Effect of Cation Valence on Thermal Expansion of $MTi_2P_3O_{12}$ (M = Na, $Ca_{0.5}$, and $La_{0.33}$) Compounds*

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The thermal expansion behavior of $MTi_2P_3O_{12}$ compounds with M = Na^+, $Ca^{2+}_{0.5}$, and $La^{3+}_{0.33}$ has been studied by high temperature X-ray diffraction. The difference in the anisotropic axial thermal expansion coefficients drastically varies for cations with varying charges but with similar sizes. The thermal expansion in this family of compounds seems to be essentially due to M–O bond expansion. A new compound $La_{0.33}Ti_2P_3O_{12}$ with hexagonal structure (a = 8.295 Å and c = 22.426 Å) is reported. © 1990 Academic Press, Inc.

Introduction

Compounds with the general formula $MM'_2P_3O_{12}$, possessing the NASICON-type structure, have been studied for interesting technological applications which include ionic conductivity (*1*), thermal expansion (TE), and many others (*2*). A large number of compounds with M = alkali, alkaline earth, and vacancy and M' = Zr, Ti, Hf, etc., form and show low and sometimes negative TE. Crystal chemical considerations have shown that the system is flexible to numerous isovalent and balanced chemical substitutions (*3*) yielding families of compounds which form the bases for both scientific understanding and a source for technologically useful product. The unusual TE properties have been attributed to

special structural features. The basic structure consists of $(Zr/Ti)_2P_3O_{12}$ units derived from corner sharing of two $(Zr/Ti)O_6$ octahedra and three PO_4 tetrahedra (*4, 5*). These units are stacked along the c direction with M atoms separating them and joined by PO_4 tetrahedra along the a and b directions with rhombohedral symmetry. In this type of polyhedral arrangement all the corners are shared resulting in a strong skeletal structure with a large number of voids (one M_1-type and three M_2-type per formula unit). The cage structure and anisotropic rotation of polyhedra result in low and sometimes negative TE and when small cation occupy these voids fast ionic conductivity can result. The bonding within the polyhedra is highly covalent and ionic between M and oxygen.

The net low volume expansion observed in many cases is because of the anisotropic axial thermal expansion coefficients (α_a and

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α_c) having opposite signs. However, such materials show hysteresis in dilatometric TE measurements due to microcracking and leading to low strength ceramic bodies. The microcracks are bound to occur at critical grain size in polycrystalline bulk of compounds having TE anisotropy. This relation between critical grain size, flectual strength, and $\Delta\alpha_{max}$ has been demonstrated in the pseudobrokite family of compounds (6). In the NASICON family of compounds, it is important to look for materials with low $\Delta\alpha_{max}$ and to understand the underlying factors governing this property. Recent studies (7) have shown that in the NASICON type of compounds, the major contribution to TE is the M–O bond; the network as such makes negligible contribution as observed in $NbZrP_3O_{12}$ where the M atom position is vacant. This approach has helped in understanding the TE behavior of $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ (7). Here we report our attempt to test this approach by studying the $MTi_2P_3O_{12}$ system where M atoms are of similar size but of differing charge. We also report the preparation of a new compound $La_{0.33}Ti_2P_3O_{12}$ whose structure is similar to previously known Na and Ca compounds.

Experimental

The compounds $NaTi_2P_3O_{12}$ (NaTP), $Ca_{0.5}Ti_2P_3O_{12}$ (CaTP), and $La_{0.33}Ti_2P_3O_{12}$ (LaTP) were prepared both by ceramic and sol–gel methods. High purity Na and Ca carbonates, La_2O_3, TiO_2, and $(NH_4)_2HPO_4$, were mixed in stoichiometric quantities and heated in stages from 200–1000°C with intermittent grinding. In the sol–gel method nitrate solution of cations was slowly added to Ti solution taken in the form of Ti-nitrate or Ti-ethoxide. The resulting gel was dried at 100°C and heated slowly to 1000°C as in ceramic method. The final heat treatment at 1200°C for 48–72 hr was in the form of a 10-mm-diameter × 3- to 5-mm-thick pellet

pressed to 5000 Kg/cm². The X-ray characterization and high temperature diffractograms were performed on a Phillips diffractometer with $CuK\alpha$ at 2θ scanning speed of 1/2 deg/min. The lattice parameters were obtained by least-squares fitting of diffraction lines in the 2θ range of 20–60 deg and with hkl obtained from the program LAZY PULVERIX (8).

Results and Discussion

The X-ray diffraction patterns of the three compounds could be indexed on the basis of a hexagonal unit cell. Though the space group $R\bar{3}c$ was sufficient to index the NaTP pattern, the CaTP and LaTP patterns contained extra low angle lines, which could not be indexed with the allowed hkl values. The analysis of the X-ray powder patterns of $M_{0.5}Ti_2P_3O_{12}$ (M = divalent cation) led us to reassign the space group to $R\bar{3}$ (9), which implies alternate vacancy and M atom occupation along the hexagonal c axis. The structure of the new compound LaTP is grossly similar to CaTP but may not exactly have the same distribution of the vacancies and the M atom. The La content of 0.33 per formula unit is consistent with the observation that in $M_xTi_2P_3O_{12}$, x = 1/z (z being the charge on the M cation). This is because the $Ti_2P_3O_{12}$ host network can accept a total of one electron from the M site. Any attempts to put La content ≥ 0.33 resulted in appearances of impurity phases. Generally, the sol–gel method, as expected, gave sharper diffraction lines. The lattice parameters are tabulated in Table I along with the ionic radii (for sixfold coordination number) for the three compounds studied.

The a unit cell parameter decreases with the increasing charge on the M cation from 1+ to 3+ while the c parameter increases. This is not expected as we have chosen cations of similar sizes (within 2%) and the c parameter should have remained constant.

TABLE I

Unit Cell Parameters, Ionic Radii, and Thermal Expansion
Parameters for $MTi_2P_3O_{12}$ Compounds

	$NaTi_2P_3O_{12}$	$Ca_{0.5}Ti_2P_3O_{12}$	$La_{0.33}Ti_2P_3O_{12}$
Space group	$R\bar{3}c$	$R\bar{3}$	—
Ionic radius (Å)	1.02	1.00	1.03
$a(\text{Å})$ (±0.01 Å)	8.49	8.38	8.29
$c(\text{Å})$ (±0.02 Å)	21.81	22.02	22.42
$\alpha_a(\times 10^{-7})$	−71.1	50.9	−1.06
	$(−44.0)^a$		
$\alpha_c(\times 10^{-7})$	158.6	9.21	6.72
	$(200.0)^a$		
Unit cell volume (Å³)	1362	1339	1336
$\alpha_v(\times 10^{-7})$	15.2	111.0	4.60
$\Delta\alpha_{max}(\times 10^{-7})$	−239.7	41.69	7.78

^{a} From Ref. (13).

For isovalent $MZr_2P_3O_{12}$ the a cell parameter decreases and the c cell parameter increases with increasing size of M atoms (10). In these cases the PO_4 tetrahedra is stretched along the c direction. The TE behavior in the NASICON family of compounds has been explained on the rotation and stretching model of the PO_4 tetrahedras (11). In the present study the PO_4 tetrahedras are stretched along the c direction as going from Na to La. The contraction of lattice in the ab plane can be attributed to increasing charge on the M atom or the number of increasing vacancies (0, 33, and 66% for NaTP, CaTP, and LaTP, respectively).

The variation of unit cell parameters with temperature obtained from high temperature X-ray diffraction experiments is shown in Fig. 1. The coefficients of thermal expansion (α) derived from these are tabulated in Table I. The values of NaTP, which was used as a test sample, agree well with those reported in the literature. The value of α_c reduces from 158.6E-7 C⁻¹ to 6.72E-7 C⁻¹. The value for α_a however is negative for Na and La compounds but positive for Ca (Table I). The reduction of α_c can be due to two or more reasons acting together: (i) The oc-

cupation of M_1 site is equal to $1/z$ (z is charge on M cation) and the host network itself contributes very little to TE. (ii) By the empirical relations found by Hazen and Prewitt (12), the $M–O$ bond expansion coefficient can be expressed as

$$\alpha_{M-O} = 32.9(0.75 - z/p) \times 10^{-6} \text{ C}^{-1},$$

where z and p are the charge and the coordination number of the M atom, respectively. The $M–O$ bond expansion, which contributes to α_c, works out to be 19.2E-6, 13.7E-6, 8.2E-6, for 1+, 2+, and 3+ cations in sixfold coordination. It is assumed here that the M atom is always going to the M_1 site and the M_2 sites are vacant. (iii) The PO_4 tetrahedras, as mentioned earlier, are stretched along the c direction and may further expand very little with heating. To determine which of these is a prime factor requires a detailed structural analysis.

The value of $\Delta\alpha_{max}$, a measure of anisotropic thermal expansion, ($= \alpha_a - \alpha_c$) is minimum for LaTP as compared to other compounds. This is very important from a practical point of view, because the critical grain size at which microcracking occurs is inversely proportional to square of $\Delta\alpha_{max}$ (6). LaTP can be a strong ceramic over a
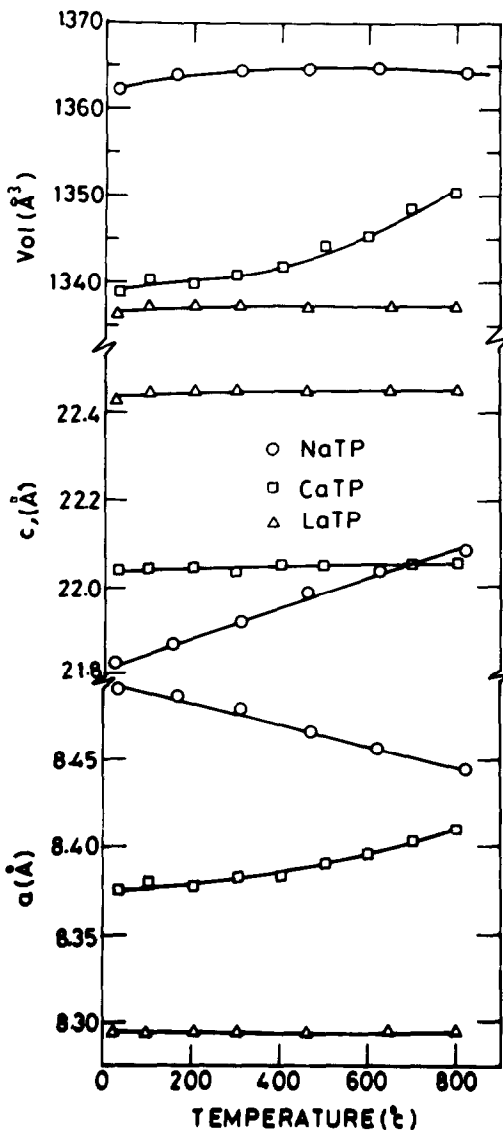
FIG. 1. Variation of lattice parameters and cell volume for $MTi_2P_3O_{12}$ (M = Na, $Ca_{0.5}$, and $La_{0.33}$) compounds.

wide range of grain size as compared to NaTP or CaTP. In conclusion we have shown that the TE in the NASICON type of compounds can primarily be accounted as due to $M-O$ bond expansion and the network itself has minimal contribution. The valence of the M atom has a pronounced effect on TE. The new compound $La_{0.33}Ti_2P_3O_{12}$ apart from having low TE coefficients also has low $\Delta\alpha_{max}$ and may be a better candidate for thermal shock resistant and related applications. The bulk TE measurements and structural details of a new compound are in progress.

Acknowledgment

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