Mechanism of low thermal expansion in the cation-ordered Nasicon structure

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Variable temperature neutron powder diffraction data are used to pinpoint the mechanism of low thermal expansivity in the Nasicon-related material $Sr_{0.5}Ti_2(PO_4)_3$; this behaviour is contrasted with that of the parent phase $NaTi_2(PO_4)_3$.

There has recently been considerable interest in materials displaying the remarkable property of negative, or very low, thermal expansivity. New materials displaying this property include $ZrP_{2-x}V_xO_7$[1] and ZrW_2O_8,[2] but by far the most widely studied types have been the Nasicon or NZP family, based on the $NaZr_2(PO_4)_3$ structure.[3–5] The NZP structure is a three-dimensional lattice consisting of vertex-linked TiO_6 and PO_4 polyhedra, with the large Na cation occupying interstitial trigonal prismatic (MI) sites spaced at intervals along the *c*-axis (Fig. 1). $NaZr_2(PO_4)_3$ itself crystallises in space group $R\bar{3}c$, having only one crystallographically distinct Na site. A wide variety of adaptations may be made to the basic NZP stoichiometry by substitutions at all three non-oxygen sites. One such series is $M_{0.5}Ti_2(PO_4)_3$, where M is a divalent cation (Ca, Sr, Ba). The Ca and Sr compounds adopt the lower symmetry $R\bar{3}$ space group owing to alternate ordering of M and vacancy along the *c*-axis, leading to crystallographically distinct MIa and MIb sites. Measurements of lattice parameter evolution *vs.* temperature, by X-ray powder diffraction, have shown that, in general, the thermal expansivity behaviour of the $R\bar{3}c$ and $R\bar{3}$ families is different, with the former showing a positive coefficient of the *c*-axis expansivity (α_c) and a negative coefficient of the *a*-axis expansivity (α_a), while the situation for the $R\bar{3}$ family is reversed.[5,6] Although a very elegant general model has been proposed to describe the thermal behaviour of these materials, in terms of cooperative rotations of linked polyhedra,[7,8] the specific issue of the contrasting behaviour of the $R\bar{3}c$ and $R\bar{3}$ series has not been satisfactorily addressed. Here, we show that this behaviour is directly related to the cation-vacancy ordering, and is due to the compressibility of the vacant site along the *c*-axis.

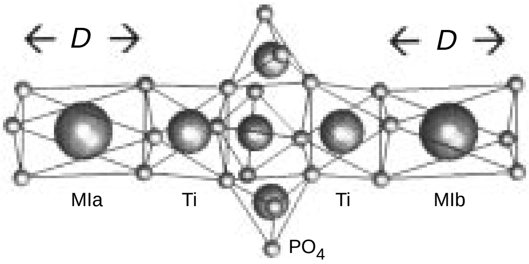

Fig. 1 Portion of the ideal NZP structure showing packing of polyhedral units along the *c*-axis. In $Sr_{0.5}Ti_2(PO_4)_3$ the MIa site (0,0,0) is fully occupied while the MIb site (0,0,1/2) is vacant. The parameter *D* refers to the O···O distance along the *c*-axis.

Samples were prepared from stoichiometric quantities of TiO_2, $(NH_4)_2HPO_4$ and Na_2CO_3 or $SrCO_3$. Thoroughly ground mixtures were preheated at 200 °C, followed by subsequent heat treatments at 600, 900 and 1000 °C with intermediate regrinding. For the Sr sample a final treatment at 1200 °C was required. Neutron diffraction data were collected on the high flux diffractometer D1B at the ILL, Grenoble, using a wavelength of 2.522 Å and a fixed detector bank covering 80° in 2θ. In order to determine the thermal evolution of the lattice parameters, a series of 123 short (*ca.* 10 min) scans was collected over the range $25 < T < 835$ °C. These scans were refined with the cyclic version of the refinement program FULLPROF[9] using the result for a run at a given temperature as input file for the following run with slightly higher temperature. Runs at selected temperatures were then chosen for detailed structural analysis. Rietveld refinement was carried out using the GSAS package.[10] The starting model for the refinement of the $Sr_{0.5}Ti_2(PO_4)_3$ structure was taken from Senbhagaraman *et al.*[11] A typical refinement consisted of 17 structural para-

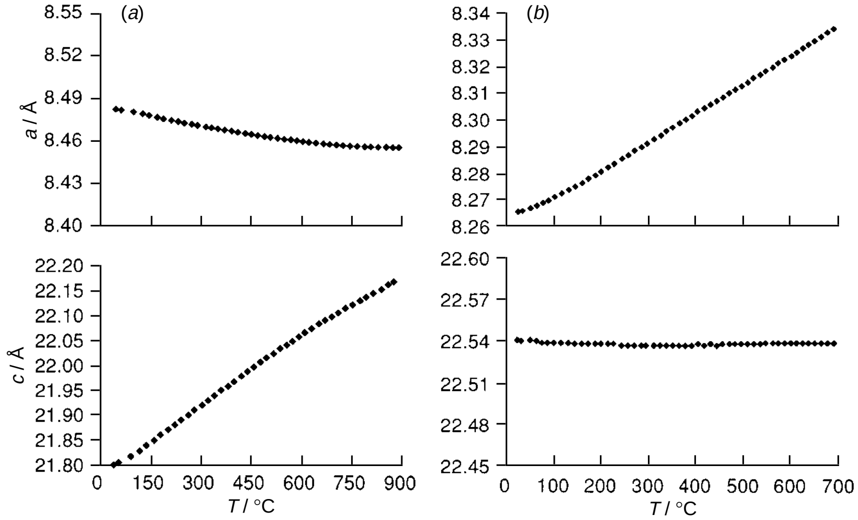

Fig. 2 Thermal evolution of lattice parameters for (*a*) $NaTi_2(PO_4)_3$ and (*b*) $Sr_{0.5}Ti_2(PO_4)_3$

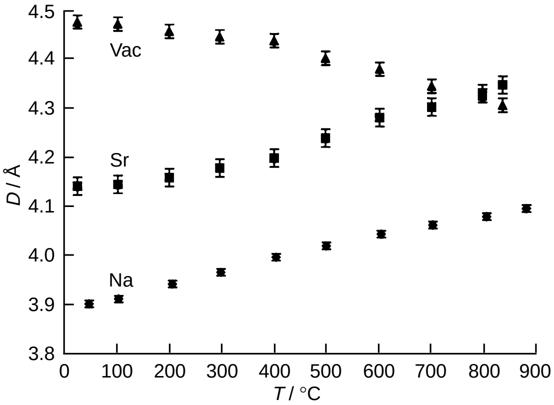

Fig. 3 Thermal evolution of the trigonal prismatic MI sites (*i.e.* O···O distance, *D*, along the *c*-axis). In $NaTi_2(PO_4)_3$ the *c*-axis expansivity is governed by 2 × *D*(Na), in $Sr_{0.5}Ti_2(PO_4)_3$ by *D*(Sr) + *D*(vac).

meters, with 400 data points and 80 contributing reflections over the range $18 < 2\theta < 98°$.

Plots of the thermal evolution of the lattice parameters for both compounds are shown in Fig. 2. Values of α_a and α_c are -5.3 and 20.8×10^{-6} °C^{-1} for $NaTi_2(PO_4)_3$ in the range 25–500 °C and 13.2 and -0.02×10^{-6} °C^{-1} for $Sr_{0.5}Ti_2(PO_4)_3$ in the range 25–800 °C, which are in good agreement with those reported by earlier studies.[5,6,12] Although thermal evolution of lattice parameters by X-ray powder diffraction has been carried out for both these samples, the present study provides, for the first time, precise structural details by neutron diffraction, which allows us to pinpoint the mechanism of their behaviour. One of the most significant trends is the near-zero expansivity of the *c*-axis for the Sr compound. It has previously been suggested that the largest contribution to the expansivity in NZP materials is the expansion of the Na–O bond itself. This governs the 'size' of the trigonal prismatic site along the *c*-axis (*i.e.* the O–O contact), which is plotted in Fig. 3. In the case of the Sr compound in $R\bar{3}$ there are two such sites to consider, the Sr site and the vacancy site, which are confirmed to be completely ordered from the refinements. It can be seen that, in the Na compound this site expands, by *ca.* 0.20 Å over the full temperature range, accounting completely for the overall expansivity α_c (two per unit cell), whereas in the Sr compound there is an expansion of the Sr site but a contraction of the vacancy site. These two almost exactly cancel out, resulting in the observed near-zero expansion coefficient, α_c. These parameters in turn result in the cooperative polyhedral rotations described by earlier workers, and lead to the expansivities along the *a*-axis. A full analysis of these effects will be the subject of a later paper, but the fundamental explanation of the *c*-axis expansivity lies simply in the relative expansion/contraction of the occupied and vacant MI sites. The anomaly previously observed in the case of $Ca_{0.5}Zr_2(PO_4)_3$, which shows the behaviour of an $R\bar{3}c$ structure rather than an $R\bar{3}$ structure[13] lies in the fact that in that case both the Ca site and the vacancy site expand with temperature, resulting in a net expansion of the *c*-axis. Apparently the smaller vacancy site in that case (*ca.* 4.1 Å at 25 °C) is not as compressible as the vacancy site in the present phase. A diffraction experiment cannot differentiate whether the unusual behaviour of the Sr phase is due to cation-ordering *per se* or merely the presence of equal numbers of filled and vacant MI sites. However, it is interesting to note that a larger value of $\alpha_c = 1.37 \times 10^{-6}$ °C^{-1} has been reported for $Ba_{0.5}Ti_2(PO_4)_3$, which crystallises in the disordered $R\bar{3}c$ structure type.[6] A comparative, detailed neutron diffraction study of the Sr and Ba materials is therefore currently in progress.

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Footnote and References

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