Thermal Expansion and Crystal Chemistry of (Sr\textsubscript{1-x}, K\textsubscript{2x})Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} Ceramic

BY DEAN-MO LIU, LI-JIAUN LIN AND CHIEN-JEN CHEN

Materials Research Laboratories, Industrial Technology Research Institute, Hsingchu, Chutung 31015, Taiwan

(Received 29 November 1994; accepted 10 May 1995)

Abstract

Thermal expansion of (Sr\textsubscript{1-x}, K\textsubscript{2x})Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} (SrKZP) (with x=0-1) ceramic was investigated using both a dilatometer and a high-temperature X-ray diffractometer. The coefficients of thermal expansion (CTEs) of the SrKZP ceramic measured by the dilatometer demonstrate a similar trend as those from high-temperature X-ray diffraction. Both measurements show an ultra-low CTE at x=0.5; nevertheless, this composition shows significant lattice thermal-expansion anisotropy (TEA), while the minimum TEA appears with composition x=0.2. Although it possessed a sufficient degree of TEA, the x=0.5 composition showed no visible microcracks or negligible microcracks over a grain size as large as 15 μm. A transition of space group from R\textsuperscript{3} to R\textsuperscript{3}c with composition between x=0.3 and x=0.5 has been observed. The crystal structure of the SrKZP ceramic with possible occupations of strontium and/or potassium within the lattice in relation to their influence on the CTEs is proposed.

Introduction

The sodium zirconium phosphate NaZr\textsubscript{2}P\textsubscript{3}O\textsubscript{12} [NZP] structure, which was first examined by Hagman & Kierkegaard (1968), shows a number of important features, such as low thermal expansion (Alamo & Roy, 1984; Agrawal & Stubican, 1985), high ionic conductivity (Goodenough, Hong & Kafalas, 1976) and enormously varied ionic substitution in the structure (Alamo & Roy, 1984). A common feature in [NZP]-type ceramics is thermal-expansion anisotropy (TEA), which usually limits their applications in practice, and arises from their opposing axial coefficients of thermal expansion (CTEs) (Oota & Hamai, 1986; Limaye, Agrawal & McKinstry, 1987; Oota, Jin & Yamai, 1989; Srikanth, Subbarao, Agrawal, Huang & Roy, 1991; Brown et al., 1992); one crystallographic direction contracts upon heating or cooling while the other expands. However, this undesired characteristic can be diminished or minimized by the incorporation of materials having opposite axial CTEs, such as (Ca\textsubscript{1-x}, Sr\textsubscript{x})Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} (Limaye, Agrawal, Roy & Mehrotra, 1991) and (Ca\textsubscript{1-x}, Mg\textsubscript{x})Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} (Brown et al., 1992), where CaZr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} has a positive CTE in the c direction and a negative CTE in the a direction while Sr\textsubscript{2}Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} and MgZr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} have negative ones in the c direction and positive ones in the a direction. Consequently, microcracking induced by TEA can be avoided or minimized to some extent.

In a previous study, the present authors demonstrated a new ceramic of an [NZP]-type compound with chemical formula (Sr\textsubscript{1-x}, K\textsubscript{2x})Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} (SrKZP), which was synthesized using the sol-gel method (Chen, 1993). The SrKZP ceramic illustrates sufficient mechanical properties compared to other [NZP]-type materials (Chen, Lin & Liu, 1994) and lower values of thermal conductivity (Liu, Chen & Lin, 1994), making the material a prime candidate for thermal insulation in further improvement of functional performance and also for structural use, especially in those situations where thermally induced stresses are critical.

In the present study, a solid solution between two end compounds, SrZr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} and KZr\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, was synthesized using a sol-gel method (Chen, 1993). The former composition exhibits expansion in the crystallographic a direction and contraction in the c direction (Limaye et al., 1987), whilst the latter contracts in the a direction and expands in the c direction (Lenain, McKinstry, Alamo & Agrawal, 1987). By the combination of these two compounds in appropriate proportions to form a single phase, a ceramic with a minimum TEA and/or a near-zero CTE can be expected. The axial CTE is determined using a high-temperature powder X-ray diffractometer. For comparison purposes, dilatometric CTE data are employed.

Experimental procedures

The single-phase (Sr\textsubscript{1-x}, K\textsubscript{2x})Zr\textsubscript{4}(PO\textsubscript{4})\textsubscript{6} ceramic was synthesized by a sol-gel method described by Chen (1993). The specimens were prepared in a cylindrical geometry 25 mm in length and 3 mm in diameter by sintering powder compacts at 1623 K for 30 min with the aid of 2 wt%Nb\textsubscript{2}O\textsubscript{5} as sintering additive. The as-sintered specimens with density above 94% of theoretical density were employed for dilatometric measurement, from room temperature to 773 K. The axial thermal expansion of the ceramic was measured for a powder form, prepared by calcination at 1128 K for 1 h with a high-temperature X-ray diffractometer (Philips PW1700).
with monochromatic Cu Kα radiation. The X-ray diffraction patterns were identified by means of a computer installed to facilitate phase analysis. The lattice parameters are determined using Cohen's least-squares fitting (Cullity, 1978). Thirteen peaks (with peak maximum) recorded at a scan speed of 0.02° s⁻¹ from 10 to 110° 2θ were selected for calculation with an R factor within 2%.

Results and discussion

**Thermal-expansion characteristics**

After calcination at 1123 K for 1 h, the powders with different potassium contents were indexed on a rhombohedral cell having typical [NZP] structure. Fig. 1 illustrates a comparison of thermal-expansion coefficients obtained from 298 to 773 K through high-temperature powder X-ray diffraction and dilatometry, respectively. The specimens employed for dilatometric measurement have a mean grain size of 3–5 μm. A similar trend in the CTE was observed in both measurements, i.e. from a positive value at x < 0.5, to near zero at x = 0.5, then down to a negative value when x > 0.5. This variation in CTE clearly substantiates the reverse effect of potassium on SrZr₄(PO₄)₆, which is analogous to the effect of ion substitution on the variation of CTE for other [NZP]-type ceramics (Brown et al., 1992; Limaye et al., 1991). However, the CTEs obtained by dilatometry have values lower than those obtained by high-temperature X-ray diffraction. A constraint effect arising from stress formation due to grain orientation would have occurred among adjacent/bonded grains within the sintered body during a dilatometric test, which results in a lower CTE (Liu & Brown, 1993; Kuszyk & Bradt, 1973). Since the cracks tend to heal as temperature increases, a proportion of the CTE for the crack-free body may therefore be compensated by this healing process, finally resulting in a lower CTE compared to that of corresponding crack-free solids. An examination by scanning electron microscopy shown in Fig. 2 with composition of x = 0.5 as a representative shows that no visible or negligible microcracks in the polished surface are observed. This suggests that the lower values of CTE in the sintered SrKZP ceramic may principally result from the constraint effect. However, for a thermal cyclic measurement on the ceramic, Fig. 3 shows a small hysteresis loop that occurs on return to room temperature, indicating that some small cracks that cannot be

![Fig. 1](image1.png)

**Fig. 1.** Thermal-expansion coefficients of SrKZP ceramic in terms of potassium content for powder and as-sintered compact forms.

By considering the strain energy in terms of the fractured surface energy, Kuszyk & Bradt (1973) have indicated that internal rupture is strongly related to polycrystalline ceramics having large thermal-expansion anisotropy (TEA). Microcracking is likely to occur once the grain size of the material exceeds a critical value, and this usually leads to lower values of CTEs due to recombination of cracks (Liu & Brown, 1993; Kuszyk & Bradt, 1973). However, for a fine-grained ceramic, the constraint effect may be negligibly small due to either a lower strain field accompanied by differential stresses or cancellation of stresses among highly randomly oriented grains (Rice, 1977).

![Fig. 2](image2.png)

**Fig. 2.** A polished surface of the SrKZP with composition x = 0.5.

![Fig. 3](image3.png)

**Fig. 3.** Thermal cyclic measurement on thermal expansion of the SrKZP ceramic shows a small hysteresis loop on return to room temperature.
Table 1. Axial CTE, TEA and lattice volume of the SrKZP ceramic obtained by a high-temperature powder X-ray diffraction analysis

| Potassium (x) | \( \alpha_a \times 10^{-6} \text{ K}^{-1} \) | \( \alpha_c \times 10^{-6} \text{ K}^{-1} \) | \( |\alpha_a - \alpha_c| \times 10^{-6} \text{ K}^{-1} \) | Volume (Å\(^3\)) |
|--------------|---------------------------------|---------------------------------|---------------------------------|---------------|
| 0.0          | 3.81                            | -2.80                           | 6.61                            | 1531.55       |
| 0.2          | 3.44                            | 2.49                            | 0.95                            | 1533.64       |
| 0.5          | -3.68                           | 6.46                            | 10.14                           | 1566.87       |
| 0.8          | -4.90                           | 6.80                            | 11.7                            | 1567.37       |
| 1.0*         | -3.40                           | 3.7                             | 7.1                             | 1568.48       |

* Data quoted from Srikanth et al. (1991).

easily identified by means of scanning electron microscopy are present.

Thermal-expansion anisotropy (TEA) of SrKZP was determined from the crystallographic axial CTE as given in Table 1. A minimum TEA was seen at \( x = 0.2 \) (i.e. \( \alpha_a = 3.44 \times 10^{-6} \text{ K}^{-1}, \alpha_c = 2.49 \times 10^{-6} \text{ K}^{-1} \) and \( \Delta \alpha = 0.95 \times 10^{-6} \text{ K}^{-1} \)), and a near-zero CTE when \( x \) approached 0.5 (i.e. \( \alpha_{\text{bulk}} = -0.3 \times 10^{-6} \text{ K}^{-1} \)); however, large TEA appears at \( x = 0.5 \) (i.e. \( \Delta \alpha = 10.1 \times 10^{-6} \text{ K}^{-1} \)). According to Cleveland & Bradt (1978), the critical grain size \( (G_{\text{cr}}) \) for a brittle solid is inversely proportional to the TEA:

\[
G_{\text{cr}} = \left( \frac{14.4 \times 10^{-3}\gamma_f}{E\Delta \alpha_{\text{max}}^2\Delta T^2} \right),
\]

where \( E \) is the elastic modulus, \( \gamma_f \) is the fracture surface energy (in J m\(^{-2}\)) of the material, \( \Delta \alpha_{\text{max}} \) represents the maximum difference in thermal-expansion anisotropy and \( \Delta T \) is the temperature difference over which the elastic strain builds up. The value for \( \gamma_f/E \) of the SrKZP ceramic has not been determined, and it may be thought to have a value similar to that for the pseudobrookite, owing to their structural resemblance, i.e. their composition of chainlike linkages of polyhedra (Alamo & Roy, 1986). The critical grain size for \( x = 0.5 \) is approximately 12 μm. Accordingly, microcracks should be seen in Fig. 4, which shows the specimen having a mean grain size of approximately 15 μm obtained by annealing at 1673 K for 24 h. Upon examination of the fractured surface with a backscatter mode in scanning electron microscopy, as depicted in Fig. 5, a number of tiny light spots embedded into the matrix grains were observed. Energy-dispersive X-ray fluorescence analysis revealed that those spots were composed primarily of the elements potassium, zirconium, and phosphorus, suggesting a crystalline KZr\(_2\)(PO\(_4\))\(_3\) phase, even though their contents are too low to be detected by X-ray diffraction. This minor phase may be caused by high-temperature decomposition, i.e. at 1673 K, and/or by some unknown chemical interactions with the additive. Therefore, the as-sintered ceramic with \( x = 0.5 \) can be strictly regarded as a ‘micro/nano-composite’ with a secondary phase having a negative bulk CTE. The matrix is therefore a potassium-deficient SrKZP ceramic with a positive CTE. Accordingly, compressive stress should be developed circumferentially in the matrix side near the interface upon cooling, which may subsequently weaken the stresses induced by the constraint effect, and consequently suppresses the formation of microcracking and displays sufficient mechanical strength (Chen et al., 1994).

**Crystal chemistry of SrKZP ceramic**

The [NZP] structure represents a large number of compounds and can be expressed by the general formula

\[
M'M''A_4B_6O_{24},
\]

where \( M' \) and \( M'' \) are holes, or vacancies, that allow ionic substitutions (Alamo & Roy, 1986). This structure is composed of a three-dimensional network of PO\(_4\)
tetrahedra sharing corners with ribbonlike ZrO$_6$ octahe-
dra to form a stable and flexible framework with a
hexagonal symmetry (Lenain et al., 1987). Prior to
substitution, SrZr$_4$(PO$_4$)$_6$ has space group $R3$ with
the $M'$ position mainly occupied by Sr atoms
(Alamo & Roy, 1986), with a ribbon of O$_3$ZrO$_3$SrO$_3$-
ZrO$_3$ZrO$_3$M"O$_3$ZrO$_3$, where $M''$ is a vacancy and is
located between the ZrO$_6$ octahedra chains with a
trigonal prismatic coordination. By the addition of K
atoms, the $a$ axial lattice parameter decreases slightly
while the $c$ lattice parameter increases (Fig. 6). The
contraction in the $a$ direction associated with an
expansion in the $c$ direction at $x < 0.3$ appears to agree
well with that observed by Alamo & Roy (1986) in other
related materials, which in turn normally involve $M'$
substitution. The $R3$ hexagonal symmetry is retained. By
further increase of potassium, i.e. $x > 0.3$, a significant
variation in lattice parameters appears, i.e. the $a$ lattice
parameter increases rapidly with the amount of potas-
sum, whilst the $c$ parameter increases only slightly, with
the accompaniment of an abrupt increase in lattice
volume as shown in Fig. 7. This rapid change in lattice
parameters indicates a transition of space group from $R3$
to $R3c$ with an additional $c$ glide resulting from
occupation of $M''$ sites by K atoms. To be more specific,
the structure can thus be viewed as a ribbon of O$_3$ZrO$_3$(Sr/K)O$_3$ZrO$_3$-
KO$_3$ZrO$_3$. The resulting crystal structure of the SrKZP
can be depicted schematically as in Fig. 8, with
$M'$ and $M''$ being partially or completely occupied.

The corresponding decrease of the CTE as well as
TEA with increasing potassium content reflects an
additive effect for such physical properties. However, it
is still unclear from the viewpoint of crystal chemistry
why ionic substitution lowers these properties and how
these substituted ions affect these properties, although a
mechanism based on the rotation of polyhedra has been
proposed by Lenain et al. (1987) to explain the ultralow
CTE characteristic of the [NZP] phase. In our opinion,
we assume that in a SrKZP single crystal the partial
substitution of Sr atoms by K atoms makes the
corresponding potassium-containing polyhedron rotate
in a direction opposite to the adjacent Sr-containing
polyhedron to result in a lattice with overall lattice
movement near zero. However, further understanding of
how $M'$ or $M''$ as well as $A$ substitutions affect the CTE
and TEA characteristics in the [NZP] structure may
provide a great advantage for design purposes.
Concluding remarks

Thermal expansion of the SrKZP ceramic has been determined using dilatometry and high-temperature powder X-ray diffraction. The two measurements demonstrate a similar trend in expansivity, i.e. the CTE changes from a positive value to nearly zero at $x = 0.5$, then changes to a negative value with further increase of potassium. Minimum thermal-expansion anisotropy is established at $x$ close to 0.2. A constraint effect due to grain orientation exists in the as-sintered ceramic, which leads to lower values of the CTE compared with that in powder form.

An abrupt change in crystallographic space symmetry from $R3$ to $R3c$ occurred when $x > 0.3$, resulting from substitution of $M''$ by the K atom, which expands the structure in the $a$ direction and increases slightly in the $c$ direction; the latter being induced mainly by the effect of atom size.

The authors gratefully acknowledge the Ministry of Economic Administration of the Republic of China for supporting this research.

References


