Yu. M. Korenev, Yu. P. Simanov, Corresponding Member of the Academy of Sciences of the USSR

A. V. Novoselova

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Abstract

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Yu. M. Korenev, Yu. P. Simanov, Corresponding Member of the Academy of Sciences of the USSR
A. V. Novoselova

On the Rhombic Modification of Beryllium Fluoride

Goldschmidt ([1]), on the basis of the closeness of the radii of Be^{2+} ($r = 0.34$ Å) and Si^{4+} ($r = 0.39$ Å), F^{-1} ($r = 1.33$ Å) and O^{2-} ($r = 1.32$ Å), suggested that beryllium fluoride should possess a structure similar to that of silicon dioxide. The structural similarity of beryllium fluoride to silicon dioxide was first experimentally discovered by Brandenberger ([2]). He found that, upon decomposition of $(NH_4)_2BeF_4$, cristobalite-like BeF_2 is formed, with the parameters of the tetragonal cell: $a = 6.60$ kX and $c = 6.74$ kX, $c/a = 1.02$.

In work ([3]) it was established that tetragonal BeF_2 at 130° transforms into a cubic modification ($a = 6.78$ kX). This transformation is analogous to the $\alpha \rightleftarrows \beta$ transformation of cristobalite (SiO_2).

In studying the NaF—BeF_2 system ([4]), in our laboratory a modification of BeF_2 was discovered that is structurally similar to low-temperature quartz. This modification of BeF_2 has a hexagonal lattice with parameters: $a = 4.72$ kX, $c = 5.18$ kX, $c/a = 1.10$.

Roy et al. ([5]) established that quartz-like BeF_2 at 220° passes into a modification similar to high-temperature quartz. The lattice parameters of this form of BeF_2 are: $a = 4.77$ kX, $c = 5.24$ kX, $c/a = 1.09$. In investigating the BeF_2—ZrF_4 system we discovered a new modification of BeF_2. This modification of BeF_2 was obtained by us from the quartz-like modification in the following way.

We prepared melts of beryllium fluoride with zirconium fluoride by driving off ammonium fluoride from a mixture of $(NH_4)_2BeF_4$ and $(NH_4)_3ZrF_7$, containing 4% ZrF_4 (relative to the simple fluorides). The driving off of ammonium fluoride was carried out in a stream of CO_2; the furnace temperature was at first slowly raised to 300°, at which temperature the greater part of NH_4F was driven off; then the temperature was raised to 400-420° and the remainder of the ammonium fluoride was driven off. X-ray investigation showed that the melt obtained contains beryllium fluoride in the form of the quartz-like modification. It was of interest to determine how zirconium fluoride affects the polymorphic transformations of BeF_2.

Earlier, in a thermographic study of the NaF—BeF_2 system ([6]), in addition to

the known modifications, one more modification of BeF_2 was found, existing in the interval 680–420°, from which, on cooling, quartz-like BeF_2 was obtained; however, it could not be detected by X-ray methods. We carried out annealing of the fluoride mixture (4% ZrF_4) at 590–600° in sealed quartz ampoules under a residual argon pressure of 10–20 mm Hg. To avoid interaction of quartz with the fluorides, the latter were placed in a nickel crucible. The annealing lasted 25 hours, after which the ampoule was cooled to room temperature.

X-ray investigation of the preparation obtained was carried out in capillaries made of Pyrex glass using cobalt radiation with an iron filter in an RKU-86 camera and copper radiation with a nickel···

filtered in the RKD chamber. The placement of the film was asymmetric. The photographs were measured on a comparator giving a reading accuracy of 0.05 mm. In all, three measurements were made by three different persons, and the mean value of $1/d^2$ was taken from the results obtained. In the photographs (rather strongly veiled), two halos from amorphous BeF_2 were clearly distinguished. The measured lines could be satisfactorily indexed in a rhombic body-centered lattice with axial parameters: $a = 10.01 \pm 0.01$ kX; $b = 13.07 \pm 0.02$ kX; $c = 16.24 \pm 0.01$ kX*. The results of the indexing are given in Table 1. Lines belonging both to quartz-like and to cristobalite-like BeF_2, as well as to zirconium fluoride, were not found in the photographs.

Table 1

Results of indexing the X-ray pattern of BeF_2

No.	I	$1/d^2_{exp}$	hkl	$1/d^2_{calc}$	No.	I	$1/d^2_{exp}$	hkl	$1/d^2_{calc}$
1	med. br.	0.0605	004	0.0606	26	weak med.	0.4208	604	0.4195
2	v. v. v. weak	0.0670	123	0.0675	27	v. v. weak	0.4433	624	0.4429
3	v. v. weak	0.0759	114	0.0764	28	v. v. weak	0.4602	615	0.4595
4	v. v. weak	0.0833	024	0.840	29	v. v. weak	0.4781	358	0.4785
5	med.	0.0936	040	0.0936	30	weak sh.	0.4952	606	0.4953
6	med. weak	0.1002	204	0.1005	31	v. v. weak	0.5140	644	0.5131
7	v. v. weak	0.1099	312	0.1107	32	v. v. weak	0.5291	547	0.5285
8	med.	0.1240	224	0.1239	33	v. v. v. weak	0.5449	194	0.5444

No.	I	$1/d^2_{\text{exp}}$	hkl	$1/d^2_{\text{calc}}$	No.	I	$1/d^2_{\text{exp}}$	hkl	$1/d^2_{\text{calc}}$
9	v. v. weak	0.1337	240	0.1335	34	v. v. weak	0.5536	?	?
10	v. weak	0.1469	323	0.1472	35	v. v. weak	0.5696	660	0.5695
11	med.	0.1546	044	0.1542	36	v. v. weak sh.	0.5872	2.0.12	0.5857
12	v. weak sh.	0.2080	325	0.2079	36	v. v. weak sh.	0.5872	646	0.5889
13	v. v.weak	0.2239	161	0.2244	37	v. v. v. weak	0.6085	725 (?)	0.6067
14	med.	0.2425	008	0.2426	38	v. v. weak	0.6279	581	0.6274
15	v. v. weak	0.2540	501	0.2530	39	v. v. v. weak	0.6483	811	0.6477
16	v. v. weak	0.2715	064	0.2712	40	v. v. v. weak	0.6791	673	0.6796
17	v. v. weak sh.	0.2847	503 (?)	0.2833	41	v. v. v. weak	0.6975	727	0.6976
18	v. v. weak	0.2960	354	0.2964	42	v. v. weak	0.7164	1.11.0	0.7178
19	weak med. sh.	0.3058	435	0.3069	43	v. v. weak	0.8637	862	0.8642
20	v. v. v. weak	0.3190	426	0.3193	44	v. weak	0.9192	5.6.11	0.9184
21	med.	0.3358	048	0.3362	45	v. weak	0.9426	3.0.15	0.9425
22	weak	0.3498	417	0.3510	46	v. weak	0.9707	0.0.16	0.9702
23	weak sh.	0.3688	611	0.3685	47	v. v. v. weak	1.0046	6.10.4	1.0045
24	v. v. v. weak	0.3855	462	0.3853	48	v. v. v. sh.	1.2785	6.8.12	1.2791

No.	I	$1/d^2_{\text{exp}}$	hkl	$1/d^2_{\text{calc}}$	No.	I	$1/d^2_{\text{exp}}$	hkl	$1/d^2_{\text{calc}}$
25	weak	0.3986	239	0.3995	49	v. v. v. sh.	1.3998	10.2.10	1.3994

The modification of BeF_2 found by us lies precisely in the temperature interval in which, according to work ([7]), the existence (by analogy with SiO_2) of a tridymite-like modification of beryllium fluoride is assumed, as is seen from the following scheme given in that article:

$$\beta Q\text{—}BeF_2 \overset{220^\circ}{\rightleftarrows} \alpha Q\text{—}BeF_2 \overset{420\text{—}450^\circ}{\rightleftarrows} T\ (?)\ BeF_2 \overset{\sim 680^\circ}{\rightleftarrows} \alpha C\text{—}BeF_2 \overset{\sim 800^\circ}{\rightleftarrows} \text{melt.}$$

$$\alpha C\text{—}BeF_2 \underset{1130^\circ}{\downarrow} \beta C\text{—}BeF_2$$

According to Gibbs ([8]), low-temperature α-tridymite (SiO_2) crystallizes in the rhombic system with parameters: $a = 9.88$ kX; $b = 17.1$ kX; $c = 16.3$ kX.

The results of indexing the X-ray pattern of Gibbs' s tridymite, presented in Shishakov' s book ([9]), as well as our photograph of dinas refractory, indicate that the lattice is body-centered.

* The small accuracy achieved in determining the parameters is explained by the indistinctness of most of the lines in the photographs.

The prominent role of reflections with all even indices permits one to speak of the presence of a subcell with a volume equal to 1/8 of the main cell. In considering the data of our table for the indexing of rhombic BeF_2, one can be convinced of its analogy with tridymite with respect to the mode of centering and the presence of a subcell. As for the absolute values of the axial parameters for the two substances being compared, then, along with a difference between the values of b, for the axes a and c we have a close similarity.

The temperature range of existence, as well as many structural properties, of the BeF_2 modification obtained by us make it possible to call it tridymite-like.

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.