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COMMUNICATION

NEW COMPOUNDS WITH NASICON-RELATED STRUCTURES OF THE TYPE $NaM'M''P_3O_{12}$ ($M' = Nb, Sb$; $M'' = Al, Ga, In, Fe$)

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Abstract—New compounds of composition $NaM'M''P_3O_{12}$ ($M' = Nb, Sb$; $M'' = Al, Ga, In, Fe$) with structures related to that of the fast ion conductor called "NASICON" have been prepared. The X-ray powder diffraction data are presented and the variation in the lattice parameters as aluminium in $NaNbAlP_3O_{12}$ is replaced by larger gallium, indium and iron ions is discussed. The lattice parameters and the resistivities of the compounds are indicative of the occupation by Na^+ of only the Type I sites.

Compounds of composition $AM_2^{IV}P_3O_{12}$ 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 types of 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 eight to ten co-ordinating 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 $Na_3Zr_2Si_2PO_{12}$ which is called 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]

We report here on the preparation and characterisation of new compounds of the type $AM'^{V}M''^{III}P_3O_{12}$.

EXPERIMENTAL

Compounds of composition $NaM'M''P_3O_{12}$ ($M' = Nb, Sb$; $M'' = Al, Ga, In, Fe$) were prepared by sequential heating of well ground appropriate stoichiometric mixtures of $NaNO_3$; Nb_2O_5 or Sb_2O_5; Al_2O_3, Ga_2O_3, In_2O_3 or Fe_2O_3; and $NH_4H_2PO_4$ at 500°C (6 h), 800°C (14 h), and at 1000°C (5 h). Compounds where $M'' = Ga$ and In required treatment at 1000°C for 16 h to achieve monophasic composition.

X-ray powder diffraction data were recorded with a Siemens D5000 diffractometer using Cu-K_α radiation. ^{57}Fe Mössbauer spectra were recorded with a microprocessor-controlled Mössbauer spectrometer using a ^{57}Co—Rh source. The drive velocity was calibrated with a ^{57}Co—Rh source and a natural iron foil. All the spectra were computer fitted. The ^{57}Fe Mössbauer chemical isomer shift data are quoted relative to metallic iron. Resistivity measurements were recorded with an EG and G

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Princeton Potentiostat Model 273A. Pellets of 2 mm thickness were prepared in a KBr press and the conductivity measured using platinum wire electrodes.

RESULTS AND DISCUSSION

The formation of monophasic compounds of composition $NaM'M''P_3O_{12}$ ($M' = Nb, Sb$; $M'' = Al, Ga, In, Fe$) was confirmed by X-ray powder diffraction. The X-ray powder diffraction data for $NaNbAlP_3O_{12}$ are contained in Table 1. The ^{57}Fe Mössbauer spectrum recorded from $NaNbFeP_3O_{12}$ (δ 0.35 mm s^{-1}, Δ 0.96 mm s^{-1}) confirmed the occupation by Fe^{3+} of the octahedral structural site in $NaNbFeP_3O_{12}$. The lattice parameters for compounds of the type $NaNbM''P_3O_{12}$ ($M = Al, Ga, In, Fe$) are shown in Table 2. The systematic increase in lattice parameters is a reflection of the increasing size[5] of the M″ ion as Al^{3+} ($r = 0.51$ Å) is replaced by Ga^{3+} ($r = 0.62$ Å), Fe^{3+} ($r = 0.64$ Å) and In^{3+} ($r = 0.81$ Å). This is depicted in Fig. 1 which shows the increase in the c lattice parameter to exceed that of the a and b lattice parameters. The trend is similar to that recently observed[6,7] when the structurally related $Nb^{V}Ti^{IV}P_3O_{12}$ phases, which contain empty Type I and Type II sites, were reacted with iron and tin. The results were interpreted in terms of the incor-

Table 1. X-ray powder diffraction data for $NaNbAlP_3O_{12}$

$h\ k\ l$	d_{obs} (Å)	d_{cal} (Å)
1 0 2	6.099	6.097
1 0 4	4.377	4.377
1 1 0	4.248	4.248
1 1 3	3.665	3.666
2 0 4	3.046	3.048
1 1 6	2.758	2.759
1 0 8	2.552	2.553
2 1 4	2.475	2.476
3 0 0	2.452	2.452
2 0 8	2.189	2.188
1 1 9	2.103	2.103
2 1 7	2.071	2.073
2 2 3	2.040	2.038
3 0 6	2.030	2.032
3 1 2	--	2.005
2 1 8	1.945	1.945
3 1 4	1.911	1.910
2 0 10	1.869	1.874
2 2 6	1.833	1.833
4 0 2	1.813	1.814
2 1 10	1.715	1.715
3 1 7	—	1.706
1 1 12	1.668	1.669
3 1 8	1.632	1.633
3 2 4	1.611	1.612
4 1 0	1.605	1.605
3 2 5	1.576	1.574
4 1 3	1.566	1.567
4 0 8	1.524	1.524
3 1 10	1.489	1.489

Table 2. Lattice parameters for compounds of the type $NaM'M''P_3O_{12}$ ($M' = Nb, Sb$; $M'' = Al, Ga, In, Fe$)

M″	$a = b \pm 0.01$ Å	$c \pm 0.01$ Å
M′ = Nb		
Al	8.49	21.78
Ga	8.54	21.98
In	8.65	22.62
Fe	8.61	22.11
M″ = Sb		
Al	8.29	21.87
Ga	8.29	22.12
In	8.34	23.08
Fe	8.38	22.22

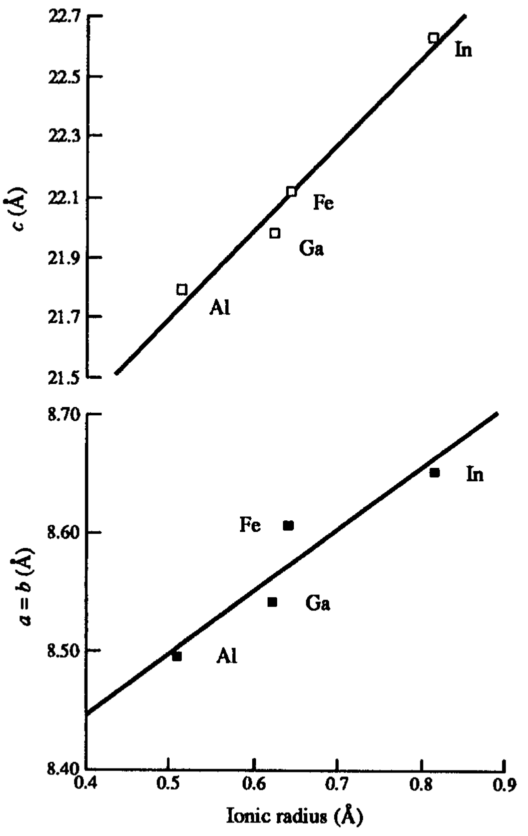

Fig. 1. Variation in lattice parameters for compounds of the type $NaNbM''P_3O_{12}$ ($M'' = Al, Ga, In, Fe$).

poration of the large Fe^{2+} and Sn^{2+} ions in the Type I sites with concomitant reduction of niobium in the host structure. We envisage that in materials of the type $NaNb^{V}M''^{III}P_3O_{12}$ the small sodium ions, which maintain electrical neutrality in the phases, are also located in the octahedral Type I sites as opposed to being distributed over both the Type I and Type II sites as in NASICON. The preliminary measurement of the resistivities of compounds of the type $NaNbM''P_3O_{12}$ recorded from pelleted samples were found to be $>10^8$ ohms at 298 K which contrasts with the fast sodium ion conduction properties of NASICON. We also associate this with the structural evidence for the occupation by sodium of only the Type I sites in $NaNbM''P_3O_{12}$.

Compounds of the type $NaSbM''P_3O_{12}$ were similar. The lattice parameters (Table 2) showed similar variations according to the size of the M″ ion.

Hence new compounds of the type $NaM'M''P_3O_{12}$ (M' = Nb, Sb; M'' = Al, Ga, In, Fe) with NASICON type structures have been prepared. It appears however that, in contrast with NASICON, the small sodium ions are incorporated only within the octahedral Type I sites and that this influences the ionic conduction properties of the materials.

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