86 *Inorg. Chem.* **2011**, *50*, 86–89
DOI: 10.1021/ic101248g

Inorganic Chemistry
Article

Single Crystal X-Ray Structure of BeF_2: α-Quartz

Pallavi Ghalsasi[†] and Prasanna S. Ghalsasi*[,‡]

[†]*Department of Physics, Indian Institute of Technology Gandhinagar, Ahmedabad 382424, Gujarat, India, and*
[‡]*Department of Chemistry, The M.S. University of Baroda, Vadodara 390002, Gujarat, India*

Received June 23, 2010

We report for the first time, the synthesis and X-ray diffraction studies of single crystals of BeF_2. The crystals were obtained during the sublimation of amorphous BeF_2 under static reduced pressure. BeF_2 crystallizes in the chiral trigonal space group $P3_121$. A single-crystal X-ray diffraction study on these crystals shows that each of the Be atoms is bonded to four F atoms, and each of the F atoms is bonded to two Be atoms with associated Be−F bond distances of 1.5420(13) and 1.5471(13) Å, showing an almost regular tetrahedron. The infrared spectrum of these crystals recorded at room temperature shows distinct peaks around 770 and 410 cm^{-1}.

Introduction

The beryllium fluoride (BeF_2) molecule has very high ionic character due to the large difference in electronegativity between the F and Be atoms.[1] Even so, its bonding is considered highly covalent in character over other alkaline earth fluorides. It is a very interesting molecule, as its gaseous form shows a CO_2-like linear structure.[2] Its molten form shows water-like resemblance,[3] and it has been a subject of research for its amorphous to amorphous transition.[4] While, in the solid state, many of the other alkaline earth metal fluorides crystallize in CaF_2 structure,[5] BeF_2 prefers a tetrahedral network. Recently (TX_4) tetrahedral units attracted considerable interest as a result of the properties of these frameworks, which include porosity, ion exchange selectivity, and unusual electronic/magnetic behaviors.[6]

The corner-sharing tetrahedral framework of SiO_2 is quite similar to that of BeF_2.[7] These striking structural similarities between SiO_2 and BeF_2 have been studied for various amorphous phases where the average structure is determined by neutron diffraction and/or Raman spectroscopy. This remarkable resemblance explained in the literature is due to similar radii (r_F = 1.33 Å; r_O = 1.32 Å) and polarizabilities of F^- and O^{2-} ions and the fact that, for both materials, the radius ratio of cation to anion is appropriate for tetrahedral bonding [$r_{Be}/r_F = 0.26$; $r_{Si}/r_O = 0.32$].[8] The strength of the Be−F bond is much less than that of the Si−O bond, and hence BeF_2 may be considered as a weaker analogue of SiO_2, having a lower melting point (540 °C), hardness, higher solubility, and chemical reactivity.

The preparation of BeF_2 by the mixing of $BeCl_2$ with excess of NaF seems to be an extremely simple procedure. But, in reality, to get pure BeF_2 and crystallize it without the presence of H_2O molecules is a challenging task. The latter difficulty is because BeF_2 has an electron-deficient beryllium atom, which readily accepts a pair of electrons to complete its octet, if suitable coordinate covalent bond donors are available. Water is such a donor, so the species $BeF_2 \cdot OH^- \cdot H_2O$ and $BeF_3^- \cdot H_2O$ predominate in the presence of water, along with BeF_4^{2-}, while their relative amounts depend on the ratio of F to Be. Note that all of these beryllofluorides would be tetrahedral, making them strictly isomorphous to a phosphate group. This peculiarity of beryllofluorides is exploited by biologists to understand protein/ATP structures.[9] On the other hand, BeF_2 is a subject of fundamental importance to the glass community, where routine techniques of formation and/or purification continue to be based on high temperature and low pressure. We used the latter approach to get the crystalline form of BeF_2, which is the subject of the present manuscript.

Experimental Section

Beryllium fluoride (BeF_2) was obtained from Alfa Aesar in the form of a white powder (99.5%, metals base). For sublimation of this commercial BeF_2 sample, a homemade stainless steel bomb was used. The description of this bomb in brief is as

*To whom correspondence should be addressed. E-mail: prasanna.ghalsasi@gmail.com.

(1) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U. K., 1997.
(2) Yu, S.; Shayesteh, A.; Bernath, P. F.; Koput, J. *J. Chem. Phys.* **2005**, *123*, 134303.
(3) Agarwal, M.; Chakravarty, C. *J. Phys. Chem. B* **2007**, *111*, 13294.
(4) (a) Yarger, J. L.; Wolf, G. H. *Science* **2004**, *306*, 820. (b) Brazhkin, V. V.; Lyapin, A. G. *J. Phys.: Condens. Matter* **2003**, *15*, 6059.
(5) Hargittai, M. *Chem. Rev.* **2000**, *100*(6), 2233.
(6) (a) Wells, A. F. *Phil. Trans. R. Soc. London, Ser. A* **1986**, *319*, 291. (b) Delgado, O. F.; Paz, F. A. A.; Dress, W. M.; Huson, D. H.; Klinowski, J.; Mackay, A. L. *Nature* **1999**, *400*, 644. (c) Foster, M. D.; Simperler, A.; Bell, R. G.; Delgado, O. F. F. *Spectrochim. Acta* **1972**, *28A*, 1103. (d) Narten, A. H. *J. Chem. Phys.* **1972**, *56*, 1905. (e) Paz, A. A.; Klinowski, J. *Nat. Mater.* **2004**, *3*, 234. (f) Zwjinenburg, M. A.; Cora, F.; Bell, R. G. *J. Am. Chem. Soc.* **2008**, *130*, 11082.
(7) Wright, A. F.; Fitch, A. N.; Wright, A. C. *J. Sol. Stat. Chem.* **1988**, *73*, 298.
(8) *CRC Handbook of Chemistry and Physics*, 63rd ed.; CRC Press: Boca Raton, FL, 1982.
(9) Petsko, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 538.

 Published on Web 12/08/2010