. Bull.* **14**:1469 (1979).
5. J. Alamo and R. Roy. *J. Am. Ceram. Soc.* **67**:C78 (1984).
6. R. Roy, D. K. Agrawal, J. Alamo, and R. A. Roy, *Mat. Res. Bull.* **19**:471 (1984).
7. D. K. Agrawal and V. S. Stubican, *Mat. Res. Bull.* **20**:99 (1985).
8. G. E. Lenain, H. A. McKinstry, S. Y. Limaye, and A. Woodword, *Mat. Res. Bull.* **19**:1451 (1984).
9. T. Oota and I. Yamai, *J. Am. Ceram. Soc.* **69**:1 (1986).
10. R. Roy, E. R. Vance, and J. Alamo, *Mat. Res. Bull.* **17**:585 (1982).
11. J. B., Goodenough, H. Y.-P. Hong, and J. A. Kafalas, *Mat. Res. Bull.* **11**:203 (1976).
12. H. Y.-P. Hong, *Mat. Res. Bull.* **11**:173 (1976).
13. B. E. Taylor, A. D. English, and T. Berzins, *Mat. Res. Bull.* **12**:171 (1977).
14. J. Alamo and R. Roy, *J. Mat. Sci.* **21**:444 (1986).
15. S. Y. Limaye, D. K. Agrawal, R. Roy, and Y. Mehrotra, *J. Mat. Sci.* **26**:93 (1991).
16. G. E. Lenain, H. A. McKinstry, and D. K. Agrawal, *J. Am. Ceram. Soc.* **68**:C224 (1985).
17. S. Komarneni, *Int. J. High Technol. Ceram.* **4**:31 (1988).
18. M. Sljukic, B. Matkovic, B. Prodic, and S. Scavnicar, *Croat. Chem. Acta* **39**:145 (1967).
19. C. Y. Huang, *Cell Parameter, Version 2.5.1* (Materials Research Laboratory, The Pennsylvania State University, University Park, 1988).
20. T. Ohashi and K. Matsuhiro, 91st Ann. Mtg. Am. Ceram. Soc., April 23–27, 1989 Paper 12-B-89.
21. D. Taylor, *Min. Mag.* **48**:65 (1984).
22. H. D. Megaw, *Crystal Structures—A Working Approach* (W. B. Saunders, Philadelphia, 1973).
23. R. A. Young, *Acta Crystallogr.* **15**:337 (1962).
24. G. E. Lenain, H. A. McKinstry, J. Alamo, and D. K. Agrawal, *J. Mat. Sci.* **22**:17 (1987).
25. L. Hagman and P. Kierkegaard, *Acta Chem. Scand.* **22**:1822 (1968).
26. R. M. Hazen, C. W. Finger, D. K. Agrawal, H. A. McKinstry, and A. J. Perrotta, *J. Mater. Res.* **2**:329 (1987).
27. M. Sljukic, M. Matkovic, B. Prodic, and D. Anderson, *Zeit. Krist. Bd.* **130**(S):148 (1969).
28. C. Y. Huang, D. K. Agrawal, and H. A. McKinstry, Unpublished data.
29. J. L. Rodrigo, P. Carrasco, and J. Alamo, *Mat. Res. Bull.* **24**:611 (1989).
30. D. Tran Qui, J. J. Capponi, J. C. Joubert, and R. D. Shannon, *J. Solid State Chem.* **39**:219 (1981).