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Hydrothermal Synthesis of Single Crystals of $LiBePO_4{\cdot}H_2O$: a Li-A(BW) Type Zeolitic Material

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Single crystals of $LiBePO_4{\cdot}H_2O$ were grown hydrothermally and characterized by X-ray structure analysis, which proved the BeO_4 and PO_4 tetrahedra linked by common corners to be distributed in a completely ordered manner establishing polar channels extending parallel to [001] which accommodate water molecules bound to Li^+ cations.

Zeolites attract wide interest both in academic and industrial research since they are able to serve as ion exchangers, as molecular sieves or as shape-selective catalysts, hence providing a great number of different applications. An ample variety of natural and synthetic zeolitic aluminosilicates are known.[1–3]

One of these is a silicate exhibiting sorptive and ion-exchange properties which was reported by Barrer and White[4] to have the composition $Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}4H_2O$. The stoichiometry of this so-called 'Li-A(BW)' zeolite was revised to $LiAlSiO_4{\cdot}H_2O$ by an X-ray structure analysis furnished by Kerr[5] using powder data only, since single crystals of sufficient size were not available.

Often structural studies on these compounds unfortunately suffer from the lack of suitable single crystals and from the nearly identical X-ray scattering power of Al and Si causing ambiguities concerning the distribution of Al and Si in the framework.

Employing building blocks different from AlO_4 and SiO_4 tetrahedra would be of great advantage for the synthesis, application and structural characterization of zeolite-like materials.[6] Gier and Stucky[7] have recently reported on the synthesis of microcrystalline $LiXYO_4{\cdot}H_2O$ samples (X = Be or Zn, Y = P or As). Based on the X-ray powder diffraction patterns they concluded these compounds to be analogues of the Li-A(BW) type zeolite with the space group $Pna2_1$ assuming that Be or Zn completely replace Al, and P or As replace Si. However, the a and b axes should be interchanged to make the systematic absences given by Gier and Stucky consistent with the space group setting.

Our single-crystal study[†,‡] proved $LiBePO_4{\cdot}H_2O$ to be in principle isostructural with $LiAlSiO_4{\cdot}H_2O$, however, with P occupying the position assigned to Al by Kerr,[5] and Be lying on the Si site in a completely ordered manner. Furthermore there is no evidence for Li sites statistically disordered as reported by Kerr. The sums of the E–O bond valences (E = P, Be or Li) calculated employing the method of Brown and Wu[9] are close to the expected values (P 5.10, Be 2.05, Li 1.01), indicating that the tetrahedral environment is well adapted to the specific requirements of the different elements.

The framework of $LiBePO_4{\cdot}H_2O$ consists of tetrahedral building blocks which are centred by Li, Be or P (Fig. 1). One corner of the Li-centred tetrahedron is occupied by a water molecule and the $Li–OH_2$ bond is the shortest in the lithium co-ordination sphere [185(2) pm]. A polar channel results extending parallel to [001]. Ionic radii provided as given by Shannon[10] the oval aperture of this channel has an effective cross-section of approximately 3.3 × 4.0 Å. This channel is filled by the water molecules bound to Li^+. A schematic view of one of these tubular units characterizing $LiBePO_4{\cdot}H_2O$ is given in Fig. 2. Atoms O(2), O(3) and O(4) are bound to P, Be and Li, whereas O(1) connects merely a P-centred tetrahedron with a Be-centred one. The atoms in the centres of adjacent tetrahedra are separated from each other almost uniformly. The shortest of these interatomic distances is 281(2) pm (P ··· Be), the longest is 309(1) pm (P ··· Li). The sums of the bond angles with O(2), O(3) and O(4), respectively, are close to 360° (Fig. 1), indicating oxygen atoms in nearly planar co-ordination. Least-squares planes fitted to these

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[†] Single crystals of $LiBePO_4{\cdot}H_2O$ were prepared under hydrothermal conditions. Beryllium sulfate (7.87 mmol) was dissolved in H_2O (8.5 cm^3) and 85% H_3PO_4 (7.4 mmol). Lithium chloride (7.87 mmol) dissolved in water (3 cm^3) was added to this solution. This mixture was adjusted to pH 7 by adding an aqueous solution (40%) of NEt_4OH yielding a colourless gel which was heated in a steel autoclave under autogeneous pressure for 8 d at 125 °C. Subsequently it was gradually cooled to room temperature over 5 d. Columnar colourless crystals of $LiBePO_4{\cdot}H_2O$ up to 0.06 mm in length were isolated in 84% yield. Differential thermal analysis in air recorded up to 550 °C revealed a single endothermic process between 405 and 435 °C. IR spectra showed the residue to be free of water of crystallization. Characteristic IR absorption data for $LiBePO_4{\cdot}H_2O$ (KBr): 3605m, 3421m, 1640w, 1159s, 1120s, 1079vs, 1057vs, 1027vs, 764s, 732s, 601vs, 576vs, 533m, 487m, 464m, 372m and 345w (sh) cm^{-1}.

[‡] Crystal data for $LiBePO_4{\cdot}H_2O$. Orthorhombic, space group $Pna2_1$ (no. 33), $a = 968.0(2)$, $b = 781.14(15)$, $c = 475.83(10)$ pm, $U = 359.8 \times 10^6$ pm^3, $Z = 4$, $M_r = 128.9$, $D_c = 2.38$ g cm^{-3}, $\mu = 6.3$ cm^{-1} (Mo-Kα), $F(000) = 256$. 734 Reflections of a single crystal with dimensions 0.04 × 0.06 × 0.06 mm were collected on a Siemens four-circle diffractometer (graphite-monochromated Mo-Kα radiation) in the ω-scan mode to $2\theta_{max} = 50°$, $T = 295$ K; a numerical absorption correction was applied. 545 Unique reflections with $|F| > 3\sigma_{|F|}$ were considered observed. Hydrogen positions could not be located. All non-hydrogen atoms except Li and Be were refined anisotropically (63 parameters, SHELXTL PLUS program package[8]). $R = 0.0567$, $R' = 0.0491$, $R_g = 0.0550$; absolute configuration $\eta = 1.8(8)$, $w = \sigma_{|F|}^{-2}\{1 - \exp[-0.5(\sin\theta/\lambda)^2]\}$, largest features in final Fourier difference synthesis $+1.14/-0.71 \times 10^{-6}$ e pm^{-3}. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Fachinformationszentrum, Karlsruhe. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

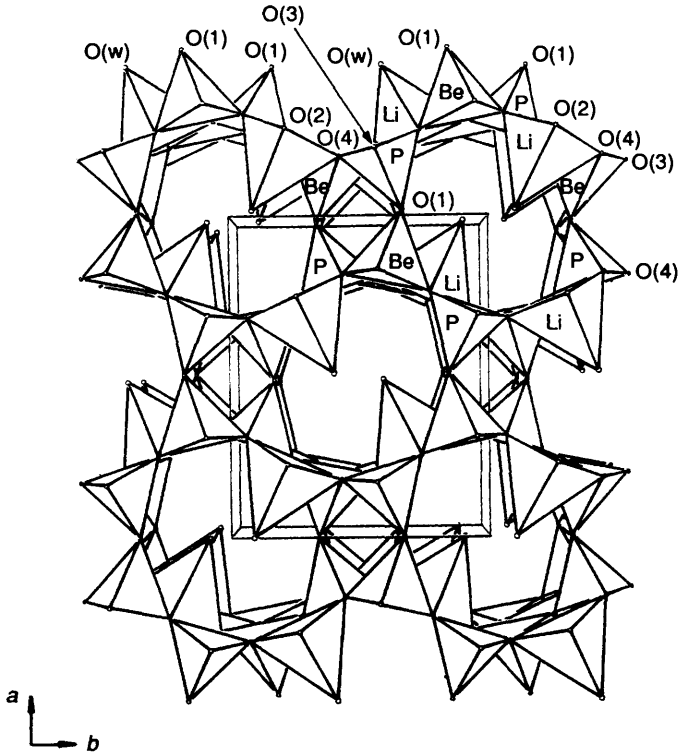

Fig. 1 A polar channel-like void extending parallel to [001] and accommodating water molecules co-ordinated to Li^+ is the characteristic structural feature of $LiBePO_4{\cdot}H_2O$. This framework is composed of tetrahedral building blocks linked by common corners to yield eight-, six- and four-membered rings, respectively. Interatomic distances (pm): P–O(1) 152.0(7), P–O(2) 152.1(7), P–O(3) 156.3(8), P–O(4) 152.9(6), Be–O(1) 161(1), Be–O(2) 165(1), Be–O(3) 164(2), Be–O(4) 160(3), Li–O(w) 185(2), Li–O(2) 196(2), Li–O(3) 196(2), Li–O(4) 197(2); selected angles (°): P–O(1)–Be 140.43(64), P–O(2)–Be 141.60(94), P–O(2)–Li 114.83(58), Be–O(2)–Li 103.32(98), P–O(3)–Be 130.75(86), P–O(3)–Li 117.96(74), Be–O(3)–Li 109.40(98), P–O(4)–Be 127.81(57), P–O(4)–Li 123.67(75), Be–O(4)–Li 103.72(84)

oxygen atoms and their bonding partners (P, Be, Li) show accordingly small deviations from planarity with mean deviations of 2 pm [O(2)], 5 pm [O(3)] and 8 pm [O(3)].

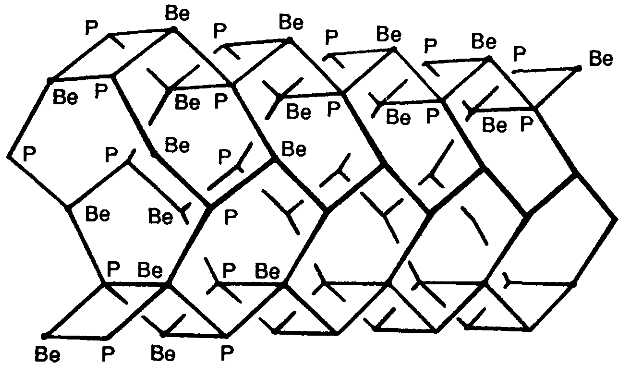

Fig. 2 A schematic view of a tubular unit in $LiBePO_4{\cdot}H_2O$. The tube axis is parallel to [001]. The connection of Be- and P-centred co-ordination tetrahedra *via* common corners yields four-, six- and eight-membered rings

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