

Synthesis and structural characterization of Na₂MnP₂O₇ crystal

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Abstract. Na₂MnP₂O₇ crystals were synthesized by hydrothermal technique. Crystals obtained are in the form of single crystals of rhombohedral morphology with lattice parameters as follows: triclinic, $P\bar{1}$, $l = 0.71069 \text{ \AA}$, $a = 6.657(3) \text{ \AA}$, $b = 6.714(6) \text{ \AA}$, $c = 6.518(4) \text{ \AA}$, $\alpha = 112.31(6)^\circ$, $\beta = 92.14(4)^\circ$, $\gamma = 83.89(5)^\circ$, $V = 268.0(3) \text{ \AA}^3$, $Z = 2$, $r_{\text{cal}} = 2$, 3.121 g/cm^3 , $m = 3.121 \text{ mm}^{-1}$, $F_{000} = 244$, goodness-of-fit on $F = 1.348$, final R indices with $[I > 3s(I)]$ $R = 0.051$ and $wR = 0.065$.

Keywords. NASICON; hydrothermal; crystal structure.

1. Introduction

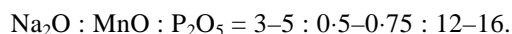
NASICON compounds were the most popular materials available for many years as source materials for high temperature battery devices. But the interest in these compounds has slowly declined because of their polycrystallinity, non-stoichiometric composition, complex conduction mechanism and host of other problems (Byrappa and Gopalakrishna 1986). Owing to these problems, scientists looked into new compounds known as NASICON analogues, which are pure phosphates and are almost free from the NASICON problems (Yoshimura *et al* 1981; Byrappa *et al* 1985a, b, 1986; Clearfield *et al* 1986; Lokanath *et al* 1999). However, these compounds always have only the triorthophosphate end members and their structures are directly related to Na₃Sc₂P₃O₁₂ (Byrappa and Gopalakrishna 1986; Lokanath *et al* 1999). We have reported for the first time high ionic conductivity in condensed phosphates which are much easier to synthesize in the form of single crystals with stoichiometric composition (Byrappa *et al* 1989; Salvador Gali *et al* 1989, 1992). We report here the synthesis and crystal structure of a new material which promises to be a good solid electrolyte.

2. Experimental

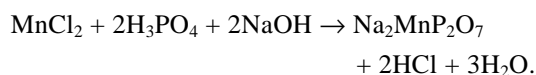
Crystals of the compound Na₂MnP₂O₇ were synthesized in teflon liners by the hydrothermal method using Morey

type autoclave at 220–250°C and 50–60 bars. The starting mixture consists of manganese oxide, 85% orthophosphoric acid and 2.5–5 M NaOH solution which acts as a mineralizer.

Na₂MnP₂O₇ crystals could be synthesized under the following molar ratio



The following reaction explains the synthesis of the compound



Light purple coloured crystals with sub vitreous lustre were obtained in the form of single crystals having sizes ranging from 1–3 mm, with well developed morphology.

Rhombohedral shaped crystal with approximate size 0.1 × 0.1 × 0.15 mm was mounted on a Rigaku AFC7S diffractometer equipped with a graphite monochromated MoK α X-ray source ($l = 0.71069 \text{ \AA}$). The unit cell parameters were obtained by using the method of short vectors followed by least squares refinement of 19 reflections. Lorentz and polarization corrections were applied.

The crystal belongs to the triclinic space group $P\bar{1}$. The structure was solved using SIR92 (Altomare *et al* 1993). The structure was refined using teXsan (Molecular Structure Corporation, USA 1995) for 923 unique reflections. The refinement was carried out by keeping all oxygen atoms as isotropic and the rest as anisotropic. The

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procedure is similar to the structure solutions of compounds reported earlier (Byrappa *et al* 1985a, b; Lokanath *et al* 1999). 101 parameters were refined using 923 observed reflections with $I > 3\sigma(I)$ to $R = 0.051$ and $wR = 0.065$.

3. Results and discussion

The positional parameters and equivalent temperature factors are given in table 1. Anisotropic parameters (U_{ij}) are listed in table 2. Table 3 gives the bond distances and

Table 1. Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Mn1	0.6503(2)	0.1145(2)	0.2253(2)	0.0111(3)
P1	1.1469(3)	0.2212(3)	0.2531(3)	0.0096(5)
P2	1.6269(3)	0.6335(3)	0.3242(3)	0.0097(5)
Na1	1.1507(6)	0.7443(6)	0.2135(8)	0.046(1)
O1	1.4306(8)	0.7431(8)	0.4348(8)	0.014(1)
O2	1.7204(8)	0.7773(8)	0.2227(9)	0.015(1)
O3	1.7843(7)	0.6173(8)	0.5127(8)	0.012(1)
O4	1.0920(7)	0.3693(8)	0.1226(8)	0.013(1)
O5	1.3267(7)	0.0587(8)	0.1441(8)	0.012(1)
O6	0.9716(7)	0.1136(8)	0.2873(9)	0.016(1)
O7	0.6249(7)	0.4052(8)	0.1605(8)	0.013(1)

Table 2. Anisotropic thermal parameters of the non-hydrogen atoms.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn1	0.0115(7)	0.0085(7)	0.0095(7)	− 0.0000(4)	− 0.0005(4)	− 0.0006(5)
P1	0.0104(10)	0.0065(10)	0.008(1)	0.0001(7)	− 0.0012(7)	− 0.0013(8)
P2	0.0130(10)	0.0059(10)	0.008(1)	− 0.0006(7)	− 0.0015(7)	− 0.0003(8)
Na1	0.043(2)	0.018(2)	0.076(3)	− 0.008(2)	− 0.039(2)	0.017(2)
O1	0.019(3)	0.014(3)	0.006(3)	0.000(2)	− 0.002(2)	0.000(2)
O2	0.022(3)	0.005(3)	0.016(3)	0.001(2)	0.000(2)	0.001(2)
O3	0.014(3)	0.009(3)	0.007(3)	0.001(2)	− 0.004(2)	− 0.003(2)
O4	0.013(3)	0.010(3)	0.014(3)	0.002(2)	− 0.000(2)	0.002(2)
O5	0.014(3)	0.010(3)	0.007(3)	0.001(2)	− 0.001(2)	− 0.001(2)
O6	0.013(3)	0.011(3)	0.021(3)	− 0.001(2)	− 0.007(2)	0.004(2)
O7	0.021(3)	0.004(3)	0.010(3)	− 0.003(2)	− 0.005(2)	− 0.001(2)

Table 3. Bond lengths (Å).

Atoms	Length	Atoms	Length
Mn1–O1	2.118(5)	P2–O1	1.494(5)
Mn1–O2	2.256(5)	P2–O2	1.549(5)
Mn1–O5	2.235(5)	P2–O3	1.612(5)
Mn1–O5	2.244(5)	P2–O7	1.500(5)
Mn1–O6	2.162(5)	Na1–O1	2.315(6)
Mn1–O7	2.137(5)	Na1–O4	2.429(6)
P1–Na1	3.111(4)	Na1–O4	2.592(6)
P1–O3	1.585(5)	Na1–O5	2.707(6)
P1–O4	1.545(5)	Na1–O6	2.511(6)
P1–O5	1.525(5)	Na1–O7	2.698(7)
P1–O6	1.502(5)		

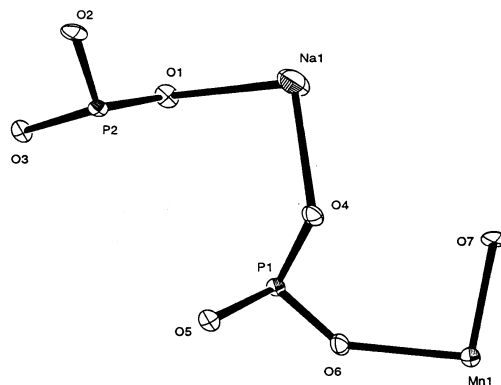


Figure 1. ORTEP of the molecule at 50% probability.

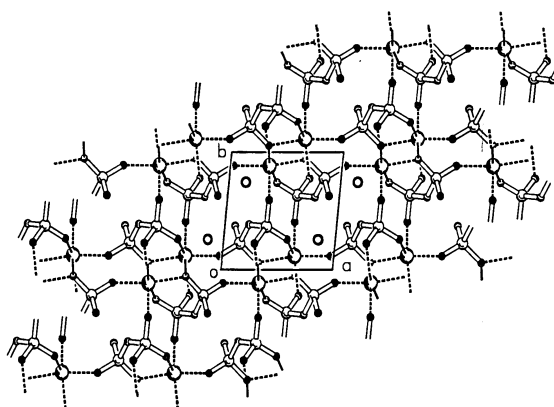


Figure 2. Packing of molecules down *c* axis.

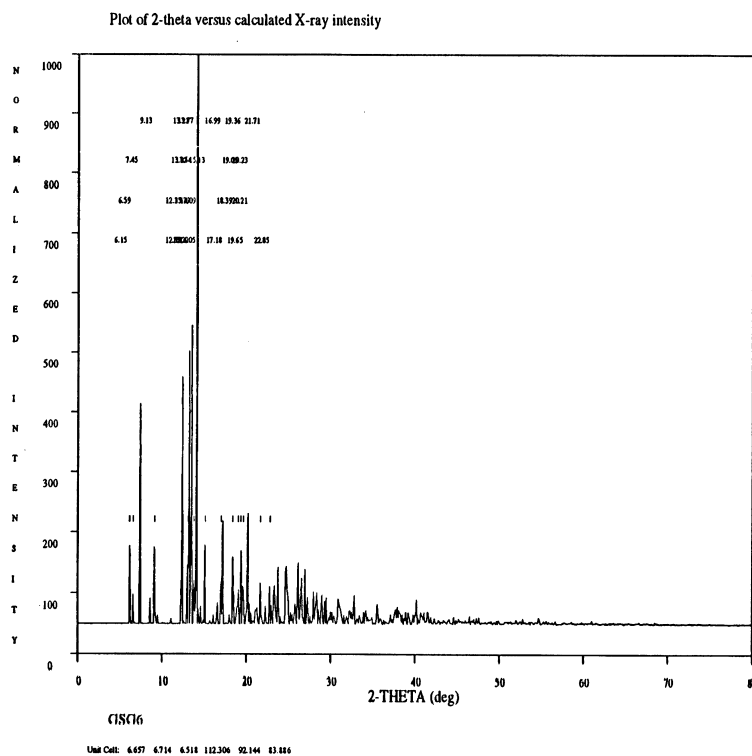


Figure 3. Powder pattern of the sample.

Table 4. Bond angles (°).

Atoms	Angle	Atoms	Angle
O1-Mnl-O2	94.9(2)	P1-Nal-O7	92.2(2)
O1-Mnl-O5	88.7(2)	O1-Nal-O4	96.4(2)
O1-Mnl-O5	168.4(2)	O1-Nal-O4	160.7(2)
O1-Mnl-O6	94.4(2)	O1-Nal-O5	83.2(2)
O1-Mnl-O7	97.5(2)	O1-Nal-O6	114.2(2)
O2-Mnl-O5	91.1(2)	O1-Nal-O7	92.7(2)
O2-Mnl-O5	83.0(2)	O4-Nal-O4	71.7(2)
O2-Mnl-O6	80.2(2)	O4-Nal-O5	152.7(3)
O2-Mnl-O7	166.9(2)	O4-Nal-O6	142.6(2)
O5-Mnl-O5	80.0(2)	O4-Nal-O7	85.9(2)
O5-Mnl-O6	171.0(2)	O4-Nal-O5	100.5(2)
O5-Mnl-O7	93.5(2)	O4-Nal-O6	83.1(2)
O5-Mnl-O6	96.4(2)	O4-Nal-O7	71.9(2)
O5-Mnl-O7	85.7(2)	O5-Nal-O6	57.4(2)
O6-Mnl-O7	94.5(2)	O5-Nal-O7	66.9(2)
Nal-P1-O3	114.5(2)	O6-Nal-O7	112.4(2)
Nal-P1-O4	142.0(2)	Mnl-O1-P2	130.9(3)
Nal-P1-O5	60.5(2)	Mnl-O1-Nal	110.7(2)
Nal-P1-O6	53.0(2)	P2-O1-Nal	118.2(3)
O3-P1-O4	103.5(3)	Mnl-O2-P2	136.5(3)
O3-P1-O5	108.5(3)	P1-O3-P2	135.7(3)
O3-P1-O6	108.6(3)	P1-O4-Nal	129.9(3)
O4-P1-O5	110.0(3)	P1-O4-Nal	120.8(3)
O4-P1-O6	113.6(3)	Nal-O4-Nal	108.3(2)
O5-P1-O6	112.2(3)	Mnl-O5-Mnl	100.0(2)
O1-P2-O2	110.1(3)	Mnl-O5-P1	124.8(3)
O1-P2-O3	108.1(3)	Mnl-O5-Nal	122.6(2)
O1-P2-O7	116.5(3)	Mnl-O5-P1	121.7(3)
O2-P2-O3	105.0(3)	Mnl-O5-Nal	95.1(2)
O2-P2-O7	111.6(3)	P1-O5-Nal	90.2(2)
O3-P2-O7	104.8(3)	Mnl-O6-P1	139.1(3)
P1-Nal-O1	96.6(2)	Mnl-O6-Nal	113.9(2)
P1-Nal-O4	166.9(2)	P1-O6-Nal	98.5(3)
P1-Nal-O4	95.4(2)	Mnl-O7-P2	128.1(3)
P1-Nal-O5	29.3(1)	Mnl-O7-Nal	98.0(2)
P1-Nal-O6	28.5(1)	P2-O7-Nal	121.4(3)

angles. Figure 1 represents ORTEP (Molecular Structure Corporation, USA 1995) diagram of the molecule with thermal ellipsoids at 50% probability. The packing of molecules down *c* axis is shown in figure 2. The material

is a good example of a three-dimensional conductor. Figure 3 represents the simulated powder pattern of the sample.

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