CRYSTAL STRUCTURE OF BiMOPO₄, M = Co, Ni. LONE PAIR LOCALIZATION

M. KETATNI ¹, O. MENTRE ² and F. ABRAHAM ²

¹Laboratoire de Chimie Analytique et de Coordination, Université Chouaïb Doukkali, Faculté des Sciences, B.P 20 El Jadida, Morocco

²Laboratoire de Cristallochimie et Physicochimie du Solide, UPRESA. C.N.R.S. 8012, E.N.S.C.L., Université des Sciences et Technologies de Lille, B. P. 108, 59652 Villeneuve d’Ascq Cedex, France

Abstract The new compound BiCoPO₄, monoclinic, P₂₁/n, a = 7.2470(1) Å, b = 11.2851(2) Å, c = 5.2260(1) Å and β = 107.843(1)°, Z = 4, was synthesized and structurally characterized by powder X-ray diffraction. It is isostructural with bismuth nickel oxyphosphate BiNiOPO₄. The crystal structure is built up from a complex tridimensional assembly of (Co/Ni)₂O₁₀ dimers linked by PO₄ groups. This forms large tunnels running along c which host Bi³⁺ cations. Smaller tunnels running along a and crossing the latter were also evidenced. It is noteworthy that the original BiNiPO₅ lattice is appreciably increased with Co²⁺ cations as the transition metal. The Bi³⁺ cation is surrounded by a strongly distorted oxygen octahedron. Reducing the Bi-O bonds to the three shortest, Bi environment can be considered as tetrahedral considering the BiO₃Lp polyhedron, Lp = 6s² lone pair. The lone pair localization was performed from electrostatic interactions and revealed Lp - Bi distance of 0.68 Å and 0.58 Å, for Co²⁺ and Ni²⁺ compounds respectively.

INTRODUCTION

Bismuth materials often display interesting properties such as superconductivity or good ionic conductivity ¹. In the course of the investigation of the phase diagram for

Phosphorus Research Bulletin Vol. 10 (1999), 155
three component systems, a growing number of compounds with the BiA_2MO_6 (A= Ca, Mg, Cd, Pb, Cu; M = P, As, V) have been found including BiCu_2PO_6 and the recent BiCu_2VO_6. Most recently, the Bi_2O_3-NiO-P_2O_5 system was investigated with the aim of finding new materials displaying interesting properties. We have isolated a new bismuth nickel phosphate of formula BiNiPO_5 adopting an original crystal structure. Attempts to prepare the homologue compounds with Cu or Zn substituting Ni failed. In contrast, the Co substitution led to the new compound BiCoPO_5. In this paper, we report the synthesis and crystal structure of this new quaternary phase.

EXPERIMENTAL

The powder of BiCoPO_5 was prepared by solid state reaction. An adequate mixture of Bi_2O_3 (Aldrich, 99.9%), CoO (Aldrich, specpur) and (NH_4)_2HPO_4 (Fluka, puriss.) was successively preheated at 300°C and 500°C in air for 10 hrs to decompose (NH_4)_2HPO_4. After grinding, the mixture was heated at 700°C for 24 hr and at 850°C for 2 days in a gold crucible and ground at the end of each period of heating. Finally the product was air-quenched. BiNiPO_5 synthesis is described in the reference.

The X-ray diffraction patterns were collected using a Siemens D5000 powder diffractometer (CuKα radiation). BiCoPO_5 diffractogram showed that this compound strongly dominated, but weak peaks of a second phase were also present. The assorted material was already encountered when preparing single crystals of Bi_6.67P_4O_20 in presence of cobalt oxide. Its crystal structure and characterisation will be published in a paper to come. The attempts to prepare single crystals of BiCoPO_5 failed. We decided to study the BiCoPO_5 crystal structure using the Rietveld refinement of its powder pattern.

DATA ANALYSIS

Powder X-ray diffraction data used for structure determination were collected at room temperature from 10 - 130° (2θ) using a step size of 0.025°(2θ) with a counting time of 40 sec per step. All the reflections can be indexed with a monoclinic cell in the space group P2_1/n and the orthorhombic I second phase as an impurity. The latter was
taken in account in the refinement with the mean of its profile matching fit (no structural model was tested but only the orthorhombic Ibam symmetry). The compound appeared to be isostructural with BiNiPO$_5$. The refined cell dimensions are $a = 7.2470(1)$Å, $b = 11.2851(2)$Å, $c = 5.2260(1)$Å and $\beta = 107.843(1)^{\circ}$, the corresponding figure of merit is $F_{30} = 75(0.00847, 47)$ for BiCoPO$_5$ and $a = 7.1664(8)$, $b = 11.206(1)$, $c = 5.1732(6)$ Å, $\beta = 107.281(6)^{\circ}$; $F_{30} = 100(0.0056, 54)$ for BiNiPO$_5$

Thus, we used the structural parameters of BiNiPO$_5$ as the starting model. The structure refinement was carried out with the Rietveld method by means of the program FULLPROF 98. Final least squares refinement on 1381 reflections with 53 refined structural parameters resulted in the residuals $R_p = 12.1\%$, $R_{wp} = 15.7\%$, $R_{Bragg} = 3.83\%$, $R_F = 2.14\%$ and $\chi^2 = 1.53\%$. The atomic parameters and isotropic thermal parameters are reported in TABLE 1

**TABLE 1** Atomic and Lp coordinates for BiCoPO$_5$ and BiNiPO$_5$ (in italic, from ref. 13)

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>B_{eq}(\text{Å}^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.1909(3)</td>
<td>0.0981(2)</td>
<td>0.1122(4)</td>
<td>0.45(4)</td>
</tr>
<tr>
<td></td>
<td>0.19137(3)</td>
<td>0.09956(2)</td>
<td>0.10964(4)</td>
<td>0.404(6)</td>
</tr>
<tr>
<td>Co</td>
<td>0.8125(8)</td>
<td>0.0853(5)</td>
<td>0.3690(13)</td>
<td>0.8(2)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8137(1)</td>
<td>0.0805(1)</td>
<td>0.3702(2)</td>
<td>0.39(2)</td>
</tr>
<tr>
<td>P</td>
<td>0.0248(12)</td>
<td>0.3479(8)</td>
<td>0.2105(19)</td>
<td>0.2(2)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.332(3)</td>
<td>0.921(2)</td>
<td>0.067(4)</td>
<td>0.9(6)</td>
</tr>
<tr>
<td></td>
<td>0.3385(7)</td>
<td>0.9172(4)</td>
<td>0.0473(9)</td>
<td>0.5(1)</td>
</tr>
<tr>
<td>O(2)</td>
<td>-0.009(3)</td>
<td>0.219(2)</td>
<td>0.298(5)</td>
<td>1.8(6)</td>
</tr>
<tr>
<td></td>
<td>-0.0147(7)</td>
<td>0.2221(4)</td>
<td>0.3138(9)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>O(3)</td>
<td>0.840(3)</td>
<td>0.422(2)</td>
<td>0.098(4)</td>
<td>0.3(5)</td>
</tr>
<tr>
<td></td>
<td>0.8294(7)</td>
<td>0.4176(4)</td>
<td>0.1131(9)</td>
<td>0.9(1)</td>
</tr>
<tr>
<td>O(4)</td>
<td>0.481(3)</td>
<td>0.468(2)</td>
<td>0.265(4)</td>
<td>1.0(5)</td>
</tr>
<tr>
<td></td>
<td>0.4841(6)</td>
<td>0.4758(4)</td>
<td>0.2450(8)</td>
<td>0.4(1)</td>
</tr>
<tr>
<td>O(5)</td>
<td>0.614(3)</td>
<td>0.171(2)</td>
<td>0.486(4)</td>
<td>0.2(5)</td>
</tr>
<tr>
<td></td>
<td>0.6106(7)</td>
<td>0.1718(4)</td>
<td>0.4856(9)</td>
<td>0.8(1)</td>
</tr>
<tr>
<td>Lp</td>
<td>0.277</td>
<td>0.127</td>
<td>0.151</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.268</td>
<td>0.122</td>
<td>0.145</td>
<td></td>
</tr>
</tbody>
</table>

Phosphorus Research Bulletin Vol. 10 (1999), 157
LONE PAIR LOCALIZATION

In cations such as Tl⁺, Pb²⁺, Bi³⁺ ... the partial hybridisation of full ns² lone pair with its np⁰ empty shell is known as the lone pair effect that forms a supplemental entity, two electrons loaded, filling the volume of about one F⁻ or O²⁻ anion. Verbaere proposed a method to determine the displacement of the ns² lone pair from its center using the Ewald's method. The mean ionicity of each chemical specy was calculated for BiCoPO₅ from the electronegativity difference of the terminal atoms. That yields +1.418 for Bi³⁺, +1.029 for Co²⁺, +1.069 for Ni²⁺ and +2.0 for P⁵⁺ and -0.889 for O²⁻. For BiCoPO₅ the lone pair was refined 0.68 Å apart. The cobalt material yielded a Bi-Lp distance of 0.58 Å.

RESULTS AND DISCUSSION

For a better understanding, the Co²⁺ and Ni²⁺ cations will be called M (for Transition Metal) in the discussion to come. M occupies the centre of a regular octahedron with M-O distances longest for Co²⁺ than Ni²⁺. That peculiar point justifies the exaggerated unit cell increasing for Co²⁺ considering the relatively equivalent ionic radii (VI : rCo²⁺ = 0.69 Å, rNi²⁺ = 0.65 Å). In both cases PO₄ tetrahedron is perfectly regular with four P-O bonds close to 1.5 Å and angles around 109°. However P-O(2) is greater for the cobalt compound yielding a wider distribution of O-P-O angles.

The O(4) atom which does not belong to the PO₄ tetrahedron is coordinated to two bismuth and two cobalt atoms, forming an irregular OBi₂M₂ tetrahedron. The studied compound must be considered as an oxophosphate and formulated BiCoPO₄. The coordination of the other oxygen atoms is 3; one bond to P, one to M and one to Bi.

BiNiPO₅ was already described in term of double mixed chains, formed by the edge sharing of Ni₂O₁₀ and Bi₂O₁₀ dimers, running along the c axis. Actually a most likely description can be done evidencing a tunnel structure occupied by Bi³⁺ hosts. Thus, the elementary building brick is formed of the connection by the O(4)-O(4) edge of two MO₆ octahedra yielding T₂O₁₀ dimers. It is noteworthy that the O(4)-O(4) distance is appreciably increased from Co²⁺ to Ni²⁺ compounds, 2.49(4) Å and 2.64(1) Å.
respectively enabling a strongest M-M metal interaction for the latter, Ni-Ni = 3.172(2), Co-Co = 3.27(1). Then one PO₄ shares its four independent O(1), O(2), O(3) and O(5) oxygen atoms to one dimer forming [PM₈O₃₆]⁵¹⁻ groups. One should therefore notice that P being placed on a general position, the obtained brick is low symmetric with four individual P-M distances ranging from 3.22 to 3.56 Å for Co, 3.24 -3.53 Å for Ni. Then, each free apex of the [PM₈O₃₆]⁵¹⁻ entities connect a PO₄ to form a complex tridimensional framework. Then, a projection of the structure along the c axis, fig. 1, clearly evidence the existence of channels running along [0 0 1]. They host Bi³⁺ cations. One must observe than two consecutive octahedra of the apparent octahedral double chains are in fact separate by PO₄ tetrahedra. The figure 1, which shows the projection of the crystal structure along a displays that feature. Smaller tunnels can be observed running along b.

FIGURE 1 : Projection of the BiCoPO₅ structure along the a and the c axis, evidencing large tunnels that host Bi³⁺ cations.

BISMUTH ENVIRONMENT

the bismuth cation has a strongly distorted octahedral coordination with three short distances at one side (O(1)⁴⁰, O(4) and O(4)⁴⁰) ranging from 2.11 to 2.29 Å and three longer on the opposite side (2.40-2.70 Å) for BiCoPO₅. These distances are
appreciably longer in the BiNiPO₅ case. As expected, the lone pair position was refined towards the center of the O(1)O(3)O(5) face that provides the largest empty space. If only the shortest three Bi - O distances are considered, the coordination polyhedron can be described as a BiO₃Lp tetrahedron, a classical environment for Bi³⁺ as shown in the Bi₉P₂ClO₁₈ material. Taking account of strong bonds between Bi³⁺ and oxygen of the tunnel walls, the channel section is considerably reduced.

REFERENCES

12 M. Ketatni, PhD dissertation, Université des Sciences et Technologies de Lille, France, April 1995.