

The Preparation and Structure of the α - and β -Quartz Polymorphs of Beryllium Fluoride

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Devitrification of vitreous BeF_2 at 355°C yields β -quartz BeF_2 which on cooling to ambient temperature undergoes a displacive transition to give the α -quartz form. Both α - and β -quartz BeF_2 have tetrahedral (BeF_4) structures which are very closely related to the corresponding SiO_2 polymorphs. At ambient temperature the Be-F bond lengths are 1.541(2) and 1.544(2) Å and the Be-F-Be angle is $144.6(2)^\circ$. For β -quartz BeF_2 at 246°C the corresponding average values in the micro-twinned structure are 1.535 Å and 150.3° , respectively. © 1988 Academic Press, Inc.

Introduction

The remarkable correspondence between the polymorphism of BeF_2 and that of SiO_2 is held (1) to be due to the similar radii [$r_{\text{F}} = 1.33$ Å; $r_{\text{O}} = 1.32$ Å (2)] and polarizabilities of the F^- and O^{2-} ions and the fact that for both materials the radius ratio is appropriate for tetrahedral bonding [$r_{\text{Be}}/r_{\text{F}} = 0.26$; $r_{\text{Si}}/r_{\text{O}} = 0.32$]. The strength of the Be-F bond is much less than that of the Si-O bond and hence BeF_2 may be considered a weakened analog of SiO_2 having a lower melting point [540°C (3)] and hardness and higher solubility and chemical reactivity (1). Despite the close relationship between the two materials, however, BeF_2 has been very much less studied than SiO_2 due to its high toxicity and water sensitivity. Thus, although the structure of vitreous BeF_2 has

been studied by both X-ray (4-13) and neutron (13, 14) diffraction, there have been no structural studies of any of the crystalline phases other than a simple measurement of lattice parameters. The present neutron diffraction study was therefore carried out in order to obtain accurate structural parameters for α - and β -quartz BeF_2 to enable a detailed comparison of the crystalline and vitreous states.

There is still confusion in the literature as to the equilibrium phase diagram and Fig. 1 was constructed mainly from the work of Roy *et al.* (15, 16). β -Cristobalite BeF_2 is obtained by heating $(\text{NH}_4)_2\text{BeF}_4$ under reduced pressure (~ 100 mm) at about 180 - 260°C (15) and transforms to α -cristobalite BeF_2 below 130°C (17-19). On further heating β -cristobalite BeF_2 melts at 543°C (15) and prolonged heating at 340 - 430°C gives

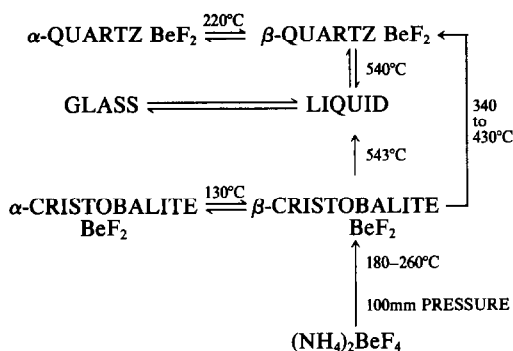


FIG. 1. The polymorphism of BeF_2 (at atmospheric pressure) (1, 15–18).

partial conversion to the β -quartz form (15, 16). β -Cristobalite BeF_2 appears, however, to be stable between 516°C and the melting point, although in this temperature range only the β -quartz form has ever been found in equilibrium with the melt in studies of binary mixtures. It has been reported that β -cristobalite BeF_2 is obtained by devitrification of the pure material at 350 and 450°C (6), but this is not consistent with results obtained by the present authors and by Taylor and Gardner (20). Roy *et al.* (16) suggest that either cristobalite BeF_2 is a metastable or low temperature form or else it is only stable just below the melting point. On cooling below the liquidus, a melt containing a small addition of LiF or NaF yields β -quartz BeF_2 (15), which transforms to the α -quartz modification below 220°C (16). The thermal expansion, of both α - and β -quartz BeF_2 , has been studied using X-ray powder diffraction techniques (16) and is remarkably similar to that of the corresponding silica polymorphs. Beryllium fluoride also forms a coesite modification, at a pressure slightly greater than that required for SiO_2 (21), and another similar to tridymite has been reported in the ZrF_4 - BeF_2 system (19). Vitreous BeF_2 may be prepared by quenching the melt and has a glass transition temperature of 325°C (3). The structure of vitreous BeF_2 is analogous

to that of vitreous SiO_2 (4–14), comprising a network of corner sharing BeF_4 tetrahedra, with a mean Be–F bond length of 1.553(5) Å (14).

Sample Preparation and Measurement

Beryllium fluoride was obtained from Merck in the form of glassy pieces 2–5 mm in size. After coarse grinding, 3 cm³ was loaded into a 12-mm-diameter cylindrical, thin-walled, vanadium sample container and sealed with a copper washer. This was then mounted in a furnace designed for powder diffraction. The diffraction pattern of the amorphous phase at room temperature was recorded on the D1A high-resolution powder diffractometer at a wavelength λ of 1.511 Å (calibrated with a Ni standard).

The temperature was then raised to 30°C above T_g ($T_g = 325^\circ\text{C}$) while scanning a small angular range for the appearance of the low-index β -quartz peaks of BeF_2 . The temperature was stabilized at 355°C and the sample left to crystallize fully for several hours. The β -quartz diffraction pattern was measured at 246°C. The scanning time was 8 hr. The sample was then allowed to cool to room temperature and the diffraction pattern of the α -quartz phase was recorded. The three patterns are shown in Figs. 2–4 as a function of the scattering angle 2θ .

Analysis and Results

The structures were refined using the Rietveld neutron powder profile refinement technique (22) with neutron scattering lengths for Be and F of 0.774×10^{-14} and 0.566×10^{-14} m, respectively. The background was estimated by linear interpolation of values obtained between the Bragg peaks. It was subtracted before refinement and reintroduced afterward for Figs. 3 and 4. The diffuse scattering visible in Fig. 4 is indicative of some disorder in agreement with the profile analysis. The expected (sta-

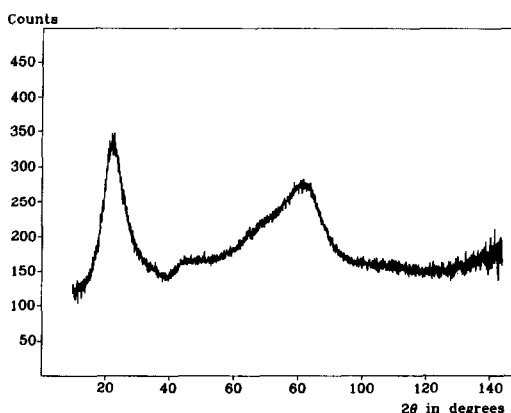


FIG. 2. The diffraction pattern for the vitreous BeF_2 starting material.

tistical) profile R -factors for the α - and β -polymorphs are respectively 3.9 and 5.4%. It was observed that the experimental resolution refined from the data differed significantly from that normally to be expected for D1A, and that the profile fit was poor

even though the agreement with peak intensities was good.

The poor profile is consistent with broadening of the diffraction peaks due to crystallite size. The mean particle dimension L in units of d normal to (h,k,l) in a powder sample is related to the integral diffraction breadth β (in radians) free from instrumental broadening by the Scherrer equation,

$$\beta = \lambda / (Ld \cos \theta). \quad (1)$$

The refinement program was therefore modified to take into account crystallite size broadening by including an additional term in the calculation of the half-width parameter. The Gaussian-peak width function took the form

$$H^2 = U \tan \theta + V \tan^2 \theta + W + X / \cos^2 \theta \quad (2)$$

where H is the full width at half-maximum height of the Gaussian peak measured at 2θ . U , V , and W were refined in the normal

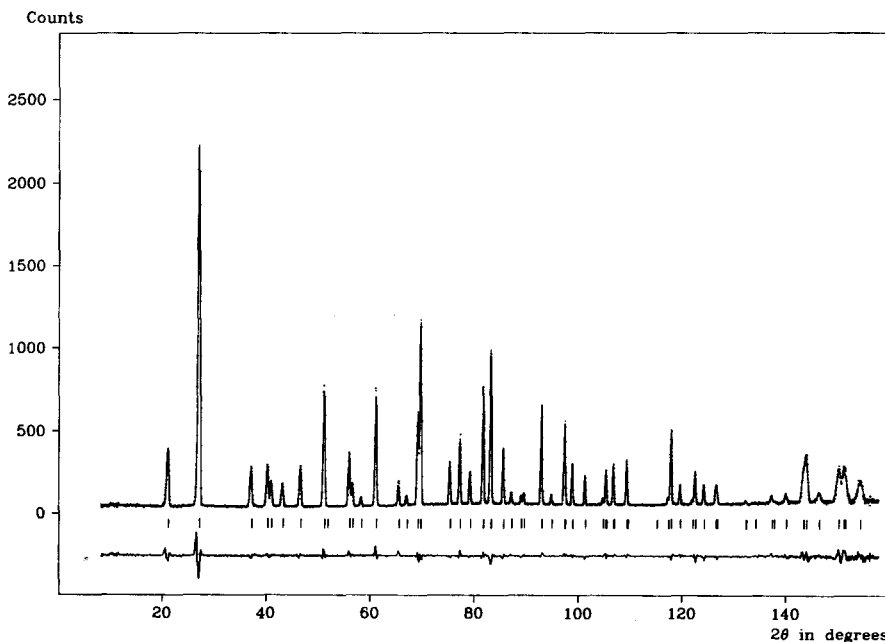


FIG. 3. The diffraction pattern for α -quartz BeF_2 showing the raw data points, Rietveld fit, positions of Bragg peaks (vertical bars), and residual.

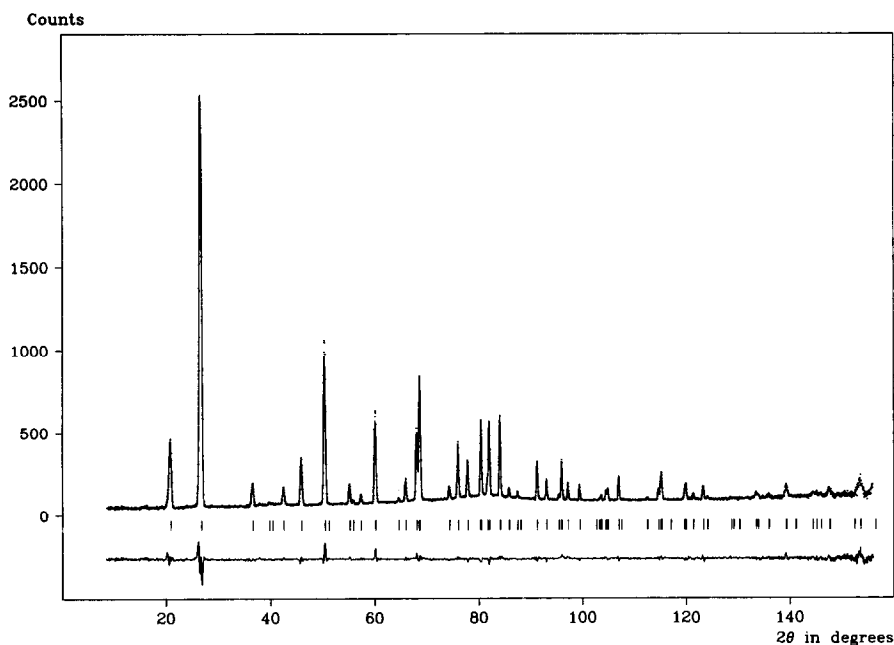


FIG. 4. Rietveld fit to the diffraction pattern for β -quartz BeF_2 (key is indicated in Fig. 3).

way, while X was adjusted by trial and error and found to give the best profile fit at a value of 0.13 (degrees²) corresponding to $L \sim 750 \text{ \AA}$.

α -Quartz BeF_2

The starting parameters for α -quartz BeF_2 were those for α -quartz SiO_2 . The final refinement gave an excellent fit to both the profile and peak intensities, with structural parameters very close to those of α -quartz SiO_2 , as shown in Table I. The refined BeF_4 tetrahedra are very regular in the α -phase, the $\text{F}-\text{Be}-\text{F}$ angles being within 0.6° of the tetrahedral angle. The six values are $108.9, 108.9, 109.5, 109.4, 110.0,$ and $110.0(2)^\circ$. The $\text{Be}-\hat{\text{F}}-\text{Be}$ bridging bond angle is $144.6(2)^\circ$, and the bond lengths are $1.541(2)$ and $1.544(2) \text{ \AA}$. The lower strength of the $\text{Be}-\text{F}$ bond shows up in the temperature factors for both Be and F, which are up to three times larger in BeF_2 than in the SiO_2 analog.

β -Quartz BeF_2

The β -phase was refined in space group $P622$ which offers the possibility of two model types. In the so-called ideal β -quartz structure the Be atoms would occupy the high symmetry $3c (\frac{1}{2}, 0, 0)$ position and the F atoms the $6j (x, 2x, \frac{1}{2})$ position. This structure type was generally accepted for β -quartz SiO_2 since the first analysis by Bragg and Gibbs (23) in 1925. More recently, however, Arnold (24) has proposed a disordered structure for the high-temperature phase corresponding to a time or space average (diffraction cannot distinguish between the two phenomena) of α_1 and α_2 Dauphiné twins. Wright and Lehmann (25) have refined the structure of β -quartz SiO_2 from both single crystal and powder data, the latter obtained under experimental conditions identical to those here, and strongly favor the disordered model over the ideal one.

The present data have been analyzed us-

TABLE I
 FINAL PARAMETERS

	α -Quartz (space group $P3_221$)		β -Quartz (space group $P6_222$)	
	BeF ₂	SiO ₂ (25)	BeF ₂	SiO ₂ (25)
T (°C)	Ambient	Ambient	246	630
a_0	4.7329(1)	4.9134	4.8060(1)	4.9977
c_0	5.1788(1)	5.4052	5.2404(1)	5.4601
	Beryllium	Silicon	Beryllium	Silicon
X	0.4706(3)	0.4701(1)	0.4806(9)	0.484
B			1.90(2)	1.46(9)
U_{11}	0.0153(7)	0.0056(2)		
U_{22}	0.0121(9)	0.0039(2)		
U_{33}	0.0079(5)	0.0052(2)		
U_{13}	$\frac{1}{2}U_{22}$	$\frac{1}{2}U_{22}$		
U_{12}	$\frac{1}{2}U_{23}$	$\frac{1}{2}U_{23}$		
U_{23}	-0.0007(5)	-0.0006(2)		
	Fluorine	Oxygen	Fluorine	Oxygen
X	0.4158(4)	0.4136(1)	0.4204(4)	0.4179(4)
Y	0.2672(3)	0.2676(1)	0.2497(9)	0.2432(8)
Z	0.1206(2)	0.1191(1)	0.1477(3)	0.1416(8)
U_{11}	0.0328(1)	0.0137(2)	0.027(3)	0.051(2)
U_{22}	0.0256(8)	0.0093(2)	0.071(1)	0.041(9)
U_{33}	0.0159(7)	0.0109(1)	0.041(3)	0.027(7)
U_{12}	0.0199(9)	0.0078(1)	0.029(1)	0.032(2)
U_{13}	0.0058(7)	-0.0030(1)	0.015(3)	-0.002(2)
U_{23}	0.0088(5)	-0.0048(1)	-0.004(2)	-0.013(6)
R_1 (%)	2.08		3.31	
R_F (%)	7.38		9.97	

ing both models, and once again the disordered model is clearly favored. The results are given in Table I, and compared to the SiO₂ analog. The refined angles for the BeF₄ tetrahedral unit suggest an almost undistorted tetrahedron, but as with the SiO₂ refinement, the disorder of the central atom is so small that correlation occurs between the anisotropic temperature factors and the amount of translational separation between the Be atoms of the α_1 and α_2 structures. With the fluorine atoms the separation is sufficiently large that the structural and temperature parameters can be independently refined. The quoted refinement is therefore based on a split Be position (three atoms in 6g) with a simple isotropic temperature factor. The refined Be-F distances are 1.495(10) and 1.572(8) Å, but the true

uncertainty of the Be position is probably greater than that quoted from statistical considerations in Table I. The average value of 1.535 Å is, however, obtained when Be is constrained in 3c ($\frac{1}{2}$, 0, 0) or relaxed to 6g (0.481, 0, 0). While the average Be-F distance appears to shorten on passing from the α - to the β -phase, the Be-F-Be angle increases from 144.6 to 150.3°. For quartz SiO₂ the angles were 143.6° (α) and 150.9° (β) (25) which accounts for the lattice expansion at the phase transition.

Discussion

It is extremely interesting to note that the polymorph obtained on the devitrification of pure, dry vitreous BeF₂ at 355°C is β -quartz BeF₂ and not the β -cristobalite form, since in the SiO₂ system only β -cristobalite is ever obtained on devitrification, even in the temperature range (867–1470°C) where tridymite might be expected to be the stable phase (26), tridymite only being obtained in the presence of a flux or solvent. Thus in its devitrification behavior BeF₂ is *not* analogous to SiO₂, which is an indication either of structural differences between the two glasses or more likely that the glass structure does not resemble that of any of the crystalline forms closely enough to cause that form to become the devitrification product. Phillips (27) has suggested that the structure of vitreous silica is granular, comprising an agglomeration of 66-Å β -cristobalite paracrystallites, the surfaces of which are noncoalescing and saturated with Si=O double bonds, and argued that the structure of vitreous BeF₂ should be similar. As discussed elsewhere (28) there are serious objections to Phillips' model for SiO₂. However, the devitrification behavior of vitreous BeF₂ reported here suggests that its structure is most unlikely to be based on β -cristobalite BeF₂ paracrystals, since in this case devitrification would almost certainly yield β -cristobalite BeF₂ and

not the β -quartz form. Note in particular that the diffraction pattern for the vitreous BeF₂ starting material in Fig. 2 shows no trace of any quartz phase which could nucleate the devitrification. Also the first diffraction peak for the glass is not coincident with the intense second Bragg peak for either of the quartz polymorphs and hence any attempt to model the glass structure by broadening the α - or β -quartz powder diffraction patterns would yield a first diffraction peak for the glass in the wrong position as demonstrated by the quasi-crystalline model calculations of Leadbetter and Wright (13). It can thus be concluded that the intermediate range order in the glass does not resemble that of the quartz polymorphs.

The similarities between the structures of the quartz polymorphs of BeF₂ and SiO₂ are striking. They extend even to the bridging bond angles, their expansion at the phase transition and the disordered structure of the β -phase. Above the transition temperature Roy *et al.* (16) find that the lattice parameters of β -quartz BeF₂, like those of the SiO₂ analog, are almost independent of temperature. The value obtained here for c_0 [5.2404(1) Å] is close to that of Roy *et al.* [$a_0 = 4.78_2$; $c_0 = 5.25_3$ Å] but a_0 [4.8060(1) Å] is somewhat higher. For the α -quartz polymorph both lattice parameters [$a_0 = 4.7329(1)$; $c_0 = 5.1788(1)$ Å] are slightly less than those of Hyde *et al.* (29) [$a_0 = 4.752(10)$; $c_0 = 5.188(10)$ Å]. The present lattice parameters for α - and β -quartz BeF₂ lead to average number densities ρ^0 of 0.02986 and 0.02862 composition units Å⁻³ respectively compared to a value ρ_g^0 of 0.02562 c.u. Å⁻³ for the glass (3). The density ratios $\rho_\alpha^0/\rho_g^0 = 1.17$ and $\rho_\beta^0/\rho_g^0 = 1.12$ are both lower than the corresponding values for the SiO₂ quartz analogs [1.20 and 1.15, respectively (3)]. On the other hand the ratio $\rho_{\text{BeF}_2}^0/\rho_{\text{SiO}_2}^0$ is closely similar (1.12₅ and 1.12₇) for the two quartz polymorphs but rather higher for the glasses (1.16), suggest-

ing that the latter differ in either their bridging bond angle distribution or their network topology.

Conclusions

The present structural study of the quartz polymorphs of BeF₂ demonstrates once again the remarkable similarity between the structural chemistries of BeF₂ and SiO₂ which for the quartz analogs includes not only the detailed bond angles but also the disorder in the β -phase. Further work is now required to extend this quantitative study to the other crystalline polymorphs and in particular to ascertain whether a similar situation exists for α - and β -cristobalite BeF₂. The present study has, however, highlighted differences in devitrification behavior, and possibly structure, between the vitreous forms of BeF₂ and SiO₂, which will be discussed further in a forthcoming paper on vitreous BeF₂ (14).

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