JOURNAL OF MATERIAL SCIENCE **33** (1998) 4007–4013

Thermal expansion studies on the Sodium Zirconium Phosphate family of compounds $A_{1/2}M_2(PO_4)_3$: effect of interstitial and framework cations

K. V. GOVINDAN KUTTY, R. ASUVATHRAMAN, R. SRIDHARAN
Materials Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India
E-mail:kug@igcar.ernet.in

Thermal expansion of the sodium zirconium phosphate (NZP) family of compounds $A_{1/2}M_2(PO_4)_3$ (A = Ca or Sr; M = Ti, Zr, Hf or Sn) has been measured in the temperature range 298–1273 K by high-temperature X-ray powder diffractometry. Some of the compounds in the series (calcium zirconium phosphate and calcium hafnium phosphate) display the typical thermal expansion behaviour of NZP compounds, namely expansion along the hexagonal *c* axis and contraction along the *a* axis. The other compounds, depending on their interstitial and framework composition, behave differently. The observed axial thermal expansion and contraction behaviour is explained on the basis of the crystal chemistry of the compounds. Low-expansion compounds in this series are identified and their expansion anisotropy examined. Infared spectra of the compounds are reported. Differential scanning calorimetry measurements on the tin compounds indicate the occurrence of a diffuse phase transformation at high temperatures. © *1998 Kluwer Academic Publishers*

1. Introduction

The sodium zirconium phosphate ($NaZr_2(PO4)_3$ (NZP)) family of compounds are characterized by a flexible framework structure belonging to the rhombohedral–hexagonal system [1]. The crystal structure is built up of corner-sharing PO_4 tetrahedra and ZrO_6 octahedra. The three-dimensionally linked interstitial space can be occupied by atoms of alkali, alkaline earth or similar elements or remain vacant. The crystal structure is amenable to a wide variety of chemical substitutions at the various crystallographic positions, thus yielding a large number of closely related compounds. The crystal chemistry of the NZP system has been described by Alamo and Roy [2]. When a typical NZP compound such as $NaZr_2(PO_4)_3$ is heated, the crystal undergoes anisotropic expansion; it expands along the hexagonal *c* axis and contracts along the *a* axis. This is due to bond angle distortions brought about by the coupled rotation of the corner-shared PO_4 and ZrO_6 polyhedra under thermal stresses [3–5]. The average linear thermal expansion of the compound is, therefore, very low. For example, Alamo and Roy [6] have reported an α_c of $25.5 \times 10^{-6}\,K^{-1}$ and an α_a of $-6.42 \times 10^{-6}\,K^{-1}$ in the temperature range 298–873 K; this gives an average expansion coefficient of $4 \times 10^{-6}\,K^{-1}$. The low thermal expansivity of NZP compounds was first observed by Boilot *et al.* [7]. Lenain *et al.* [8] have provided a structural model that explains this behaviour, and the model has been verified by Hazen *et al.* [5] by means of high-temperature X-ray diffractometry. A large number of NZP compounds have been investigated in the search for low-thermal-expansion materials. Taylor [9] and Brewal and Agrawal [10] have reviewed the thermal expansion behaviour of NZP compounds and compiled the available information.

Recently, we have examined [11] the effect of variation in framework composition on the thermal expansivity of two series of NZP compounds, one with sodium as the constant interstitial ion and the other with the interstitial positions vacant. The tin-containing compounds in both the series were found to behave anomalously [11, 12], and this was explained as a space group change [13] taking place with temperature in these compounds. In the present work, we have examined a family of NZP compounds wherein 50% of the interstices, called A_1 sites, along the hexagonal *c* axis are vacant. We have studied the effect of variation in interstitial and framework composition on the thermal expansivity of the NZP compounds with Ca and Sr as the interstitial ions and Ti, Zr, Hf and Sn as the framework ions. Thermal expansion of some of these compounds has been measured by other investigators. Roy *et al.* [14] have carried out extensive thermal expansion work on the calcium titanium phosphate ($Ca_{1/2}Ti_2(PO_4)_3$) family of compounds and discovered many near-zero expansion ceramics in this system. Limaye *et al.* [15] have reported the synthesis and thermal expansion of a series of alkaline earth-containing NZP compounds, namely $A_{1/2}Zr_2(PO_4)_3$

(A = Mg, Ca, Sr or Ba). They found that $Ca_{1/2}Zr_2(PO_4)_3$ and $Sr_{1/2}Zr_2(PO_4)_3$ show reverse axial anisotropy as well as opposite bulk thermal expansivity. Detailed analysis of the X-ray powder patterns of the titanium analogues $A_{1/2}Ti_2(PO_4)_3$ (A = Ca, Sr or Ba) by Senbhagaraman *et al.* [16, 17] has established that the space group of this type of compounds is $R\bar{3}$, which means alternate vacancy and A atom occupation along the hexagonal *c* axis. Recently, Huang *et al.* [18] have studied the thermal expansion behaviour of a series of compounds in the $ATi_2(PO_4)_3$ family, with various alkali and alkaline earth elements as the interstitial A ions.

We have carried out the synthesis and expansion measurements of all the compounds in the present series under identical conditions, compared their axial thermal expansion as a function of temperature and attempted to explain the variation in thermal expansion in terms of the crystal chemistry of the compounds.

2. Experimental methods

The compounds were synthesized by solid-state reactions starting from the following materials: ZrO_2 (NFC, India), HfO_2 (NFC, India), TiO_2 (Alpha, USA), SnO_2 (Johnson–Matthey, UK), $CaCO_3$ (Sarabhai, India), $SrCO_3$ (Sarabhai, India) and $NH_4H_2PO_4$ (CDH, India). Stoichiometric amounts of the reactants were ground together using an agate mortar and pestle and heated in air at 623 K for about 8 h (to decompose the ammonium dihydrogen phosphate). The amorphous mass so obtained was ground well and calcined in air at 873 K for about 7 h, and subsequently at 1200 K for about 15 h (to decompose the carbonate). The powder mixture was ground again and heated in air at 1473 K for 5 h. The powders were then pelletized (diameter, 12.5 mm; thickness, 2–3 mm) using a tungsten carbide-lined die and plunger under a load of 4 tons and sintered in air at 1473 K for 24 h.

The products were characterized by X-ray powder diffraction. A Siemens D 500 X-ray powder diffractometer coupled to a high-temperature attachment (Seifert HDK 2.1) was employed for product phase identification as well as the measurement of axial thermal expansion in the temperature range 298–1273 K. The experimental system has been explained in detail elsewhere [19]. In the high-temperature chamber, the sample is mounted as a thin layer on a tantalum strip that was resistively heated at programmed rates. The sample temperature was monitored by a thermocouple spot welded at the rear of the sample carrier strip. All measurements were carried out in a vaccum of about 10^{-5} Torr.

Hexagonal lattice parameters at different temperatures were calculated by measuring the angles corresponding to well-defined reflections in the 2θ range 18–50°. A typical set of reflections considered were as follows: (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4), (3 0 0), (2 2 0), (3 0 6), (1 2 8), (0 2 10), (1 3 4), (2 2 6) and (2 1 10). The angles were determined by step scanning in 2θ steps of 0.02° with counting times of 1 or 2 s per step. The hexagonal lattice parameters were calculated by the least-squares method using the NBS software AIDS83. The maximum error in the measured values were 0.005 Å in *a* and 0.05 Å in *c*. The lattice parameters, *l* were fitted against temperature (in kelvins) to the polynomial expression

$$l = x + yT + zT^2 \tag{1}$$

The average axial expansion coefficient, α_l, between the temperatures, T_1 and T_2, was calculated by the equation

$$\alpha_l = \frac{l_2 - l_1}{l_1(T_2 - T_1)} \tag{2}$$

The average volume expansion coefficient, α_v, was also calculated similarly. The average linear expansion coefficient, $\bar{\alpha}$, was calculated by the expression

$$\bar{\alpha} = \frac{\alpha_v}{3} = \frac{2\alpha_a + \alpha_c}{3} \tag{3}$$

The infrared spectra of the compounds were recorded in the 1300–400 cm^{-1} range using the KBr disc technique, on a Digilab FTS 15/90 Fourier transform infrared spectrometer at a resolution of 4 cm^{-1}. Differential scanning calorimetry (DSC) measurements were carried out on a Setaram DSC 111 equipment, in air at a heating and cooling rate of 5 °C min^{-1}. About 50 mg of the samples contained in alumina crucibles were employed in the measurements.

3. Results and discussion

3.1. Phase analysis

The compounds $A_{1/2}M_2(PO_4)_3$ (A = Ca or Sr; M = Ti, Zr, Hf or Sn) have been synthesized. $A_{1/2}Sn_2(PO_4)_3$ and $A_{1/2}Hf_2(PO_4)_3$ have been synthesized for the first time in the present study. X-ray diffraction patterns of the product obtained from the heat treatment of the starting powder mixture at 1200 K showed the onset of formation of the NZP phases; unreacted metal oxides and pyrophosphates were found to be the predominant phases at this stage. After soaking at 1473 K for 5 h, NZP compounds were seen to be the major phase; only traces of the pyrophosphates were detected. After the final sintering, traces of SnO_2 and TiO_2 were left as impurity phases in the tin- and titanium-containing compounds respectively; the other compounds of the series were obtained as a single phase with NZP structure. The X-ray diffraction patterns could all be indexed on the $R\bar{3}$ space group, as reported by Senbhagaraman *et al.* [16, 17]. Table I

TABLE I Measured lattice parameters, *a* and *c*, and cell volumes, *v*, of the NZP compounds

Compound	*a* (Å)	*c* (Å)	Cell volume ($Å^3$)
CaZrP	8.777	22.66	1511.74
SrZrP	8.690	23.33	1525.55
CaHfP	8.740	22.62	1496.15
SrHfP	8.658	23.29	1511.69
CaTiP	8.368	22.00	1334.40
SrTiP	8.303	22.59	1348.49
CaSnP	8.363	22.64	1371.43
SrSnP	8.313	23.12	1383.22

TABLE II Coefficients of the expression $l = x + yT + zT^2$ used to fit the lattice parameters, a (x_1, y_1, z_1) and c (x_2, y_2, z_2) against temperature (in Kelvin)

Compound	x_1	y_1	z_1	x_2	y_2	z_2
CaZrP	8.8088	-1.263×10^{-4}	6.631×10^{-8}	22.581 22	2.854×10^{-4}	-7.014×10^{-8}
SrZrP	8.68465	1.811×10^{-5}	5.38×10^{-10}	23.302 98	8.747×10^{-5}	-2.201×10^{-8}
CaHfP	8.74596	-1.848×10^{-5}	-6.168×10^{-9}	22.569 8	1.576×10^{-4}	7.565×10^{-9}
SrHfP	8.64883	3.441×10^{-5}	-1.285×10^{-8}	23.296 24	-4.671×10^{-5}	5.447×10^{-8}
CaTiP	8.35642	3.497×10^{-5}	1.511×10^{-8}	22.004 08	-6.23×10^{-6}	2.241×10^{-8}
SrTiP	8.29355	2.002×10^{-5}	3.946×10^{-8}	22.602 19	-6.218×10^{-5}	3.781×10^{-8}
CaSnP	8.32882	1.25×10^{-4}	-3.66×10^{-8}	22.690 47	-2.128×10^{-4}	1.893×10^{-7}
SrSnP	8.2816	1.141×10^{-4}	-3.365×10^{-8}	23.088 11	1.13×10^{-4}	-7.453×10^{-8}

TABLE III Lattice parameters, a and c, of some NZP compounds containing sodium and calcium ions in the interstices

Compound	a (Å)	c (Å)	Reference
$NaZr_2(PO_4)_3$	8.806	22.77	[11]
	8.808	22.75	[9]
CaZrP	8.777	22.66	This study
	8.789	22.68	[9]
$NaHf_2(PO_4)_3$	8.769	22.86	[11]
	8.772	22.662	[22]
CaHfP	8.740	22.62	This study
$NaTi_2(PO_4)_3$	8.495	21.83	[11]
	8.49	21.81	[21]
CaTiP	8.368	22.00	This study
	8.38	22.02	[21]
$NaSn_2(PO_4)_3$	8.504	22.55	[11]
	8.5002	22.541	[12]
CaSnP	8.363	22.64	This study

shows the measured lattice parameters and cell volumes of the compounds at room temperature. The lattice parameters of the zirconium- and titanium-containing compounds are in agreement with the literature data. Table II lists the coefficients of the polynomial expression used to fit a (x_1, y_1, z_1) and c (x_2, y_2, z_2) against temperature (in kelvin).

In all the four sets of compounds (i.e., those containing Ti, Zr, Hf and Sn in the framework), the strontium compounds are characterized by higher c and cell volume, v, and lower a compared with the Ca analogues. This can be attributed to the larger size of the Sr (2 +) ion compared with the Ca (2 +) for a given coordination number [20]. The presence of the bulkier Sr (2 +) instead of Ca (2 +) in the interstices increases the size of the SrO_6 distorted octahedra and hence stretches the bridging tetrahedra in the c direction. This causes a simultaneous contraction along the a axis, leading to an increase in c and a decrease in a. This is much like the large thermal expansion of the Na-O bond, causing an increase in c and a simultaneous decrease in a in $NaZr_2(PO_4)_3$ as a result of the coupled rotation of the ZrO_6 and PO_4 polyhedra under thermal stresses [3].

Table III shows the lattice parameters of the calcium compounds measured in the present study together with those of the corresponding monosodium compounds taken from the literature [9, 11, 21, 22]. Some trends are evident. Ca (2 +) and Na (1 +) have comparable sizes for the same coordination number in oxide lattices. An increase in the lattice parameter c and decrease in a as the valency of the interstitial ion increases from Na (1 +) to Ca (2 +) can be noticed in the case of $Ca_{1/2}Ti_2(PO_4)_3$ (CaTiP) and $Ca_{1/2}Sn_2(PO_4)_3$ (CaSnP) when their lattice parameters are compared with those of the respective monosodium analogues. In their studies on $NaTi_2(PO_4)_3$, CaTiP and $La_{1/3}Ti_2(PO_4)_3$, Senbhagaraman and Umarji [21] have noticed such a change, in spite of the ionic radius of the interstitial ions being almost the same [20]. However, such a trend is not apparent when the lattice parameters of $Ca_{1/2}Zr_2(PO_4)_3$ (CaZrP) and $Ca_{1/2}Hf_2(PO_4)_3$ (CaHfP) are compared with those of the corresponding sodium compounds. The axial expansion behaviour of the titanium and tin compounds is also different from that of the zirconium and hafnium analogues, as discussed in the next section.

3.2. Axial thermal expansion

Fig. 1 shows the percentage variation in the lattice parameters and unit-cell volume with temperature for all the eight compounds. CaZrP and CaHfP expand along the hexagonal c axis and contract along the a axis, while their strontium analogues $Sr_{1/2}Zr_2(PO_4)_3$ (SrZrP) and $Sr_{1/2}Hf_2(PO_4)_3$ (SrHfP) expand along both the axes. CaTiP and CaSnP show expansion along the a and c axes. In $Sr_{1/2}Ti_2(PO_4)_3$ (SrTiP) and $Sr_{1/2}Sn_2(PO_4)_3$ (SrSnP), a and the unit-cell volume increase significantly with increasing temperature, whereas c remains almost unchanged. In the tin compounds, the measurements could be carried out only up to 1073 K on account of the onset of sample degradation in the high-temperature X-ray diffraction chamber under the measuring conditions employed.

While the observed axial expansion behaviour of CaZrP agrees with that found by Limaye *et al.* [15], the behaviour of SrZrP does not; however, it is in line with the results of Oota and Yamai [3] and Huang *et al.* [23]. The decrease in c and increase in a with increasing temperature in SrZrP as observed by Limaye *et al.* [15] may be caused by an A site disordering; some of the Sr ions may have entered the larger A_{II} sites which connect in the a–b plane. The behaviours of CaZrP and CaHfP are similar to that of sodium zirconium phosphate [3] ; however, the expansion coefficient along c axis is much lower (about $7.5 \times 10^{-6} K^{-1}$) than that of $NaZr_2(PO_4)_3$ (about

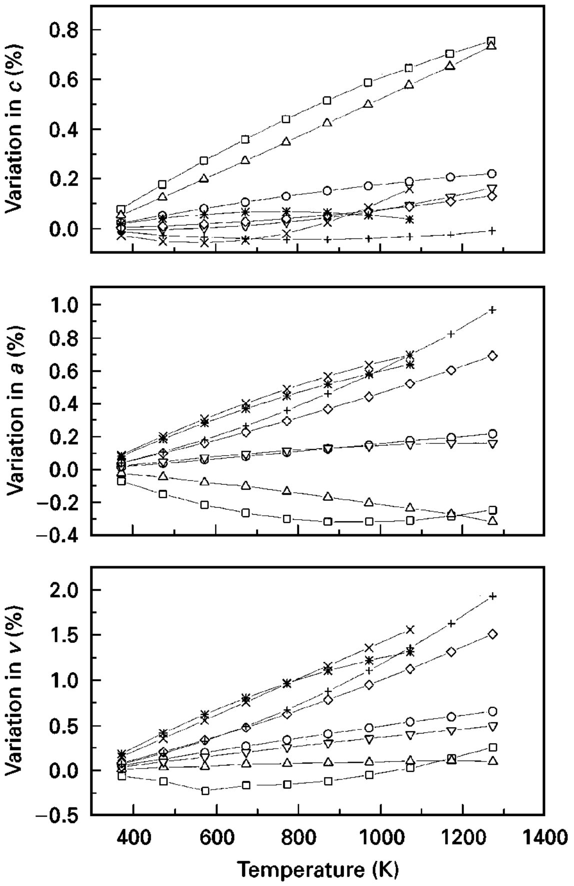

Figure 1 Axial cell volume expansion of the NZP compounds at different temperatures. (□), CaZrP; (○), SrZrP; (△), CaHfP; (▽) SrHfP; (◇), CaTiP; (+), SrTiP; (×), CaSnP; (*), SrSnP.

$25 \times 10^{-6}\,K^{-1}$). The difference between the sodium and calcium analogues in their thermal expansion characteristics must be due to the difference in the thermal expansion coefficients of the Na–O and Ca–O bonds in the AO_6 polyhedra of the compounds. The Ca–O bond, being stronger, can be expected to show a smaller expansion. On the basis of the crystallographic data on a large number of compounds, Hazen and Prewitt [24] have tabulated the expansion coefficients of many compounds characterized mainly by oxide polyhedra and derived the empirical relationship that a given cation–oxygen polyhedron (AO_6, AO_4 etc.) exhibits nearly the same expansion coefficient in different compounds. They suggested the empirical function

$$\alpha = 32.9(0.75 - Z\rho) \times 10^{-6}\,K^{-1} \qquad (4)$$

for the average thermal expansion of a metal–oxygen bond, where Z represents the charge on the metal ion and ρ its coordination number. The average expansion coefficients for the Na–O and Ca–O bonds work out to be $19.2 \times 10^{-6}\,K^{-1}$ and $13.8 \times 10^{-6}\,K^{-1}$, respectively. Thus, the smaller expansion coefficient of the Ca–O bond gives rise to a smaller expansion along the c axis and a concomitantly smaller contraction along the a axis in CaZrP and CaHfP, when compared with the axial length changes in the monosodium analogues.

TABLE IV Average axial and volume expansion coefficients between room temperature and the highest temperature of measurement (1073 K for the tin compounds and 1273 K for the others)

Compound	$\bar{\alpha}_a$	$\bar{\alpha}_c$	$\bar{\alpha}_v$	$\bar{\alpha} = \bar{\alpha}_v/3$	Anisotropy, $\lvert\bar{\alpha}_a - \bar{\alpha}_c\rvert$
CaZrP	− 2.57	7.74	2.55	0.85	10.31
SrZrP	2.24	2.28	6.65	2.22	0.04
CaHfP	− 3.29	7.52	0.92	0.31	10.81
SrHfP	1.66	1.67	5.01	1.67	0.01
CaTiP	6.99	1.31	15.41	5.14	5.68
SrTiP	9.88	− 0.14	19.73	6.58	9.74
CaSnP	8.95	2.05	20.05	6.68	6.90
SrSnP	8.07	0.50	16.88	5.63	7.57

In SrZrP and SrHfP, the extent of expansion along the c axis is much smaller than that of the corresponding calcium compounds. For example, the mean coefficient of thermal expansion along the c axis between room temperature and 1273 K for CaZrP is $7.74 \times 10^{-6} K^{-1}$ while that for SrZrP is $2.28 \times 10^{-6}\,K^{-1}$; the values for CaHfP and SrHfP are $7.52 \times 10^{-6}\,K^{-1}$ and $1.67 \times 10^{-6}\,K^{-1}$, respectively. (Table IV lists the average axial expansion coefficients of the eight compounds between room temperature and the highest temperature of measurement.) This decrease is brought about by the larger ionic radius of the strontium ion compared with that of the calcium ion (1.18 Å and 1.00 Å, respectively, for six-fold coordination). Owing to the larger ionic size of the interstitial Sr(2+) ion, the interlinking PO_4 tetrahedra in SrZrP and SrHfP become very stretched along the c axis even at room temperature, and this strain in the structure minimizes further expansion along the c axis as the temperature is raised. The constraint causing contraction along the a axis does not exist now in the structure, and consequently the two materials show a thermal expansion along the a axis also.

It can be seen from Fig. 1 that the magnitudes of axial expansion and contraction at different temperatures in CaHfP are smaller than those in CaZrP; the variation in c with temperature in SrHfP is smaller than that in SrZrP while the variations in a are almost the same in the two compounds. This seems to be the manifestation of the slight covalency of the Hf–O bond in comparison with the Zr–O bond, as commonly seen in oxide compounds.

Regarding the axial thermal expansion of CaTiP, the present results are in agreement with those of previous workers [17, 18]; as regards SrTiP, our results broadly agree with those of Huang *et al.* [18]. In the case of CaTiP, an increase in both a and c with increasing temperature is noticed. However, it is well known [14] that sodium titanium phosphate displays the same axial expansion behaviour as that of sodium zirconium phosphate, namely, expansion along c and contraction along a. The predominance of the large expansion of the Na–O bond in both the compounds may be responsible for this. The reason for the increase in both a and c with increasing temperature could be the predominance of anion–anion interaction. The very small ionic radius or the Ti(4 +) ion can allow anion–anion contact in the TiO_6 octahedra in CaTiP. On account of such anionic interactions, compounds such as TiO_2 which are characterized by TiO_6 octahedra in the structure exhibit much larger thermal expansion than do other structurally related compounds [25]. In CaTiP, the anion–anion proximity can be decreased by the simultaneous increase in *a* and *c* under thermal stresses. In SrTiP, the large size of the Sr(2+) ion prevents any significant expansion along the *c* axis; in fact, a very small contraction is observed along this axis between room temperature and 1273 K (Table IV). The *a* axis, however, shows a larger thermal expansion compared with that in CaTiP, signifying the coupled nature of the framework polyhedral twists that cause the axial length changes.

In CaSnP and SrSnP, the expansion coefficient along *a* axis is much higher than that along the *c* axis. The behaviour is almost similar to that of sodium tin phosphate [12] in the temperature range of measurement. The reason for this variation may also be the same as that proposed by Alamo and Rodrigo [13] for the lattice parameter variation in sodium tin phosphate, namely, a space group change. The fully filled nature of the d orbitals of the tin ion (unlike those of the Ti, Zr and Hf ions) makes it easier to bend or distort the O–Sn–O and Sn–O–P bends, thereby making the structure a little more close packed. For this reason, a second-order type of phase transformation is also encountered in $NaSn_2(PO_4)_3$ [13] and $NbSn(PO_4)_3$ [11] at high temperatures. The very small magnitude of thermal expansion along the *c* axis in SrSnP is perhaps due to the large size of the divalent Sr ion in the interstices, as discussed before in the case of SrTiP.

In order to verify the occurrence of a phase transformation in the tin compounds in the present study, DSC experiments were carried out. The results are shown in Fig. 2. The base line shifts in the DSC traces indicate a second-order phase transformation taking place over a range of temperature, starting at around 573 K in CaSnP and at around 473 K in SrSnP.

A plot of the room-temperature lattice parameters versus the tetravalent ionic radius (Fig. 3) also brings out the structural peculiarity of the tin compounds. The lattice parameters *a* of the titanium and tin compounds are very close, although the tetravalent ionic radii of Ti and Sn are quite different. An extraordinary decrease in the lattice parameter, *a*, of the tin compounds is thus indicated here. This is perhaps the manifestation of the relative rotation of the PO_4 and SnO_6 polyhedra, as described by Alamo and Rodrigo [13] in the case of $NaSn_2(PO_4)_3$. The variation in *c* however, does not follow that in *a*. The change in *c* is linear in the case of the Sr compounds, as a result of the large ionic radius of the interstitial Sr ion and the consequent stretching of the bridging PO_4 tetrahedra in the *c* direction. In the case of the calcium-containing series, the *c* parameter of the tin compound lies above the line joining the *c* values of the other two, indicating a slight elongation along the *c* axis in this compound. This enhancement of *c* in CaSnP must be the offshoot of the large decrease in *a* discussed already. In the sodium series of compounds, there is a linear variation in *c* with the tetravalent ionic radius [12]; the large stretching due to the NaO_6 distorted octahedra [3–5] which connect along the *c* axis appears to be responsible for this behaviour.

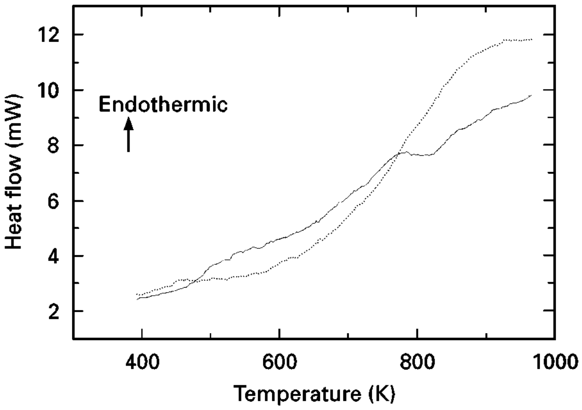

Figure 2 DSC traces of CaSnP (…) and SrSnP (——).

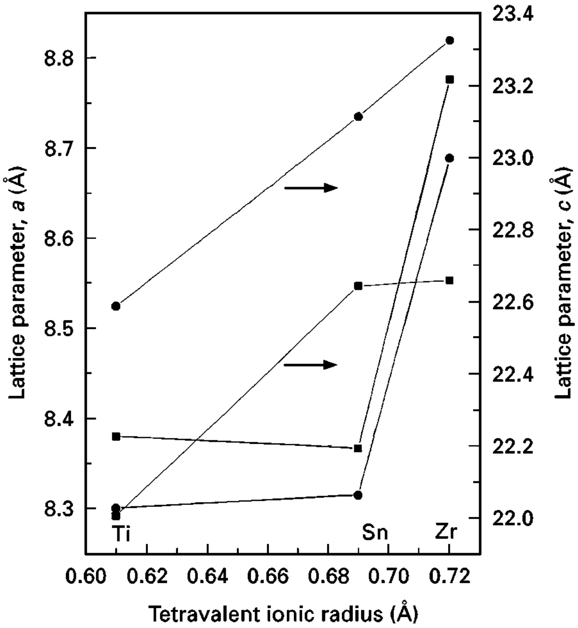

Figure 3 Variation in the lattice parameters with the tetravalent ionic radius of the NZP compounds. (■), Ca; (●), Sr.

A perusal of Table IV shows that CaZrP, SrZrP, CaHfP and SrHfP are low-expansion ceramics. The calcium compounds show high expansion anisotropy, whereas the Sr analogues are characterized by negligible anisotropy.

3.3. Infrared spectra

The infrared spectra of the compounds under study are shown in Fig. 4. Absorption bands due to the stretching ($1250–900\,cm^{-1}$) and bending (650–400 cm^{-1}) of the phosphate groups are observed, as expected [26, 27], in the form of two groups of vibrational frequencies separated by a narrow transparency window. The spectra of CaZrP, SrZrP, CaHfP and SrHfP are very similar, especially in the region of the bending frequencies. Slight differences are, however, noticed when the calcium and strontium analogues

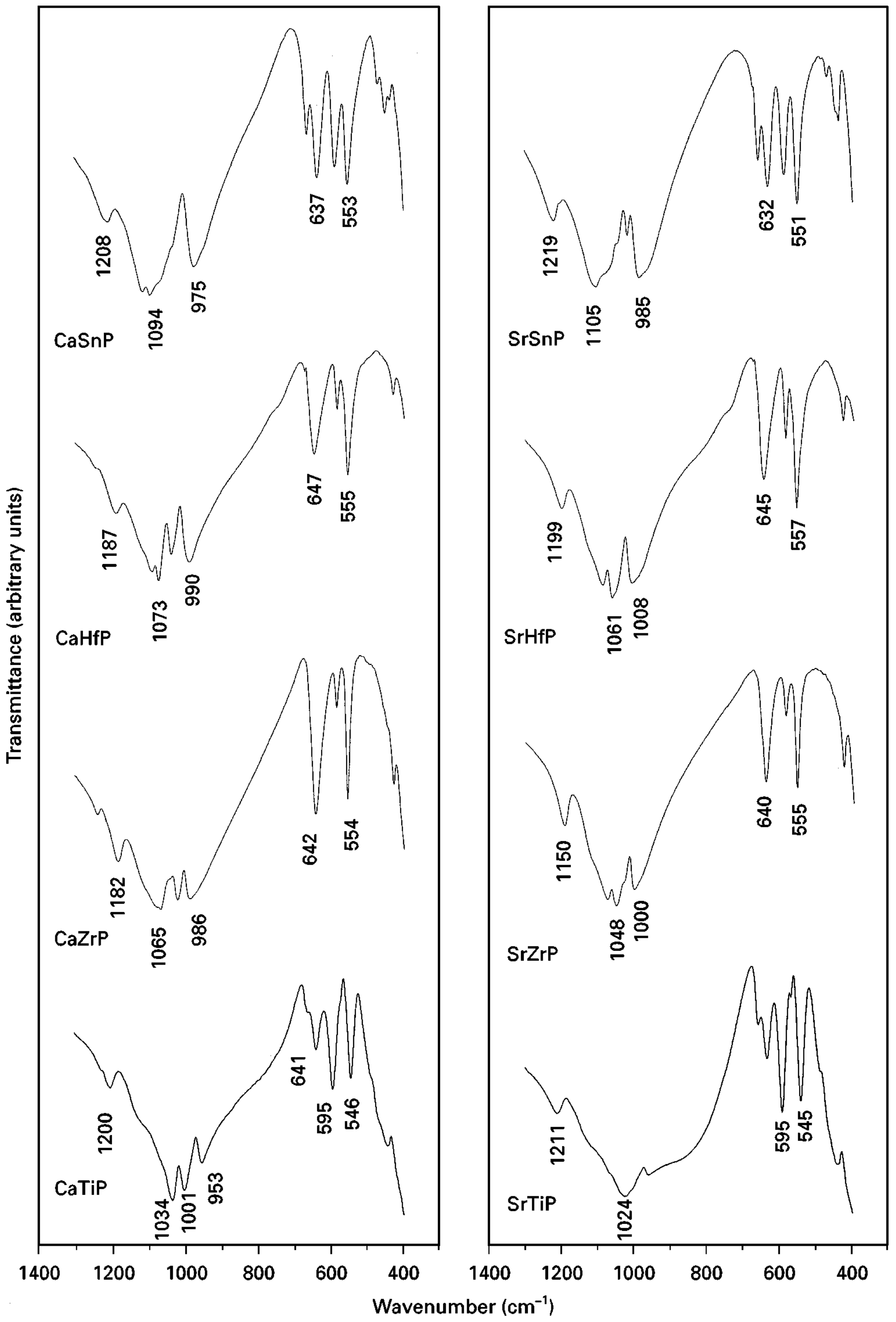

Figure 4 Infrared spectra of the NZP compounds.

are compared. For example, the absorption bands at 1235 and 1021 cm^{-1} present in CaZrP are absent in SrZrP, and the band at 1038 cm^{-1} present in CaHfP is absent in SrHfP. The tin and titanium pairs of compounds display different spectra; the frequencies corresponding to the bending vibrations are nearly identical in the spectra of their calcium and strontium analogues. In the tin and titanium pairs, the bending vibrational region has more absorption bands than displayed by the zirconium and hafnium pairs. (The lattice expansion behaviour of the tin and titanium compounds is also different from that of the zirconium and hafnium compounds.) All these are manifestations of the combined effect of the framework cations (transition metals Ti, Zr and Hf, and the main group element Sn), the interstitial ions (Ca and Sr), and the vacancies along the *c* axis on the PO_4 tetrahedra in the solids.

4. Conclusions

The thermal expansion measurements on NZP compounds of the formula $A_{1/2}M_2(PO_4)_3$ ($A = Ca$ or Sr; $M = Ti, Zr, Hf$ or Sn), carried out from room temperature to a maximum of 1273 K by means of high-temperature X-ray powder diffractometry, indicate that the expansion behaviour of the compounds depends significantly on the nature of the interstitial and framework cations. The extent of stretching of the bridging PO_4 tetrahedra (the O–P–O bond angles), the proximity of the neighbouring oxide ions in the MO_6 octahedra (O^{2-}–O^{2-} repulsion) and the possibility of A-site disordering seem to be some of the key factors to be considered in explaining the expansion behaviour of the NZP compounds.

Acknowledgements

We thank Mr Jose Joseph for experimental assistance in the high-temperature X-ray measurements, and Mr K. Sankaran for providing the infrared spectra. We are grateful to Professor U.V. Varadaraju, Materials Science Research Centre, Indian Institute of Technology, Madras, for going through the manuscript and offering valuable comments.

References

1. H. Y. -P. HONG, *Mater. Res. Bull.* **11** (1976) 173.
2. J. ALAMO and R. ROY, *J. Mater. Sci.* **21** (1986) 444.
3. T. OOTA and I. YAMAI, *J. Amer. Ceram. Soc.* **69** (1986) 1.
4. D. K. AGRAWAL, C. -Y. HUANG and H. A. McKINSTRY, *Int. J. Thermophys.* **12** (1991) 697.
5. R. M. HAZEN, L. W. FINGER, D. K. AGRAWAL, H. A. McKINSTRY and A. J. PERROTTA, *J. Mater. Res.* **2** (1987) 329.
6. J. ALAMO and R. ROY, *J. Amer. Ceram Soc.* **67** (1984) C78.
7. J. P. BOILOT, J. P. SALANIE, G. DESPLANCHES and D. LePOTIER, *Mater. Res. Bull.* **14** (1979) 1469.
8. G. E. LENAIN, H. A. McKINSTRY, J. ALAMO and D. K. AGRAWAL, *J. Mater. Sci.* **22** (1987) 17.
9. D. TAYLOR, *Brit. Ceram. Trans. J.* **90** (1991) 64.
10. E. BREWAL and D. K. AGRAWAL, *Brit. Ceram. Trans.* **94** (1995) 27.
11. K. V. GOVINDAN KUTTY, R. ASUVATHRAMAN, C. K. MATHEWS and U. V. VARADARAJU, *Mater. Res. Bull.* **29** (1994) 1009.
12. J. L. RODRIGO and J. ALAMO, *ibid.* **26** (1991) 475.
13. J. ALAMO and J. L. RODRIGO, *ibid.* **27** (1992) 1091.
14. R. ROY, D. K. AGRAWAL, J. ALAMO and R. A. ROY, *ibid.* **19** (1984) 471.
15. S. Y. LIMAYE, D. K. AGRAWAL and H. A. McKINSTRY, *J. Amer. Ceram. Soc.* **70** (1987) C232.
16. S. SENBHAGARAMAN, T. N. GURU ROW and A. M. UMARJI, *Solid State Commun.* **71** (1989) 609.
17. *Idem., J. Mater. Chem.* **3** (1993) 309.
18. C. -Y. HUANG, D. K. AGRAWAL and H. A. McKINSTRY, *J. Mater. Sci.* **30** (1995) 3509.
19. S. RAJAGOPALAN, K. V. G. KUTTY, H..K. JAJOO, S. K. ANANTHAKRISHNAN and R. ASUVATHRAMAN, Indira Gandhi Centre for Atomic Research, Kalpakkam, Report 96 (1988).
20. R. D. SHANNON, *Acta Crystallogr. A* **32** (1976) 751.
21. S. SENBHAGARAMAN and A. M. UMARJI, *J. Solid State Chem.* **85** (1990) 169.
22. J. -M. WINAND, A. RULMONT and P. TARTE, *ibid.* **93** (1991) 341.
23. C. -Y. HUANG, D. K. ARGAWAL and H. A. McKINSTRY, *J. Mater. Res.* **9** (1994) 2005.
24. R. M. HAZEN and C. T. PREWITT, *Amer. Mineral.* **62** (1977) 309.
25. H. D. MEGAW, in "Crystal structures: a working approach" (W. B. Saunders Philadelphia, PA, 1973), p. 422.
26. P. TARTE, A. RULMONT, M. LIEGEOIS-DUYCKAERTS, R. CAHAY and J. M. WINANAD, *Solid State Ionics* **42** (1990) 177.
27. G. V. SUBBA RAO, U. V. VARADARAJU, K. A. THOMAS and B. SIVASANKAR, *J. Solid State Chem.* **70** (1987) 101.

Received 4 November 1996
and accepted 11 May 1998