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# The Structural Characterization of $Sn_{0.5}NbTiP_3O_{12}$ and $Fe_{0.33}NbTiP_3O_{12}$

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The structural chemistry of the compounds $NbTiP_3O_{12}$, $Sn_{0.5}NbTiP_3O_{12}$, and $Fe_{0.33}NbTiP_3O_{12}$ has been investigated by X-ray powder diffraction and Mössbauer spectroscopy. The results show that the $Sn^{2+}$ and $Fe^{2+}$ cations are located only in the octahedral Type I sites of the $NbTiP_3O_{12}$ structure. Whereas the $Fe^{2+}$ ions are positioned approximately centrally in these sites, half of the $Sn^{2+}$ ions are displaced by ca. 0.3 Å along [001]. © 1992 Academic Press, Inc.

## Introduction

The structural properties of phases corresponding to the general formulation $A^{1+}M_2^{4+}P_3O_{12}$ involve the corner sharing of $PO_4$ tetrahedra with $MO_6$ octahedra to produce three-dimensional linked channel networks in which the $A$ ions are located (*1–4*). In these types of materials, the $A$ ions can occupy two different types of sites (*3*). The Type I sites (one per formula unit) have a distorted octahedral coordination and are situated between two $MO_6$ octahedra along the $c$-axis to produce ribbons of $O_3MO_3$ $AO_3MO_3$. The Type II sites (three per formula unit) are larger, with 8–10 coordinating oxygen ions, and are located between the ribbons. The structure is highly flexible and amenable to substitution on the $A$,$M$, or phosphorus sites to form a wide variety of isostructural materials.

The Type I and Type II site occupancies in the channels may also be varied to form phases in which the number of $A$ ions per formula lies between four (full channels) and zero (empty channels). For example, the compound $Na_3Zr_2Si_2PO_{12}$, commonly known as Nasicon, has sodium ions in both Type I and Type II sites and has attracted significant attention due to its high $Na^+$ ion mobility (*1, 2*). The compound $NbTiP_3O_{12}$, which has a similar framework structure but with completely empty channels, has recently been shown to be capable of incorporating several large ions of electropositive elements (*5*). Recent preliminary studies by $^{57}Fe$- and $^{119}Sn$-Mössbauer spectroscopy (*6*) have shown that iron and tin are incorporated in $NbTiP_3O_{12}$ as $Fe^{2+}$ and $Sn^{2+}$. In this paper we report on the structural characterization of the compounds $Fe_{0.33}NbTiP_3O_{12}$ and $Sn_{0.5}NbTiP_3O_{12}$ by X-ray powder diffraction and Mössbauer spectroscopy.

## Experimental

The compound $NbTiP_3O_{12}$ was prepared by the sequential heating of a stoichiometric mixture of niobium(V) oxide, titanium(IV) oxide (anatase), and ammonium dihydrogen

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phosphate in air at 200°C (12 hr), 600°C (6 hr), 900°C (15 hr), 1000°C (5 hr), and finally at 1300°C (1 hr). Tin and iron were incorporated into $NbTiP_3O_{12}$ to give materials of composition $Sn_{0.5}NbTiP_3O_{12}$ and $Fe_{0.33}NbTiP_3O_{12}$ by heating $NbTiP_3O_{12}$ with the appropriate powdered elemental metal at 900°C (24 hr) in evacuated sealed quartz tubes.

X-ray powder diffraction patterns were recorded with a Picker X-ray diffractometer in step-scan mode by counting for 30 sec for each step of 0.02° of $2\theta$ over a range of 10° to 70° of $2\theta$ using Cu$K\alpha$ radiation. Structural parameters were refined by the Rietveld method using a program similar to that previously described (*7*). A contribution from a $NbPO_5$ impurity phase was also refined.

Mössbauer spectra were recorded at 298 K with a microprocessor controlled Mössbauer spectrometer using $^{57}$Co–Rh and $Ca^{119m}SnO_3$ sources. The drive velocity was calibrated with a $^{57}$Co–Rh source and a natural iron foil. All the spectra were computer fitted by constraining the areas of the peaks representing each doublet to be equal and with all peaks of equal linewidth.

## Results and Discussions

The atomic coordinates of $NbTiP_3O_{12}$ were refined using the space group $R\bar{3}c$ and initial atomic coordinates previously reported (*8*) for the compound Nasicon of composition $Na_3Zr_2Si_2PO_{12}$. A pseudo-Voigt peak shape function was adopted. The isotropic thermal parameters for the two types of oxygen atoms were constrained to be equal, and since the niobium and titanium atoms were found to be randomly distributed on the octahedral sites, a single temperature factor was assigned to these atoms. The observed and calculated X-ray powder diffraction patterns for $NbTiP_3O_{12}$ are shown in Fig. 1, and the refined structural parameters are presented in Table I.

### $Sn_{0.5}NbTiP_3O_{12}$

The incorporation of tin within the $NbTiP_3O_{12}$ lattice has been shown (*5*) to give materials of composition $Sn_{0.5}NbTiP_3O_{12}$. A preliminary examination by $^{119}$Sn-Mössbauer spectroscopy showed (*6*) the tin to be incorporated as $Sn^{2+}$, and subsequent more comprehensive studies of this material have confirmed this (Fig. 2, Table II). The occurrence in the spectra of a partially superimposed singlet and doublet of similar area suggests that the $Sn^{2+}$ cations occupy two types of sites within the three-dimensional interspace of $NbTiP_3O_{12}$. The possibility that the Mössbauer data could be interpreted in terms of two quadrupole split doublets with the large peak representing the superimposed high velocity components of the two species was examined. However, the need to apply additional constraints in order to achieve satisfactory convergence mitigated against the adoption of this model.

The refinement of the X-ray powder diffraction data (Fig. 1) revealed the $Sn^{2+}$ cations to be incorporated entirely in the octahedral Type I sites, but their thermal ellipsoids were highly anisotropic with the maximum amplitude (mean square displacement 0.057 Å$^2$) directed along [001]. Since the Mössbauer spectrum clearly indicated two distinct $Sn^{2+}$ species, it was assumed that the anisotropic temperature factors were indicative of a split site. Therefore, in the final refinement half the tin atoms were located centrally (position 6*b*) while the other half were allowed to move off the mirror plane, along [001], (position 12*c*) to give a fit to the data (Table III) in which the *R*-factors were identical to those obtained when the data were fitted to tin in a single site. Using the split site model in which the vibrations were constrained to be isotropic, the tin atoms which were not constrained to the mirror plane were displaced by ca. 0.3 Å. The thermal factors for niobium and titanium were held equal, as were those for the two types of tin atoms. The refined parame-

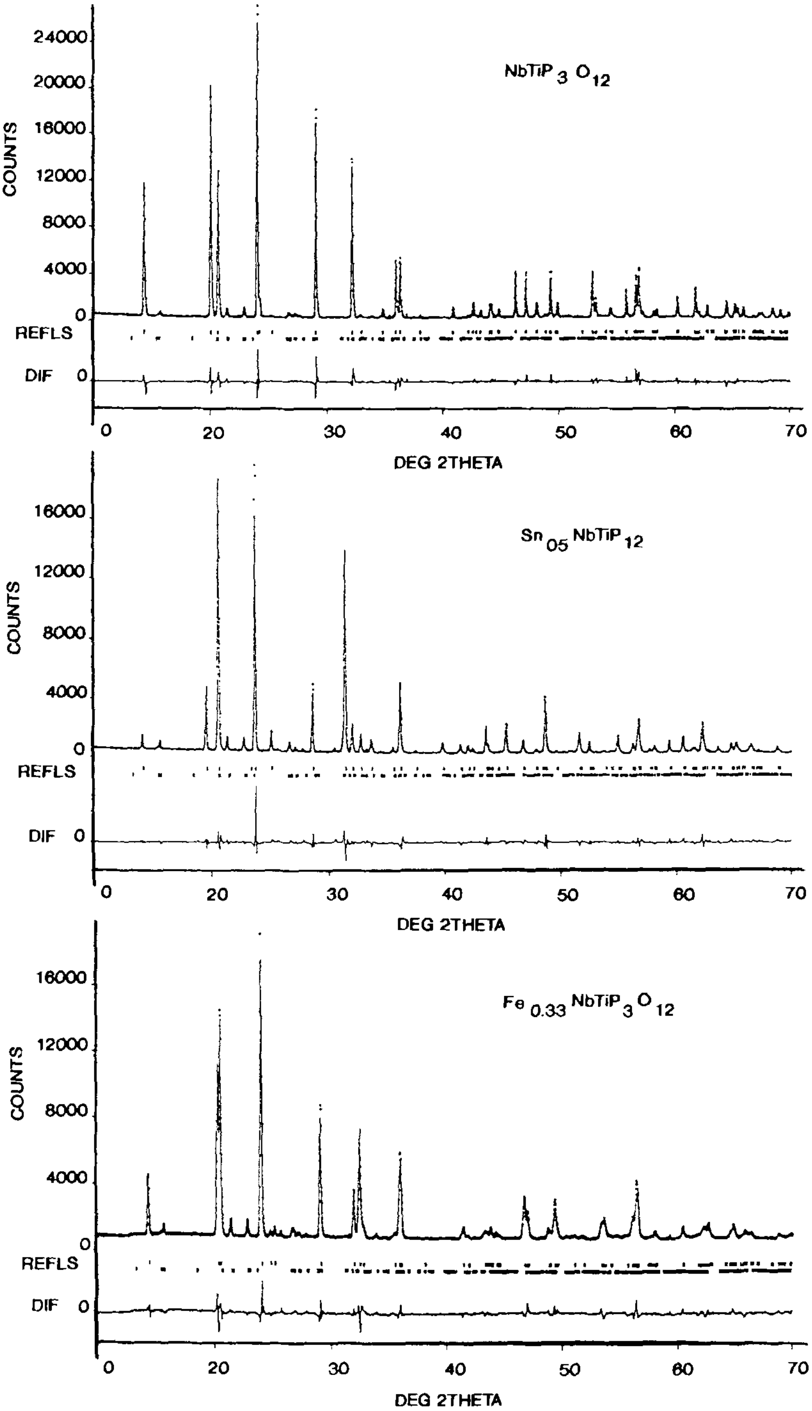

FIG. 1. X-ray powder diffraction patterns recorded from $NbTiP_3O_{12}$, $Sn_{0.5}NbTiP_3O_{12}$, and $Fe_{0.3}$ $NbTiP_3O_{12}$.

TABLE I

REFINED STRUCTURAL PARAMETERS FOR $NbTiP_3O_{12}$

| Atom | $x$ | $y$ | $z$ | $B$(Å$^2$) | Unit cell occupancy |
|---|---|---|---|---|---|
| Nb/Ti | 0 | 0 | 0.1415(1) | 0.40(2) | 12 |
| P | 0.2820(4) | 0 | $\frac{1}{4}$ | 0.8(1) | 18 |
| O(1) | 0.1700(6) | 0.9688(3) | 0.1941(2) | 0.0(1) | 36 |
| O(2) | 0.1940(5) | 0.1661(6) | 0.0899(2) | 0.0(1) | 36 |

*Note.* $a$ = 8.558(1) Å; $c$ = 21.977(1) Å; $R_I$ = 5.68%; $R_p$ = 8.96%; $R_{wp}$ = 11.95%; $R_{exp}$ = 3.62%.

ters are presented in Table III. The refined tin occupancies, equivalent to 0.523(3) tin atoms per formula unit, are acceptable bearing in mind the presence of the second phase, $NbPO_5$.

The structural data are consistent with the $^{119}$Sn-Mössbauer spectra. The singlet component may be associated with the location of approximately half of the $Sn^{2+}$ species in a regular octahedral site, while the quadrupole split absorption is indicative of a more distorted coordination for the remaining $Sn^{2+}$ ions.

It is notable that the $^{119}$Sn-Mössbauer chemical isomer shift data are more positive than those previously reported for $Sn^{2+}$ in oxygen coordination (*9*). The results are consistent with the X-ray refinement, which showed the octahedral tin atoms to be surrounded by six oxygen atoms at 2.62 Å and the remaining tin atoms to be coordinated by three oxygen atoms at 2.36 Å and three at 2.89 Å. Given that the four Sn–O bonds in SnO are 2.22 Å long (*10*), the more positive $^{119}$Sn-Mössbauer chemical isomer shift data can be attributed to the higher coordination of $Sn^{2+}$ and the longer Sn–O distances in $Sn_{0.5}NbTiP_3O_{12}$. Such $Sn^{2+}$ species may be viewed as being highly ionic in character.

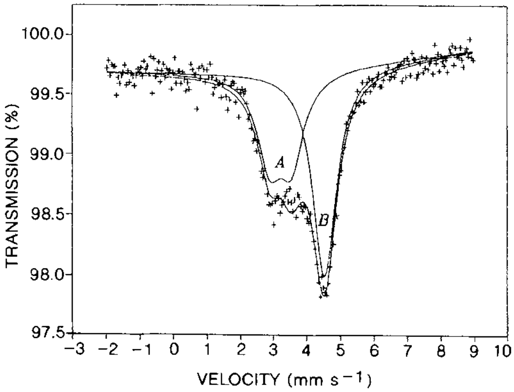

FIG. 2. $^{119}$Sn-Mössbauer spectrum recorded from $Sn_{0.5}NbTiP_3O_{12}$ at 298 K.

The above structural description involving the displacement of only half the $Sn^{2+}$ ions is unusual, but can be rationalized by a close examination of the structure (Fig. 3).

The Type I octahedral sites are trigonally elongated along [001] and share faces perpendicular to [001] with $(Nb/Ti)O_6$ octahedra above and below. Statistically, 25% of the Type I sites will be linked only to $TiO_6$ octahedra, 25% only to $NbO_6$ octahedra, and 50% to one $TiO_6$ octahedron and one $NbO_6$ octahedra. The charge balance mechanism, which results from the incorporation of $Sn^{2+}$ ions into the structure, will involve reduction of the $Ti^{4+}$ or $Nb^{5+}$ ions. Irrespective of the precise nature of this process, for $Sn_{0.5}NbTiP_3O_{12}$ we would expect the retention of the mirror plane symmetry at the tin site when it is linked to either two titanium or two niobium octahedra, but not when bounded by one $TiO_6$ and one $NbO_6$. Hence it is quite reasonable to expect the $Sn^{2+}$ ions to be distributed over two sites with equal concentrations. For such a model the nio-

TABLE II

$^{119}$Sn-MÖSSBAUER PARAMETERS RECORDED FROM $Sn_{0.5}NbTiP_3O_{12}$ AT 298 K

| Site | $\delta$ ($SnO_2$) ± 0.01 (mm $sec^{-1}$) | $\Delta$ ± 0.01 (mm $sec^{-1}$) | $\Gamma$ ± 0.01 (mm $sec^{-1}$) | Area ± 3 (%) |
|---|---|---|---|---|
| A | 3.15 | 0.68 | 0.90 | 46 |
| B | 4.47 | — | 0.90 | 54 |

bium or tin ions adjacent to the Sn(1) sites would be expected to have slightly different $z$-coordinates as compared with those linked to the Sn(2) sites. It therefore appears significant that the Nb/Ti isotropic temperature factor in $Sn_{0.5}NbTiP_3O_{12}$ is very much higher than in $NbTiP_3O_{12}$ and $Fe_{0.33}NbTiP_3O_{12}$ and thereby provides additional support for the proposed structural features. However, the adoption of undistorted sites is rare for $Sn^{2+}$ ions, since the lone pair electrons are normally stereochemically active. The results suggest that the lone pair electrons are primarily in the stereochemically inactive 5$s$ orbital. This may be a reflection of the high cation repulsions which result from this rare location of tin in a site which involves the face-sharing of octahedra containing very highly charged niobium and titanium cations.

### *$Fe_{0.33}NbTiP_3O_{12}$*

The incorporation of iron within the $NbTiP_3O_{12}$ structure gives (*5*) compounds of composition $Fe_{0.33}NbTiP_3O_{12}$ in which the iron is present as $Fe^{2+}$ (*6*). The X-ray powder diffraction pattern recorded from the compound of composition $Fe_{0.33}NbTiP_3O_{12}$ is shown in Fig. 1, and the structure was refined assuming that iron occupies only one type of site. Isotropic thermal factors were assumed for all atoms. The refined structural parameters are presented in Table IV. The results show that iron is located in the octahedral Type I sites and that the Type II sites remain empty.

The result is endorsed by a consideration of the $^{57}$Fe-Mössbauer spectrum recorded from $Fe_{0.33}NbTiP_3O_{12}$ over a narrow velocity range (Fig. 4, Table V). The spectrum was best-fitted to five separate components. The component B is characteristic of $Fe^{3+}$, and we associate this with a small amount of oxidized iron either at the surface of the host lattice or present as an impurity phase which is below the limits of detectability by X-ray powder diffraction. The component A is characterized by a large quadrupole

TABLE III

REFINED STRUCTURAL PARAMETERS FOR $Sn_{0.5}NbTiP_3O_{12}$

|  | $x$ | $y$ | $z$ | $B$(Å$^2$) | Unit cell occupancy |
|---|---|---|---|---|---|
| Nb/Ti | 0 | 0 | 0.1462(1) | 1.41(8) | 12 |
| P | 0.2843(4) | 0 | $\frac{1}{4}$ | 1.1(1) | 18 |
| Sn(1) | 0 | 0 | 0 | 2.9(2) | 1.57(1) |
| Sn(2) | 0 | 0 | 0.0144(1) | 2.9(2) | 1.57(1) |
| O(1) | 0.1708(7) | 0.9671(9) | 0.1957(4) | 0.7(2) | 36 |
| O(2) | 0.1915(7) | 0.1663(7) | 0.0931(3) | 0.7(2) | 36 |

*Note.* $a = b = 8.574(1)$ Å; $c = 22.730(1)$ Å; $R_I = 4.04\%$; $R_p = 8.18\%$; $R_{wp} = 10.92\%$; $R_{exp} = 3.94\%$.

TABLE IV

REFINED STRUCTURAL PARAMETERS FOR $Fe_{0.33}NbTiP_3O_{12}$

| | $x$ | $y$ | $z$ | $B$(Å$^2$) | Unit cell occupancy |
|---|---|---|---|---|---|
| Nb/Ti | 0 | 0 | 0.1409(1) | 0.29(9) | 12 |
| P | 0.2835(7) | 0 | $\frac{1}{4}$ | 1.3(2) | 18 |
| Fe | 0 | 0 | 0 | 3.0(7) | 2.23(6) |
| O(1) | 0.1803(8) | 0.984(1) | 0.1930(4) | −0.1(2) | 36 |
| O(2) | 0.1900(8) | 0.1605(8) | 0.0845(4) | −0.1(2) | 36 |

*Note.* $a = b = 8.614(1)$ Å; $c = 21.448(1)$ Å; $R_I = 6.01\%$; $R_p = 6.41\%$; $R_{wp} = 8.06\%$; $R_{exp} = 2.79\%$.

splitting, and we associate this with the presence of a small amount (ca. 5%) of $Fe^{2+}$ in the Type II sites which is also undetected by X-ray powder diffraction. The major features of the spectrum constituted by components C, D, and E and representing ca. 88% of the total iron content may be associated with $Fe^{2+}$ in approximately octahedral oxygen coordination. The result is consistent with the X-ray diffraction data, but the Mössbauer spectrum implies that the octahedrally coordinated $Fe^{2+}$ may occupy a distribution of similar sites. It is possible that these sites arise as a consequence of the random disposition of niobium and titanium ions in different oxidation states in the $NbTiP_3O_{12}$ structure which, as shown in Fig. 3, may have a direct influence on the displacement of the $Fe^{2+}$ ion from regular octahedral oxygen coordination. The high temperature factor

TABLE V

$^{57}$Fe-MÖSSBAUER PARAMETERS RECORDED FROM $Fe_{0.33}NbTiP_3O_{12}$ AT 298 K

| Site | δ(Fe) ± 0.03 (mm sec$^{-1}$) | Δ ± 0.03 (mm sec$^{-1}$) | Γ ± 0.03 (mm sec$^{-1}$) | Area ± 3 (%) |
|---|---|---|---|---|
| A | 1.23 | 2.26 | 0.35 | 5 |
| B | 0.37 | 1.06 | 0.35 | 5 |
| C | 1.28 | 1.48 | 0.35 | 18 |
| D | 1.31 | 1.04 | 0.35 | 36 |
| E | 1.33 | 0.66 | 0.35 | 36 |

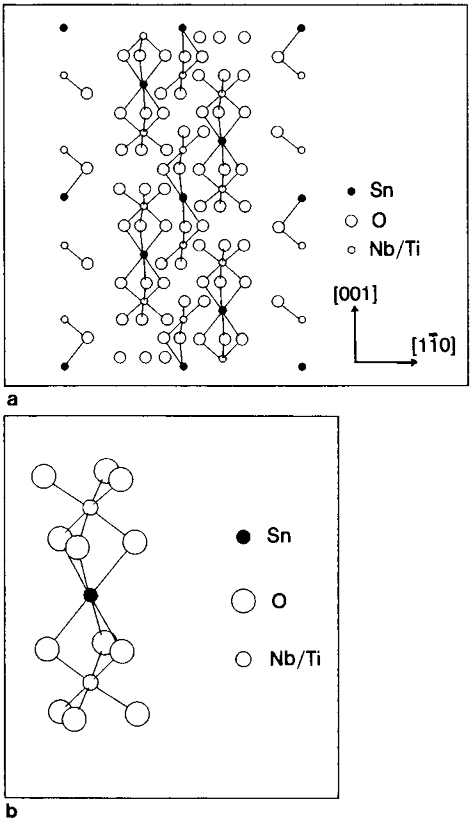

FIG. 3. (a) The structure of $Sn_{0.5}NbTiP_3O_{12}$ viewed along [110] with the phosphorus atoms omitted for clarity. (b) The coordination of tin around the octahedral Type I sites.

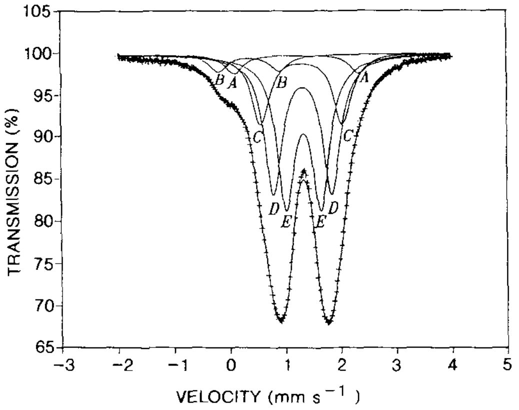

FIG. 4. $^{57}$Fe-Mössbauer spectrum recorded from $Fe_{0.33}NbTiP_3O_{12}$ at 298 K.

for iron (Table IV) is consistent with such disorder. The decidedly positive $^{57}$Fe-Mössbauer chemical isomer shifts for the $Fe^{2+}$ species (*11*) in $Fe_{0.33}NbTiP_3O_{12}$ may be associated with the average iron–oxygen bond lengths of 2.376 Å. These distances are about 0.2 Å longer than normally found in $Fe^{2+}$ octahedrally coordinated to oxygen (see, for example (*12*)), and we envisage the presence of $Fe^{2+}$ species which are highly ionic in character.

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