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Syntheses, Crystal Structures, and Characterization of Bismuth Phosphates

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The syntheses of the three forms of bismuth phosphate have been optimized, and the resulting single phases have been characterized by thermal analysis, infrared spectroscopy, and powder X-ray diffraction. Two phases may be obtained at room temperature, one trigonal (slightly hydrated) and another monoclinic with a monazite-type structure. The crystal structure of the trigonal phase, (stoichiometry $BiPO_4 \cdot 0.67H_2O$, space group $P3_121$; $a = 6.9885(2)$ Å, $c = 6.4867(2)$ Å, $Z = 3$; $R_{WP} = 5.6\%$, $R_F = 3.6\%$) has been refined by the Rietveld method. The structure contains channels that run parallel to the c axis where the water molecules are located. This water is coordinated directly to the bismuth atoms and stabilizes this form respect to the monazite-type $BiPO_4$ under the synthetic conditions. But the trigonal phase is metastable (at room temperature it spontaneously loses all the crystallization water in 2 months) and is transformed irreversibly to the monazite-type structure. The crystal structure of this second form (stoichiometry $BiPO_4$, space group $P2_1/n$; $a = 6.7626(1)$ Å, $b = 6.9516(1)$ Å, $c = 6.4822(1)$ Å, $\beta = 103.74(1)°$) has been refined to $R_{WP} = 6.6\%$ and $R_F = 3.7\%$. The monazite-type $BiPO_4$ slowly transforms into the high-temperature monoclinic form when it is heated above 600 °C. The crystal structures of these three phases present some important similarities which are described in detail.

Introduction

Bismuth phosphate is known to crystallize in three modifications.[1] The most stable form of $BiPO_4$ is the monazite-type[2,3] structure (LTMBIP, low-temperature monoclinic $BiPO_4$). Another phase may be synthesized at room temperature, which crystallizes slightly hydrated in the trigonal system (TBIP, trigonal $BiPO_4$). The framework of TBIP was determined by Mooney-Slater[1] although the water was not located. A third phase is formed upon heating LTMBIP at high temperature (HTMBIP, high-temperature monoclinic $BiPO_4$). The crystal structure of HTMBIP was recently determined from single-crystal X-ray diffraction.[4] The nature of the different transformations in this system presented some controversy. Mooney-Slater[1] asserted that the transformation from LTMBIP to HTMBIP is reversible and spontaneous at room temperature although Masse and Durif[4] concluded that this transformation is first order and irreversible. Mooney-Slater[1] also reported that TBIP may lose the water without detectable effect on the structure and, hence, suggested that water is not necessary to stabilize the structure; she claimed that crystals thus dried can be kept for years with no deterioration.

On the other hand, bismuth phosphates are reported to be good catalysts in different reactions. Bismuth phosphate, pure or doped with molybdenum, catalyzes the synthesis of butyraldehyde from 1-butanol.[5] In this case the presence of a gas flow with O_2 is needed to maintain the activity and selectivity of the catalyst.[6] Another important reaction catalyzed by $BiPO_4$ is the synthesis of nitriles from formamides.[7] The reaction takes place through the loss of a water molecule with the formation of isonitrile that isomerizes nitrile. Bismuth phosphate has also been studied as catalyst of the synthesis of benzene and acrolein from propylene.[8,9]

In order to understand the chemistry and catalytic activity of these bismuth phosphates, we have performed a systematic investigation of the syntheses and crystal structures of these compounds. We have also studied the transformations that take place in this system.

Experimental Section

Bismuth phosphate may be obtained using the method described by Mooney-Slater.[1] An acidified solution of a phosphate and a salt of bismuth was stirred and heated. Depending upon the temperature and pH, the resulting precipitate may be TBIP, LTMBIP, or a mixture of both. Lower temperature and acidity favor the growth of TBIP, in agreement with what Mooney-Slater reports.

However, to avoid the possible presence of impurity phases in the final product, we decided to use as starting materials polyphosphoric acid and bismuth oxide. The resulting compounds are bismuth phosphate and water. A typical synthesis was carried out as follows. Bi_2O_3 was slowly added to the polyphosphoric acid at a temperature between 140 and 160 °C, with constant stirring, up to a Bi:P molar ratio of 1:5. The constant stirring was needed to achieve a complete dissolution of the Bi_2O_3. The colorless solution was cooled and then hydrolyzed with water at a temperature ranging from 50 to 60 °C. The white precipitate was washed thoroughly with water to remove the excess of phosphoric acid. Under these conditions, a single phase of trigonal bismuth phosphate is obtained. Another possibility is to use aqueous phosphoric acid (85% w/w) and bismuth oxide, but the attack of H_3PO_4 solution upon Bi_2O_3 at reflux temperature leads to LTMBIP.

Monazite-type $BiPO_4$ was synthesized from phosphoric acid and Bi_2O_3. It was also prepared by heating TBIP at 300 °C for 2 days. LTMBIP was accidentally obtained from TBIP at room temperature. This reaction is spontaneous and complete in 2 months, the decomposition rate being reduced at lower temperatures. HTMBIP was synthesized by heating TBIP or LTMBIP at 750 °C for 3 days.

For chemical analysis, the solids were dissolved in a nitric acid solution. The phosphorus content was determined colorimetrically by the phosphomolybdate complex method. The bismuth content was obtained by complexometric analysis using pyrocatechol violet as indicator. The water content was obtained from the weight change after heating at 400 °C and

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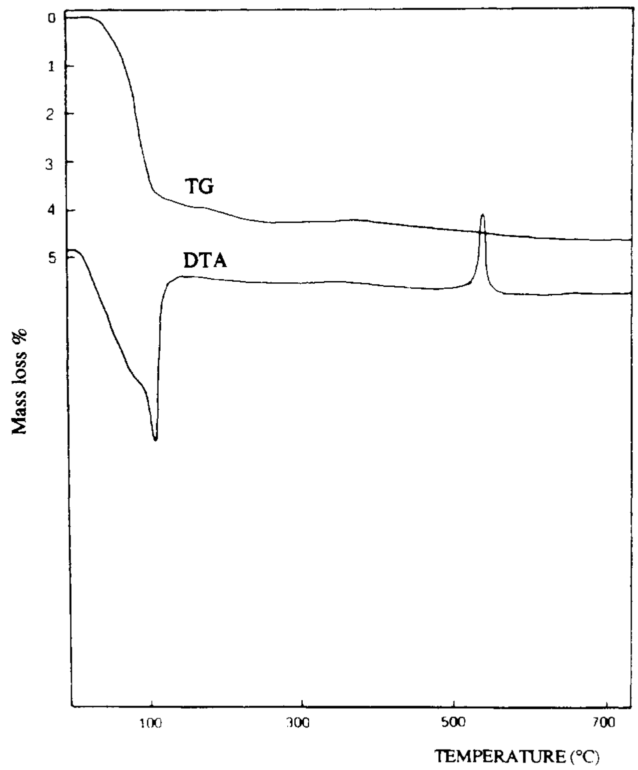

Figure 1. Thermal analysis (TGA and DTA) for $BiPO_4 \cdot 0.67H_2O$.

from the thermal study. The results gave a stoichiometry $BiPO_4$ for LTMBIP and $BiPO_4 \cdot xH_2O$ (with x ranging from 0.65 to 0.75) for TBIP.

Combined thermogravimetric (TGA) and differential (DTA) thermal analyses were carried out in air on a Rigaku Thermoflex apparatus at a heating rate of 10 K/min with calcined Al_2O_3 as the reference. Pycnometric density measurements were performed with reagent grade acetone of density 0.7899 g cm^{-3} as the filling solution.[10,11] X-ray powder diffraction patterns were recorded on a Siemens D501 automated diffractometer using graphite-monochromated Cu Kα radiation. The diffraction profile used to refine the structure of TBIP was collected in the 2θ range 13–94° by counting for 20 s/0.03° step. The data for LTMBIP were recorded between 10 and 119° (2θ) by counting for 16 s/0.03° step. These data were transferred to a VAX 8530 computer for Rietveld analysis[12] by the GSAS program[13] using a pseudo-Voigt peak shape function, corrected for asymmetry at low angles, and a refined background function. The infrared spectra were recorded on a Perkin-Elmer 883 spectrometer using a dry KBr pellet containing 2% sample.

Results and Discussion

Thermal Analysis. The TGA–DTA curves for trigonal $BiPO_4$ are displayed in Figure 1. The DTA curve shows a broad endotherm between room temperature and 260 °C and a sharp exotherm centered at 550 °C. The endotherm is associated with a loss of weight that corresponds to ≈0.73 water molecule, which includes that adsorbed in the surface and the structural water (0.67 molecule per formula). The exotherm at 550 °C, without any associate weight loss, is due to the phase transition from the monazite-type $BiPO_4$ to the high-temperature form. Mooney-Slater[1] described two exotherm effects, one centered between 200 and 250 °C and the second between 600 and 700 °C. The first exotherm has not been observed in our studies. When the water is released, the structure changes to monazite-type; we observed the second exotherm, but at a slightly lower temperature.

Table 1. Structural Parameters for $BiPO_4 \cdot 0.67H_2O$ in Space Group $P3_121$

Cell Data

$a = 6.9885(2)$ Å	$c = 6.4867(2)$ Å	$V = 274.36(1)$ Å^3
$Z = 3$	$\rho_{exp} = 5.66$ g cm^{-3}	$\rho_{crys} = 5.77$ g cm^{-3}

Atomic Parameters

atom	sym pos	*x*	*y*	*z*	*B* (Å^2)
Bi	3b	0.4690(2)	0.0000	$^5/_6$	0.77(3)
P	3a	0.4366(10)	0.0000	$^1/_3$	0.2(1)
O(1)	6c	0.3644(14)	0.1441(14)	0.4524(11)	0.9(1)
O(2)	6c	0.6234(14)	0.1139(19)	0.1750(11)	0.9(1)
O(w)	6c	–0.007(9)	0.091(5)	0.245(3)	0.9(1)

Table 2. Bond Distances (Å) and Selected Angles (deg) for $BiPO_4 \cdot 0.67H_2O$

Bi–O(1)	×2	2.896(7)	P–O(1)	×2	1.540(10)
Bi–O(1)	×2	2.369(9)	P–O(2)	×2	1.534(9)
Bi–O(2)	×2	2.561(8)	O(1)–P–O(1)	×1	98.3(8)
Bi–O(2)	×2	2.418(7)	O(1)–P–O(2)	×2	117.9(5)
Bi–O(w)	×$^2/_3$	2.66(2)	O(1)–P–O(2)	×2	107.8(3)
			O(2)–P–O(2)	×1	107.5(9)

TBIP. The powder pattern of trigonal $BiPO_4$ was autoindexed by using the program Treor[14] from the accurately measured positions of the first 20 nonoverlapping reflections. A trigonal cell of dimensions $a = 6.983(2)$ Å and $c = 6.482(2)$ Å, was obtained with figures of merit $M_{20} = 74$[15] and $F_{20} = 81$ (0.010, 23).[16] This cell is similar to that reported by Mooney-Slater[1] (space group $P3_121$; $a = 6.966(1)$ Å, $c = 6.460(2)$ Å), so we attempted to fit the X-ray profile of TBIP with the data given by this author as starting model in the $P3_121$ space group. The scale factor, background, zero-shift, peak shape parameters, cell constants, atomic coordinates, and isotropic temperature factors were varied to convergence. At this stage, a difference Fourier map revealed the position of the oxygen of the water present in the structure. Due to two very short O–O contacts, a maximum of one-third of the site may be occupied. The occupation factor of this oxygen was set to 0.333, and no attempts to refine it were carried out. Including the oxygen of the water molecule in the model improved the fit notably; R_F decreased from 5.4 to 3.6% (R factors defined in refs 12 and 13). The final refinement, with the stoichiometry $BiPO_4 \cdot 0.67H_2O$ (hydrogen atoms not located), converged to $R_{WP} = 5.6\%$, $R_P = 4.2\%$, and $R_F = 3.6\%$. Results of the refinement are given in Table 1, and the final observed, calculated, and difference profiles are shown in Figure 2. Final bond distances and angles are given in Table 2.

LTMBIP. The powder pattern of low-temperature monoclinic $BiPO_4$ was indexed by following the above described procedure. A monoclinic cell of dimensions $a = 6.761(2)$ Å, $b = 6.952(2)$ Å, $c = 6.482(2)$ Å, and $\beta = 103.78(2)°$ was obtained with figures of merit $M_{20} = 23$ and $F_{20} = 32$ (0.017, 37). This cell is similar to that reported by Kokkoros[2] for $CePO_4$ (space group $P2_1/n$; $a = 6.83$ Å, $b = 7.05$ Å, $c = 6.48$ Å, $\beta = 103.6°$), so we attempted to fit the X-ray profile of LTMBIP with the structural parameters of $CePO_4$ as the starting model in space group $P2_1/n$. The final refinement converged to $R_{WP} = 6.6\%$, $R_P = 4.4\%$, and $R_F = 3.7\%$. Results of the refinement are given in Table 3, and the final observed, calculated, and difference profiles are shown in Figure 3. Final bond distances and angles are given in Table 4.

HTMBiP. The powder pattern of high-temperature monoclinic $BiPO_4$ was indexed on a monoclinic cell of dimensions $a = 4.885(1)$ Å, $b = 7.074(1)$ Å, $c = 4.707(1)$ Å, and $\beta = 96.289(8)°$. This cell is very close to that reported by Masse and Durif[4] ($a = 4.871$ Å, $b = 7.073$ Å, $c = 4.709$ Å, $\beta = 96.24°$). As this structure was well determined from single-crystal intensity data, no attempt to refine its crystal structure was done.

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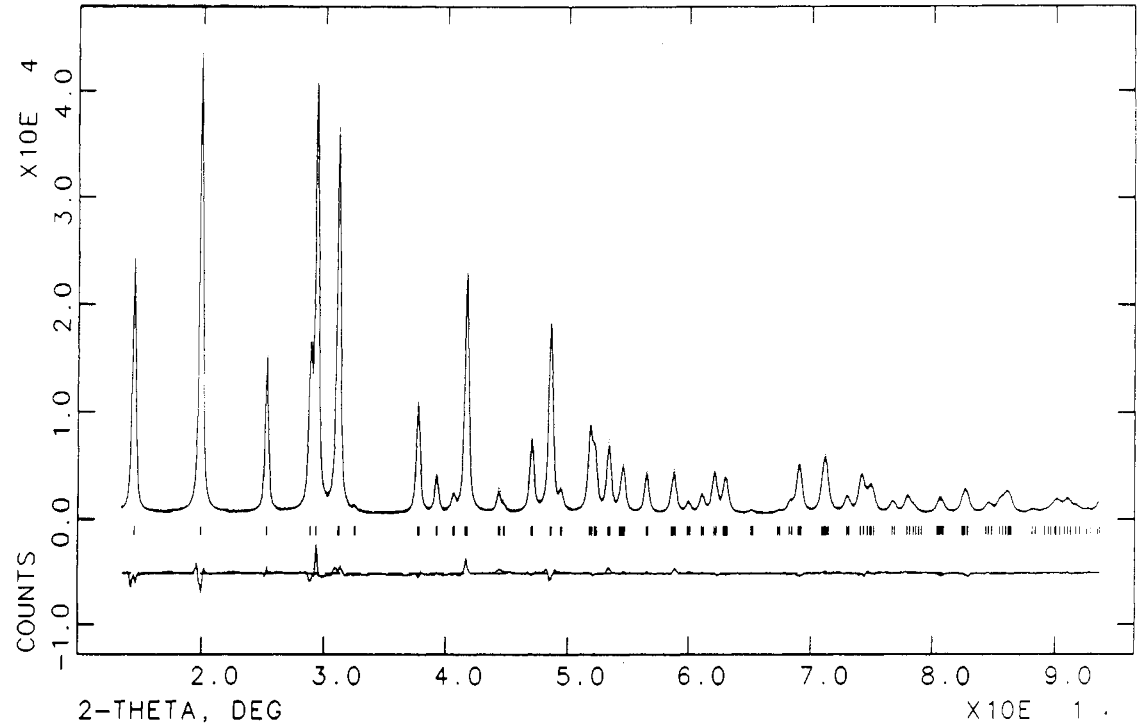

Figure 2. Final observed (points), calculated (full line), and difference X-ray profiles for $BiPO_4 \cdot 0.67H_2O$.

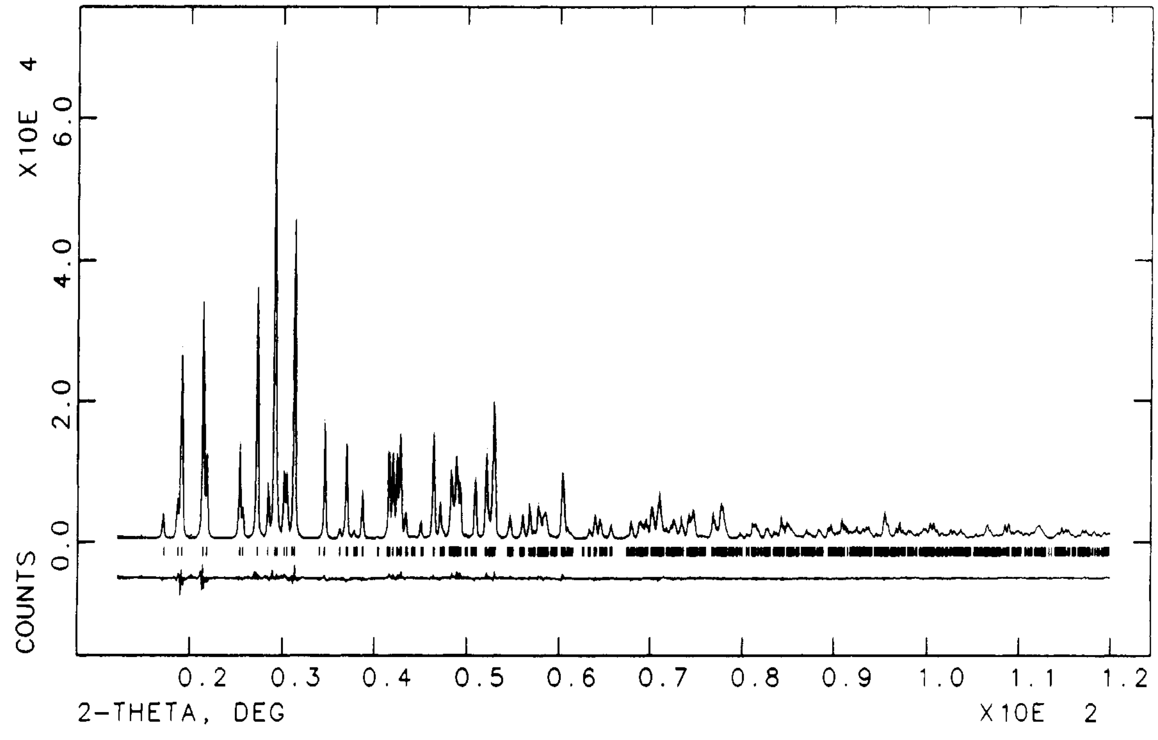

Figure 3. Final observed (points), calculated (full line), and difference X-ray profiles for monazite-type $BiPO_4$.

Description and Comparison of the Structures. The three modifications of bismuth orthophosphate show important similarities in their structural features which are somewhat obscured by the different symmetries and by the choice of coordinate systems. We take as the basic type, for sake of comparison, the Bi-monazite monoclinic structure. The structure can be thought of as the stacking along the monoclinic *a* axis of layers having the thickness of half the (100) spacing $0.5d_{100} \approx 3.28$ Å. These layers, depicted in Figure 4c, contain PO_4 tetrahedra and bismuth atoms in the same stoichiometry as in the whole structure. Each Bi atom is bonded to five oxygen atoms in the same layer, three oxygens of different tetrahedra at distances 2.49, 2.52, and 2.46 Å, and two oxygen atoms belonging to the fourth tetrahedron at 2.33 and 2.49 Å. The link between layers is due to the bonds of the Bi atoms to two oxygen atoms in one neighboring layer at 2.44 and 2.48 Å and to one oxygen atom in the other neighboring layer at 2.68 Å. Within each layer, chains running parallel to the *c* axis can be distinguished. In these chains Bi atoms alternate with PO_4 tetrahedra, in such a way that the bismuth atom is close to two oxygen atoms in one tetrahedron (2.33 and 2.48 Å) and one oxygen atom in the other tetrahedron (2.52 Å).

The trigonal form of $BiPO_4$ contains structural water coordinated directly to the bismuth atoms at 2.66 Å. This water is located in the channels parallel to the *c* axis (see Figure 4b and Figure 5). The maximum amount of water that it is possible to accommodate in the structure is 0.67 molecule per formula unit, in good agreement with the value obtained from the thermal analysis. This water stabilizes the trigonal form, and when this

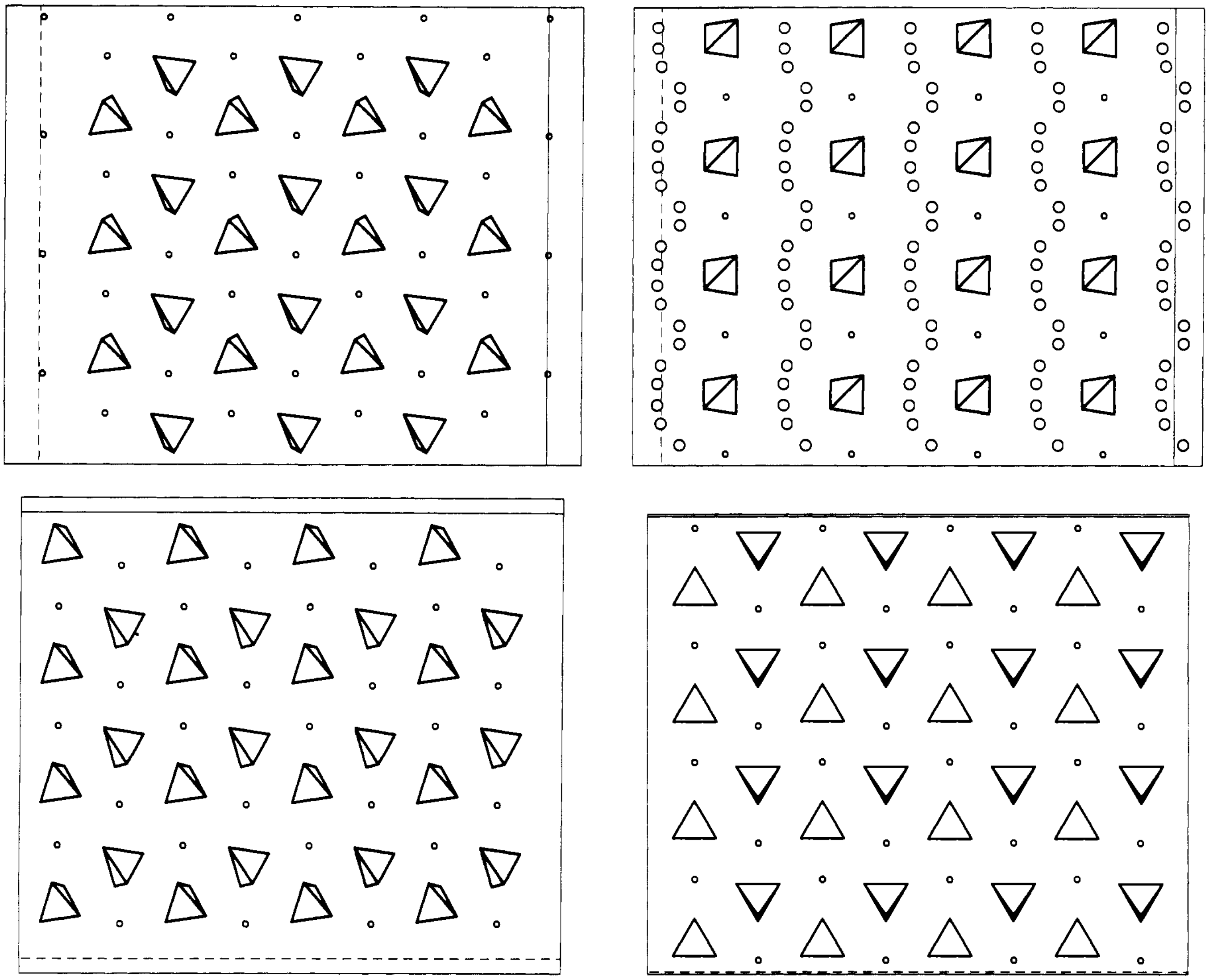

Figure 4. Comparison of the structural features of the three modifications of $BiPO_4$. In all drawings small circles are Bi atoms. (a) Upper left: Orthogonal projection onto the (100) plane of a layer $0.55d_{100}$ thick in the trigonal modification. The center of the layer is at $x = {}^1/_2$. (b) Upper right: Same as in (a), for a layer at $x = 0$, having a thickness $0.45d_{100}$. Large circles represent water molecules. These layers alternate with those of the type in figure 4a, packing along the a^* axis. (c) Lower left: Orthogonal projection onto the (100) plane of the layer at $x \approx 0.25$, $0.5d_{100}$ in thickness of the monoclinic monazite-type structure LTMBIP. Layers like this alternate with others at $x \approx 0.75$, which are their mirror images, to build the complete structure. (d) Lower right: Orthogonal projection onto the $(\bar{1}01)$ plane of the high-temperature monoclinic modification.

Table 3. Structural Parameters for Low-Temperature Monoclinic $BiPO_4$ in Space Group $P2_1/n$

Cell Data

$a = 6.7626(1)$ Å $b = 6.9516(1)$ Å $c = 6.4822(8)$ Å $\beta = 103.736(1)°$
$V = 296.018(8)$ Å^3 $Z = 4$ $\rho_{exp} = 6.75$ g cm^{-3} $\rho_{crys} = 6.82$ g cm^{-3}

Atomic Parameters

atom	sym pos	x	y	z	B (Å^2)
Bi	4e	0.2858(1)	0.1442(1)	0.0872(1)	0.82(2)
P	4e	0.2961(8)	0.1614(7)	0.6113(7)	0.75(9)
O(1)	4e	0.2612(13)	0.0097(12)	0.4419(15)	0.01(11)
O(2)	4e	0.3803(12)	0.3280(15)	0.5221(14)	0.01(11)
O(3)	4e	0.4533(13)	0.1043(13)	0.8148(13)	0.01(11)
O(4)	4e	0.1223(15)	0.1992(13)	0.7072(14)	0.01(11)

Table 4. Bond Distances (Å) and Selected Angles (deg) for Low-Temperature Monoclinic $BiPO_4$

Bi–O(1)	2.523(9)	Bi–O(4)	2.478(9)	O(1)–P–O(2)	105.9(6)
Bi–O(1)	2.562(8)	Bi–O(4)	2.476(9)	O(1)–P–O(3)	113.8(6)
Bi–O(2)	2.681(8)	P–O(1)	1.500(10)	O(1)–P–O(4)	115.5(6)
Bi–O(2)	2.493(10)	P–O(2)	1.468(10)	O(2)–P–O(3)	106.8(6)
Bi–O(3)	2.443(9)	P–O(3)	1.537(9)	O(2)–P–O(4)	116.5(7)
Bi–O(3)	2.330(8)	P–O(4)	1.478(9)	O(3)–P–O(4)	98.1(6)

phase is dehydrated, the structure changes to the monazite-type form. The structure of TBIP contains layers (see Figure 4a) which are almost identical with the layers that make up the above described Bi-monazite structure. The layers are parallel to the (100) planes and are located at $x = 0.5$. Each Bi atoms is linked to six oxygen atoms that belong to four PO_4 tetrahedra within the layer. Two oxygens from two different tetrahedra are at 2.37 and 2.56 Å; the other four oxygens belong to two tetrahedra with distances 2.42 Å (×2) and 2.96 Å (×2). These layers contain chains of PO_4 tetrahedra alternating with Bi atoms, which run parallel to the c axis. The layers above described pack along the a axis alternating with layers also parallel to (100) and located at $x = 0$ (Figure 4b). In these layers, chains of Bi atoms and PO_4 tetrahedra crystallographically identical to the chains present in the layer at $x = 0.5$ alternate along the trigonal b axis with tunnels where a statistical distribution of water molecules is located. The alternate stacking of these two kinds of layers along the a axis produces a structure which is looser than the monazite-type structure. Just from these packing considerations, and neglecting the presence of water, one would expect a density $\rho_{trigonal} = {}^5/_6\rho_{monazite}$, while the observed ratio is $\rho_{trigonal} = 0.812\rho_{monazite}$, in quite good agreement with the predicted value. The link between layers is due to two Bi–O bonds at 2.37 and 2.56 Å.

The monoclinic high-temperature modification of $BiPO_4$ is very similar to the monazite type although this similarity is partially concealed by the choice of the cell parameters. The cell parameters given by Masse and Duriff[4] are $a = 4.871$ Å, $b =$

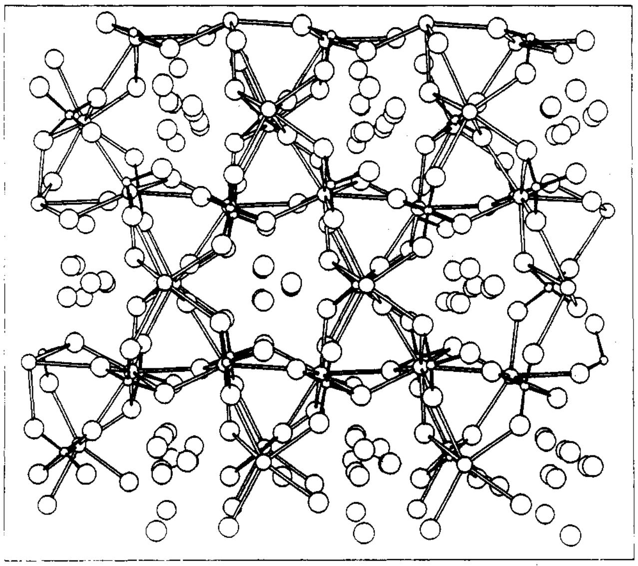

Figure 5. Perspective view along the *c* axis of $BiPO_4 \cdot 0.67H_2O$. All the available positions for the water are shown. Large circles represent oxygen atoms; smallest circles are P atoms.

7.073 Å, $c = 4.709$ Å, and $\beta = 96.24°$; space group $P2_1/m$. If we take a new coordinate system related to this by the equations $\mathbf{a}' = -\mathbf{a} + \mathbf{c}$, $\mathbf{b}' = \mathbf{b}$, and $\mathbf{c}' = \mathbf{a} + \mathbf{c}$, the resulting cell parameters in this nonstandard setting are $a' = 7.134$ Å, $b' = 7.073$ Å, $c' = 6.397$ Å, and $\beta' = 91.95°$; space group $B2_1/m$. These parameters are similar to those of the monazite modification and reveal the true affinities between both polymorphs. In fact, the high-temperature phase contains layers very similar to those already described in the monazite and trigonal forms. A layer, which has the orientation of the ($\bar{1}01$) planes referred to the original coordinate frame, or the (100) planes in the proposed primed system, is represented in Figure 4d. The layer is made up of chains of PO_4 tetrahedra and Bi atoms, running in the [101] direction. Each Bi atom is linked to two oxygen atoms belonging to one tetrahedron, at 2.32 and 2.88 Å, and to two more oxygen atoms in the other tetrahedron, each at 2.53 Å. Two mirror-equivalent bonds (2.35 Å) connect the Bi to oxygens in two more tetrahedra that belong to neighboring chains, making a total of six Bi–O intralayer bonds. The links between the layers are due to two Bi–O bonds of 2.91 and 2.15 Å.

The rearrangement involved in passing from the trigonal type to the monazite type is relatively slight; the remaining half of the layers are unaffected. One can expect, as Mooney-Slater seems to have observed,[1] that a single crystal of the trigonal form would produce upon phase transformation a bundle of monazite-type oriented fibers, having their *c* axes parallel to the original trigonal *c* axis. The transformation from the metastable trigonal $BiPO_4 \cdot 0.67H_2O$ to monazite-type $BiPO_4$ is spontaneous at room temperature and irreversible. We have observed a complete transformation in air, at room temperature in 2 months. All attempts to hydrate monazite-type $BiPO_4$ at different temperatures to obtain the trigonal form have failed. The transformation from monazite-type to the high-temperature form is irreversible and requires a small rotation of the tetrahedra to adopt a more symmetric (and slightly more volume-consuming) arrangement, with no modification of the essential topological features. A consequence of the increase in symmetry of the tetrahedra network is that an approximate *B*-centering present in the monazite structure now becomes exact, and hence we can select a smaller primitive unit cell, which makes it more difficult to detect the high degree of similarity between both structures.

Infrared Study. The IR spectrum of trigonal $BiPO_4 \cdot 0.67H_2O$ is shown in Figure 6. The main absorption band in the region of hydroxyl stretching is centered at 3495 cm^{-1} and is assigned to the stretching vibration, ν(O–H), of the water coordinated directly to the bismuth atoms. The shoulder at 3560 cm^{-1} is probably due to ν(O–H) of the water adsorbed in the surface of the sample. The band near to 1600 cm^{-1} is typical of the H–O–H bending vibration. The very intense band centered at 1010 cm^{-1} is due to the ν_3 stretching vibration of the PO_4 group. Only one band can be seen in this region although the PO_4 group has here

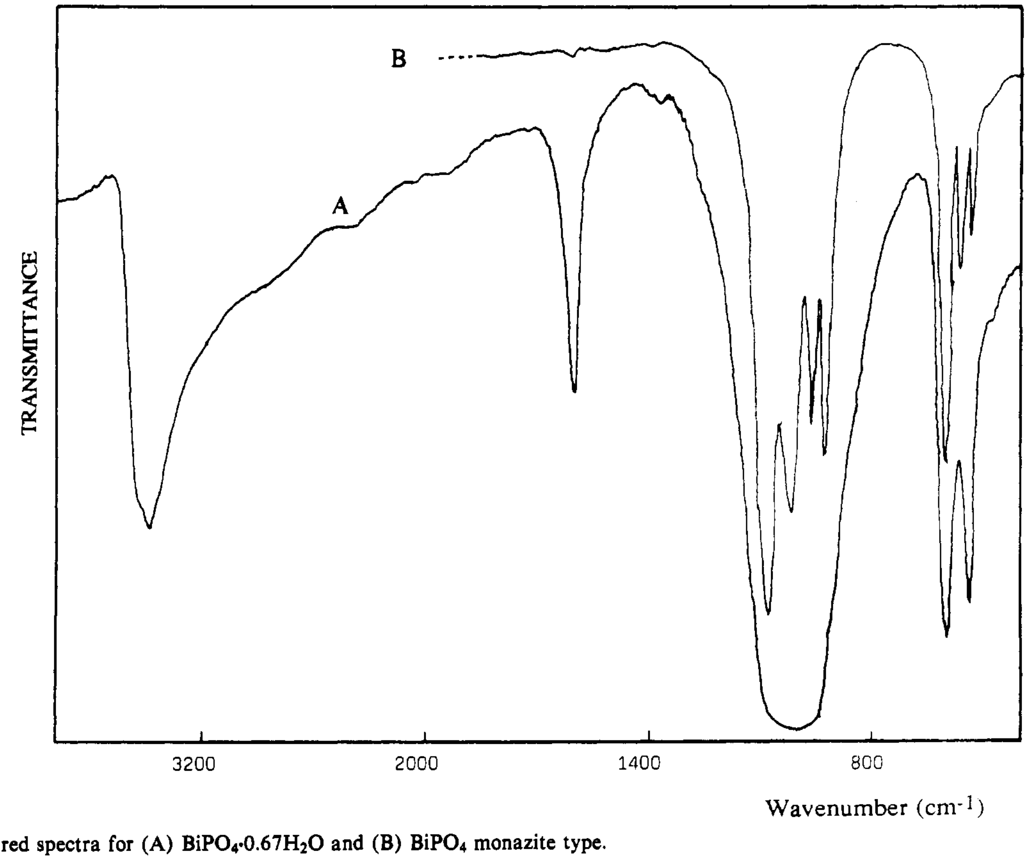

Figure 6. Infrared spectra for (A) $BiPO_4 \cdot 0.67H_2O$ and (B) $BiPO_4$ monazite type.

a C_2 symmetry (see Table 2) but the P–O distances are almost identical and so the symmetry becomes pseudo-T_d. The bands centered at 600 and 535 cm^{-1} are assigned to δ(O–P–O) and ν_4(PO$_4$), respectively.[17]

The PO$_4$ group is nonregular in the case of LTMBIP (see Table 4), and so the IR bands in the region of 1000 cm^{-1} were very complex because the symmetry falls from pseudo-T_d to C_1. Indeed, three bands can be seen at 1073, 1010, and 955 cm^{-1} in this region.

Conclusions

The stable phase in the Bi–P–O system is monoclinic with a monazite-type structure. A second phase may be prepared at room temperature; this phase crystallizes slightly hydrated in the trigonal system and it is metastable. The structure contains channels where the water molecules, coordinated directly to the bismuth atoms, are located. At room temperature the trigonal phase spontaneously loses the crystallization water and is transformed irreversibly to the monazite-type structure. The crystal structures of these two phases have been refined by the Rietveld method. The monazite-type BiPO$_4$ transforms slowly to the high-temperature monoclinic form when it is heated above 600 °C. The structural changes in the transformation LTMBIP → HTMBIP are very slight (a small rotation of the PO$_4$ tetrahedra), which is consistent with a reversible transformation according to Mooney-Slater,[1] but our experimental data show that HTMBIP is stable at room temperature for a long time (at least 10 months), indicating that the kinetics of this hypothetical reaction would be very slow. The structural similarities between the three phases have been presented.

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