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

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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

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Table 1. Crystal Data and Structure Refinement for BeF_2

identification code	wyo104m
empirical formula	BeF_2
fw	47.01
temp	100(2) K
wavelength	0.71073 Å
cryst syst	trigonal
space group	$P3_121$
unit cell dimensions	a = 4.7390(5) Å, α = 90°
	b = 4.7390(5) Å, β = 90°
	c = 5.1875(8) Å, γ = 120°
vol	100.89(2) $Å^3$
Z	3
density (calculated)	2.321 Mg/m^3
absorption coeff	0.318 mm^{-1}
F(000)	66
cryst size	$0.40 \times 0.26 \times 0.20$ mm^3
Θ range for data collection	3.93−29.15°
index ranges	$-6 \leq h \leq 6, -6 \leq k \leq 6, -6 \leq l \leq 6$
reflns collected	752
independent reflns	167 [R(int) = 0.0257]
completeness to θ = 29.15°	88.8%
absorption correction	semiempirical from equivalents
refinement method	full-matrix least-squares on F^2
data/restraints/params	167/0/16
goodness-of-fit on F^2	1.141
final R indices [$I > 2\sigma(I)$]	R1 = 0.0186, wR2 = 0.0409
R indices (all data)	R1 = 0.0187, wR2 = 0.0410
absolute structure parameter	3(2)
largest diff. peak and hole	0.107 and −0.131 e $Å^{-3}$

follows. Two rectangular nickel plates were welded to the top flange of a stainless steel cylindrical vessel to provide surface area for condensation of the sublimed BeF_2. A Teflon O-ring was tightly fixed inside the groove of the top flange, and the bomb was heated in a Watlow furnace for 2−3 h at 250 °C until the Teflon O-ring melted to form a proper shape, so as to provide a good seal. After bringing the bomb to room temperature, the above-mentioned BeF_2 powder was loaded in a nickel crucible, which was then kept inside the bomb. The bomb was kept under dynamic vacuum (10^{-4} Torr) conditions for 24 h and then heated at 800 °C inside the furnace for 7 days, with a continuous flow of cold water through the top flange. The bomb was then allowed to cool down to room temperature slowly, keeping the water supply on. Colorless, transparent, spherical beads of vitreous BeF_2 were obtained from the nickel crucible, while the single crystalline α-quartz form of BeF_2 was observed at the inner surface of the top flange. The crystals were of the size $0.4 \times 0.3 \times 0.20$ mm^3 and hard in nature. The yield of the pure crystals was around 10%. We have not standardized the process of single crystal formation yet. But, we always observed the formation of single crystalline α-quartz BeF_2 (near the top flange inside the bomb) during the preparation of BeF_2 glass.

BeF_2 crystals diffract very poorly. The collected X-ray diffraction data, using a Bruker SMART APEXII with a CCD detector, revealed reverse twinning. A twin law (−1 0 0 0 −1 0 0 0 1) was applied in the refinement, which led to a satisfactory solution. This is done by applying the TWIN command in the .ins file. The exact percentage of two domains was found to be 42 and 58%.

Table 2. Atomic Coordinates ($\times$ 10^4) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for BeF_2[a]

	x	y	z	U(eq)
F(1)	4164(3)	2671(2)	2131(2)	26(1)
Be	4700(4)	0	3333	17(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for BeF_2[a]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	32(1)	24(1)	28(1)	9(1)	6(1)	18(1)
Be	18(1)	16(1)	17(1)	1(1)	1(1)	8(1)

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2[\, h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}\,]$.

Table 4. Bond Lengths [Å] and Angles [deg] for BeF_2[a]

F(1)−Be	1.5420(13)
F(1)−Be#1	1.5471(13)
Be−F(1)#2	1.5420(13)
Be−F(1)#3	1.5471(13)
Be−F(1)#4	1.5471(13)
Be−F(1)−Be#1	144.71(9)
F(1)−Be−F(1)#2	109.77(17)
F(1)−Be−F(1)#3	108.92(2)
F(1)#2−Be−F(1)#3	109.83(6)
F(1)−Be−F(1)#4	109.83(6)
F(1)#2−Be−F(1)#4	108.92(2)
F(1)#3−Be−F(1)#4	109.56(13)

[a] Symmetry transformations used to generate equivalent atoms. #1: $-x+y+1, -x+1, z-1/3$. #2: $x-y, -y, -z+2/3$. #3: $-x+1, -x+y, -z+1/3$. #4: $-y+1, x-y, z+1/3$.

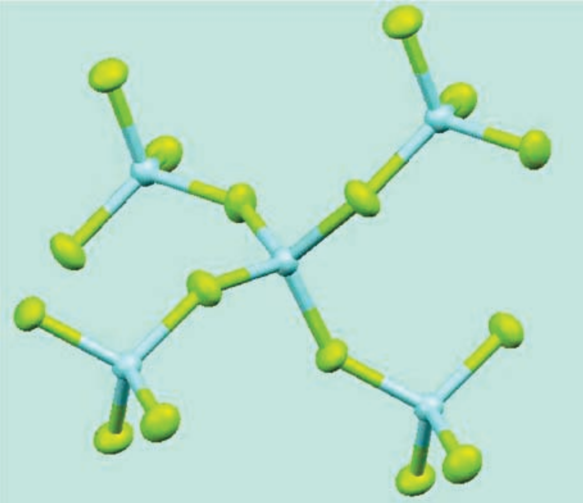


Figure 1. View of the BeF_2 network. Thermal ellipsoids are drawn at 30% probability.

Results and Discussion

BeF_2 crystallizes in the chiral trigonal space group $P3_121$. Satisfactory refinement of the structure confirms the choice of the space group. Crystal data along with the details of the data collection and refinement are shown in Table 1. Table 2 presents the final atomic coordinates and equivalent isotropic displacement parameters, and Table 3 shows anisotropic displacement parameters with ESDs in parentheses, which are calculated for this crystal. Although the crystal belongs to a chiral space group, the handedness of the BeF_2 network could not be determined, as the Mo Kα radiation was used for the data collection and also due to the weakly diffracting nature of the crystal. The Be atom is located on a 3b Wyckoff site, and the F atom is located on a 6c Wyckoff site. Figure 1 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 (for details, refer to Table 4). These values slightly differ in the values obtained using neutron diffraction measurements on powdered BeF_2, 1.541(2) and 1.544(2) Å. The Be atom is in a near tetrahedral geometry,

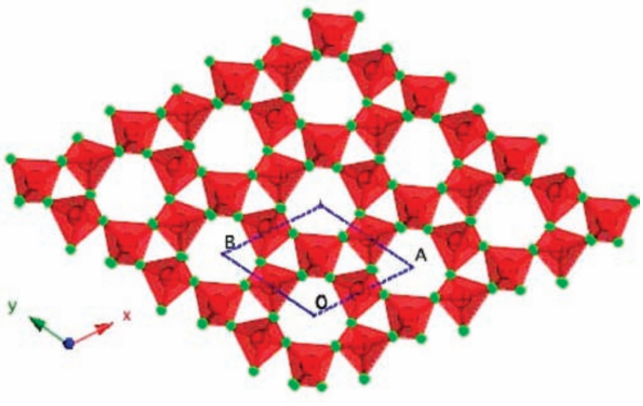


Figure 2. Packing diagram of BeF_4 tetrahedral network along the *z* axis to show α-quartz type polymorph.

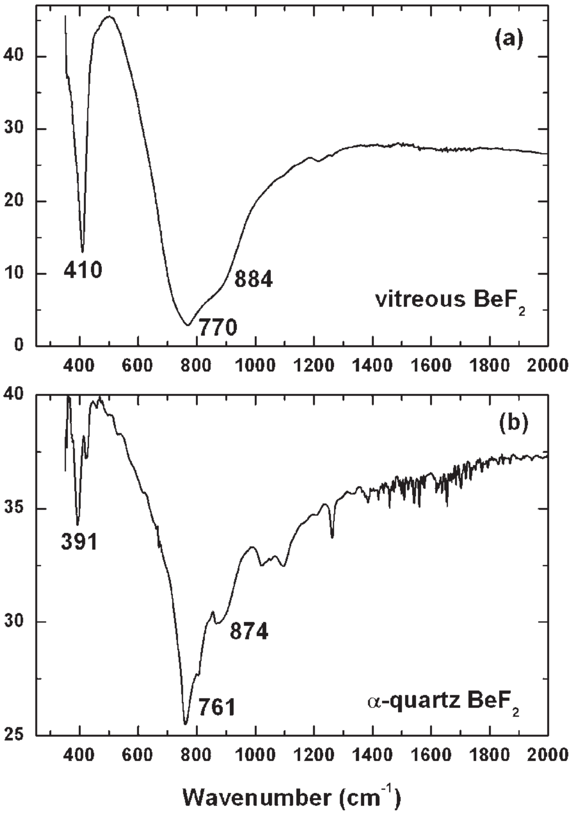
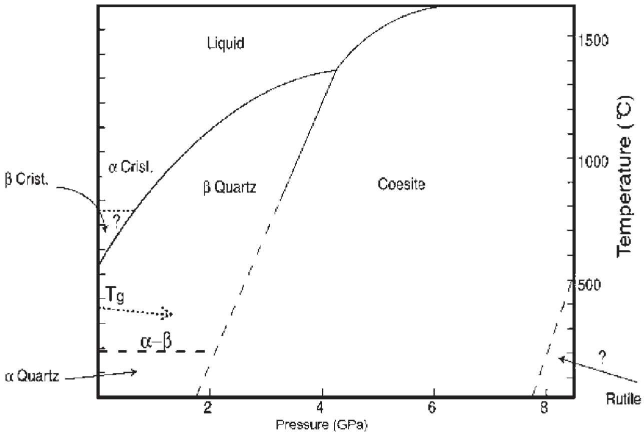


Figure 3. Infrared spectra of vitreous BeF_2 (a) and α-quartz BeF_2 (b) under ambient conditions.

and the Be−F−Be unit is bent with a bond angle of 144.71(9)°. Figure 2 shows that these BeF_4 tetrahedra are arranged in a typical α-quartz type structure, similar to that of SiO_2. The Supporting Information includes a tabulated comparison of structural parameters of BeF_2 from the literature and the present work to those of SiO_2.

Figure 3 shows a comparison of infrared spectra of vitreous BeF_2 obtained as transparent colorless beads (a) and of α-quartz BeF_2 (b). The infrared spectrum of vitreous BeF_2 shows peaks around 410 and 770 cm^{-1} attributed to the Be−F stretching vibrations in the BeF_4 tetrahedron.[10] The shoulder at 880 cm^{-1} is suggested to be due to presence of oxygen in the sample. There have been no reports on the Raman and infrared mode assignments for BeF_2 based on group theory. A comparison of the infrared spectra with that of SiO_2 indicates that the peak around 410 cm^{-1} is associated with a TO−LO pair and the peak at 770 cm^{-1} with a TO mode.[10] The infrared spectrum of α-quartz BeF_2 shows the same modes slightly red-shifted with featured sharp peaks.

Scheme 1. The Polymorphism of BeF_2 (reprinted with permission from ref 12. Copyright 2002, Materials Research Society).



While glassy BeF_2 is being used commercially in infrared optics due to its useful optical properties, very little has been known about its crystalline varieties. This is because, like silica and germanium dioxide, beryllium fluoride possesses a Be/F radius ratio of ~0.3, a figure which allows compounds of the AX_2 type to exist in the glassy form. This was initially well supported by X-ray methods.[11] The structural relationship between silica and BeF_2 is now established, and the equilibrium phase diagram for BeF_2 is outlined in Scheme 1, which shows possible structural forms, supported by neutron, powder X-ray, and other techniques.[12] Thus, BeF_2 is predicted to exist in tetragonal and trigonal structures, similar to silica. In the present work, we have obtained single crystals of BeF_2 for the first time, which are trigonal in nature. In the future, we would like to crystallize other forms of BeF_2.[13]

Conclusion

We have reported the synthesis of single crystals of the α-quartz polymorph of BeF_2 for the first time. Single crystals were obtained not by the standard procedure of synthesis of BeF_2, but by a sublimation technique. Single-crystal X-ray diffraction data on these BeF_2 crystals have shown structural analogy with SiO_2, and not with alkaline earth metal fluorides. We would like to study further various polymorphs of BeF_2 like α- and/or β-cristobalite and α- and/or β-quartz as a function of pressure. A comparison of high pressure data of the β-quartz form with that of vitreous BeF_2 will be very

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important as the structure of vitreous BeF_2 is supposed to be close to that of β-quartz.

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Supporting Information Available: Crystallographic information file (CIF) for the single-crystal X-ray diffraction data, a comparison of structural parameters of α-quartz structures of BeF_2 (literature and present work) with SiO_2, and preparation of BeF_2. This information is available free of charge via Internet at http://pubs.acs.org.