JOURNAL OF MATERIALS SCIENCE **35** (2000) 3359 – 3364

New [NZP] materials for protection coatings. Tailoring of thermal expansion

E. BREVAL, H. A. McKINSTRY, D. K. AGRAWAL
Materials Research Laboratory, Penn State University, University Park, PA 16802 USA.
E-mail: EXB6@psu.edu

[NZP] (the $NaZr_2P_3O_{12}$-Family) materials can be selected for synthesizing new thermal shock resistant ceramic coatings with a thermal expansion that can be tailored to match that of the substrate, and to possess a low thermal expansion anisotropy. The tailoring technique will involve the selection of a suitable pair of compositions which, upon being mixed to form a crystalline solution, will possess the desired thermal expansion coefficient and will have negligible thermal expansion anisotropy. This can be done when the axial thermal expansion for one end member is larger in the *a*-direction than in the *c*-direction and vice versa for the other end member. © *2000 Kluwer Academic Publishers*

1. Introduction

1.1. Scope

The purpose of this paper is to emphasize that [NZP]-family materials can be tailored so that it is possible to match the thermal expansion of structural materials. Many high temperature applications involve a strong and thermally stable material, for example stainless steel, with a ceramic protection. If the two materials have different thermal expansions a delamination between them can occur [1–8]. Another desired property of the protection material is a very low anisotropy in its axial thermal expansion coefficients to avoid microcracking during cooling from high temperatures [9–14]. The work presented in this publication is not an experimental study, but it is intended as a guide for the users of protective material to select an [NZP] composition with the optimum thermal expansion properties.

1.2. [NZP] materials

The family of [NZP] materials is already known not only for its low thermal expansion, but also for the possibility of ionic substitution for the purpose of creating new materials with desired properties. [NZP] has a 3-D framework structure [5, 6, 15–18] with ZrO_6 octahedra corner linked to PO_4 tetrahedra. The parent composition of [NZP] is $NaZr_2P_3O_{12}$, from which its name, NZP, is derived. The general structural formula is $[M'][M''][A_2^{IV}][B_3^{V}]O_{12}$, where M' and M'' are interstitial sites partly occupied by Na. A and B are lattice sites occupied by Zr and P, respectively. Most [NZP] materials have a hexagonal structure [9, 16, 17].

Many [NZP] compounds have been synthesized, and the thermal expansion and thermal expansion anisotropy values for some of these have been reported. A review of some of these results appears in an earlier work [15]. New candidates for compositions with low thermal expansion anisotropy can be found as crystalline solutions between known end members with already known lattice thermal expansions [15–27]. Crystalline solutions, containing one or more elements on the M-site, the A-site, and/or the B-site are shown below:

The two M-sites can be occupied by:	H, Li, Na, K, Rb, Cs, NH_4, Ag, Cu, Mg, Ca, Cd, Sr, Ba, Fe, Zn, RE, or Nb
The A site can be occupied by:	Mg, Mn, Zn, Ni, Cu, Co, Al, Cr, Fe, Y, Zr, La, In, Yb, Sc, Ga, Nd, Ge, Sn, Ti, Hf, or Nb
The B site can be occupied by:	P, Al, Si, As, V, or S.

The axial thermal expansion in the *a*-directions are α_a and in the *c* direction α_c. One of these axial thermal expansions is often negative. The average thermal expansion of a polycrystalline body (α_{av}) is $(2\alpha_a + \alpha_c)/3$. The thermal expansion anisotropy is $\alpha_c - \alpha_a$.

1.3. Examples of applications

The application of high temperature thermal barriers and corrosion resistant coatings with the required mechanical properties for a specific application can produce cost-effective substrate-coating systems [8, 14, 28]. The importance of matching the thermal expansion of the coating material with the substrate components and of obtaining a low thermal expansion anisotropy can therefore not be overemphasized. Two patents describe the favorable thermal expansion properties of [NZP] materials [1, 2]. One is a high

0022–2461

temperature thermal barrier with compositions in the series $Ca_{1-x}Mg_xZr_4(PO_4)_6$ [2, 7, 20], which have been shown to have low thermal expansion. In the patent [2] it was found that for $x = 0.5$, it resulted in a relatively low thermal expansion ($0.26 \cdot 10^{-6\circ}C^{-1}$) material. For coating applications an optimum composition was found to be $x = 0.4$ in this system with the average thermal expansion of $0.1 \cdot 10^{-6\circ}C^{-1}$ and a thermal expansion anisotropy of $5.3 \cdot 10^{-6\circ}C^{-1}$. The other patent [1] describes $Ba_{1+x}Zr_4\ P_{6-2x}Si_{2x}O_{24}$ [1, 8, 21], which has shown possibilities in the coating of carbon-carbon composite materials. The optimum composition was $x = 0.25$ in this system. The average thermal expansion was $0.74 \cdot 10^{-6\circ}C^{-1}$ and the thermal expansion anisotropy was $1.8 \cdot 10^{-6\circ}C^{-1}$.

1.4. Acoustic emission due to microcracking during cooling

Thermal expansion anisotropy of materials for high temperature applications in non-cubic materials is widely discussed [1, 13]. It can lead to microcracking in a polycrystalline ceramic during cooling due to uneven contraction (or expansion) of the material in different crystallographic directions [9]. One of the best described examples is the monoclinic Nb_2O_5 [9, 30]; the thermal expansion anisotropy is explained by the distortion of the coordination polyhedra in the Nb_2O_5 lattice during heating or cooling. It is a well described example of thermal expansion anisotropy in a polycrystalline material which, during cooling from elevated temperatures, leads to microcracking, which has been connected with acoustic emission activities [9, 30].

2. Crystalline solution [NZP] compositions from two end members

Several crystalline [NZP] solutions are reported for which $\alpha_a < \alpha_c$ for one end member and $\alpha_a > \alpha_c$ for the other. Each end member shows extensive microcracking during cooling and high acoustic emission [11, 12, 15]. An intermediate composition will exist for which there is nearly zero thermal expansion anisotropy and therefore no microcracking during cooling. By using the axial thermal expansion data for known compositions it should be possible to estimate the thermal expansion data for intermediate compositions.

2.1. $Ca_{1-x}Mg_xZr_4P_6O_{24}$

Examples of this crystalline solution in which the axial thermal expansions change with the composition were discussed in Section 1.3. The system $Ca_{1-x}Mg_xZr_4(PO_4)_6$ [2, 7, 20] is monoclinic for high values of x, but hexagonal for $0 \leq x \leq 0.5$. The axial thermal expansion in the a-direction increases less than the axial thermal expansion in the c-direction, i.e. $\alpha_a < \alpha_c$ for all values of x, therefore it is not possible within this system to select a composition for which the axial thermal expansion anisotropy is zero.

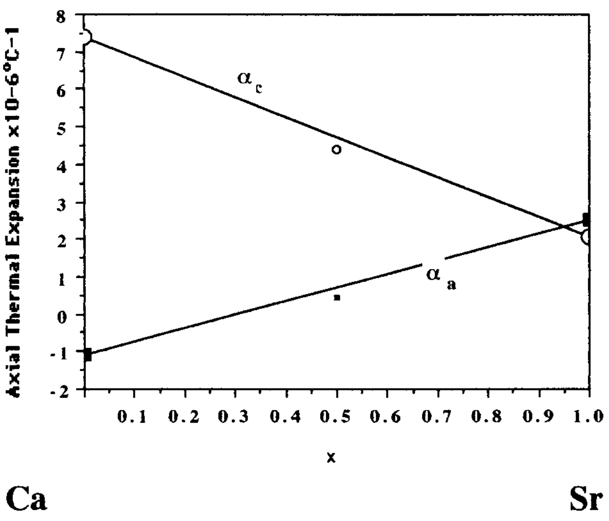

Figure 1 Axial thermal expansions in the system $Ca_{1-x}Sr_xZr_4\ P_6O_{24}$ ($0 \leq x \leq 1$). The measured values for α_a and α_c for the end members $CaZr_4P_6O_{24}$ and $SrZr_4P_6O_{24}$ [18, 21, 22] are shown with large markers, and the interpolations are shown as straight lines. The measured values for α_a and α_c for the composition $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$(23) are shown with small markers.

2.2. $Ca_{1-x}Sr_xZr_4P_6O_{24}$

For $CaZr_4P_6O_{24}$ the axial thermal expansion is smaller in the a-direction than in the c-direction ($\alpha_a < \alpha_c$). The axial thermal expansion for $SrZr_4P_6O_{24}$ is larger in the a-direction than in the c-direction ($\alpha_a > \alpha_c$) [11, 18, 21, 22]. See Fig. 1. This indicates that between the end members, $CaZr_4P_6O_{24}$ and $SrZr_4P_6O_{24}$, there exists an intermediate composition with zero thermal expansion anisotropy.

It can be estimated, assuming linearity as sketched using straight lines in Fig. 1, that the predicted axial thermal expansion values for $x = 0.5$ is $\alpha_a = \sim 0.65 \cdot 10^{-6\circ}C^{-1}$ and $\alpha_c = 4.72 \cdot 10^{-6\circ}C^{-1}$. An actual investigation of the thermal expansion data for this material was carried out [23] and the results were found to be relatively close to the predicted values, namely $\alpha_a = 0.45 \cdot 10^{-6\circ}C^{-1}$ and $\alpha_c = 4.38 \cdot 10^{-6\circ}C^{-1}$. Fig. 1 shows that there is some deviation from linearity between the end members $CaZr_4P_6O_{24}$ and $SrZr_4P_6O_{24}$.

There have been many attempts to correlate the thermal expansion anisotropy and the amount of microcracking during cooling [1,12, 21, 22]. Originally, the axial thermal expansions up to 1000°C were known only for the end members $CaZr_4P_6O_{24}$ and $SrZr_4P_6O_{24}$ [1, 12, 18, 21, 22]. The extensive microcracking during cooling of the end members was compared to the microcracking of the intermediate compositions ($Ca_{1-x}Sr_xZr_4P_6SO_{24}$) ($x = 0.25$, $x = 0.5$, and $x = 0.75$), which all gave approximately the same low amount of microcracking during cooling [11]. It was therefore assumed [1, 12] that the compound $Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$ ($x = 0.5$) had the lowest anisotropy in this series. However, according to Fig. 1 the composition for $x \sim 0.95$ should have zero thermal expansion anisotropy and therefore show the lowest amount of microcracking. There is therefore reason to believe that the relationship between the amount of microcracking during cooling and the value of the anisotropy is not monotonic linear. This may require a new investigation

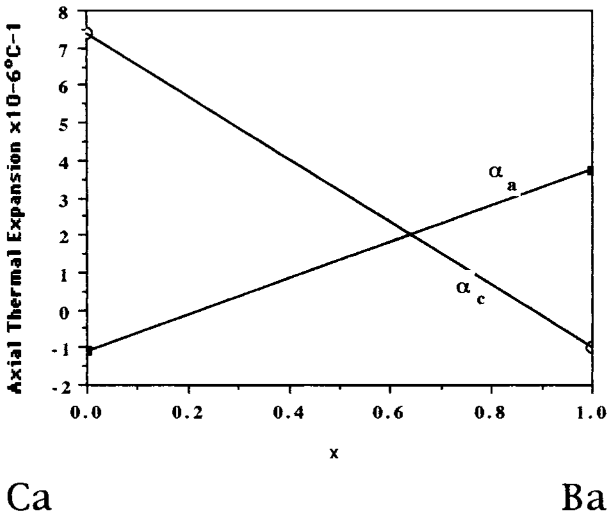

Figure 2 Axial thermal expansions for $Ca_{1-x}Ba_xZr_4P_6O_{24}$ with $CaZr_4P_6O_{24}$ and $BaZr_4P_6O_{24}$ as end members [21, 22]. The estimated thermal expansion data for intermediary compositions are shown as straight lines between the end members.

of the underlying cause of microcracking during cooling [12, 29].

2.3. $CaZr_4P_6O_{24}$ and $BaZr_4P_6O_{24}$

Crystalline solutions with $CaZr_4P_6O_{24}$ and $BaZr_4P_6O_{24}$ as end members [21, 22] have not been reported. The thermal expansion for the a-parameter is negative for the Ca-end-member and positive for the Ba-end-member and vice versa for the c-parameter. The axial thermal expansions for crystalline solutions between the end members are not known, but it may be speculated that they can be described as interpolated lines between the end members as shown in Fig. 2, though the actual shape may deviate from a straight line. It should therefore be possible to find an intermediary composition with zero thermal expansion anisotropy.

3. [NZP] thermal expansion properties due to M- and B-site substitutions

The mechanism of the axial thermal expansion can be explored by a comparison within series of [NZP] compositions with selected ionic substitutions. There are reported many [NZP] compositions with substitutions at the M-sites, the A-site and the B-site [13–27]. However, thermal expansion data is not abundant for A-site substituted [NZP], but a reasonable amount of data can be found for M-site and B-site substituted [NZP] [7–11, 13–16, 18–28, 30–33]. In the following section thermal expansion data for [NZP] materials is compiled with Zr only at the A-site, but with substitutions at the M-sites and B-site. The intent is to provide the reader with tools to predict thermal expansion data for other systems with different A-site ions.

3.1. Data for the systems $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$, M = 2Na, Ca, Sr, and Ba

TABLE I The thermal anisotropy, $\alpha_c - \alpha_a$ for the composition $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$, M = 2Na, Ca, $Ca_{0.5}Sr_{0.5}$, Sr, and Ba for $x = 0$ and $x = 0.37$

M Me^+ or Me^{2+}	$\alpha_c - \alpha_a$ ($x = 0$) $\cdot 10^{-6}$°C^{-1}	$\alpha_c - \alpha_a$($x = 0.37$) $\cdot 10^{-6}$°C^{-1}	Ref.
Na	25.5	25.3	24
Ca	8.5		18, 21, 22
$Ca_{0.5}Sr_{0.5}$	7.1	10.3	23
Sr	−0.3	6.9	2, 20, 21, 22
Ba	−4.8	5.2	2, 20, 21, 22

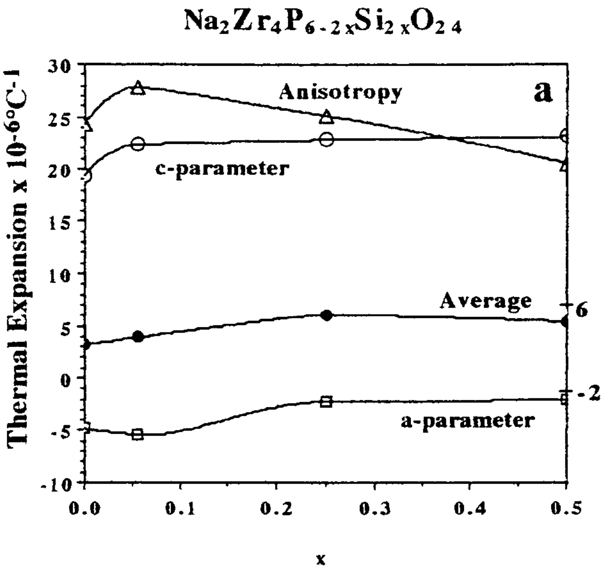

Figure 3 Variation of axial thermal expansion coefficients from room temperature up to 1000°C as a function of the content of silicon (x) in $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$, where M = 2Na (a) [24], $Ca_{0.5}Sr_{0.5}$ (b) [23], Sr (c) [21], and Ba (d)[21]. Note the difference in the scale of the thermal expansion. (*Continued.*)

The changes in the lattice in which phosphorus is substituted by silicon is well described for the system $Na_{1+y}Zr_2Si_yP_{3-y}O_{12}$. This system is often called the Nasicon system [24]. The most studied compositions range from $y = 2$ to $y = 2.2$. These compositions are technically important since they have a maximum sodium ionic conductivity and also a low thermal expansion anisotropy, though the thermal expansion is not especially low [4]. When comparing with other [NZP] systems with an M^{+2} ion at the M site it is more consistent to write the formula as $(2Na)_{1+x}Zr_4\,P_{6-2x}Si_{2x}O_{24}$. See Table I and Fig. 3a., which show the thermal expansion coefficients up to 1000°C for $0 \leq x \leq 0.5$, a range in which all Nasicon compositions are hexagonal.

Two other good examples are $Sr_{1+x}Zr_4P_{6-2x}\,Si_{2x}O_{24}$ and $Ba_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ [28]. A member of the latter system ($x = 0.25$) has been shown to be a good coating material for high temperature applications because of low thermal expansion, low thermal expansion anisotropy and a minimum of microcracking during cooling [1, 18, 12, 21, 28]. In both of these systems the axial thermal expansions change with the value of x. For $x = 0$ the thermal expansion in the a-direction, α_a, is larger than the thermal expansion in the c-direction, α_c, whereas for $x = 0.5$ $\alpha_a < \alpha_c$. This means that between the two values of x (0 and 0.5) there exists a composition for which the axial thermal expansions match, wherefore the anisotropy is zero. See Fig. 3c

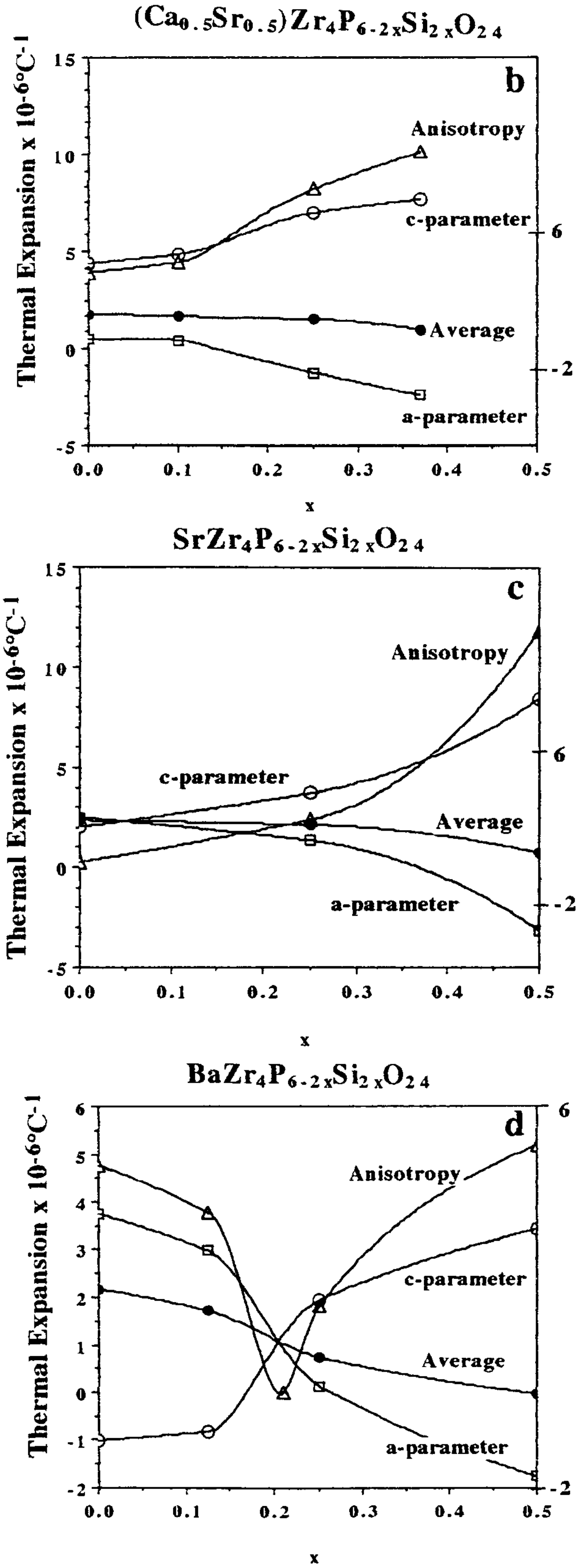

Figure 3 (*Continued.*)

and d. The thermal expansion data [23] for the system $(Ca,Sr)_{1+x}Zr_4P_{6-2x}$ $Si_{2x}O_{24}$ are plotted in Fig. 3b. See also Table I.

From these examples it is possible to deduce some generalizations. Zero thermal expansion appears on Fig. 3 as cross-over points between the thermal expansions of the a-axis and the c-axis. With decreasing ionic M-site radius there is a shift of this point towards smaller x-values. For M-site ions being $(Ca_{0.5}Sr_{0.5})$ or Na the lines do not cross at-all, and therefore these series do not contain any zero thermal expansion compositions. However, for the M-site ion being Ca/Sr, the thermal axial thermal expansions do show some convergence towards smaller x-values, but there is nearly no convergence for the still smaller Na ion.

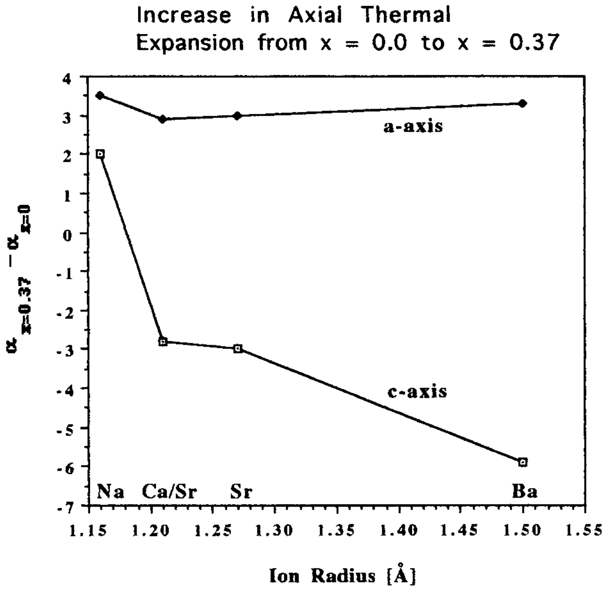

Figure 4 Increase in axial thermal expansion from no substitution of P by Si in the composition $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ ($x = 0$) to partly Si-substituted P ($x = 0.37$) with increasing size of the ion at the M-position.

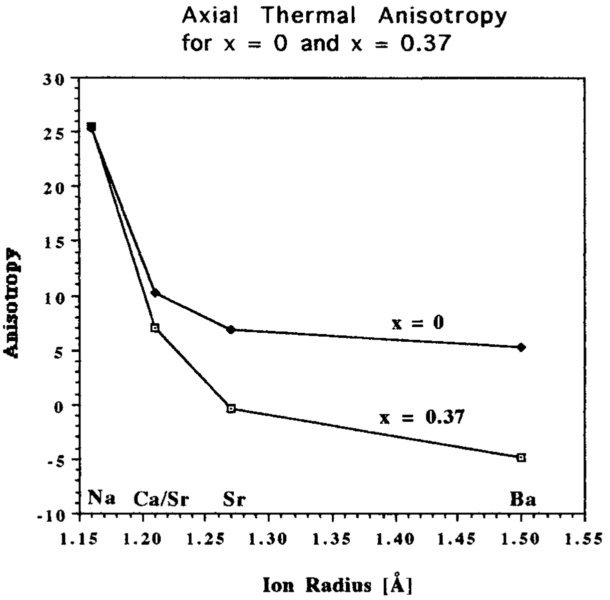

Figure 5 Axial thermal expansion anisotropies ($\alpha_c - \alpha_a$) for zero substitution of P by Si in the composition $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$ ($x = 0$) and partly Si-substituted P ($x = 0.37$) with increasing size of the ion at the M-position.

3.2. M- and B-site substituted [NZP]. General trends in thermal expansion behavior

An alternative way of plotting the results shown in Fig. 3 is shown in Figs 4 and 5 for the systems $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$, M = 2Na, Ca, Sr, and Ba. Fig. 4

TABLE II [NZP] type candidates for end members to design new coating [NZP] materials [15, 18, 22, 23, 25–27, 31–33]

Material	Thermal expansion $[^\circ C^{-1} \cdot 10^{-6}]$	
	α_{av}	$\alpha_c - \alpha_a$
$Na_{2.5}Zr_2P_{1.5}Si_{1.5}O_{12}$	6.7	12.6
$KZr_2P_3O_{12}$	0	11.7
$SrZr_4P_6O_{24}$	2.4	−0.3
$BaZr_4P_6O_{24}$	2.17	−4.77
$Ca_{0.5}Sr_{0.5}Zr_4P_6O_{24}$	−0.1	1.8
$Ba_{1.25}Zr_4P_{5.5}Si_{0.5}O_{24}$	−0.29	6.14
$KTi_2P_3O_{12}$	2.6	8.4
$CaTi_4P_6O_{24}$	6.74	−6.21
$La_{0.33}Ti_4P_6O_{24}$	0.8	0.2
$Ca_{1.4}Mg_{0.4}Zr_4P_6O_{24}$	5.3	1.65
$NbZrP_3O_{12}$	−1.9	4.6
$Sr_{0.125}Nb_{0.25}Zr_{1.5}P_3O_{12}$	2.4	0.3
$Sr_{1.125}Zr_4P_{5.5}Si_{0.5}O_{24}$	2.13	2.38

shows the difference in thermal expansion anisotropy between a partial substitution of Si for P ($x = 0.37$) and the unsubstituted composition ($x = 0$) as plotted against the size of the M-site ion. With Si substitution for P there is hardly any influence on the thermal expansion of the a-parameter with increasing size of the M-site ion, but the thermal expansion of the c-parameter strongly decreases with increasing size of the M-site ion. Fig. 5. shows the axial thermal anisotropies for $x = 0$ and $x = 0.37$ for the systems $M_{1+x}Zr_4P_{6-2x}Si_{2x}O_{24}$, M = 2Na, Ca, Sr, and Ba. Both of these anisotropies decrease with increasing site-M size ion. For $x = 0.37$ the anisotropy decreases more, and it changes sign for a site-M ion radius smaller than about 1.25 Å

4. Discussion

4.1. [NZP] protection material

The purpose of this study was to predict which new [NZP] compositions have desired thermal expansion and near zero thermal expansion anisotropy, and which therefore could be used to protect other materials. This can be done by selecting suitable [NZP] end members [15, 18, 22, 23, 25–27, 31–33] some of which are shown Table II, and comparing the thermal expansion data with those of commonly used structural substrate materials. The coating material should have a thermal expansion matching that of the substrate. At the same time it should have zero or minimum thermal expansion anisotropy. Note that although the thermal expansion anisotropy $\alpha_c - \alpha_a$ is not necessarily especially low for the end members as seen in Table II, yet for the selection of end members $\alpha_c - \alpha_a$ should be positive for one end member and negative for the other.

4.2. An example of an NZP coating material

A coating for certain ceramic substrate materials with relatively low thermal expansion such as Brick Materials, Certain Glasses, Porcelain, and carbon fibers could be found when choosing adequate [NZP] end members for example the Ca/Ba system as shown in Fig. 2. In this system an ideal [NZP] structures would have zero thermal expansion anisotropy and a thermal expansion around $3 \cdot 10^{-6} {}^\circ C^{-1}$, which is also the thermal expansion of many ceramic substrates.

5. Conclusions

When choosing among already known [NZP] family compositions there are possibilities by certain substitutions to create new materials with:

1) desired thermal expansion
2) near-zero thermal expansion anisotropy.

Acknowledgements

Supported in part by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as a part of the Ceramic Technology Project of the Materials Development Program, Under Contract DE-AC05-84OR21400 with Martin-Marietta Systems, Inc.

References

1. S. Y. LIMAYE, D. K. AGRAWAL and H. A. MCKINSTRY, US Patent no. 4,801,566 (1989).
2. J. BROWN, D. HIRSCHFELD, D-M. LIU, Y. YANG, T. LI, R. E. SWANSON, S. VAN AKEN and J-M. KIN, US Patent no. 5,102,836 (1992).
3. R. W. DAVIDGE and D. J. GREEN, *J. Mater. Sci.* **3**(6) (1968) 629.
4. T. V. TVERGAARD and J. W. HUTCHINSON, *J. Amer. Ceram. Soc.* **71**(3) (1988) 157.
5. F. A. HUMMEL, *Interceram.* **33**(6) (1984) 27.
6. R. ROY, D. K. AGRAWAL and H. A. MCKINSTRY, *Annu. Rev. Mater. Sci.* **19** (1989) 59.
7. T. K. LI, D. A. HIRSCHFELD and J. J. BROWN, *J. Mater. Res.* **9**(8) (1994) 2014.
8. D. K. AGRAWAL, G. HARSHÉ, E. BREVAL and R. ROY, *ibid.* **11**(12) (1996) 3158.
9. W. R. BUESSEM and F. F. LANGE, *Interceram* **15**(3) (1996) 229.
10. N. SRIDHAR, W. YANG, D. J. SROLOVITZ and E. R. FULLER, *J. Am. Ceram. Soc.* **77**(5) (1994) 123.
11. E. BREVAL, D. K. AGRAWAL and E. C. SUBBARAO, in Ceramic Transactions of the American Ceramic Society Annual Meeting April 1993, Cincinnati, Ohio, in the Series Low-Expansion Materials, Ceramic Transaction. V 52, edited by D. P. Stinton and S. Y. Limaye, Westerville Ohio (1994) p. 35.
12. V. SRIKANTH, E. C. SUBBARAO, D. K. AGRAWAL and C-Y HUANG, *J. Am. Ceram. Soc.* **74**(2) (1991) 365.
13. E. BREVAL, V. SRIKANTH and E. C. SUBBARAO, *ibid.* **78**(9) (1995) 2541.
14. A. C. D. CHAKLADER and F. BRADLEY, in Proceedings at UNITEC '89, Vol. 2, edited by L. J. Trostel Jr., (American Ceramic Society for UNITECR, 1989) 1225.
15. E. BREVAL and D. K. AGRAWAL, *British Ceramic Transactions* **94**(1) (1995) 27.
16. L. O. HAGMAN and P. KIERKEGAARD, *Acta Chem. Scand.* **22** (1968) 1822.
17. J. P. BOILOT, G. COLLIN and Ph. COLOMBAN in "Progress in Solid State SubsElectrolytes" edited by T. A. Wheat, A. Ahmad and A. Kuriakose ERP/MSL 83-94(TR), Energy, Mines and Resources, Ottawa, Canada (1989) p. 91.
18. C.-Y. HUANG, A Thesis in Ceramic Science, Penn State University, 1990.
19. E. BREVAL, H. A. MCKINSTRY and D. K. AGRAWAL, *British Ceramics Transactions and Journal* **93**(6) (1994) 239.
20. T. K. LI, D. A. HIRSCHFELD, S. VANAKEN, Y. YANG and J. J. BROWN, *J. Mater. Sci.* **8**(11) (1993) 2954.

21. D. K. AGRAWAL, C.-Y. HUANG and H. A. MCKINSTRY, *International Journal of Thermophysics* **12**(4) (1984) 697.
22. C.-Y. HUANG, D. K. AGRAWAL and H. A. MCKINSTRY, *J. Mater. Sci.* **9**(8) (1994) 2005.
23. E. BREVAL, H. A. MCKINSTRY and D. K. AGRAWAL, *J. Am. Ceram. Soc.* **81**(4) (1998) 926.
24. H. Y.-P. HONG, *Mat. Res. Bull.* **11** (1976) 173.
25. T. OTA, P. JIN and I. YAMAI, *J. Mater. Sci. Lett.* **12** (1993) 1348.
26. R. BROCHU, M. LOUËR, M. ALAMI, M. ALQARAOUI and D. LOUËR, *Mat. Res, Bull.* **32**(1) (1997) 113.
27. D. TAYLOR, *British Ceramics, Transactions and Journal* **83–93** (1984–1993).
28. R. NAGESWARAN, J. ZHENG and S. Y. LIMAYE Report ORNL/96/34, Oak Ridge National Laboratory, Research sponsored by U.S. Department of Energy (1995) 248.
29. V. SRIKANTH, E. C. SUBBARAO and G. V. RAO, *Ceramics International* **18** (1992) 251.
30. W. R. MANNING, O. HUNTER, JR., F. W. CALDERWOOD and D. W. STACY, *J. Am. Ceram. Soc.* **55**(7) (1972) 42.
31. PH. COLOMBAN and E. MOUCHON, *Solid State Ionics* **72** (1994) 209.
32. R. BROCHU, M. EL-YACOUBI, M. LOUËR, A. SERGHINI, M. ALAMI and D. LOUËR, *Mat. Res, Bull.* **32**(1) (1997) 15.
33. I. YAMAI and T. OTA, *J. Am. Ceram. Soc.* **76**(2) (1993) 487.

Received 23 April
and accepted 10 December 1999