

Synthesis and Structures of New Borophosphates ($B_{1-x}M_x$)PO₄ (M=Mn,Fe,Co,Ni,Cu) with Orthorhombic Low-Cristobalite Type

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Abstract: The first reported ($B_{1-x}M_x$)PO₄ (M = Mn, Fe, Co, Ni, Cu) compounds were synthesized by high temperature solid state methods and the structures refined from X-ray powder data. The transition metal substitutions on the boron site stabilized the structure to the orthorhombic low-cristobalite type with average volumes per tetrahedral unit 30% larger than that in BPO₄ and novel catalytic properties are expected. The magnetic data indicate the 3+ valences for the metals.

Keywords: Transition-metal borophosphate, synthesis, structure, magnetic property.

Two modifications of BPO₄, the tetragonal high-cristobalite¹ and the hexagonal high pressure phase², have been found. The high-cristobalite phase has long been used as multi-functional catalyst³. We report here the synthesis, structure refinements of new borophosphates with low-cristobalite structure stabilized by transition metals Mn, Fe, Co, Ni and Cu, and their magnetic properties.

All the starting reagents: H₃BO₃, NH₄H₂PO₄, MnO₂, Fe₂O₃, Co(CH₃COO)₂·4H₂O, Ni(CH₃COO)₂·4H₂O, CuO were in AR purities and well ground, pre-reacted at 700°C for 4 h and finally reacted at 1300°C for 8 h, and then cooled down to room temperature.

XRD⁴: X-ray powder diffraction data were collected on a Rigaku-D/max automatic powder diffractometer with graphite-monochromated Cu K α radiation ($\lambda = 1.54056\text{\AA}$) and $\omega-2\theta$ scan mode. The unit cell parameters were obtained by least-square fits of the powder diffraction data. The structure refinements were carried out by using Rietveld method and program package DBWS-9006PC. The atomic positional parameters obtained for the prototype AlPO₄⁵ were used as starting parameters. The final refinements showed partial substitutions of boron site by heavy transition metals Mn, Fe, Co, Ni and Cu. The figure of merits (R_p , R_{bragg}) for the powder profile refinements are (6.84%, 3.82%), (7.68%, 6.97%), (6.51%, 9.91%), (10.58%, 11.58%) and (3.27%, 4.86%) for Mn, Fe, Co, Ni and Cu compounds respectively.

The magnetic susceptibility of the Fe, Co and Cu compounds were measured in a temperature range of 2 - 300K with external magnetic field of 5 Tesla using a Quantum Design SQUID magnetometer.

The new substitutional compounds were shown to be isostructural with the orthorhombic low-cristobalite structure. Crystallographic data: orthorhombic, space group C222₁, Z = 4. (B_{0.58}Mn_{0.42})PO₄, a = 7.0863 (1) Å, b = 7.0804 (1) Å, c = 6.9914 (5) Å, V = 350.79 (3) Å³, Mr = 124.3, Dx = 2.352 g/cm³, F (000) = 242; (B_{0.54}Fe_{0.46})PO₄, a = 7.0850 (6) Å, b = 7.1035 (6) Å, c = 6.9997 (3) Å, V = 352.28 (7) Å³; Mr = 126.5, Dx = 2.384 g/cm³, F (000) = 246; (B_{0.58}Co_{0.42})PO₄, a = 7.046 (1) Å, b = 7.031 (1) Å, c = 6.9494 (5) Å, V = 344.28 (3) Å³, Mr = 126.0, Dx = 2.430 g/cm³, F (000) = 244; (B_{0.66}Ni_{0.34})PO₄, a = 7.0800 (5) Å, b = 7.0841 (4) Å, c = 6.9898 (3) Å, V = 350.58 (6) Å³, Mr = 122.1, Dx = 2.312 g/cm³, F (000) = 240; (B_{0.70}Cu_{0.30})PO₄, a = 7.0853 (3) Å, b = 7.0781 (3) Å, c = 6.9879 (2) Å, V = 350.45 (4) Å³, Mr = 121.6, Dx = 2.304 g/cm³, F (000) = 236.

The average bond distances in the PO₄ tetrahedra are 1.586, 1.690, 1.601, 1.577 and 1.634 Å, in (B,M)O₄ are 1.658, 1.534, 1.628, 1.665 and 1.623 Å for Mn, Fe, Co, Ni and Cu compounds respectively. They are slightly larger than the P-O and B-O bond values of 1.52 and 1.46 Å. The transition metals led to deformation of all the tetrahedra and quite anisotropic expansion of the structure.

The average volumes per cation-O₄ tetrahedral unit are 87.7, 88.1, 86.1, 87.6 and 87.6 Å³ for Mn, Fe, Co, Ni and Cu respectively which are about 30% larger than that found in BPO₄ (62.5 Å³) with high-cristobalite structure. Furthermore, the size of the tunnel along the [110] direction has been enlarged to 3.0 Å × 4.6 Å comparing to the triangle opening of 2.4 Å in the BPO₄. It may be concluded that the new compounds have much more open structure and are more porous than the boron orthophosphate. It seems reasonable to expect novel properties by considering that the BPO₄ is a multi-functional catalyst.

The variations of the magnetic susceptibility with temperature follow the Curie-Weiss law. The deduced numbers of Bohr magnetons (μ_B) for the Fe, Co and Cu compounds are 5.5, 5.8 and 2.6 per mole-ions respectively and close to their theoretical values for the 3+ valences (Fe³⁺: 5.7-6.0, Co³⁺: 5.1-5.7, Cu³⁺: 2.9 - 3.9)°.

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