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Thermal expansion behaviour of $M'Ti_2P_3O_{12}$ (M'=Li, Na, K, Cs) and $M''Ti_4P_6O_{24}$ (M''=Mg, Ca, Sr, Ba) compounds

C.-Y. HUANG*, D.K. AGRAWAL, H.A. McKINSTRY
Intercollege Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

The [NZP] family has been attracting considerable attention because of its potential in thermal shock-resistant applications. The compounds $M'Ti_2P_3O_{12}$ (M' = Li, Na, K, Cs) and $M''Ti_4P_6O_{24}$ (M'' = Mg, Ca, Sr, Ba) belong to this new family of low-expansion materials. The results of a systematic study undertaken to investigate the thermal expansion behaviour of these materials are reported. A correlation between the ionic size and lattice expansion was also attempted, and compounds possessing lowest bulk thermal and low anisotropy were identified.

1. Introduction

The compounds belonging to the crystal family of [NZP] have been receiving considerable attention since the parent composition $NaZr_2P_3O_{12}$ was first reported by Goodenough *et al.* [1] to have potential use as a super-ionic conductor, and several isostructural compositions in this family, reportedly possessing low-expansion characteristics as shown by Roy and co-workers [2–4]. The compounds $M'Ti_2P_3O_{12}$ (M' = Li, Na, K, Cs) and $M''Ti_4P_6O_{24}$ (M'' = Mg, Ca, Sr, Ba) belong to this [NZP] family, and are isostructural with $NaZr_2P_3O_{12}$. The most interesting part of this [NZP] family is its unique crystal structure which explains all its interesting properties. $NaZr_2P_3O_{12}$, the prototype composition, belongs to the rhombohedral crystal system with space group $R\bar{3}c$ with six formula units in a unit cell. 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 from these rigid but deformable polyhedra. Each ZrO_6 octahedron is then connected to six PO_4 tetrahedra and each PO_4 tetrahedron is connected to four ZrO_6 octahedra [5]. The sodium or other substituting ions are located at the interstitial sites created by the framework. This open framework structure offers a wide variety of ionic substitution at different lattice sites. For instance, almost all of the alkali and alkaline earth cations can be substituted for the Na^+ ion; Cr^{3+}, Ti^{4+}, Hf^{4+}, Ge^{4+}, Sn^{4+}, and Ta^{5+} for Zr^{4+}; and Si^{4+}, As^{5+}, and S^{6+} for P^{5+} [6].

Some of the [MTP] compositions also show ionic conductivity, for example, $LiTi_2P_3O_{12}$ demonstrates high ionic conductivity [7, 8]. The thermal expansion of NTP was first reported by Alamo and Roy in 1984 [2] and they also observed a high degree of anisotropy in its lattice thermal expansion. Oota and Yamai [9] and Rodrigo *et al.* [10] have also studied the thermal expansion of $NaTi_2(PO_4)_3$, $KTi_2(PO_4)_3$ and other related compounds. Rodrigo *et al.* used the Rietveld method [11–13] to interpret high-temperature X-ray diffraction data. For $NaTi_2(PO_4)_3$ the calculated α_a was $-4.4 \times 10^{-6}\,°C^{-1}$ and $\alpha_c = 20 \times 10^{-6}\,°C^{-1}$ from room temperature to 800 °C, where α is the coefficient of thermal expansion. Yamai and Oota [14] found that the thermal expansion of $KTi_2(PO_4)_3$ is also anisotropic. Recently, Senbhagaraman *et al.* [15] have studied and refined the crystal structure of $CaTi_4(PO_4)_6$ and $SrTi_4(PO_4)_6$, and found that in the case of CaTP, both *a* and *c* axes expand with temperature, while in SrTP, the *c* axis contracts and the *a* axis expands. However, so far no systematic study on the thermal expansion behaviour of [MTP]: $M'Ti_2P_3O_{12}$ and $M''Ti_4P_6O_{24}$ compounds has been reported. In this study, we have investigated the thermal expansion behaviour of these compounds using high-temperature X-ray diffractometry and dilatometry.

2. Experimental procedure

2.1. Sample preparation

The alkali and alkaline earth titanium phosphates ($M'Ti_2P_3O_{12}$ and $M''Ti_4P_6O_{24}$) investigated in this study were synthesized by powder-mixing (the solid-state reaction) method by using dry oxide powders as precursors. The starting materials were alkali or alkaline earth carbonates (M'_2CO_3 or $M''CO_3$), titanium oxide (TiO_2), ammonium dihydrogen phosphate ($NH_4H_2PO_4$). Stoichiometric amounts of these starting powders were weighed, hand-mixed and ground in acetone with an agate mortar and pestle. The

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*Present address: Department of Mineral Engineering, National Cheng Kung University, Tainan, Taiwan 70101.

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homogenized mixture was air dried, and heat treated at 170 °C for 16 h to remove H_2O, at 600 °C for 4 h to remove NH_3, and finally, calcined at 900 °C for 16 h to decompose carbonates. Before each heat treatment the mixture was ground and mixed again to ensure good homogeneity and, subsequently, completion of the reaction. After calcination the mixture was ground to -325 mesh (44 µm) and pressed into pellets (25 mm diameter and about 5 mm thick) with a pressure of about 150 MPa. A few drops of binder (15% polyvinyl alcohol, PVA) were sometimes added to enhance green density. The pellets were finally sintered in the temperature range 1000–1200 °C for 48 h, depending on the composition.

2.2. Phase identification

An automated X-ray diffractometer (Scintag PAD V, Scientific Computer and Instruments) was used for phase identification of the prepared samples. The X-ray diffraction patterns were obtained from 10°–70° 2θ at a speed of $2^\circ\ 2\theta\ \mathrm{min}^{-1}$ and were compared with the corresponding Joint Committee on Powder Diffraction Standards (JCPDS) patterns. There were no JCPDS patterns for $MgTi_4P_6O_{24}$; therefore, its pattern was indexed by comparison with that of CaTP. In most cases, the prepared samples showed single-phase material; sometimes a minor amount of unreacted TiO_2 was observed.

2.3. Bulk linear thermal expansion measurements

The bulk linear thermal expansion of sintered samples were measured with a push-rod dilatometer (Theta Industries, Inc., Port Washington, New York). The dilatometer consists of a split furnace with a maximum operating temperature of 1200 °C, a programmable temperature controller with which the heating and cooling rates can be set, two fused silica push rods, a linear expansion measuring device (linear variable differential transformer, LVDT), a signal conditioner to use with LVDT, and an X–Y recorder to record temperature and expansion. A 0.5% precision of the system is claimed by the manufacturer. The dilatometer uses two push rods to measure the difference of thermal expansion between a sample and a reference material (fused silica) so that any possible system error can be cancelled, assuming that the same error occurs to both push rods. The dimensions of the sample and the reference material used were about 25 mm × 5 mm × 5 mm. The heating and cooling rate of the furnace was set at $4\ ^\circ\mathrm{C\ min}^{-1}$, and an intermediate temperature, as well as the peak temperature (1000 °C) was set and maintained for 30 min in order to ensure that the temperature of the sample was in equilibrium with the temperature of the furnace.

2.4. Axial thermal expansion measurements

The measurements of axial thermal expansion were made by using a high-temperature X-ray diffractometer. The dimensions of the unit cell were determined from each X-ray diffraction pattern obtained at various temperatures up to 1000 °C. The coefficients of thermal expansion in different crystallographic directions were calculated from the change of the cell dimension within a temperature range. The X-ray diffractometer made by Picker X-ray Corporation, uses a copper radiation with a nickel filter and a sodium iodide scintillation counter. The diffractometer is also equipped with a stepping motor which is automated by a microcomputer (Apple II plus) and is capable of scanning at a minimum step of 0.005° 2θ. The computer is interfaced and programmed so that it can control the scanning step and counting period, and can also collect the data. The diffractometer is also equipped with a high-temperature furnace [16]. The computer reads the temperature output from a digital thermometer and instructs the power supply to provide a proper portion of the maximum output to the furnace. After the temperature inside the furnace is stabilized, it can be maintained within less than 1° C.

A preliminary scan (fast scan) is made first in order to decide the range of each peak position for a subsequent slow scan. The fast scan is set at 0.1° 2θ steps and a counting time of 4 s at each step, from 10°–162° 2θ. The stored data are analysed by a computer program (Peaks Finder), in which the least-squares method is used to fit sections (0.7 ° 2θ per section) of the diffraction pattern. Following the preliminary scan, the slow scan was carried out and the data collected for each peak were analysed by a curve-fitting computer program in order to determine the peak position precisely. The program applied the nonlinear least-squares method to fit the profile of an X-ray diffraction peak, which was assumed to be a double Cauchy distribution.

Finally, the peak positions and the matching Miller indices are input to a computer program (Cell Parameter version 2.6) which is capable of calculating the lattice parameters of cubic, tetragonal, orthorhombic, hexagonal, and monoclinic crystals. The Cell Parameter program applies Cohen's method [17], which is based on the least-squares multiple regression method, to perform the calculation.

The measured cell parameters, a and c (in the hexagonal system), at different temperatures can then be used to calculate the average axial thermal expansion coefficients, $\bar{\alpha}_a$ and $\bar{\alpha}_c$, by

$$\bar{\alpha}_a = \frac{1}{a_1}\left[\frac{a_2 - a_1}{T_2 - T_1}\right] \tag{1a}$$

and

$$\bar{\alpha}_c = \frac{1}{c_1}\left[\frac{c_2 - c_1}{T_2 - T_1}\right], \tag{1b}$$

where a_1 and c_1 are the cell parameters at temperature T_1; and a_2 and c_2 are the cell parameters at temperature T_2.

3. Results and discussion

3.1. Phase identification

The room-temperature X-ray powder diffraction patterns of the prepared samples were obtained. Most of these patterns were indexed in the hexagonal system for convenience (although they are rhombohedral). They were further examined as to whether or not they belong to the space group $R\bar{3}c$, depending on whether the indices satisfy the extinction rule ($h0l$:$l = 2n$) of this space group. All the alkali (monovalent) titanium phosphates are rhombohedral and belong to the space group $R\bar{3}c$. CaTP and SrTP are rhombohedral but belong to the space group $R\bar{3}$, this has been confirmed recently by Senbhagaraman *et al.* [15]. $MgTi_4P_6O_{24}$ and $BaTi_4P_6O_{24}$, are also rhombohedral but belong to the space group $R\bar{3}c$.

3.2. Lattice parameters and axial thermal expansion

The room-temperature lattice parameters of M′TP and M″TP are presented in Table I. The variation of lattice parameters with temperature is illustrated in Fig. 1a and b. In $LiTi_2P_3O_{12}$, the a-parameter varies little, while the c-parameter and the volume of the unit cell increase between 25 and 1000 °C. In $NaTi_2P_3O_{12}$, the a-parameter decreases, and the c-parameter and the volume of unit cell increase between 27 and 1000 °C. In $KTi_2P_3O_{12}$, the a-parameter decreases between 22 and 500 °C, and then increases between 500 and 1000 °C, while the c-parameter increases between 22 and 1000 °C, and the volume of unit cell varies little between 22 and 200 °C, and then increases between 200 and 1000 °C. In $RbTi_2P_3O_{12}$, both lattice parameters and the cell volume increase between 28 and 600 °C. Measurements above 600 °C could not be made in this compound.

In $MgTi_4P_6O_{24}$ the a-parameter remains practically constant with temperature up to 800 °C, and the c-parameter and the cell volume both increase between 27 and 1000 °C. In $CaTi_4P_6O_{24}$, the a-parameter and the volume of unit cell increase linearly between 26 and 1000 °C, while the c-parameter varies little between 26 and 300 °C, and then increases between 300 and 1000 °C. In $SrTi_4P_6O_{24}$ the a-parameter and the volume of the unit cell increase between 25 and 1000 °C, but the c-parameter remains unchanged between 25 and 800 °C, and then decreases between 800 and 1000 °C. In $BaTi_4P_6O_{24}$, the a-parameter and the volume of unit cell increase between 23 and 1000 °C, while the c-parameter remains unchanged up to 300 °C, and then increases between 300 and 1000 °C.

TABLE I Lattice parameters and volume of the unit cell of $M'Ti_2P_3O_{12}$ and $M''Ti_4P_6O_{24}$ at room temperature

Compound	a (nm)	c (nm)	Vol (10^{-3} nm^3)
$LiTi_2P_3O_{12}$	0.85115	2.08554	1308.46
$NaTi_2P_3O_{12}$	0.84871	2.17719	1358.14
$KTi_2P_3O_{12}$	0.83585	2.30749	1396.17
$RbTi_2P_3O_{12}$	0.82888	2.35666	1402.20
$MgTi_4P_6O_{24}$	0.85028	2.09174	1309.67
$CaTi_4P_6O_{24}$	0.83582	2.20042	1331.26
$SrTi_4P_6O_{24}$	0.82866	2.25932	1343.57
$BaTi_4P_6O_{24}$	0.83426	2.30190	1387.46

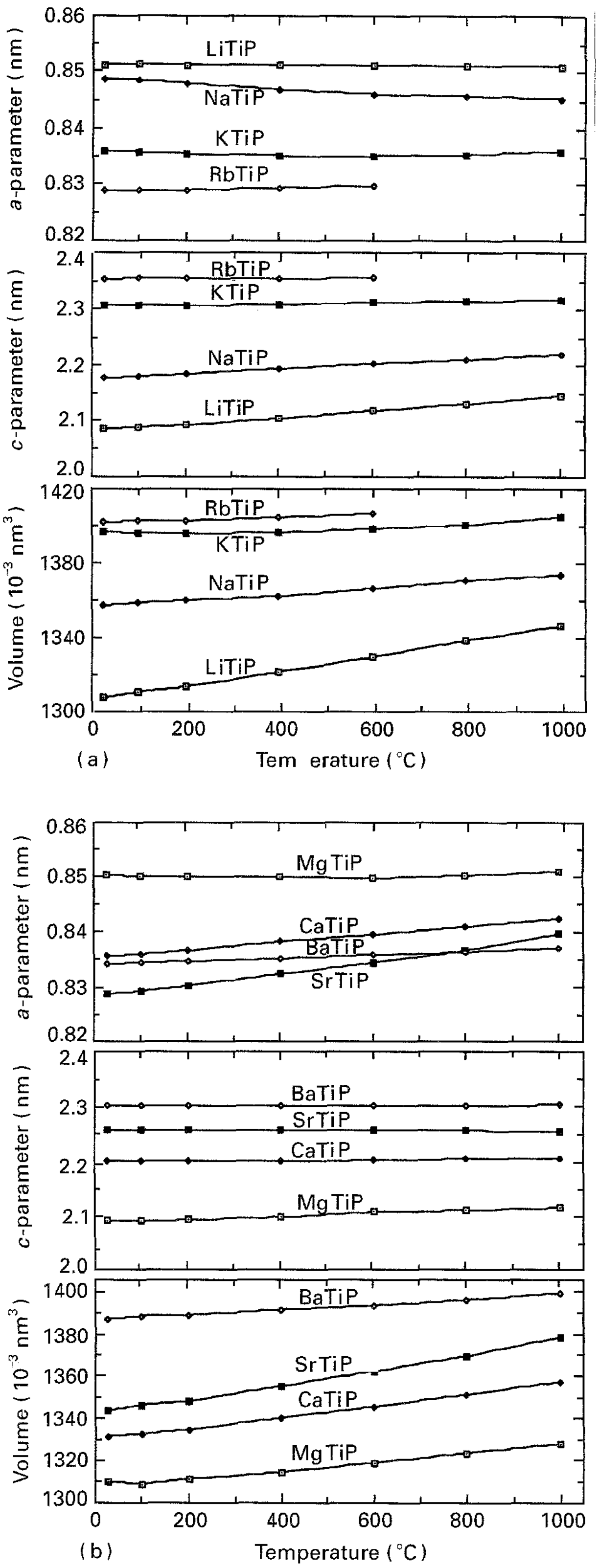

Figure 1 Variation of cell parameters and volume of (a) alkali titanium phosphates and (b) alkaline earth titanium phosphates with temperature.

It is to be noted that the a-parameter becomes smaller, and the c-parameter and the cell volume become larger as a larger alkali or alkaline earth ion is substituted into the [NZP] structure. It is normal that the substitution of a larger ion increases the cell dimension (as in the case of the c-parameter), but it is not normal that such a substitution would decrease the a-parameter. However, this phenomenon can be

TABLE II Average axial thermal expansion coefficients of (α in $10^{-6}\,°C^{-1}$) of $M'Ti_2P_3O_{12}$ and $M''Ti_4P_6O_{24}$ compounds.

Compounds	$\bar{\alpha}_a$	$\bar{\alpha}_c$	$\bar{\alpha}_V/3$	$\lvert\bar{\alpha}_a - \bar{\alpha}_c\rvert$	Temperature range (°C)
$LiTi_2P_3O_{12}$	− 0.05	30.59	10.16	30.64	25–1000
$NaTi_2P_3O_{12}$	− 3.88	20.74	4.28	24.62	27–1000
$KTi_2P_3O_{12}$	0.21	5.73	2.05	5.52	25–1000
$RbTi_2P_3O_{12}$	1.88	3.15	2.31	1.27	28–600
$MgTi_4P_6O_{24}$	0.89	12.54	4.78	11.65	27–1000
$CaTi_4P_6O_{24}$	8.77	2.56	6.74	6.21	28–1000
$SrTi_4P_6O_{24}$	14.04	− 1.83	8.79	15.87	25–1000
$BaTi_4P_6O_{24}$	3.73	1.37	2.95	2.36	28–1000

explained on the basis of the coupled rotation of the polyhedra [18]. There is an exception to this trend, that is the *a*-parameter of $BaTi_4P_6O_{24}$ is larger than that of $SrTi_4P_6O_{24}$ (the size of Ba^{2+} is larger than the size of Sr^{2+}) from room temperature to 600 °C, although it becomes smaller above 800 °C. This may be due to the fact that these two compounds do not belong to the same space group symmetry.

In order to examine the variation of the axial thermal expansions with the compositions, the average axial thermal expansion coefficients, $\bar{\alpha}_a$ and $\bar{\alpha}_c$, and one-third of the average volume thermal expansion coefficient, $\bar{\alpha}_V/3$, which is an equivalent of the estimated bulk linear thermal expansion coefficient, are listed in Table II. Also listed in the table is the absolute value of the difference between the average axial thermal expansion coefficients, $|\bar{\alpha}_a - \bar{\alpha}_c|$, which is a measure of the degree of anisotropy in the axial thermal expansions.

Fig. 2 shows the variation of $\Delta a/a$, $\Delta c/c$, and $\Delta V/V$ with temperature for alkali titanium phosphates. $\Delta a/a$ of $LiTi_2P_3O_{12}$ and $RbTi_2P_3O_{12}$ is mostly positive and that of $NaTi_2P_3O_{12}$ and $KTi_2P_3O_{12}$ is mostly negative. $\Delta c/c$ and $\Delta V/V$ are all positive or near zero. $\bar{\alpha}_c$ is always larger than $\bar{\alpha}_a$ of the compounds in this group (Table II). As the composition changes from $LiTi_2P_3O_{12}$ to $RbTi_2P_3O_{12}$ (smaller to larger alkali ion) $\bar{\alpha}_a$ and the $\bar{\alpha}_c$ approach each other (Fig. 3) and also reach a smaller $\bar{\alpha}_V/3$ and $|\bar{\alpha}_a - \bar{\alpha}_c|$ (Table II). In this group, $RbTi_2P_3O_{12}$ has relatively small thermal expansion and the smallest anisotropy.

Fig. 4 shows the variation of $\Delta a/a$, $\Delta c/c$, and $\Delta V/V$ with temperature for alkaline earth titanium phosphates. $\Delta a/a$ is always positive or near zero, $\Delta c/c$ is always positive except for that of $SrTi_4P_6O_{24}$, and $\Delta V/V$ is always positive. In general, a relatively small expansion in one direction is always coupled with a relatively large expansion in another, except for $BaTi_4P_6O_{24}$. For $MgTi_4P_6O_{24}$, $\bar{\alpha}_c$ is larger than $\bar{\alpha}_a$; and for the other three compounds in this group, $\bar{\alpha}_c$ is smaller than $\bar{\alpha}_a$ (Fig. 5), which is similar to the case of $SrZr_4P_6O_{24}$ and $BaZr_4P_6O_{24}$, but it is different from the case of other compounds listed in Table II (larger $\bar{\alpha}_c$ and smaller $\bar{\alpha}_a$).

There is no clear dependence of the thermal expansion on the size of the alkaline earth ion in alkaline earth titanium phosphates (Fig. 5); however, if the compounds with the same space group symmetry are compared with each other (i.e. $MgTi_4P_6O_{24}$ and $BaTi_4P_6O_{24}$, $R\bar{3}c$; $CaTi_4P_6O_{24}$ and $SrTi_4P_6O_{24}$, $R\bar{3}$), $\bar{\alpha}_a$ increases and $\bar{\alpha}_c$ decreases as a larger alkaline earth ion is substituted (Table II).

Among these titanium-based NZP compounds, $BaTi_4P_6O_{24}$ is the best choice for low thermal expansion applications because it has a smaller $\bar{\alpha}_a$ and the

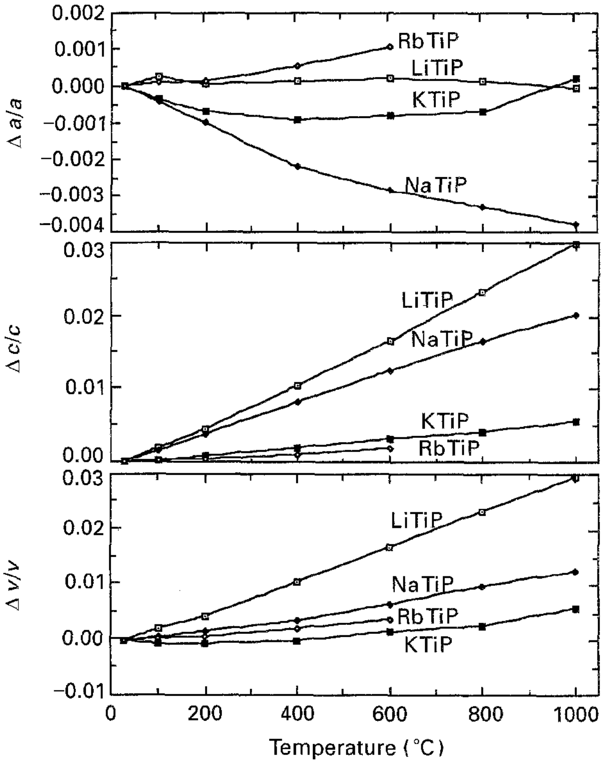

Figure 2 Variation of axial and volume thermal expansions of alkali titanium phosphates with temperature.

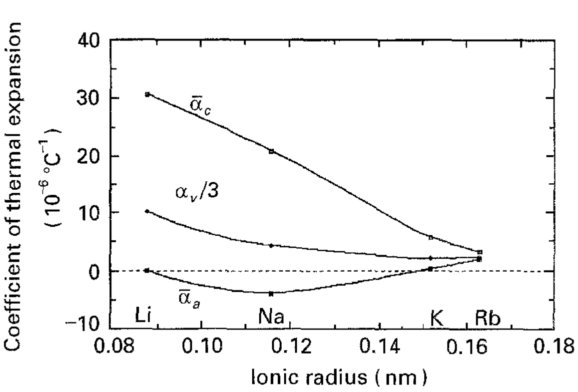

Figure 3 Variation of axial thermal expansion coefficients with the size of alkali ion in alkali titanium phosphates.

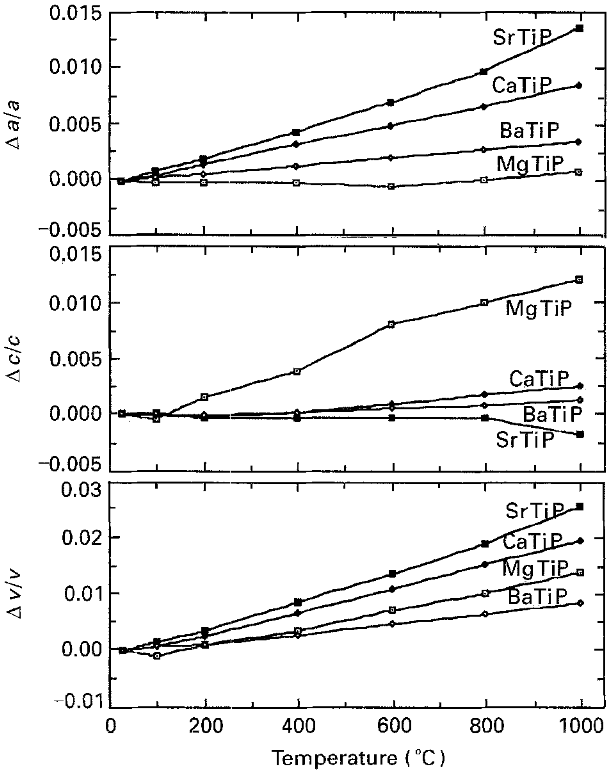

Figure 4 Variation of axial and volume thermal expansions of alkaline earth titanium phosphates with temperature.

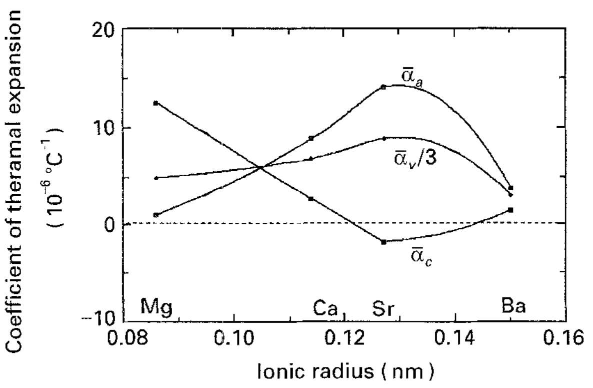

Figure 5 Variation of axial thermal expansion coefficients with the size of alkaline earth ion in alkaline earth titanium phosphates.

smallest $\bar{\alpha}_c$, $\bar{\alpha}_V/3$, and $|\bar{\alpha}_a - \bar{\alpha}_c|$ between room temperature and 1000 °C (Table II).

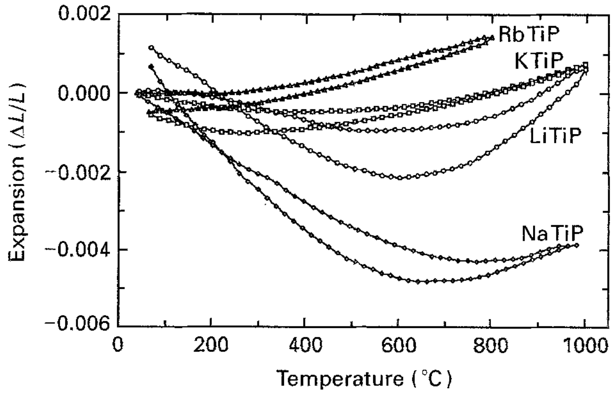

Figure 6 Thermal expansion curves of alkali titanium phosphates obtained by dilatometry.

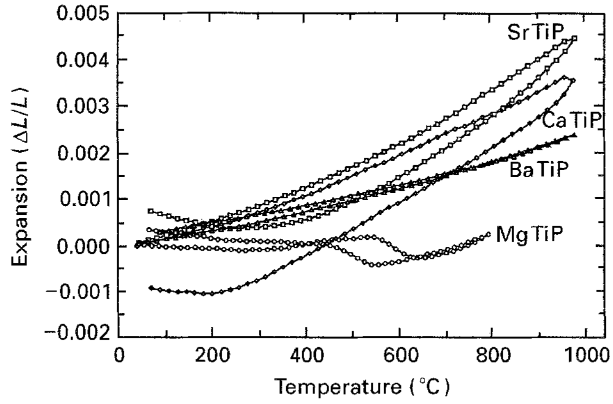

Figure 7 Thermal expansion curves of alkaline earth titanium phosphates obtained by dilatometry.

TABLE III Coefficients of bulk linear thermal expansion (α in 10^{-6} °C^{-1}) of $M'Ti_2P_3O_{12}$ and $M''Ti_4P_6O_{24}$ compounds.

Compounds	Bulk linear expansion		
	$\bar{\alpha}_{ave}$	$\bar{\alpha}_{up}$	$\bar{\alpha}_{down}$
$LiTi_2P_3O_{12}$	−0.11	0.70	−0.91
$NaTi_2P_3O_{12}$	−4.55	−3.97	−5.13
$KTi_2P_3O_{12}$	0.99	0.73	1.25
$RbTi_2P_3O_{12}$	2.15	1.84	2.46
$MgTi_4P_6O_{24}$	0.06	0.30	−0.18
$CaTi_4P_6O_{24}$	4.22	3.84	4.60
$SrTi_4P_6O_{24}$	4.28	4.72	3.84
$BaTi_4P_6O_{24}$	2.40	2.48	2.32

3.3. Bulk linear thermal expansion

The results of the dilatometric measurements on M′TP and M″TP are shown in Figs 6 and 7, respectively. For each sample at least two measurements were made to ensure the reproducibility of the data. The hysteresis and the permanent dimension change in a ceramic specimen after the dilatometric measurement are common features of the materials possessing anisotropic thermal expansion characteristics. The bulk linear thermal expansion coefficients as calculated from the plots are listed in Table III. For alkali titanium phosphates (Fig. 6 and Table III), the bulk linear thermal expansion increases and the hysteresis decreases with the size of the alkali ion, with the exception of $LiTi_2P_3O_{12}$, which exhibits a higher thermal expansion than $NaTi_2P_3O_{12}$, and a larger hysteresis loop. For alkaline earth titanium phosphates (Fig. 7 and Table III), when the compounds with the same space group symmetry are being considered, the bulk linear thermal expansion increases and the hysteresis decreases with the size of the alkaline earth ion. $BaTi_4P_6O_{24}$ shows almost no hysteresis in its thermal expansion behaviour. In general, the compound with a larger alkali or alkaline earth ion (at the sodium position in the NZP structure) has a larger bulk linear thermal expansion (not necessarily a larger absolute value) and a smaller hysteresis.

4. Conclusion

The bulk and axial thermal expansions of $M'Ti_2P_3O_{12}$ (M' = Li, Na, K, Cs) and $M''Ti_4P_6O_{24}$ (M'' = Mg, Ca, Sr, Ba) compounds were investigated. It was observed that there is a trend between the composition and the cell parameters. As the larger alkali ions or alkaline earth ions are substituted into the M'TP or M''TP compounds, the cell dimensions become smaller in the *a*-direction and larger in the *c*-direction. The high-temperature X-ray data indicated that the axial thermal expansion in the *c*-direction was larger than in the *a*-direction in the case of M'TP, and this trend is reversed in M''TP. Based on this study, it is suggested that $RbTi_2P_3O_{12}$ and $BaTi_4P_6O_{24}$ may be proved potential candidates for low thermal expansion applications.

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