Impetus for solvothermal synthesis technique: synthesis and structure of a novel 1-D borophosphate using ionic liquid as medium

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Abstract

A novel borophosphate compound has been synthesized under solvothermal conditions using ionic liquid as a medium and structurally characterized by single-crystal X-ray diffractions. The compound crystallizes in the monoclinic, space group $P2(1)/n$, $a = 8.089(8)$ Å, $b = 13.977(12)$ Å, $c = 8.441(8)$ Å, $\beta = 112.517(11)°$, $Z = 2$, $V = 881.7(14)$ Å^3, $R_1 = 0.03$, w$R_2 = 0.079$ and $S = 1.01$. Its structure consists of a 1-D straight chain that is built of the alternative linkage of mutually perpendicular four-member rings. Other characterizations by IR and thermal and elemental analyses are also described.
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1. Introduction

The hydrothermal technique was originally the domain of geochemists and mineralogists having interest in simulating mineral formation. In fact, the hydrothermal technique may be regarded as a special case of a chemical transport reaction [1–5]. Typical hydrothermal reactions are carried out in the temperature ranging between 100°C and 250°C under autogenous pressure, in which three potential advantageous characteristics of this reaction are apparent [1]. The reduced viscosity of solvent enhances the diffusion processes so that solvent extraction of solids and crystal growth from the solution is favored [2]. This technique has recently been adopted for the synthesis of a wide variety of metastable materials [6,7]. However, some disadvantages are observed from the investigation on the solid-state synthetic methods at an intermediate temperature. First, the participation of water in the hydrolysis reaction and high proclivity of water to occupy the vacant sites in alkali and transition metal coordination spheres often limit the use of the hydrothermal method for metals Sn and Sb, etc. to the preparation of new oxo- and thiometalates and the synthesis of solvent-free phases. Second, to withstand the pressures involved in solvothemal syntheses, a special reaction vessel is usually required to avoid an explosion. The solvothermal technique developed for the higher pressures and temperatures has remained confined to specialized laboratories. Therefore, the approaches to reduce the reliance on traditional solvents, such as water, methanol, amines, acetonitrile, etc., will be of tremendous importance in solving these problems. The search for alternatives to the common solvents for the solvothermal synthetic technique is one of the most challenging issues in the materials science.

An ionic liquid comprised of only ions is a liquid at a low temperature of ($<100°C$) and possesses a wide range of liquid, negligible vapor pressure, high electrical conductivity, wide electrochemical windows, tolerance to strong acids, relatively low viscosity ($<100°C$), high solvability, non-coordination and excellent thermal and chemical stability [8–10]. These characteristics of the ionic liquids may make them significant as a potential medium for solvothermal synthesis. Our research focuses mainly on the systematic investigation of solid-state synthetic methods at an intermediate temperature for the preparation of the new solid-state materials with the designed structure and the useful chemical and physical properties.

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One of the most promising areas is the preparation of the compound combining both borate and phosphate groups in the materials field, as most of the best known materials with optical and electro-optical application are either borates or phosphates such as BBO (β-BaB$_2$O$_4$), KDP (KH$_2$PO$_4$), etc. In the last few years, some compounds combining both borate and phosphate groups have been synthesized by the high-temperature synthesis (molten salt) and the low temperature-high pressure approach (solvothermal technique) and structurally characterized [11]. Today, the structural chemistry of borophosphate anions has been already extending from isolated species, oligomer, rings and chains to layers and frameworks [12], but the total amount and the varieties of the borophosphates are still lacking. We had prepared an unprecedented borophosphate (NH$_3$CH$_2$CH$_2$NH$_3$)$_2$B$_2$P$_4$O$_{14}$(OH)$_2$ by a new solvothermal technique using ionic liquid as a medium. Its structure consists of a 1-D straight chain that is built of the alternative linkage of mutually perpendicular four-member rings. Here, we report the synthesis and structure of this compound.

2. Experimental

All reagents were commercially available and no further purification was carried out. IR spectrum was recorded on a Nicolet NEXUS-670 FT-IR spectrometer in the KBr matrix in the range of 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was carried out at a heating rate of 5°C/min in a nitrogen atmosphere of 30 mL/min from 25°C to 800°C with a TGA/SDTA851^e.

A mixture containing boric acid, phosphoric acid (85 wt%), ethylenediamine and 1-butyl-3-methylimdazolium chloride in a molar ratio of 3:6:4.5:2.2 was loaded into a thick wall Pyrex tube (7 mL capacity, the reactant was added to a total volume of 1 mL), which was sealed under vacuum, and held in an oven at 110°C for 6 days. The single-phase colorless prism crystals were obtained after washing with deionized water. IR (KBr pellet, cm^{-1}): 3204(s), 3016(w), 2912(w), 2825(w), 2769(w), 2676(w), 2572(w), 2491(w), 2037(w), 1622(m), 1534(m), 1479(m), 1134(s), 1079(m), 954(s), 894(m), 816(m), 584(m), 540(m) and 455(m) cm^{-1}.

The data for the crystals (0.20 mm × 0.20 mm × 0.1 mm) were collected on a Rigaku Mercury CCD area detector with graphite monochromated Mo$K\alpha$ radiation. The data were collected at a temperature of -80 ± 1°C to a maximum 2θ value of 55.0°. Of the 7016 reflections that were collected, 2004 reflections were unique ($R_{int} = 0.027$). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were isotropically refined. The final cycle of full-matrix least squares refinement on F^2

was based on 1761 observed reflections and 177 variable parameters. Details of the data collection, structure solution and refinement are given in Table 1. The CIF file of single-crystal refinement is deposited. CCDC 207003.

3. Results and discussion

The non-hydrogen coordinates and equivalent isotropic displacement parameters as well as the selected bond lengths and angles are listed in Tables 2 and 3, respectively. The asymmetric unit of the compound consists of one tetrahedral B^{3+} site, two tetrahedral P^{5+} site and eight oxygen atoms (Fig. 1). Both boron and

Table 1
Crystallographic data for (NH$_3$CH$_2$CH$_2$NH$_3$)$_2$B$_2$P$_4$O$_{14}$(OH)$_2$

Formula	(NH$_3$CH$_2$CH$_2$NH$_3$)$_2$B$_2$P$_4$O$_{14}$(OH)$_2$
fw	527.5
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (Å)	8.089(8)
b (Å)	13.977(12)
c (Å)	8.441(8)
β (deg)	112.517(11)°
Z	2
V (Å^3)	881.7(14)
D_c (g/cm^3)	1.980
μ (cm^{-1})	5.24
F (000)	540
Crystal size (mm^3)	0.20 × 0.20 × 0.1
No. of data collected/unique	7016/2004 ($R_{int} = 0.027$)
GOF	1.01
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.03, 0.079
Max., min. peak and hole (e Å^{-3})	0.52, -0.37

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] w$R_2 = \left[\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2\right]^{1/2}$.

Table 2
Non-hydrogen atomic coordinates and equivalent isotropic displacement parameters for (NH$_3$CH$_2$CH$_2$NH$_3$)$_2$B$_2$P$_4$O$_{14}$(OH)$_2$

Atom	x	y	z	B_{eq}[a]
P(1)	0.44728(6)	0.60133(3)	$-0.16701(6)$	0.622(10)
P(2)	0.88602(6)	0.48806(3)	$-0.24716(6)$	0.604(10)
B(1)	0.7597(3)	0.4934(2)	0.0217(3)	0.74(4)
O(1)	0.3098(2)	0.59061(10)	$-0.0810(2)$	1.12(3)
O(2)	0.6316(2)	0.57291(10)	$-0.0305(2)$	1.05(3)
O(3)	0.8090(2)	0.45517(10)	$-0.1136(2)$	1.06(3)
O(4)	1.0901(2)	0.46334(10)	$-0.1647(2)$	1.08(3)
O(5)	0.4036(2)	0.53021(10)	$-0.3166(2)$	1.13(3)
O(6)	0.4502(2)	0.70367(10)	$-0.2160(2)$	1.05(3)
O(7)	0.8101(2)	0.42046(10)	$-0.3983(2)$	1.05(3)
O(8)	0.8548(2)	0.59230(10)	$-0.2897(2)$	1.04(3)
N(1)	0.2313(2)	0.34247(13)	$-0.3712(3)$	1.09(4)
N(2)	0.6347(2)	0.2408(1)	$-0.4298(3)$	1.18(4)
C(1)	0.4196(3)	0.3069(2)	$-0.3156(3)$	1.29(4)
C(2)	0.4475(3)	0.2723(2)	$-0.4724(3)$	1.19(4)

[a] $B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha$.

Table 3
Selected bond lengths (Å) and bond angles (deg)

P(1)–O(1)	1.550(2)	P(1)–O(2)	1.547(2)
P(1)–O(5)	1.538(2)	P(1)–O(6)	1.492(2)
P(2)–O(3)	1.552(2)	P(2)–O(4)	1.565(2)
P(2)–O(7)	1.516(2)	P(2)–O(8)	1.499(2)
B(1)–O(2)	1.468(3)	B(1)–O(1)	1.470(3)
B(1)–O(4)	1.476(3)	B(1)–O(3)	1.449(3)
O(1)–P(1)–O(2)	106.61(11)	O(1)–P(1)–O(5)	109.96(10)
O(2)–P(1)–O(5)	107.38(10)	O(1)–P(1)–O(6)	108.21(9)
O(3)–P(2)–O(4)	105.06(12)	O(3)–P(2)–O(7)	106.32(10)
O(2)–B(1)–O(1)	43.83(9)	O(4)–P(2)–O(8)	111.93(9)
O(1)–B(1)–O(4)	110.59(17)	O(1)–B(2)–O(3)	103.38(18)
O(2)–B(1)–O(4)	126.09(13)	O(3)–B(2)–O(4)	113.99(16)

Hydrogen bonds (Å)

N(1)···O(8)	2.825(2)	N(2)···O(7)	2.846(2)
N(1)···O(4)	2.954(2)	N(2)···O(6)	2.905(2)
N(1)···O(5)	2.924(2)	N(2)···O(8)	2.762(2)
N(1)···O(6)	2.700(2)	O(5)···O(7)	2.463(3)
O(5)···O(2)	2.486(3)	O(5)···O(6)	2.549(3)
O(1)···O(5)	2.529(3)		
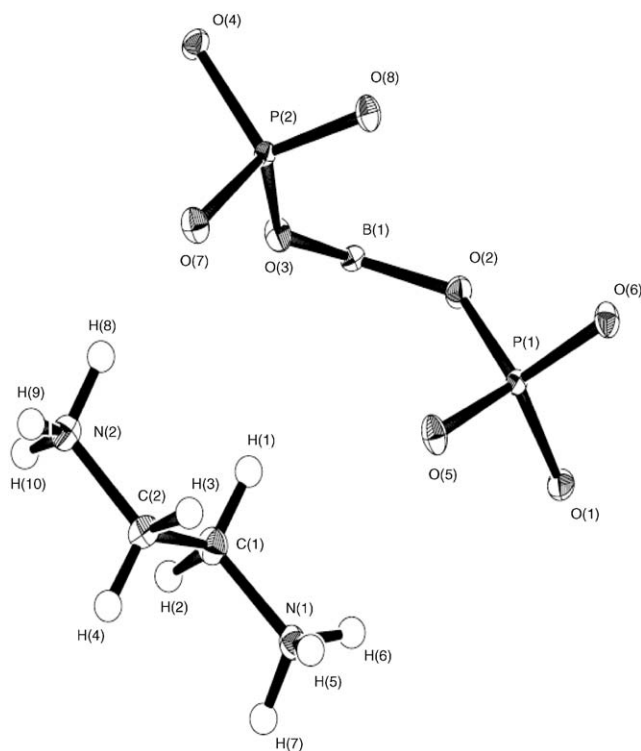
Fig. 1. ORTEP plot of 1, $(NH_3CH_2CH_2NH_3)_2B_2P_4O_{14}(OH)_2$.

Fig. 2. One-dimensional straight chain structure viewed along the c-axis.

phosphorus atoms adopt tetrahedral coordination with P–O distance of 1.492(2)−1.565(2) Å and with B–O distance of 1.449(3)−1.476(3) Å, respectively.

The anionic framework is a new tetrahedral chain and has not been previously observed in not only aluminosilicate and aluminophosphate structures but also in borophosphate compounds. To our knowledge, the characteristic geometry of all known borophosphates that are comprised of one-dimensional chains is in the fold or helix structure [13], 11(h). The crystal structure of the compound consists of 1-D straight chains, which run parallel to (001), of alternatively linked four-member rings perpendicular to each other (Figs. 2 and 3). The infinite straight chain is built of four-member rings of the tetrahedra along the central borate chain, in such a way that all vertices of the BO_4 groups participate in bridging functions with PO_4 tetrahedra. The phosphate groups occupy the borders of the mutually perpendicular four-member rings along the chain with two terminal oxygen atoms. Bond valence sum calculations and the comparisons of the P–O bonds show that the O(5) atoms are –OH groups [14]. This infinite four-ring connectivity is commonly seen in other tetrahedral structures, such as the sodalite and sodium zincophosphate frameworks [15,16]. However, its straight chain configuration appears to be unique here. The chains are bonded together via hydrogen bond interactions formed between the ammine groups of the organic amine dications and the oxygen atoms of the anions, and the
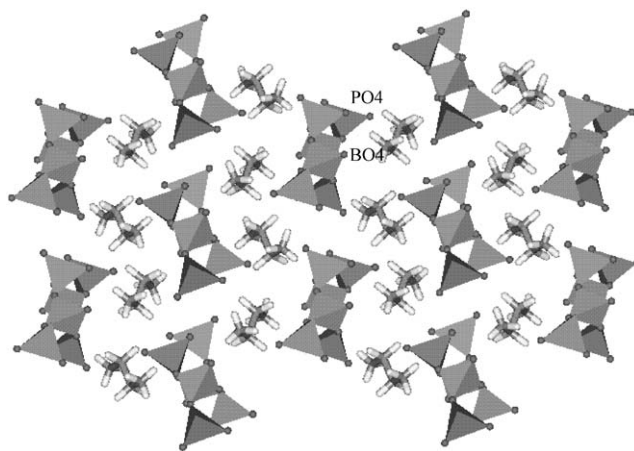

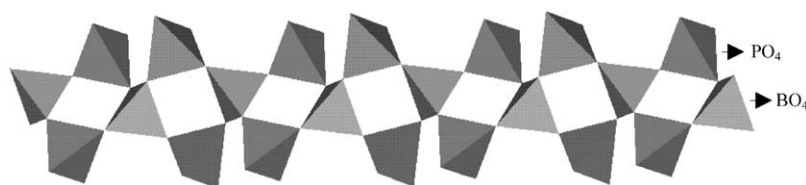Fig. 3. Figure showing a view of the one-dimensional chain structure along the a-axis.
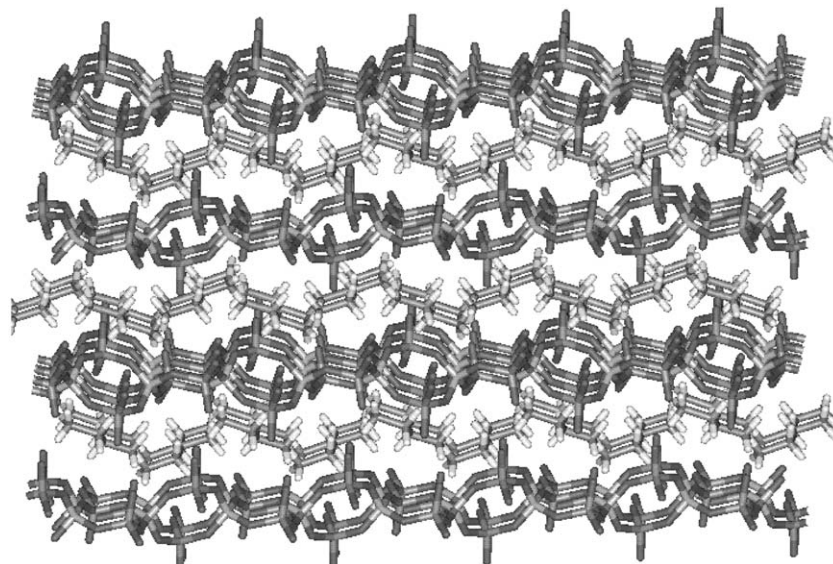
Fig. 4. Structure of a sheet in the *ab* plane.

hydrogen bonds of the inter-chains (Table 3), thus forming a two-dimensional sheet (Fig. 4).

Thermal loss weight is a two-stage process. The first weight loss of 24% is observed between 346°C and 435°C and attributed to the loss of ethylenediamine molecules (cal. 23%). A gradual loss of mass 21% at the second stage in the range from 435°C to 620°C is attributed to the loss of the hydroxyl that is formed by combining framework oxygen atoms with protons.

It is noteworthy that the results demonstrate that this synthetic technique can be readily used to construct new metastable compounds. The ability to expand this synthetic technique to the preparation of the borate, phosphate and borophosphate with novel structure in our interesting projects is also desirable, and it allows access to a variety of possibly metastable phases unobtainable by the common soventothermal method.

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