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Thermal expansion studies of substituted CTP derivatives

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Abstract. Several new Na, Y and Zr substituted derivatives of $Ca_{0.5}Ti_2(PO_4)_3$ (CTP) have been synthesized. These derivatives retain the hexagonal structure of the parent (CTP) compound with minor changes in lattice parameters. Linear thermal expansion coefficients (α) have been obtained using a high sensitivity dilatometer.

Keywords. CTP; phosphates; thermal expansion.

1. Introduction

$Ca_{0.5}Ti_2(PO_4)_3$ and $NaZr_2(PO_4)_3$ commonly called CTP and NZP have been the subject of numerous investigations (Goodenough *et al* 1976; Hong 1976; Roy *et al* 1984; Alamo and Roy 1986; Ota *et al* 1989; Limaye *et al* 1991; Kutty *et al* 1994) due to their possible applications as ionic conductors and low-thermal expansion materials. Among other possible applications is the ability of the members of the [CTP] family to immobilize radionuclides as reported by Roy *et al* (1985). The CTP structure consists of TiO_6 octahedra and PO_4 tetrahedra sharing all their corners such that each TiO_6 octahedra is connected to six PO_4 tetrahedra and each PO_4 tetrahedron connected to four TiO_6 octahedra. These units are repeated alternating with MO_6 octahedra (M = Na, Ca etc.) along the *c*-axis to form chains which in turn are connected through the phosphate groups to neighbouring chains (figure 1). Such a structural network results in various kinds of holes which are occupied by Na or Ca ions in NZP and CTP respectively. The crystal chemistry and details of the range of ionic substitutions possible in the CTP structure have been given by Alamo and Roy (1986). These studies have shown that a rich substitution chemistry is possible in these compounds which bring about a wide-ranging thermal expansion behaviour. The thermal expansion in these materials is anisotropic. The anisotropic behaviour is attributed to the M–O bonds (M = Na, Ca) which expand more than the other bonds in the network.

Although various ionic substitutions have been carried out in the CTP structure the influence of trivalent rare-earth or Y ions on the structure and thermal expansion properties is unknown except for one report on $La_{0.33}Ti_2(PO_4)_3$ (Senbhagaraman and Umarji 1990) although recently several Zr-containing compounds of the type $Ln_{0.33}Zr_2(PO_4)_3$ have been reported (Alami Talbi *et al* 1994). We have therefore attempted to synthesize and characterize Y doped CTP materials. Furthermore we have studied Na doping in Ca sites and Zr doping in Ti sites to see the effect on the thermal expansion properties, knowing that $Ca_{0.5}Ti_2(PO_4)_3$ has a positive linear thermal expansion coefficient (α) while the other end member ($NaTi_2(PO_4)_3$, $Ca_{0.5}Zr_2(PO_4)_3$) have a negative α.

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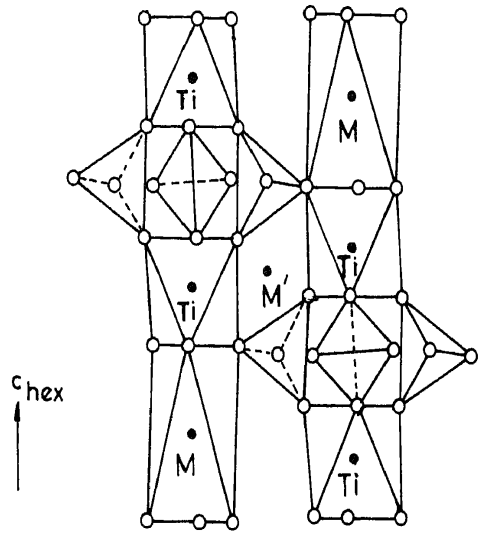

Figure 1. Structural model of CTP, showing the MO_6 and PO_4 interconnected polyhedra.

In this article we report the synthesis, characterization and thermal expansion studies of the above compounds. We have also studied the effect of codoping Nb in Ti sites and Si in P sites in $Ca_{0.5}Ti_2(PO_4)_3$.

2. Experimental

Pure and doped $Ca_{0.5}Ti_2(PO_4)_3$ type CTP phases were prepared by solid state reactions. Stoichiometric quantities of $CaCO_3$, Na_2CO_3, Y_2O_3, TiO_2, ZrO_2, SiO_2 (fumed amorphous), Nb_2O_5 and $(NH_4)_2HPO_4$ were mixed thoroughly in acetone and dried. The powders were heated at 623 K (4h) and 1173 K (18h). These were mixed with 5% solution of PVA (few drops) and then pelletized and heated at 1323 K for 16 h. The Nb and Si containing samples were heated only up to a maximum temperature of 1273 K. Powder XRD patterns were obtained at room temperature using a JEOL-JDX-8P diffractometer with CuKα radiation. The lattice parameters were calculated by a least squares fitting procedure of the observed *d*-values.

Thermal expansion measurements were carried out on sintered pellets using a high sensitivity dilatometer based on linearly variable differential transformer (LVDT) principle (Senbhagaraman 1995). The measurements were carried out in the range 300 to 900 K on samples of length 4 to 6 mm. The temperature was increased at the rate of 2·2 K/min and measured with an accuracy of $\pm$ 1 K using a type K thermocouple. The coefficient of linear thermal expansion (α) was obtained from the slopes of the $\Delta l/l$ vs temperature plots and had an accuracy of $\pm 0{\cdot}5 \times 10^{-6}$K.

3. Results and discussion

The general formula of the CTP structure may be written as $MM'_3Ti_2P_3O_{12}$ where M can be Na, Ca, Sr, while M′ is mainly Na or K. The M and M′ ions occupy the holes formed by the network of PO_4 and TiO_6 units (figure 1). In $NaTi_2(PO_4)_3$ the M sites are

Table 1. Lattice parameters and the linear thermal expansion coefficient (α) for the various CTP type materials studied.

Composition	Lattice parameters		
	a(Å)	c(Å)	'α' ($10^{-6}K^{-1}$)
$Ca_{0.5}Ti_2(PO_4)_3$	8·347(3)	21·95(1)	6·5[+]
$Ca_{0.4}Na_{0.2}Ti_2(PO_4)_3$	8·371(4)	21·91(2)	6·3
$Ca_{0.3}Na_{0.4}Ti_2(PO_4)_3$	8·410(2)	21·915(7)	7·0
$Ca_{0.35}Y_{0.1}Ti_2(PO_4)_3$	8·349(3)	21·90(1)	6·8
$Ca_{0.4}Y_{0.1}Ti_2(PO_4)_3$	8·339(3)	21·89(1)	7·1
$Ca_{0.3}Na_{0.1}Y_{0.1}Ti_2(PO_4)_3$	8·360(3)	21·91(1)	7·0
$Ca_{0.5}Ti_{1.9}Zr_{0.1}(PO_4)_3$	8·362(4)	21·93(2)	9·4
$Ca_{0.5}Ti_{1.75}Zr_{0.25}(PO_4)_3$*	8·346(3)	21·94(1)	8·7
$Ca_{0.5}Ti_{1.9}Nb_{0.1}P_{2.9}Si_{0.1}O_{12}$	8·387(3)	21·96(1)	6·8
$Ca_{0.5}Ti_{1.8}Nb_{0.2}P_{2.8}Si_{0.2}O_{12}$	8·396(2)	21·962(8)	7·7

[+]Reported value $5·1 \times 10^{-6}$; Roy *et al* 1984
*ZrO_2(5%) impurity present.

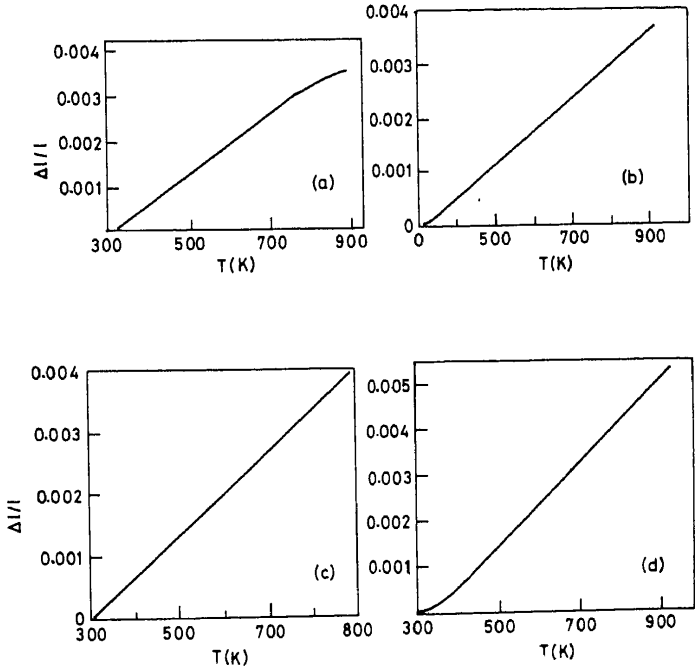

Figure 2. Variation of ($\Delta l/l$) with temperature for (**a**) $Ca_{0.5}Ti_2(PO_4)_3$, (**b**) $Ca_{0.4}Na_{0.2}Ti_2(PO_4)_3$, (**c**) $Ca_{0.35}Y_{0.1}Ti_2(PO_4)_3$ and (**d**) $Ca_{0.5}Ti_{1.9}Zr_{0.1}(PO_4)_3$.

fully occupied while in $Ca_{0.5}Ti_2(PO_4)_3$ only half of these sites are filled. In both these cases the M′ sites are empty. In compositions like $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (NASICON) the excess Na(x) goes into the M′ sites. The compositions chosen by us (table 1) aim to replace the Ca ions by Y or Na or both. Table 1 lists the various compositions, the refined lattice parameters (hexagonal lattice) and the average coefficient of linear thermal expansion (α). It is to be noted that all the compositions chosen are charge

balanced except for one, $Ca_{0.4}Y_{0.1}Ti_2(PO_4)_3$. From the powder XRD patterns all the phases obtained were pure except in the $Ca_{0.5}Ti_{1.75}Zr_{0.75}(PO_4)_3$ sample which had ~5% ZrO_2 impurities. Earlier reports (Roy *et al* 1984) also find impurity phases like ZrO_2 or ZrP_2O_7 in Zr rich samples.

In figure 2 we show some representative plots of $(\Delta l/l)$ as a function of temperature. We find that the plots are nearly linear. In $Ca_{0.5}Ti_2(PO_4)_3$ (figure 1a) we find that the plot deviates from linearity at high temperatures, beyond 750 K.

The lattice parameters of $Ca_{0.5}Ti_2(PO_4)_3$ is close to that reported in the literature. The 'α' value of $Ca_{0.5}Ti_2(PO_4)_3$, 6.5×10^{-6}/K is slightly higher than that reported earlier (Roy *et al* 1984). Since these are average α values, measured on polycrystalline samples such deviation may be explained due to microstructural differences among these samples. The Na-doped samples show an increase in the a-parameter and a decrease in the c-parameter compared to the pure CTP phase. The 'α' values fall from 6.5×10^{-6}/K in the $Ca_{0.5}Ti_2(PO_4)_3$ to 6.3×10^{-6}/K in $Ca_{0.4}Na_{0.2}Ti_2(PO_4)_3$ which is what one would expect since the end member, $NaTi_2(PO_4)_3$, has an α of -5.5×10^{-6}/K. But on increasing the Na content further, e.g. $Ca_{0.3}Na_{0.4}Ti_2(PO_4)_3$ we note that the α value of 7.0×10^{-6}/K is slightly larger than for pure CTP. It should however be noted that in $NaTi_2(PO_4)_3$ α is highly sample dependent as the thermal expansion anisotropy is very high ($\alpha_c - \alpha_a = 24 \times 10^{-6}$/K) (Rodrigo *et al* 1989; Senbhagaraman and Umarji 1990). So unless the microstructural effects are minimized it is difficult to predict how each ceramic sample of the solid solution would behave.

On substituting Y or Na + Y at the Ca sites the a-parameter does not change significantly while the c-parameter decreases (table 1). The 'α' values are slightly higher than that of pure CTP. Substituting Zr in the Ti sites leads to minor changes

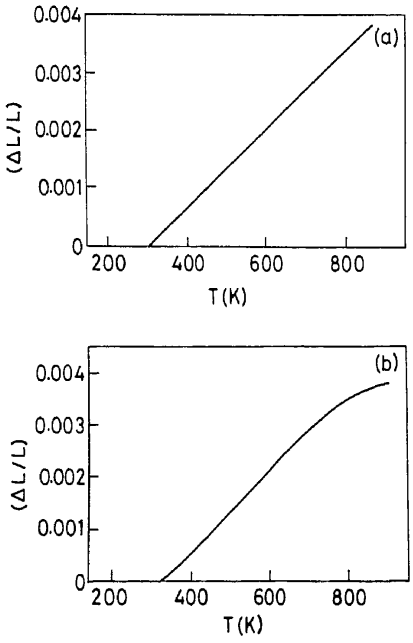

Figure 3. Variation of $(\Delta l/l)$ with temperature for **(a)** $Ca_{0.5}Ti_{1.9}Nb_{0.1}P_{2.9}Si_{0.1}O_{12}$ and **(b)** $Ca_{0.5}Ti_{1.8}Nb_{0.2}P_{2.8}Si_{0.2}O_{12}$.

in the lattice parameters, but the α-values are significantly higher ($\sim 9 \times 10^{-6}$/K) than pure CTP.

We have simultaneously substituted small amounts of Nb in Ti sites and Si in P sites (to maintain charge balance). We obtain nearly pure phases of the type $Ca_{0.5}Ti_{2-x}Nb_xP_{3-x}Si_xO_{12}$ ($x \leqslant 0.2$). Our studies have shown that fumed amorphous silica needs to be used for these reactions to obtain monophasic samples. We also note very minor amounts of TiO_2 ($\sim 2\%$) as impurity if heated to higher temperatures (> 1000°C) and longer periods. The expansion ($\Delta l/l$) was linear with temperature till 870°C in the $x = 0.1$ sample but deviated from linearity for the $x = 0.2$ sample after 750°C (figure 3). α increases with x as seen in table 1 and is larger than that of CTP.

4. Conclusions

The above study shows that various substitutions like Na, Y, Na + Y can be carried out in the CTP host lattice. The linear thermal expansion coefficients (α) are however close to that of CTP. The study also shows that substitution is also possible at Ti sites by Zr where the α values are larger than the parent value. Simultaneous substitution of Nb at Ti site and Si at P site also does not lower the α values.

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