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The oxidation states of titanium and niobium in compounds of composition $Sn_xNbTiP_3O_{12}$ ($0 < x \leqslant 0.50$): an XPS study

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Abstract—The oxidation states of titanium and niobium in compounds of composition $Sn_xNbTiP_3O_{12}$ ($0 < x \leqslant 0.50$) have been examined by X-ray photoelectron spectroscopy. The incorporation of tin as Sn^{2+} within the $NbTiP_3O_{12}$ structure results in the partial reduction of Ti^{4+} to Ti^{3+} and of Nb^{5+} to Nb^{4+}. The Ti 2*p* and Nb 3*d* core levels are characterized by high binding energies, suggesting highly ionic character in the Ti—O and Nb—O bonds. © 1997 Elsevier Science Ltd

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Compounds of composition $A^{I}M_2^{IV}P_3O_{12}$ have structures which involve the corner sharing of PO_4 tetrahedra with MO_6 octahedra, thereby producing a three-dimensional linked channel network in which the A ions can be located [1–4]. The A ions can occupy two different sites within the channels [3]. The type I sites have a distorted octahedral coordination and are situated between two MO_6 octahedra along the *c* axis to produce ribbons of $O_3MO_3AO_3MO_3$. The type II sites are larger with 8–10 coordinating oxygen ions and are located between the ribbons. The structure is amenable to substitution on the A, M or phosphorus sites and a wide range of isostructural materials can be formed. The occupancy of the type I and II sites can also be varied from four to zero. For example, the compound $Na_3Zr_2Si_2PO_{12}$, Nasicon, has sodium ions in both type I and II sites and has attracted considerable interest because of its high sodium-ion mobility [1,2].

The white compound of composition $NbTiP_3O_{12}$ with vacant type I and II sites also adopts the Nasicon-type structure and has been shown to be capable of direct reaction with several electropositive metals to give blue–black solids in which the metallic species are incorporated within the vacant sites [5]. We have shown [6,7] that the reaction of $NbTiP_3O_{12}$ with elemental tin to give compounds of the type $Sn_xNbTiP_3O_{12}$ ($0 < x \leqslant 0.50$) involves the incorporation of Sn^{2+} within the octahedral type I sites of the $NbTiP_3O_{12}$ structure. The charge balance mechanism, which results from the incorporation of Sn^{2+} ions within the structure has, on the basis of limited Ti K-edge XANES data [7], been associated with the reduction of Nb^{5+} as opposed to Ti^{4+}. However, since no systematic study of the maintenance of electrical neutrality has been described, we report here on our examination of charge balance in these materials by X-ray photoelectron spectroscopy (XPS).

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 phosphate in air at 200 (12 h), 600 (6 h), 900 (15 h), 1000 (5 h) and finally at 1300°C (1 h). Tin was incorporated into $NbTiP_3O_{12}$ to give materials of composition $Sn_xNbTiP_3O_{12}$

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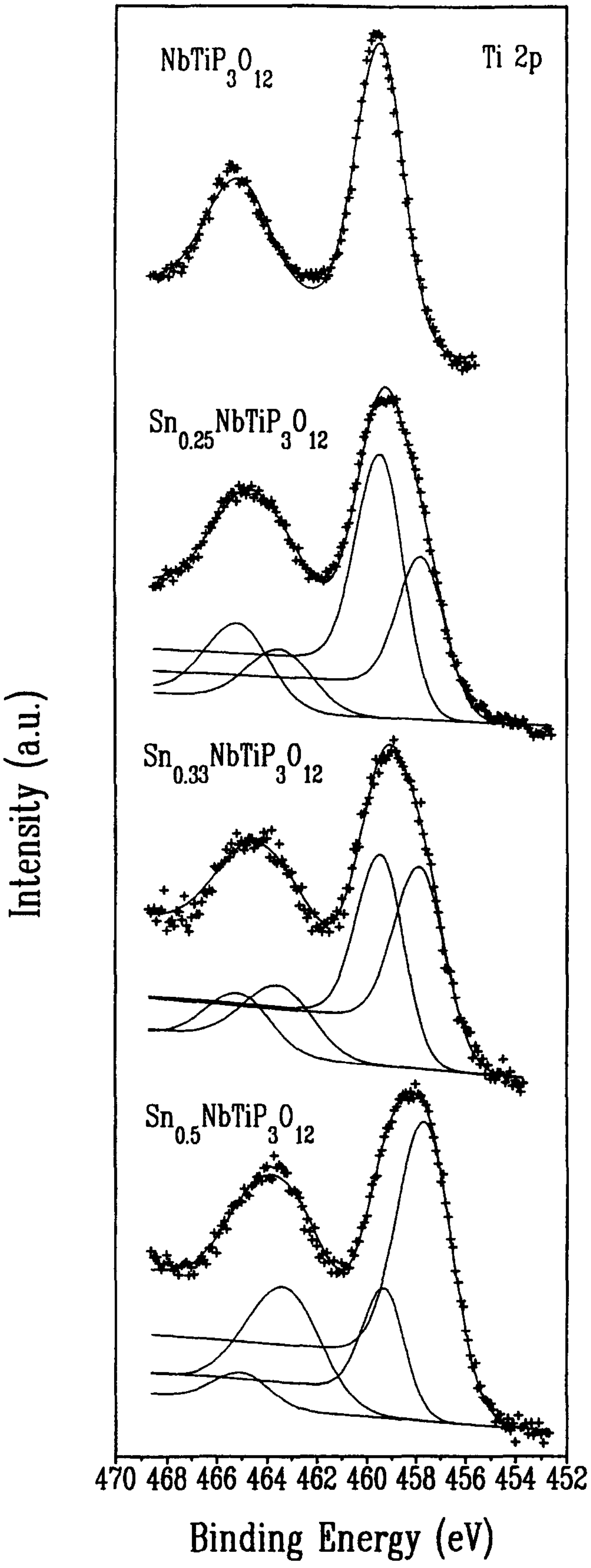

Fig. 1. Ti 2*p* X-ray photoelectron spectra recorded from the compounds $Sn_xNbTiP_3O_{12}$ ($0 \leqslant x \leqslant 0.50$)

($0 < x \leqslant 0.50$) by heating $NbTiP_3O_{12}$ with the powdered elemental metal at 900°C (24 h) in evacuated sealed quartz tubes.

XPS data were recorded with a triple channeltron CLAM2 analyser under an operating vacuum better than 1.10^{-8} torr using Al-$K\alpha$ radiation and a constant analyzer transmission energy of 20 eV. The powdered samples were supported on double-sided adhesive conductive carbon tape. All the spectra were recorded at take-off angles of 90°. All binding energies were charge-corrected to the C 1*s* signal which was set at 284.6 eV. Sample charging was checked by recording C 1*s* spectra both before and after the accumulation of each Ti 2*p* and Nb 3*d* spectrum and was found to be less than 0.1 eV. All the spectra were computer-fitted using a program based on procedures described in the literature [8]. The binding energies are accurate to ± 0.2 eV.

RESULTS AND DISCUSSION

The Ti 2*p* spectra recorded from the compounds $Sn_xNbTiP_3O_{12}$ ($0 \leqslant x \leqslant 0.50$) are shown in Fig. 1. The binding energies and the relative intensities obtained from the fit of the data are collected in Table 1. The Ti 2*p* spectrum recorded from white $NbTiP_3O_{12}$ showed only a spin-orbit doublet. The binding energy of the Ti $2p_{3/2}$ level of 459.5 eV is $\sim$ 0.5–0.7 eV larger than that reported for TiO_2 and $\sim$ 1 eV larger than that observed for Ti^{4+} in compounds such as $CaTiO_3$ or $SrTiO_3$ [9]. The result indicates that the Ti^{4+}—O bonds in $NbTiP_3O_{12}$ are more ionic in character than in other compounds in which Ti^{4+} is coordinated by oxygen and we associate this with the polarization of the Ti^{4+}—O bonds by the inductive effect of the P—O bonds [10]. The Ti 2*p* spectra recorded from the blue-black compounds $Sn_xNbTiP_3O_{12}$ ($0.25 \leqslant x \leqslant 0.50$) were characterized by broader lines than those recorded from $NbTiP_3O_{12}$. The peaks were deconvoluted into two contributions (Fig. 1, Table 1). One of the contributions is similar to that observed in the spectrum recorded from $NbTiP_3O_{12}$, the second appeared at lower binding energy (Ti $2p_{3/2} = 457.7$ eV) and we associate this with titanium in a lower oxidation state, probably Ti^{3+} (the Ti $2p_{3/2}$ binding energy of titanium in Ti_2O_3 is 457.2 eV [11]). The results suggest that the incorporation of tin into the $NbTiP_3O_{12}$ structure results in some reduction of Ti^{4+} to Ti^{3+}. The results, Table 1, also indicate that the extent of Ti^{4+} to Ti^{3+} reduction increases when larger concentrations of tin are incorporated within the structure.

Table 1. Ti $2p_{3/2}$ binding energies in the compounds $Sn_xNbTiP_3O_{12}$ ($0 \leqslant x \leqslant 0.50$)

Compound	BE (eV)	I_{rel} (%)	Assignment
$NbTiP_3O_{12}$	459.5	100	Ti^{4+}
$Sn_{0.25}NbTiP_3O_{12}$	459.5	60	Ti^{4+}
	457.8	40	Ti^{3+}
$Sn_{0.33}NbTiP_3O_{12}$	459.5	48	Ti^{4+}
	457.8	52	Ti^{3+}
$Sn_{0.50}NbTiP_3O_{12}$	459.3	22	Ti^{4+}
	457.7	78	Ti^{3+}

Table 2. Nb $3d_{5/2}$ binding energies in the compounds $Sn_xNbTiP_3O_{12}$ ($0 \leqslant x \leqslant 0.50$)

Compound	BE (eV)	I_{rel} (%)	Assignment
$NbTiP_3O_{12}$	208.2	100	Nb^{5+}
$Sn_{0.25}NbTiP_3O_{12}$	208.1	84	Nb^{5+}
	206.7	16	Nb^{4+}
$Sn_{0.33}NbTiP_3O_{12}$	208.1	77	Nb^{5+}
	207.0	23	Nb^{4+}
$Sn_{0.50}NbTiP_3O_{12}$	208.0	80	Nb^{5+}
	206.7	20	Nb^{4+}

The Nb 3*d* spectra recorded from the compounds $Sn_xNbTiP_3O_{12}$ ($0 \leqslant x \leqslant 0.50$) are shown in Fig. 2. The binding energies and the relative intensities obtained from the fit of the data are collected in Table 2. The Nb 3*d* spectrum recorded from $NbTiP_3O_{12}$ showed only a spin-orbit doublet. The binding energy of the Nb $3d_{5/2}$ level, 208.2 eV, is $\sim$ 0.8–1.0 eV higher than that observed for Nb_2O_5 [12] and is similar to that of Nb^{5+} in ionic compounds such as $NbCl_5$ [12]. We therefore associate this binding energy with a highly ionic Nb^{5+} species. The Nb 3*d* spectra recorded from the compounds $Sn_xNbTiP_3O_{12}$ ($0.25 \leqslant x \leqslant 0.50$) were broader than that recorded from $NbTiP_3O_{12}$ and were deconvoluted into two different contributions (Fig. 2, Table 2). One contribution was similar to that observed in the spectrum recorded from $NbTiP_3O_{12}$ and the second appeared at a lower binding energy (Nb $3d_{5/2} = 206.7$ eV). We associate this second contribution with Nb^{4+} species resulting from the partial reduction of Nb^{5+} ions in $NbTiP_3O_{12}$ after the incorporation of tin into the structure as Sn^{2+}. The results show that the extent of Nb^{5+} to Nb^{4+} reduction is less than that of Ti^{4+} to Ti^{3+} which implies that the reduction of Ti^{4+} ions is more easily achieved in these materials than the reduction of Nb^{5+}. It is interesting to note that the sum of the relative intensities given in Tables 1 and 2 for the Ti^{3+} and Nb^{4+} species fit reasonably well with values necessary to achieve electrical neutrality in these materials. For example, since the reactant metallic tin donates two electrons which reduce either Ti^{4+} or Nb^{5+} in the $NbTiP_3O_{12}$ structure, the compound $Sn_{0.25}NbTiP_3O_{12}$ may be formulated as $Sn_{0.25}(Nb^{5+})_{1-y}(Nb^{4+})_y(Ti^{4+})_{1-z}(Ti^{3+})_zP_3O_{12}$, and the experimentally determined value of $y+z = 0.56$ agrees well with the expected value of 0.50. Simi-

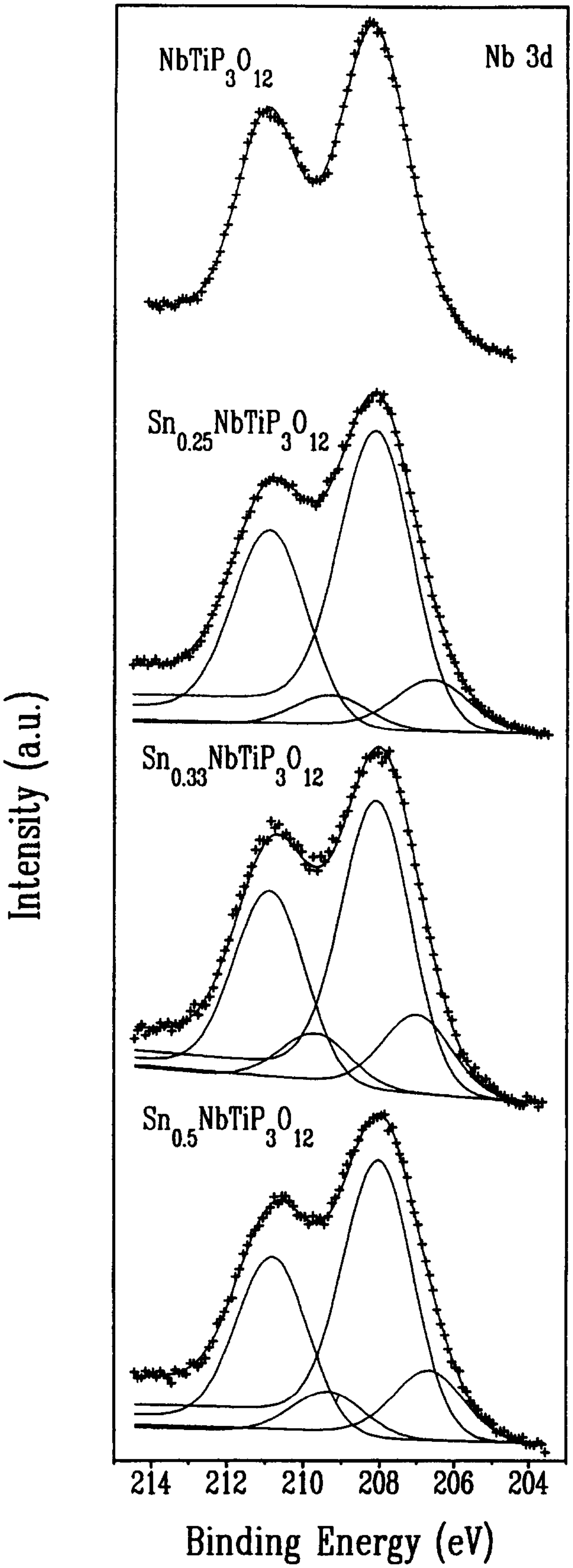

Fig. 2. Nb 3*d* X-ray photoelectron spectra recorded from the compounds $Sn_xNbTiP_3O_{12}$ ($0 \leq x \leq 0.50$)

larly, for the compounds $Sn_{0.33}NbTiP_3O_{12}$ and $Sn_{0.5}NbTiP_3O_{12}$, where $y+z$ would be expected to be 0.66 and 1, respectively, the experimentally determined values of 0.75 and 0.98 correlate remarkably well.

In a previous paper [7] we reported, on the basis of Mössbauer spectroscopy and X-ray powder diffraction data, that the upper limit of tin which can be accommodated within the channels of the $NbTiP_3O_{12}$ structure is achieved at *ca* $x = 0.5$. On the basis of limited Ti K-edge XANES data [7], it was assumed that Ti^{4+} was not reduced on incorporation of tin as a Sn^{2+} ion and that the material of composition $Sn_{0.5}NbTiP_3O_{12}$ corresponded to the situation where all the Nb^{5+} is reduced to the tetravalent form. The present work demonstrates a clear reduction of Ti^{4+} to Ti^{3+} as well as of Nb^{5+} to Nb^{4+} and endorses earlier magnetic susceptibility measurements [13] which showed $Sn_{0.5}NbTiP_3O_{12}$ to be paramagnetic at temperatures down to 4.2 K with the effective magnetic moment being consistent with the presence of Ti^{3+} and/or Nb^{4+}. We have also recorded the XPS data (Ti $2p$ and Nb $3d$ spectra) from $Sn_{0.66}NbTiP_3O_{12}$ and $Sn_{1.00}NbTiP_3O_{12}$ (which were shown by X-ray powder diffraction and ^{119}Sn Mössbauer spectroscopy to contain unreacted metallic tin [14]) and they are similar to those recorded from $Sn_{0.5}NbTiP_3O_{12}$. It therefore seems that it is not possible to reduce more than 75–80% of Ti^{4+} to the trivalent form or more than 20–25% of Nb^{5+} to the tetravalent form upon incorporation of tin, possibly because of the complex electrostatic interactions which can arise within the structure as a result of the existence of a large number of cations in different oxidation states.

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