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X-ray powder diffraction and IR study of $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ and $NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$

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$NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ was prepared by hydrothermal synthesis and was characterized by X-ray powder difraction and IR method. The title compound was synthesized from $MgCl_2\cdot 6H_2O$, $NaBO_3\cdot 4H_2O$, and $(NH_4)_2HPO_4$ with variable molar ratios using hydrothermal method by heating at 165 °C for 3 days. The X-ray powder diffraction data was indexed in hexagonal system, the unit cell parameters were found to be as $a = 9.428$, $c = 15.82$ Å, $Z = 4$ and the space group is $P6_122$. It is isostructural with $M^IM^{II}(H_2O)[BP_2O_8]$ type compounds where $M^I = Na$, K; $M^{II} = Mg$, Mn, Fe, Co, Ni and Zn. In addition $NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$ was also synthesized the first time in this research. Its unit cell parameters and hkl values were in good agreement with the sodium magnesium compound. The unit cell parameters are $a = 9.529$, $c = 15.736$ Å. The indexed X-ray powder diffraction data of both compounds which were not reported in the literature is presented in this work. The IR data of $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ is also reported. *© 2000 Kluwer Academic Publishers*

1. Introduction

Borophosphates are intermediate compounds of the systems M_xO_y-B_2O_3-P_2O_5-(H_2O) which contain complex anionic structures built of BO_4, BO_3 and PO_4 groups. A first approach to the development of a structural chemistry of borophosphates is based on the linking principles of the primary building units following the general line of silicate crystal chemistry [1–3].

Most of the compounds already known contain anionic partial structures in which phosphorus and boron are tetrahedrally surrounded by oxygen. But there are a lot of examples in which boron also shows trigonal - planar coordination. The borophosphate, $CoB_2P_3O_{12}(OH)\cdot C_2H_{10}N_2$, was described as an open - framework structure formed from corner-sharing BO_4 and PO_4 tetrahedra as well as CoO_6 octahedra [4]. In the structure of $Pb_3[BP_3O_{12}]$, boron and phosphorus are also tetrahedrally coordinated by oxygen and the polyhedra form one-dimensional infinite helices that contain two additional PO_4 groups connected to the BO_4 unit [5]. The crystal structure of $Na_5[B_2P_3O_{13}]$ contains BO_4 and PO_4 tetrahedra which share common vertices to form one dimensional infinite chains of $[B_2P_3O_{13}]$ [6, 7]. On the other hand, $Co_5BP_3O_{13}$ contains planar BO_3 groups that are linked to PO_4 tetrahedra to form dimeric $[BPO_6]^{4-}$ units [8]. The structure of α - $Zn_3(BO_3)(PO_4)$ contains isolated trigonally planar BO_3 and tetrahedral PO_4 units which are not joined together [9]. Shi *et al* [10]. also stated that the crystal structure of isotypic rare earth borophosphate compounds, $Ln_7O_6(BO_3)(PO_4)_2$, contains isolated BO_3 triangles and PO_4 tetrahedras as in the case of α-$Mg_3[BPO_7]$ [3, 11].

Although the definite number of crystal structures of borophosphates known up to now is rather small, a first approach to a structural chemistry of borophosphates is proposed by Kniep *et al* [12]. in which crystal structure of borophosphates are first divided into anhydrous and hydrated phases. According to this classification and the molar ratio of B : P; trigonal or tetrahedral coordination of B and ring structures were observed.

Molecular sieve compounds are a class of crystalline solids which because of their porous nature have wide uses for catalytic and adsorption purposes [13]. Since BPO_4 itself is an effective catalyst in a variety of dehydration, hydration, alkylation, oligomerization and rearrangement reactions, incorporation of borophosphate groups into microporous metal-borophosphates offers the potential for enhanced catalytic efficiency, as well as hydrolytic stability and the additional catalytic activitiy of the metal centers of the framework [14–16].

In this work hydrothermal preparation of $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ and $NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$ were accomplished using different reactions with different molar ratios of the reactants. The powder

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products were analyzed by X-ray powder diffraction and IR methods.

2. Experimental

2.1. Substances

$MgCl_2{\cdot}6H_2O$, $NaBO_3{\cdot}4H_2O$, and $(NH_4)_2HPO_4$ (from Merck)

2.2. Instrumentation

X-ray powder diffraction patterns (XRD) taken by using Philips diffractometer with PW 1050/25 goniometer and Co ($K\alpha$ 30–40 kV, 10–20 mA, $\lambda = 1.79021$ Å) radiation and Huber Diffractometer with Cu ($K\alpha_1$ 30–40 kV, 10–20 mA, $\lambda = 1.54051$ Å).

Nicolet 510 FT-IR Infrared Spectrometer was used in the region 400–4000 cm^{-1}. Spectra of solid samples were obtained from KBr pellets with 100 : 30 (wt/wt) KBr to product ratio.

The heating of teflon coated autoclave was done with Electro-mag oven with the heating range of 50–300°C.

Crystals were photographed with Jeol Scanning Electron Microscope (SEM) 6400 (JSN-6400) and the quantitative analysis of Mg, and Na have been done with Energy Dispersive X-ray analyzer (EDX) (20 kV).

Inductively Coupled Plasma (ICP Leeman Lab.Inc., DRE Direct Reading Echelle) was used for the analysis of Mg, Na, P and B.

2.3. Procedure

The hydrothermal synthesis was started from mixtures (totally 8 g) of $MgCl_2{\cdot}6H_2O$, $NaBO_3{\cdot}4H_2O$, and $(NH_4)_2HPO_4$ in various molar ratios (Table I). Required amount of H_2O and concentrated HNO_3 (given in Table I) was added to dissolve this solid mixture at 90 °C, then the total volume was reduced to 10 ml by evaporation of water. The highly viscous solution ($pH < 1$) was filled into Teflon coated autoclave (degree of filling 60%) and treated at 160 °C for three days. In the second set of experiments, instead of $NaBO_3{\cdot}4H_2O$, H_3BO_3 was used in the mixture for hydrothermal synthesis in different ratios, so that sodium cation was excluded.

3. Results and discussion

As it is seen from the Table I, $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ was obtained almost in all experiments. The formation of this compound does not depend on the composition of the reactants.

The X-ray powder patterns of product washed with H_2O and washed with concentrated HNO_3 was the same. It was not soluble in HNO_3. For comparison purposes the X-ray powder patterns of original product, washed with H_2O and washed with HNO_3 are given in Fig. 1a–c respectively.

Single crystals of $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ was synthesized by Kniep [17] *et al.* in 1997 under mild hydrothermal conditions. They carried out the experiment at 150 °C in 25–30% aqueous HCl solutions by mixing Na_2HPO_4, $Na_2B_4O_7{\cdot}10H_2O$ and $MgHPO_4$ within approximately 2 weeks and obtained single crystals which have a size of up to 0.5 mm. The crystal structure of $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ was solved and found to be hexagonal. They reported that $M^IM^{II}(H_2O)_2[BP_2O_8]{\cdot}H_2O$, ($M^I$ = Na, K; M^{II} = Mg, Mn, Fe, Co, Ni, Zn) compounds are isotypic.

The product obtained in this experiment in the powder form was indexed in the hexagonal system with the unit cell parameters of $a = 9.428$, $c = 15.82$ Å, $Z = 4$, space group $P6_122$ (No:178) which are in agreement with the single crystal data. The indexing of the X-ray powder diffraction pattern of $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ is given in Table II.

In the second set of experiments it was found that when the ratio of the initial reactants are 3 : 1.5 : 5.5, a new product, $NH_4Mg(H_2O)_2[BP_2O_8]{\cdot}H_2O$, was formed which have the same *d*-spacings with the sodium compound and seems to be isostructural. The IR data showed the presence of NH_4 ion. This compound was also indexed in hexagonal system and the unit cell parameters are $a = 9.529$, $c = 15.736$ Å. The X-ray powder data is included in Table II for comparison

TABLE I Hydrothermal reactions of $MgCl_2{\cdot}6H_2O + NaBO_3{\cdot}4H_2O + (NH_4)_2HPO_4$

Exp.No	Compositions $MgCl_2{\cdot}6H_2O{\cdot}NaBO_3{\cdot}4H_2O$ $(NH_4)_2HPO_4$	Solvent (ml) H_2O/HNO_3	Duration (Day)	Temp. (°C)	Phases Present
B1	3.3 : 3.3 : 3.3	20 / 2	3	165	$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B1.1	B1 washed with H_2O				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B1.2	B1 washed with conc.HNO_3				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B1.1F	B1 heated		6h	500	Amorphous
B4	3.5 : 1.5 : 5	20 / 3	3	165	$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B4.1	B4 washed with H_2O				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B4.2	B4 Washed with conc.HNO_3				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B4F	B4 heated		6h	500	Amorphous
B4YY	3.5 : 1.5 : 5 (B4 repeated)	20 / 3	3	165	$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B4YY H_2O	B4YY heated at 350 °C		6h	350	Amorphous
B6	1 : 7.5 : 1.5	20 / 6	3	165	$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B6.1	B6 Washed with Hot Water				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B6F	B6 heated		6h	500	Amorphous
B9	2 : 2.5 : 5.5	15 / 3	3	165	$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B9.1	B9 Washed with Hot Water				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B9.2	B9 Washed with conc.HNO_3				$NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$
B9F	B9 heated		6h	500	Amorphous

TABLE II The X-ray powder diffraction data of $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ and $NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$

$NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$				$NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$		
	d-spacing Å				*d-spacing* Å	
Int.	*Obs.*	*Calc.*	*h k l*	*Int.*	*Obs.*	*Calc.*
6	8.1700	8.1649	1 0 0	6	8.2538	8.2524
100	7.2727	7.2555	1 0 1	100	7.3086	7.3083
20	5.6831	5.6812	1 0 2	25	5.6830	5.6945
25	4.7213	4.7140	1 1 0	20	4.7640	4.7675
18	4.5142	4.5177	1 1 1	9	4.5601	4.5601
20	4.4360	4.4298	1 0 3	8	4.4272	4.4268
25	4.0809	4.0824	2 0 0	31	4.1259	4.1262
30	3.9519	3.9529	2 0 1	23	3.9922	3.9912
20	3.6334	3.6278	2 0 2	22	3.6539	3.6542
5	3.5561	3.5594	1 0 4	5	3.5533	3.5511
85	3.2247	3.2281	2 0 3	76	3.2431	3.2430
60	3.0827	3.0860	2 1 0	41	3.1186	3.1191
55	3.0275	3.0289	2 1 1	49	3.0579	3.0596
45	2.9493	2.9502	1 0 5	43	2.9398	2.9406
25	2.8725	2.8750	2 1 2	25	2.8988	2.8996
10	2.8404	2.8406	2 0 4	14	2.8466	2.8473
55	2.7190	2.7216	3 0 0	35	2.7503	2.7508
8	2.6651	2.6635	2 1 3	5	2.6806	2.6809
43	2.6362	2.6367	0 0 6	52	2.6227	2.6227
12	2.5715	2.5736	3 0 2	12	2.5961	2.5967
10	2.4169	2.4185	3 0 3	12	2.4352	2.4361
5	2.3019	2.3012	1 1 6	5	2.2963	2.2976
8	2.2642	2.2589	2 2 2	12	2.2795	2.2800
20	2.1802	2.1771	3 1 2	8	2.1980	2.1977
12	2.1499	2.1518	2 2 3	11	2.1692	2.1690
30	2.0378	2.0379	3 1 3	30	2.0378	2.0379
30	2.0378	2.0379	1 1 7	28	2.0335	2.0331
20	2.0231	2.0244	4 0 1	-	-	-
10	1.9218	1.9219	1 0 8	8	1.9134	1.9134
13	1.8930	1.8937	3 0 6	-	-	-
10	1.8718	1.8732	3 2 0	5	1.8931	1.8932
10	1.8585	1.8602	3 2 1	11	1.8799	1.8797
12	1.8226	1.8227	3 2 2	8	1.8399	1.8407
-	-	-	4 0 4	13	1.8271	1.8271
6	1.7795	1.7797	2 0 8	7	1.7756	1.7756
10	1.7385	1.7387	3 0 7	8	1.7407	1.7407
10	1.7191	1.7179	3 1 6	5	1.7245	1.7245
17	1.6880	1.6880	4 1 3	18	1.7034	1.7032
5	1.6654	1.6650	2 1 8	5	1.6638	1.6638
10	1.6311	1.6313	2 2 7	13	1.6354	1.6350
14	1.6143	1.6145	2 0 9	11	1.6099	1.6099
5	1.5538	1.5531	1 0 10	5	1.5467	1.5457
6	1.5145	1.5148	4 0 7	8	1.5199	1.5200
20	1.4753	1.4751	2 0 10	5	1.4700	1.4703
7	1.4421	1.4422	3 2 7	7	1.4482	1.4481
5	1.4082	1.4078	2 1 10	7	1.4055	1.4049
8	1.3596	1.3599	3 2 8	14	1.3641	1.3640

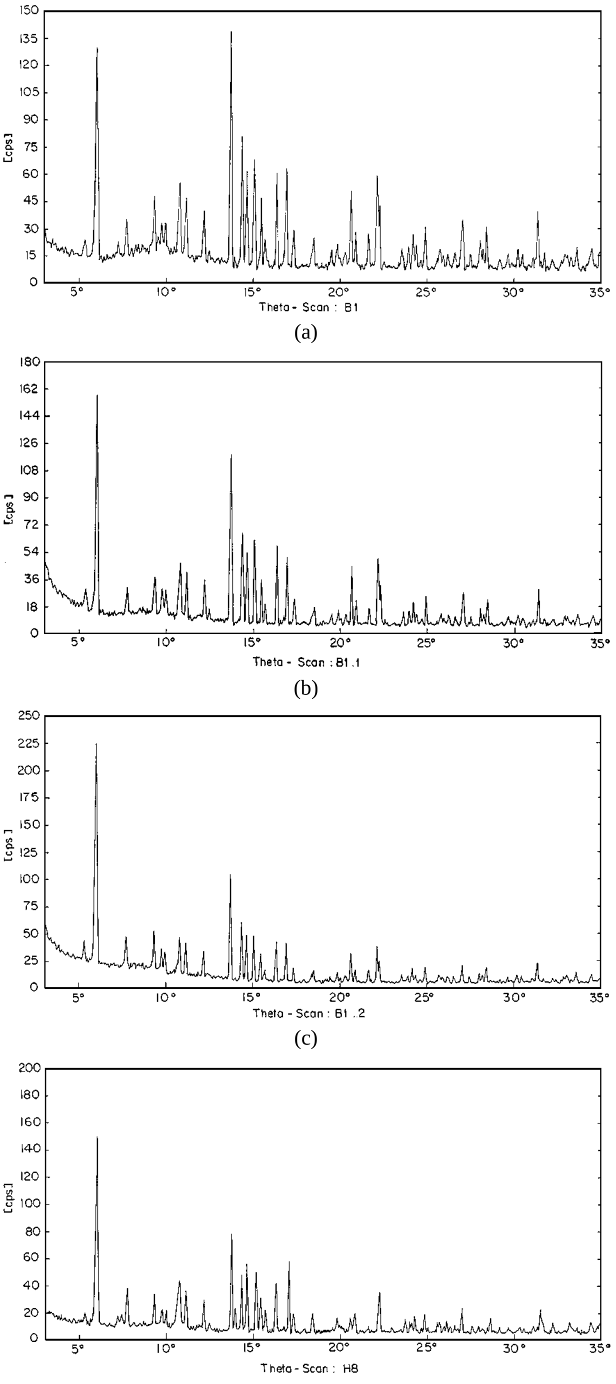
purposes [11] and its X-ray powder diffraction pattern is given in Fig. 1d. The full characterization of this compound left for future investigation.

3.1. Crystal structure

According to the crystal model done by Kniep *et al.* [17], the condensation of PO_4 and BO_4 tetrahedra through common vertices leads to tetrahedral ribbons $^{1/\propto}[BP_2O_8]^{3-}$, which are arranged around 6_1 screw axes to form helices. The spiral ribbons are built from four rings of tetrahedra in which the BO_4 and PO_4 groups alternate. Each BO_4 tetrahedron also belongs to the adjacent four-ring of tetrahedra along the ribbon, in such a way that all vertices of the BO_4 groups participate in bridging functions with PO_4 tetrahedra which is shown in Fig. 2.

3.2. IR study

In the IR spectrum of the product, two water bands occurring at 3354 and 3558 cm^{-1} are due to water molecules occupying different positions [18]. The band at 3558 cm^{-1} is due to hydrogen bonding between the hydrated molecules and other one at 3354 cm^{-1} shows the bond between anion and coordinated water (Fig. 3a). The absence of the peak at 1440 cm^{-1} proves the absence BO_3 functional group in the structure. The absence of band for P-O-P (at around 740 cm^{-1}) satisfies postulate done by Kniep *et al* [12]. According to



(a)

(b)

(c)

(d)

Figure 1 (a) The X-ray powder pattern of $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ (original product) (b) The X-ray powder pattern of the product washed with H_2O (c) The X-ray powder pattern of the product washed with HNO_3 (d) The X-ray powder pattern of $NH_4Mg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ (original product).

these supplementary principles, in borophosphate compounds P-O-P linking is not observed. The stretching modes of a free PO_4^{3-} anion with T_d symmetry has four internal modes of vibrations [19–22], $\nu_3(PO_4) = 1107$, 1024 cm^{-1}, $\nu_1(PO_4) = 954$, $\nu_4(PO_4) = 576$, and $\nu_2 = 482$ cm^{-1} are also present in the IR spectra of product. The IR Frequencies of $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ and $NH_4Mg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ were given in Table III. In the IR spectra of $NH_4Mg(H_2O)_2[BP_2O_8]{\cdot}H_2O$, the strong band at 1447 cm^{-1} is due to N-H stretching vibration (Fig. 3b).

The thermal dehydration of this compound is a two step process. The dehydration at lower

TABLE III The IR Frequencies of $NaMg(H_2O)_2[BP_2O_8]{\cdot}H_2O$ and $NH_4Mg(H_2O)_2[BP_2O_8]{\cdot}H_2O$

Frequency (cm^{-1})	**Assignments**
3558	Hydrogen bond between the water molecules
3354	Hydrogen bond between borate anion and coordinated water
1202, 1159	$\nu_{P=O}$
1103, 1024	$\nu_3(BO_4)$, $\nu_3(PO_4)$
959	$\nu_1(PO_4)$
882	$\nu_1(BO_4)$
850	ν_{as} B-O-P
681	ν_s B-O-P
650	δBOP
576	$\nu_4(BO_4)$, $\nu_4(PO_4)$
482	$\nu_2(PO_4)$

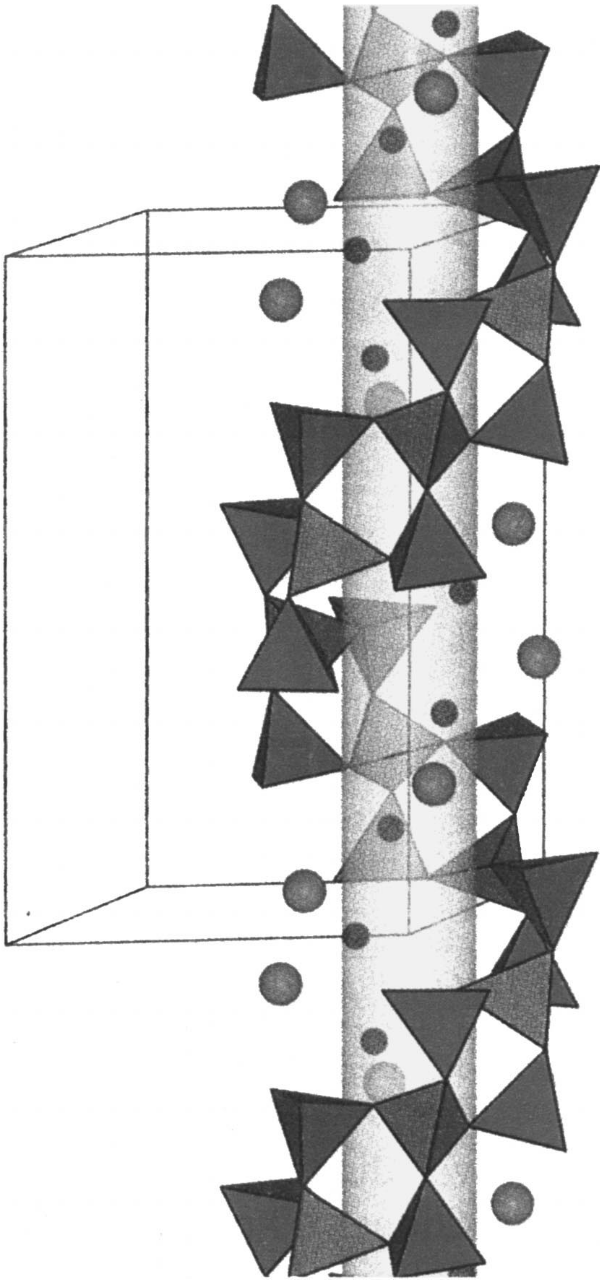
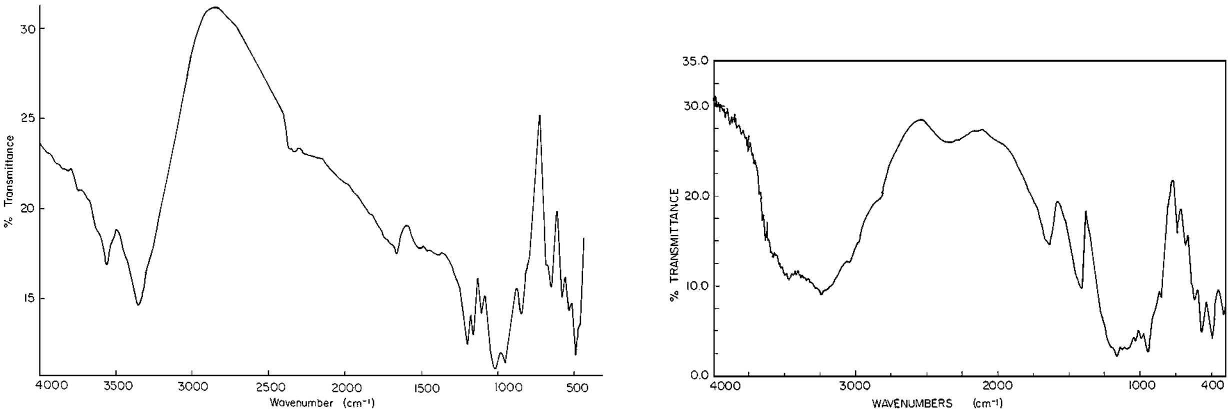
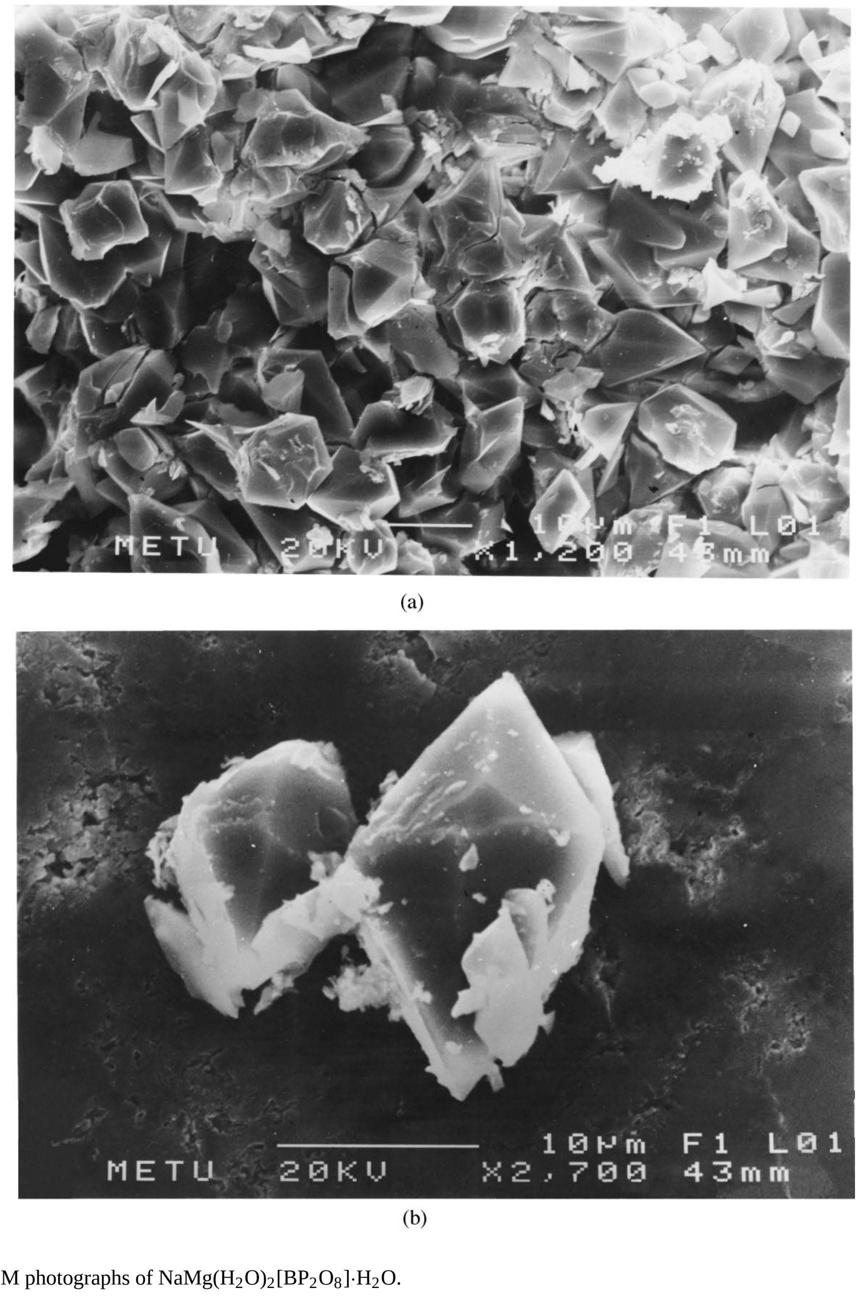


Figure 2 Tetrahedral helices $1/\infty[BP_2O_8^{3-}]$ in the crystal structure of M^IM^{II} $(H_2O)_2[BP_2O_8]{\cdot}H_2O$ [17].



(a) (b)

Figure 3 (a) The IR spectra of $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ (b) The IR spectra of $NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$.



(a)

(b)

Figure 4 (a, b) The SEM photographs of $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$.

temperature (around 150 °C) converts the formula into $NaMg(H_2O)[BP_2O_8]$ with the release of 2 moles of H_2O. According to Kniep *et al.* [17], the water of crystallization (spiral structure within the channels of the M^{I}-borophosphate double helices) and one mole of coordination water (at the M^{II} centers) are released in a collective process. The M^{II} centers are then only pentacoordinate. The crystalline dehydration products $M^{I}M^{II}(H_2O)[BP_2O_8]$ can be described as microporous borophosphates with channel structures. At higher temperatures (at 500 °C), release of the last mole of coordination water leads to X-ray amorphous product. Bands due to both coordinated and hydrated water disappeared and there was a minor change in the structure due to rupture of hydrogen bonds. The interpretation of the IR spectra revealed some broad features between 1200–650 cm^{-1} due to overlapping of P-O and B-O vibrational interactions so characteristic assignments may not very well established as stated by Tarte *et al.* [23]. Only tentative assignments can be proposed for the lower frequency bands in the 680–480 cm^{-1} region. These may be assigned to chain vibrations which have a mixed stretching -bending character [24].

3.3. Analysis

The ICP analysis showed that washed product contains 410 ppm (3.72% wt/wt) B, 843 ppm (7.74% wt/wt) Mg and 803.5 ppm (7.4% wt/wt) Na. In addition EDX analysis showed that weight percent of Mg and Na are same. Theoretically, $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ contains 3.64% (wt/wt) B, 7.61% (wt/wt) Na and 7.94% (wt/wt) Mg. This shows the ratio of Na : Mg : B is around 1 : 1 : 1.

The SEM photographs of the product are given in Fig. 4a and b which show the hexagonal structure clearly as a single crystals and bulk of single crystals.

4. Conclusion

In this study, $NaMg(H_2O)_2[BP_2O_8]\cdot H_2O$ and $NH_4Mg(H_2O)_2[BP_2O_8]\cdot H_2O$ were obtained and their X-ray powder and indexing data and IR analysis was presented the first time in this reseach. It was also shown that the obtained product is insoluble in H_2O and conc.HNO_3.

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