

**Crystal Chemistry of  $M^{2+}Be_2P_2O_8$  Beryllophosphates: a Comparison with Aluminosilicates.** F. Hatert, F. Dal Bo, M. Baijot. University of Liège, Laboratory of Mineralogy B18, B-4000 Liège, Belgium. E-mail: [fhatert@ulg.ac.be](mailto:fhatert@ulg.ac.be)

Beryllophosphates are very fascinating since their structures can be compared to those of aluminosilicates and borosilicates. In order to study in more details the crystal chemistry of beryllophosphates, we decided to investigate the  $M^{2+}$ -Be- $PO_4$ - $H_2O$  system ( $M^{2+} = Ca, Sr, Pb, Ba, Zn, Cd$ ), by using hydrothermal synthesis techniques at low temperature (200°C) and low pressure (autogenous pressure), and at high temperature (400°C and 600°C) and high pressure (1 kbar). During these syntheses, different beryllophosphates were obtained:  $CaBe_2P_2O_8$ ,  $SrBe_2P_2O_8$ ,  $PbBe_2P_2O_8$  and  $BaBe_2P_2O_8$ . These compounds have large stability fields and are observed in all the hydrothermal syntheses, whatever the temperature and pressure conditions applied.  $CaBe_2P_2O_8$  and  $SrBe_2P_2O_8$  are the synthetic analogues of minerals named hurlbutite [1] and strontiohurlbutite [2], respectively.  $CaBe_2P_2O_8$ ,  $SrBe_2P_2O_8$  and  $PbBe_2P_2O_8$  crystallized in the same space group and are isostructural. Their structure consists of corner-sharing  $BeO_4$  and  $PO_4$  tetrahedra assembled in 4- and 8-membered rings; these rings are nearly perpendicular to the  $a$  axis. The 4-membered rings consist of a pair of tetrahedra pointing upwards (U) and a pair of tetrahedra pointing downwards (D), and therefore UUDD type rings are observed. The 8-membered rings are formed by linking four 4-membered rings, and show only one pattern: DDUDUUDU.  $BeO_4$  and  $PO_4$  tetrahedra are also connected by corner-sharing to form a double crankshaft chain running along the  $a$  axis. The bivalent cations are located in the 8-membered rings and occur in 7+3-coordinated polyhedron, characterized by 7 short bonds and 3 long bonds. Actually, all these characteristics are typical of the structure of paracelsain [ $BaAl_2Si_2O_8$ ], an aluminosilicate belonging to the feldspar family. The relationship between beryllophosphates and aluminosilicates is not surprising [3] since the O atoms shared only between the Be and P tetrahedra or only between the Al and Si tetrahedra receive in both cases exactly the same Pauling bond valence sums (1.75). It also happens in the case of borosilicates [4] and other synthetic compounds such as  $SrGa_2Si_2O_8$  and  $SrGa_2Ge_2O_8$  [5]. A review of the literature indicated that a lot of compounds with the general formula  $M^{2+}T^{3+}_2T^{4+}_2O_8$  or  $M^{2+}T^{2+}_2T^{5+}_2O_8$  showed a paracelsian-type structure.  $BaBe_2P_2O_8$  exhibits a structure completely different from those of other beryllophosphates investigated in this study. The structure of  $BaBe_2P_2O_8$  is based on a double layer of tetrahedra containing both

beryllium and phosphorus in a 1/1 ratio. These tetrahedra are assembled in 6-membered rings forming channels parallel to the  $c$  axis. Parallel to the  $a$ - $b$  plane, a ring is connected to 6 other rings to form an infinite layer. In the  $c$  direction, the tetrahedra are also linked by their apical oxygen, thus forming a double layer with all tetrahedra of the same layer pointing in one direction. These layers are connected by the Ba atoms, located in a twelve-coordinated polyhedron. The Ba polyhedron has a very regular hexagonal shape and showed 12 identical bonds of 2.976(2) Å length. This barium beryllium phosphate is isostructural with dmisteinbergite, a hexagonal polymorph of  $CaAl_2Si_2O_8$  [6].

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