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Studies on the Intergrowth Structures in Indium(In) Borophosphates

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Several indium borophosphates have been reported recently, including $KIn[BP_2O_8(OH)]$(I) and $NaIn[BP_2O_8(OH)]$(II). The latter two compounds were synthesized under mild hydrothermal conditions, and have the same molar ratio (M^1:In:B:P:O:H) in molecular formula but with different structure types. Compound I crystallizes in the triclinic system with space group $P\bar{1}$ (No.2), $a=0.52638(4)$ nm, $b=0.84791(5)$ nm, $c=0.81469(9)$ nm, $\alpha=91.1741(7)$ °, $\beta=93.061(7)$ °, $\gamma=79.823(5)$ °, $V=0.3573$ nm^3, Z=2; while compound II possesses a monoclinic structure with space group $P2_1/n$ (No.14) with $a=0.5177(1)$ nm, $b=1.6815(3)$ nm, $c=0.7684(2)$ nm, $\beta=94.10(3)$ °, $V=0.6672(2)$ nm^3, Z=4. Eight-membered-ring and six-membered-ring are formed by alternating borate, phosphate tetrahedra and In-coordination octahedron sharing corners via common oxygen atoms in compound I and II respectively. The polyhedra in the structure are oriented along certain direction to form alternating layered fragments. These two structure types can be considered as intergrowth structures, which consist of the same layered fragments growing in different orientations. Other structure intergrowth possibilities are also expected in similar systems. CSD: I , 409583; II , 413343.

Keywords: intergrowth structure   borophosphate   hydrothermal synthesis   indium

0   Introduction

The chemistry of metal borophosphates has attracted many scientists due to the potential applica-

tion of this group of compounds as functional materials in the last several years[1]. A large variety of new structure types have been observed among compounds synthesized by mild hydrothermal

methods. In the course of our systematic investigations on borophosphates, a series of compounds have been reported, in which the anionic structural components are built up from M^{III}-O (M^{III}=Al, Ga, In and Fe) and $B_xP_yO_z$ units[2~17]. The units are connected in different ways to form cluster anions and one-, two-, or three-dimensional arrangements.

In these compounds, the charge balances are provided by alkali metal or ammonium ions (M^I=Na^+, K^+, Rb^+, Cs^+, NH_4^+) occupying the channels in most compounds. The size as well as the charge and nature of the countercations are important factors in determining the structures of the compounds formed. In the present paper, we mainly discuss the effect of M^I cation size on the intergrowth structures in compounds with different countercations.

Several compounds, $M^I In[BP_2O_8(OH)]$ (M^I=$Na^{+[11,12]}$, $K^{+[13]}$, $Rb^{+[14]}$, $NH_4^{+[15]}$), $K_2Fe_2[B_2P_4O_{16}(OH)_2]^{[17]}$ and $NaIn[BP_2O_8(OH)]$ with a new structure type were reported recently. $KIn[BP_2O_8(OH)]$ and $NaIn[BP_2O_8(OH)]$ with two different types are good cases for discussing cation-size effect on structure.

1　Crystal Structure

The crystal structure of KIn $[BP_2O_8$ (OH)] and NaIn $[BP_2O_8$ (OH)] were established by X-ray single crystal diffraction methods. Selected crystallographic data are summarized in Table 1, and selected average bond lengths are shown in Table 2. The coordination tetrahedra around the B and P atoms in compound I and II are quite regular with average bond lengths of 0.1467 nm, 0.1468 nm and 0.1531 nm, 0.1533 nm, respectively. The indium atoms have octahedral coordination with some deformation in both compounds. For InO_6, the In-O bond distances range from 0.2110 nm to 0.2179 nm with average bond length of 0.2133 nm in compound I; and from 0.2096 nm to 0.2202 nm with average bond length of 0.2136 nm in compound II. All the average bond distances are consistent with those typical values observed in borophosphates. On the basis of bond strength calculation[18], the bond vaence sums for counterpart

atoms have similar values as illuminated in Table 2 in both compounds. All bond valence sums of selected atoms are closed to their chemical valences in the two compounds except indium atoms with a slight deviation due to their distorted octahedral coordination, which shows the reliability of the determined structures.

Table 1　Selected Crystallographic Data for Compounds I and II

compound	I	II
formula	$KIn[BP_2O_8(OH)]$	$NaIn[BP_2O_8(OH)]$
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a / nm	0.52638(4)	0.5177(1)
b / nm	0.84791(5)	1.6815(3)
c / nm	0.81469(9)	0.7684(2)
α / (°)	91.741(7)	90
β / (°)	93.061(7)	94.10(3)
γ / (°)	79.823(5)	90
Z	2	4
V / nm³	0.35730(5)	0.6672(2)

Table 2　Selected Average Bond Length ($BL_{av.}$) and Bond Valence Sums (BVS) in Compound I and II

compound	$BL_{av.}$ / nm			BVS		
	In-O	P-O	B-O	In	P	B
I	0.2133	0.1531	0.1467	3.21	4.87	3.07
II	0.2136	0.1533	0.1468	3.20	4.86	3.08

The isolated anionic fragment $[B_2P_4O_{16}(OH)_2]^{8-}$ in both compounds are composed of cluster radicals, each built of two B and two P tetrahedra linked in a centrosymmetric four-membered ring and of two terminal P tetrahedral attached to the ring (Fig.1). Each In octahedron linking with six tetrahedra
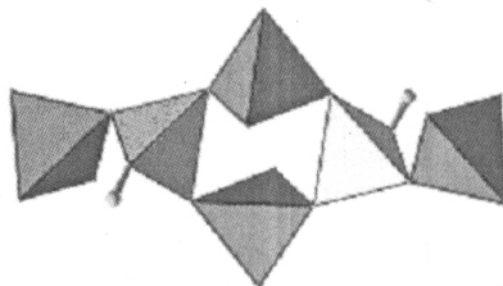

Fig.1　Isolated $[B_2P_4O_{16}(OH)_2]^{8-}$ in compound I and II

(including five P tetrahedra and one B tetrahedron) via common oxygen corners results in overall three-dimensional framework which contains elliptical channels. Potassium and sodium ions are distributed within the cavities in compound I and II, respectively, and the polyhedral representation of the structures is shown in Fig.3 and Fig.4. Same as in other reported borophosphates, there are no condensations of the P tetrahedra observed.

CSD: I, 409583; II, 413343.

2　Result and Discussion

The two compounds with the same stoichiometry but with two different structure types represent a good example of illustrating cation size effect. Here comound I containing K possesses the triclinic structure while the Na compound has the monoclinic symmetry. A comparison of the structures of compound I and II revealed some substantial differences.

In compound I, the elliptical cross section of the channels are defined by eight-membered octahedral/tetrahedral rings (8-MR), including two In coordination octahedra, four phosphate and two borate-groups (Fig.2(a)). The size of the 8-MR cavity is about 0.89×0.40 nm^2 (distances between $O \cdots O$ atoms). In compound II, six-membered rings (6-MR) are formed by the alternative connection of two InO_6 octahedra with three phosphate and one borate tetrahedra (Fig.2(b)) with cavity size nearly 0.59×0.50 nm^2 (distances between $O \cdots O$ atoms). The cavities in the framework of compound I (8-MR) are substantially larger than those in compound II (6-MR); this associated with the difference in the size of M^1 ions. The radius of Na$^+$ is about 0.097 nm while the radius
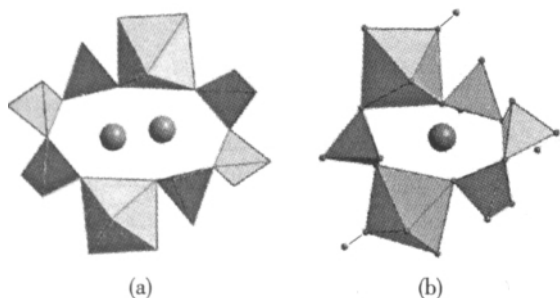
of K$^+$ are claimed to have the value of 0.133 nm. The K-O distances range from 0.2773 nm to 0.3038 nm in compound I and the Na-O distances range from 0.2434 nm to 0.2705 nm in compound II, so that the six-memebered ring can no longer "tolerate" K$^+$ anymore, and results in different polyhedral arrangement. In compound I, polyhedra are arranged perpendicular to the a-axis in an ordered fashion to form layered fragment slanting to left. In compound II, octahedron and tetrahedron are arranged pair-wise in a herringbone fashion along the a-axis to form layered fragment inclining to left and right. Here we mark the two kinds of layers containing different fragment inclining to left and right as layer l and r, respectively; m and n stand for the elementary layer number of layer l and r respectively. So if $m=0$ and
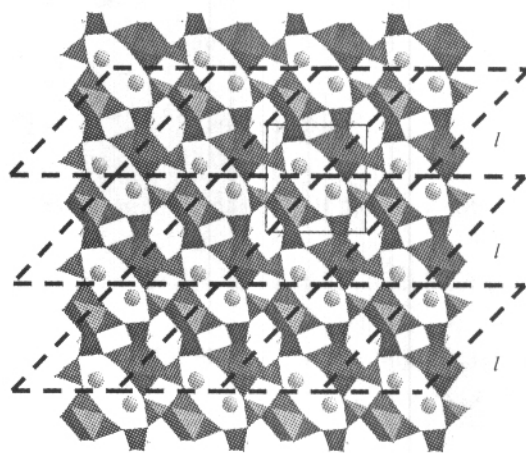

Fig.2　(a) 6-MR in compound I (b) 8-MR in compound II

Fig.3　Crystal structure of compound I viewed from the
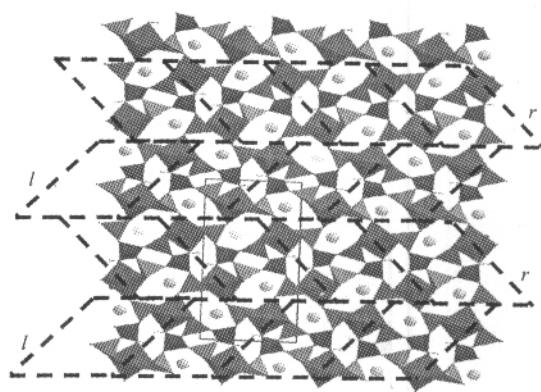c axis (the fragments are indicated by dashed lines)

Fig.4　Crystal structure of compound II viewed from the
a axis (the fragments are indicated by dashed lines)

$n=1$ (all layer l stacked), we get the structure of compound I (Fig.3); if $m=1$ and $n=1$ (layer l and r stacked alternatively), then we get the structure of compound II (Fig.4). These kinds of structure relationships are denoted as intergrowth structures and the concept is very useful when one try to understand complicated structures.

Crystal structures of such kind of compounds show us rich structural chemistry, and there are still many borophosphates with several structural types containing the third main group elements. Since the cation sizes of M^I have strong influence on the structures. In these systems, other structures with different combinations of intergrown fragment numbers m and n are expected with proper tuning of small/large cation ratio in the compounds. The relationship between the cation sizes and the structure types need further studies.

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