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 $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$

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Introduction

The framework compound $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_12$ (named NASICON) is an excellent fast sodium ion conductor [1]. However, it cannot be grown as a single crystal; and in our laboratory and elsewhere [2] it has been shown that it cannot be prepared as a pure monophase. The presumed scandium analog $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ [labelled here as NASICON(Sc)] can be prepared as a stoichiometric single crystal [3] and has come under considerable study. It is an excellent solid electrolyte in its own right. However, it has its own unique crystal chemistry which is not the same as the $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_12$ parent compound [4,5]. Efforts have been made to correlate its structural phase changes and its ionic conductivity [4,6,7,8]. However, considerable confusion exists in the literature as to the structure of the stable polymorphic modifications. At room temperature $\text{Na}_3\text{Sc}_2\text{PO}_12$ is variously described as monoclinic C2/c [3], monoclinic C/c [5] and rhombohedral R3c [8,9]. The "intrinsic" structure has even been stated as being dependent on whether the sample is a sintered powder, a powdered crystal [8] or a single crystal [9]. There is general agreement that at least one high-temperature phase is rhombohedral [8,9,10 but not 3].

In this paper we shall present neutron and x-ray diffraction data that confirm the nature of the transition from an ordinary-conducting, high temperature phase to a still higher temperature, superionic-conducting phase. We shall also discuss the unresolved discrepancies associated with the lower temperature conducting phases and present appropriate optical, x ray and neutron diffraction data. These data will be correlated with ionic conductivity measurements as a function of temperature.

Experimental

Polycrystalline $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ powder was prepared by solid state reaction of Sc_2O_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Na}_2\text{C}_2\text{O}_4$ or by solid state reaction of Sc_2O_3 and NaH_2PO_4 . Single crystals were grown from fluxed melts of $\text{ScPO}_4:\text{Na}_2\text{P}_2\text{O}_7$ either unseeded [4], or seeded according to the classic Kyropoulos method. Extensive primary and secondary twinning is observed [4] in the virgin crystals, or is readily introduced upon handling the crystals or cycling through the 64°C transition. This prevalent domain structure is responsible for several inconsistencies in the single crystal results reported in the literature and is the reason why all the present data are obtained using powder diffraction procedures.

X-ray diffraction data were obtained on a G.E. XRD diffractometer. Neutron diffraction data were taken on the high-resolution, multi-detector, powder diffractometer at the NBS research reactor. They were refined by the Rietveld procedure. Optical microscopy was carried out on the Zeiss Universal equipped with a ultra-precision (± 0.01 °C) hot stage for transmitted polarized light. Procedures for measuring the ionic conductivity have been described elsewhere [7].

Results and Conclusions

There are at least four polymorphic modifications of pure, stoichiometric $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$. Figure 1 presents x-ray data for powdered crystals at temperatures well away from the observed transition temperatures. The same results are obtained for NASICON(Sc) prepared by solid state syntheses. Ionic conductivity data and DTA analyses have already been presented [7] for typical solid state syntheses.

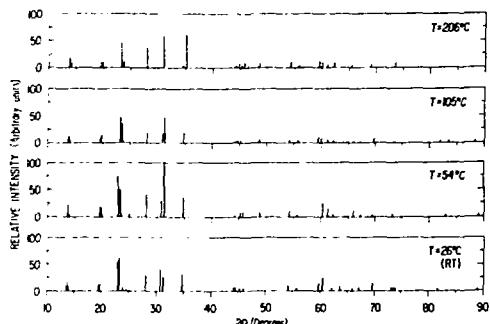


Fig. 1. X-ray diffraction of flux-grown powdered crystals of NASICON(Sc), $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$. Overlapping reflections with Al, Be or the Si internal standard are omitted. Cu K α .

At room temperature, the refined neutron diffraction data confirm the Cc space group reported by Efremov and Kalinin [5] but with $a = 16.0449(24)$, $b = 8.9225(15)$, $c = 9.0656(13)$, $\beta = 126.918^{\circ}(21)$, $R_{\text{wp}} = 17.5\%$, and $R_{\text{expected}} = 7\%$. We shall call this polymorph A.

Between 25°C and 64°C, a second polymorph appears as indicated in Fig. 1. The structure is monoclinic but has not yet been refined. The A \leftrightarrow B transition is clearly dependent on sample stoichiometry and purity [4,11].

At 64°C, a third polymorph C appears. It is rhombohedral R3c. Using hexagonal axes, $a = 8.9273(2)$, $c = 22.3668A$, $R_{\text{wp}} = 6.28\%$ and $R_{\text{e}} = 3.8\%$ at 100°C. B \leftrightarrow C is accompanied by a fivefold increase in ionic conductivity but only a small decrease in activation energy from 0.56 eV to 0.45 eV. A, B and C are ordinary ionic conductors.

At 166°C, the high temperature polymorph D appears. It is the superconducting phase of NASICON(Sc). It, too, is rhombohedral R3c with $a = 8.9274(1)$, $c = 22.5493(6)A$, $R_{\text{wp}} = 5.81\%$ and $R_{\text{e}} = 3.87\%$ at 225°C. The activation energy for Na^+ motion in phase D is only 0.15 eV.

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Table 1. Atomic parameters for NASICON (Sc), $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ at 100 °C and 225 °C. Space group = R_{3c}.
 100 °C a = 0.9273(7), c = 22.3669(6) Å
 225 °C a = 0.9274(1), c = 22.5493(6) Å

| 100 °C. Phase C. Ordinary Na^+ conductor. | | | | | | | | | | |
|--|-------------|---------|--------|------------|--|---------------|---------------|---------------|---------------|---------------|
| Atom | Coordinates | | | Occupation | Anisotropic Thermal Parameters (Å ²) | | | | | |
| | x/a | y/b | z/c | | θ_{11} | θ_{22} | θ_{33} | θ_{12} | θ_{13} | θ_{23} |
| Na(1) | 0.0000 | 0.0000 | 0.0000 | 0.1647(49) | 26.201 | 26.201 | 1.848 | 13.100 | 0.000 | 0.000 |
| Na(2) | 0.6399 | 0.0000 | 0.2500 | 0.3353(49) | 1.023 | 1.305 | 12.448 | 0.653 | 1.378 | 2.755 |
| Sc | 0.0000 | 0.0000 | 0.1490 | | 0.725 | 0.725 | 1.494 | 0.362 | 0.000 | 0.000 |
| P | 0.2929 | 0.0000 | 0.2500 | | 0.823 | 0.520 | 1.506 | 0.260 | -0.050 | -0.100 |
| O(1) | 0.1857 | -0.0250 | 0.1948 | | 1.959 | 2.061 | 3.760 | 1.282 | -1.550 | 0.631 |
| O(2) | 0.3118 | -0.1595 | 0.2561 | | 1.373 | 0.446 | 2.414 | 0.594 | -0.395 | 0.401 |

| 225 °C. Phase D. Superionic Na^+ conductor. | | | | | | | | | | |
|--|-------------|---------|--------|------------|--|---------------|---------------|---------------|---------------|---------------|
| Atom | Coordinates | | | Occupation | Anisotropic Thermal Parameters (Å ²) | | | | | |
| | x/a | y/b | z/c | | θ_{11} | θ_{22} | θ_{33} | θ_{12} | θ_{13} | θ_{23} |
| Na(1) | 0.0000 | 0.0000 | 0.0000 | 0.1332(42) | 40.670 | 40.670 | -0.107 | 20.335 | 0.000 | 0.000 |
| Na(2) | 0.6356 | 0.0000 | 0.2500 | 0.3668(42) | 0.818 | 1.068 | 20.587 | 0.534 | 3.088 | 6.177 |
| Sc | 0.0000 | 0.0000 | 0.1494 | | 1.122 | 1.122 | 1.501 | 0.561 | 0.000 | 0.000 |
| P | 0.2919 | 0.0000 | 0.2500 | | 0.470 | 1.220 | 1.256 | 0.610 | -0.112 | -0.224 |
| O(1) | 0.1827 | -0.0306 | 0.1955 | | 2.554 | 1.900 | 3.142 | 1.506 | -1.492 | -0.191 |
| O(2) | 0.3118 | -0.1594 | 0.2575 | | 1.582 | 0.475 | 2.493 | 0.433 | -0.591 | 0.340 |

Table 1 indicates that the C \leftrightarrow D transition from the ordinary to the superionic phase has as its salient feature the appearance of vacancies on the previously full Na(1) sites. Full occupation of Na(1) is 0.1667 and full occupation of the Na(2) site is 0.5000. Figure 2 is a view of the structure perpendicular to the c axis. The anisotropies in the thermal factors demonstrate that fast Na-ion motion in phase D 's from a Na(1) site to a Na(2) site. Na does not

move between equivalent Na(1) sites or between equivalent Na(2) sites. In effect, the Na ion is moving in a "dogleg" fashion from Na(1) to Na(2). These conclusions are in agreement with the optical, thermal and conductivity data.

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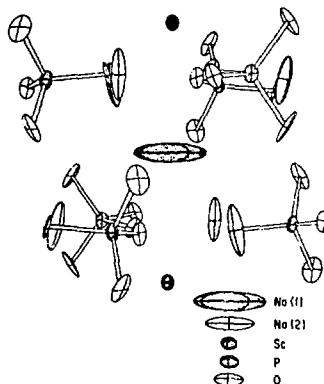


Fig. 2. Structure of NASICON(Sc), $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$, in both high temperature, R_{3c} phases C and D. Ordinary phase C is stable from 64 to 160 °C. Superionic phase D is stable above 166 °C. Viewed perpendicular to the c axis.