Chromatographic Determination of the Phosphate Anions in Crystalline and Glassy $Na_4NbP_3O_z$*,†

B. C. SALES AND B. C. CHAKOUMAKOS

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056

High-performance liquid chromatography (HPLC) measurements on crystalline and glassy $Na_4NbP_3O_z$ prove that the crystalline phase is a pyrophosphate and that the glassy material contains a distribution of phosphate anions with anions up to five PO_4 tetrahedra in length. Powder X-ray diffraction data for a new trimetaphosphate crystalline phase with the composition $Na_3NbP_3O_x$ are also reported. © 1993 Academic Press, Inc.

Introduction

Crystalline $Na_4NbP_3O_z$ was found by Jazouli *et al.* (*1, 2*) to exhibit a reversible crystalline-to-glass phase change. On the basis of Raman and optical investigations, these workers concluded that the crystalline phase was an orthophosphate with a structure similar to the NASICON structure; hence the crystalline composition was given as $Na_4Nb(PO_4)_3$. Very few orthophosphates convert to the glassy phase by conventional melt quenching, which made this material even more intriguing. This observation was also made by Prabakar and Rao (*3*), who concluded on the basis of magic-angle spinning (MAS) ^{31}P nuclear magnetic resonance (NMR) spectroscopy that the local phosphorus environments were quite different in the glassy and crystalline forms of Na_4 $Nb(PO)_4$. They suggested that the crystalline material was actually a metaphosphate,

which would account for the relative ease of glass formation as well as the change in local environments suggested by the NMR spectra. If single crystals of $Na_4NbP_3O_z$ could easily be produced, X-ray or neutron diffraction techniques could precisely determine the structure. For the glassy phase, however, diffraction techniques provide limited structural information.

High-performance liquid chromatography (HPLC) provides another approach to the resolution of some of the structural questions concerning crystalline and glassy $Na_4NbP_3O_z$. The HPLC technique is only sensitive to the distribution of phosphate anions present in the solid, and is applicable to a large number of metal phosphate materials. From the point of view of HPLC, the metal phosphate solids of interest can be described as consisting of "spaghetti-like" chains of corner-linked PO_4 tetrahedra. These chains (anions) are in turn bonded to each other by metal cations (e.g., Na, Nb). A crystalline phosphate of this type generally has a phosphate anion of only one specific length in its structure, while an amorphous solid is characterized by a distribution of chains of different length. The HPLC technique works for most metal phosphate solids because of the way that

these solids dissolve in high-pH solutions containing a chelating agent (EDTA). In these solutions, the phosphate solids dissolve without breaking the bridging P–O–P bonds of the phosphate anions (4, 5); i.e., entire phosphate anions are transported into the solution intact (congruent dissolution). Therefore, if the dissolution step is done properly, the distribution of phosphate anions in solution accurately mirrors the distribution of phosphate anions in the solid. Once the anions are in solution, they can be separated and counted using a modern HPLC system. The presence of the chelating agent in the solutions is apparently critical in dealing with high-field-strength cations such as Nb^{5+}, because otherwise, the cations tend to form metal complexes with the phosphate anions in solution. Selected crystalline-phosphate standards are used to calibrate the HPLC system so that a particular peak in the chromatogram can be assigned unambiguously to a known phosphate anion. A detailed description of the HPLC system used in our laboratory has been given previously (6, 8).

Synthesis

Crystalline and glassy $Na_4NbP_3O_z$ specimens were prepared as described by El Jazouli et al. (2). Stochiometric amounts of Na_2CO_3, Nb_2O_5, and $NH_4H_2PO_4$ were thoroughly ground together, pressed into a pellet, and then heated in air in a Pt crucible at 200°C for 2 hr, 400°C for 4 hr, and 650°C for 15 hr. The material was removed from the Pt crucible, reground, re-pressed, and fired at 650°C in air for another 60 hr. The powder X-ray pattern from the resulting material (Fig. 1a) was in good agreement with the pattern reported by Prabkar and Rao (3). The general topology of the X-ray pattern, however, is not similar to that of NASICON (9). A portion of the crystalline $Na_4NbP_3O_z$ was converted into a glass by heating the material in a Pt crucible to a temperature of about 800°C and then simply turning off the furnace. This material was found to be an
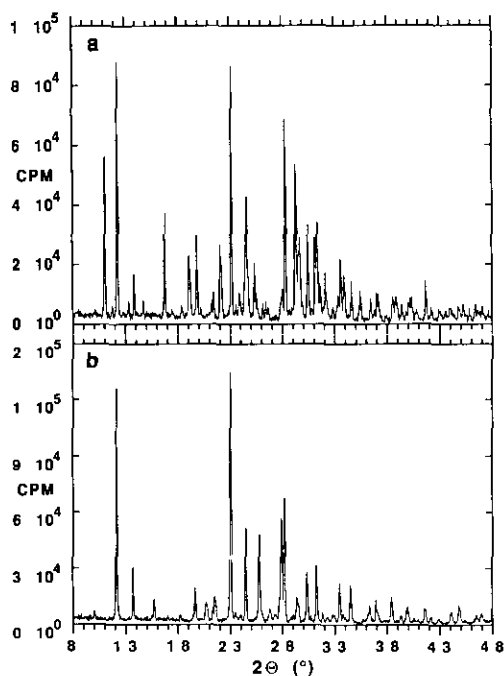

FIG. 1. Powder X-ray diffraction patterns (Cu$K\alpha$ radiation) from (a) $Na_4NbP_3O_z$ and (b) $Na_3NbP_3O_z$.

unusually good glass former, since cooling the melt at rates as low as 4°C/hr resulted in very little, if any, crystallization.

Results and Discussion

A small portion of crystalline $Na_4NbP_3O_z$ was lightly ground into a powder, partially dissolved in the chromatography solution, filtered, and injected into the HPLC system. The resulting chromatogram (Fig. 2a) clearly shows that $Na_4NbP_3O_z$ is a pyrophosphate and not an orthophosphate as originally suggested. The distribution of phosphate anions in the glass was analyzed in a similar fashion and the chromatogram from the glass is shown in Fig. 2b. As expected, in addition to the pyrophosphate anions present in the parent crystalline material, the glass contains both shorter and longer phosphate anions. In the glass, the average chain length must remain close to 2 in order to maintain formal charge balance between the phosphate anions and the metal
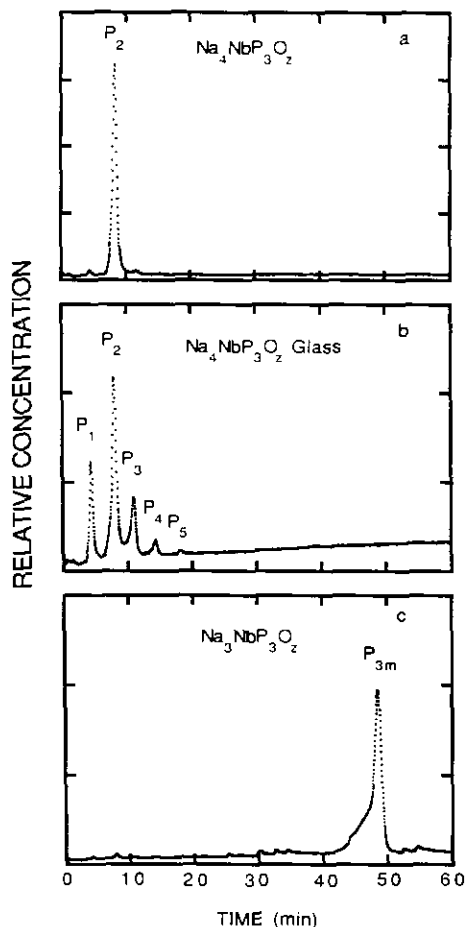
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FIG. 2. Chromatograms from (a) crystalline $Na_4Nb P_3O_z$, (b) $Na_4NbP_3O_z$ glass, and (c) crystalline $Na_3Nb P_3O_z$. Phosphate anions consisting of 1, 2, 3, . . . , n corner-linked PO_4 tetrahedra are labelled in the figure as P_1, P_2, P_3, . . . , P_n. The cyclic phosphate anion, trimetaphosphate, is denoted by P_{3m}.

cations. From the chromatogram shown in Fig. 2b, the average chain length was calculated to be 1.75.

Since $Na_4NbP_3O_z$ clearly appears to be a pyrophosphate, this suggests that the formula be written as $Na_6(NbO)_2(P_2O_7)_3 \cdot Na_2O$. The presence of niobyl groups was also suggested by the Raman data of Jazouli et al. (2). Since it was not obvious on the basis of formal charge balance alone how to incorporate the extra Na_2O into the pyrophosphate formula, crystalline samples of

$Na_3NbP_3O_z$ were prepared using the same synthesis conditions that were used to prepare $Na_4NbP_3O_z$. The x-ray pattern from this material (Fig. 1b) is quite different from that of $Na_4NbP_3O_z$ and is simpler, indicating a crystalline phase with higher symmetry. The chromatogram from this material was quite surprising (Fig. 2c). $Na_3NbP_3O_z$ was expected to be a pyrophosphate, but the chromatogram clearly shows only one type of anion, a trimetaphosphate anion, P_{3m}.

TABLE I

X-RAY DIFFRACTION PATTERN (CuKα RADIATION) FOR $Na_3NbP_3O_z$

2Θ(°)	d(Å)	Relative intensity
9.97	8.86	5
12.09	7.31	93
13.66	6.47	22
15.66	5.65	10
18.15	4.88	4
19.57	4.53	12
20.58	4.31	9
20.71	4.28	8
21.25	4.18	6
21.48	4.13	11
22.98	3.869	100
24.43	3.642	38
25.73	3.462	36
26.73	3.334	6
27.26	3.270	3
27.62	3.228	3
27.85	3.203	42
28.13	3.171	50
29.33	3.044	10
30.30	2.948	20
31.20	2.865	23
31.79	2.814	5
32.14	2.784	2
32.83	2.727	4
33.41	2.681	16
34.45	2.602	15
36.27	2.476	8
36.92	2.434	10
38.36	2.346	11
39.25	2.295	3
39.86	2.261	7
41.54	2.173	7
42.09	2.146	3
42.84	2.110	2
44.03	2.056	5
44.79	2.023	8

The trimetaphosphate anion $(P_3O_9)^{-3}$ consists of three PO_4 tetrahedra in a ring. The powder diffraction intensity data for this new crystalline phosphate phase are given in Table I.

Two other crystalline Na–Nb–P–O solids were also synthesized, Na$_2$NbP$_3$O$_z$ and Na$_5$NbP$_3$O$_z$. X-ray diffraction and HPLC indicated that these samples were multiphase. Taken together, the present results suggest that part of the reason that the pyrophosphate Na$_4$NbP$_3$O$_z$ forms a glass so easily is its close proximity to the trimetaphosphate phase Na$_3$NbP$_3$O$_z$. The results also show that the phosphate-anion characterization of a new crystalline phosphate phase with indirect techniques such as Raman or NMR spectroscopy is, at best, difficult.

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