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Physical properties of $BeAl_2O_4$ single crystals

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Physical properties of Czochralski-grown single crystal $BeAl_2O_4$ are reported. Data on hardness, thermal expansion, thermal conductivity, and elastic constants are tabulated as a function of crystallographic orientation. Results indicate that the properties of $BeAl_2O_4$ compare favourably with those of Al_2O_3.

1. Introduction

The mineral chrysoberyl ($BeAl_2O_4$) has physical properties, including high hardness values and high thermal diffusivity, low density, and the luminescent and lasing behaviour of the Cr^{3+}-doped variety ("alexandrite") [1], that make it an interesting candidate for a variety of applications.

Chrysoberyl crystal growth by a variety of methods has been described in the literature. Farrel and Fang [1] reported flux growth of chrysoberyl and alexandrite. Linares [2] achieved successful Czochralski and flux growth of small single crystals. In addition, existing patents deal with hydrothermal synthesis [3], Verneuil growth [4] and vapour growth [5] of chrysoberyl crystals.

In this work, we summarize the known properties of chrysoberyl and report our physical property measurements on large single crystals grown by the Czochralski technique [6].

2. Known properties of chrysoberyl

2.1. Structure

Chrysoberyl, $BeAl_2O_4$, crystallizes in the orthorhombic system with space group *Pnma;* $a = 9.404$ Å; $b = 5.476$ Å; and $c = 4.427$ Å [7, 8]. The structure is built upon approximate hexagonal close packing of oxygen ions, with Al^{3+} and Be^{2+} ions occupying octahedral and tetrahedral sites, respectively. The deviations from exact hexagonal close packing of oxygen ions are manifested in the appearance of two types of octahedrally co-ordinated sites, Al_I, possession inversion symmetry, and Al_{II}, a mirror site; the larger Al_{II} size is preferred by substitutional Cr or Fe ions [8].

The assignment in the literature of the lattice-parameter designations a and b is inconsistent in that Dana [9] uses $a = 5.476$ Å and $b = 9.404$ Å, whereas Bragg and Brown [7] originally assigned $a = 4.24$ Å, $b = 9.39$ Å and $c = 5.47$ Å. These discrepancies must be taken into account in interpreting morphological features of crystals and orientation-dependent properties. In this paper, we will adhere to the assignment used by Newnham [8], i.e. $a = 9.404$ Å, $b = 5.476$ Å and $c = 4.727$ Å. The X-ray density is $3.69\,g\,cm^{-3}$.

2.2. Phase relationships

$BeAl_2O_4$ is a congruent melting compound (m.p. = 1870° C) in the $BeO–Al_2O_3$ systems. A continuous series of solid solutions exist between $BeAl_2O_4$ and the isostructural compound $BeCr_2O_4$ [8]. Fe^{3+} also substitutes readily into the Al_{II} site, up to 50 at.% (based on both Al_I and Al_{II} sites) [8].

2.3. Optical properties

Chrysoberyl is optically biaxial, positive with indices: $\alpha = 1.746$, $\beta = 1.748$ and $\gamma = 1.756$, and $2\nu = 45°$ (sodium line, room temperature). Principal vibration direction X is parallel to the c direction, and Y is parallel to the a direction [9]. (In the reference, Y is parallel to b. In the present work, a- and b-axes have been interchanged for internal consistency, and to comply with Newnham's assignment of lattice-parameter designations.)

3. Experimental results and discussion

3.1. Microhardness

We have made Knoop microhardness measurements, using a Lietz Durimet Hardness Tester,* on the three crystallographic axes and in various directions in $BeAl_2O_4$. The Knoop microhardness of $BeAl_2O_4$ was measured as a funtion of indentor orientation on each principal face. The results are shown in Fig. 1. The hardness variations for the (1 0 0) and (0 1 0) faces are nearly identical, showing a strong minimum when the long axis of the indentor is parallel to [0 0 1]. Because the flow produced by a Knoop indentor is at right angles to the long axis, the operative slip system(s) has slip planes in the [0 0 1] zone, and slip direction in the (0 0 1) plane.

The hardness variation on the (0 0 1) face shows high average hardness values with weak minima when the short diagonal (i.e. shear direction) is parallel to [1 1 0]. The lack of strong anistropy on the (0 0 1) face indicates the operation of multiple slip systems.

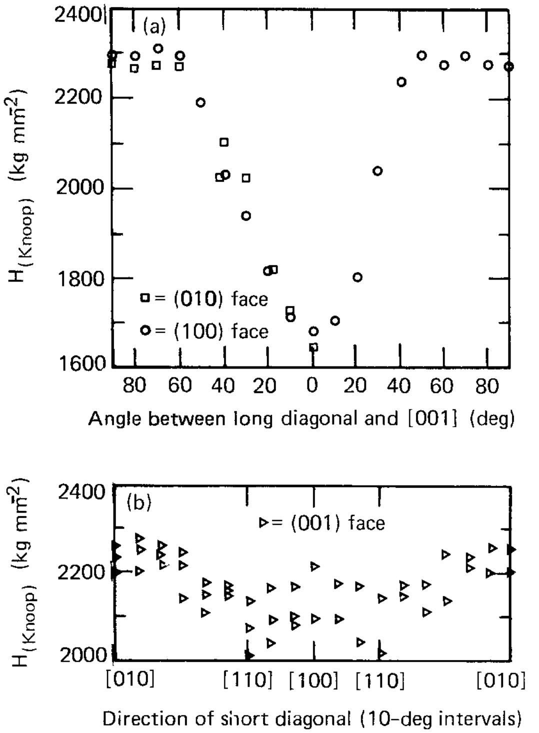

Figure 1 Knoop microhardness measurements of $BeAl_2O_4$ crystal (100 g load, 15 sec): (a) versus angle between long diagonal and [0 0 1], and (b) versus direction of short diagonal.

These results indicate that prismatic slip of the hexagonal oxygen sublattice in $BeAl_2O_4$ occurs at a lower stress than basal slip, the reverse of the behaviour of sapphire. Oxygen sublattice prismatic slip in $BeAl_2O_4$ would correspond to systems of the type [1 1 0] (1 1 0) with the Burgers vector $b = 10.88$ Å or [0 1 0] (1 1 0) with $b = 5.476$ Å. (In Al_2O_3, $b = 8.22$ Å for prismatic slip.)

Basal slip of the oxygen sublattice of $BeAl_2O_4$ would involve systems of the type [1 0 0] (0 0 1), $b = 9.404$ Å, or [1 3 0] (0 0 1), $b = 12.58$ Å ($b =$ 4.75 Å for basal slip in Al_2O_3.) Thus the cation sublattice of $BeAl_2O_4$ favours prismatic slip over basal slip, because the elastic energy (proportional to b^2) of the smallest basal-slip dislocation is about three times larger than that of the prismatic [1 1 0] (1 0 0) distortion.

Knoop hardness measurements on the (0 0 1) face of a sapphire crystal gave an HK-100 value of 1815 kg mm^{-2}, which is significantly lower than values obtained on a number of orientations of $BeAl_2O_4$. The 1815 kg mm^{-2} value was the average of 30 indentations.

3.2. Thermal conductivity

The room temperature thermal conductivity of $BeAl_2O_4$ was measured by Dr Ray Taylor of the Thermophysical Properties Research Center at Purdue University. The thermal conductivities of three faces of a 1 cm oriented cube and of reference samples of yittrium aluminium garnet and gadolinium gallium garnet were measured by the thermal comparator method. The measured values of $BeAl_2O_4$ shown in Table I are compared with those of BeO and Al_2O_3. The lack of anisotropy shown in these thermal conductivity measurements on $BeAl_2O_4$ should not be taken as real, because the thermal comparator method of measurement inherently averages the heat flux over a range of directions. The fact that $BeAl_2O_4$ has a lower thermal conductivity than either Al_2O_3 or BeO is

TABLE I Thermal conductivities of $BeAl_2O_4$, Al_2O_3, and BeO at 300 K

Material	Thermal conductivity (W cm^{-1} °C)
$BeAl_2O_4$ (all orientations)	0.23
Al_2O_3	0.35
BeO	3.7

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*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the US Department of Energy to the exclusion of others that may be suitable.

consistent with its more complex orthorhombic structure and greater number of chemical components.

3.3. Sound velocities and elastic constants

The fast- and slow-shear wave and longitudinal-wave sound velocities for propagation along the principal directions in chrysoberyl have been determined at room temperature by the pulse-echo technique, using a 1 cm, polished, oriented cube. The values, measured to within about 1%, are shown in Table II. Six of the nine independent elastic constants can be calculated from these data and are shown in Table III. Measurements of the velocities in diagonal directions are required for determination of the remaining constants.

The ultrasonic attenuation at 500 MHz was measured at 0.6 dBμsec^{-1} for longitudinal waves and 0.9 dBμsec^{-1} for shear waves. However, truly exponential decay curves were not obtained, probably because of slightly nonparallel cube faces. Pending better measurements, these values must be considered upper bounds.

TABLE II Sound velocities of $BeAl_2O_4$

Direction of propagation	Longitudinal mode (10 cm sec^{-1})	Shear mode (10^5 cm sec^{-1})	
		"fast"	"slow"
⟨1 0 0⟩	10.8	6.40	6.19
⟨0 1 0⟩	11.2	6.42	6.27
⟨0 0 1⟩	11.75	6.25	6.20

TABLE III Elastic constants of $BeAl_2O_4$

Elastic constant	10^{11} Pa	Elastic constant	10^{11} Pa
C_{11}	4.32	C_{44}	1.45
C_{22}	4.64	C_{55}	1.52
C_{33}	5.11	C_{66}	1.42

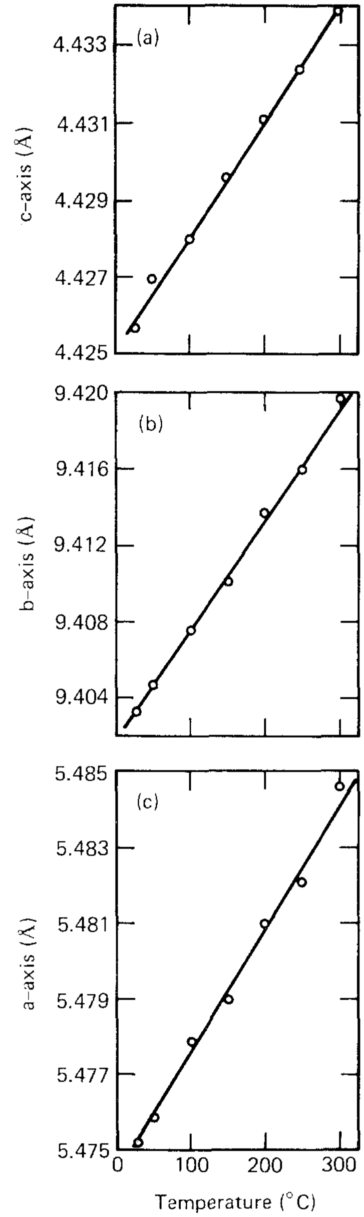

Figure 2 Thermal expansion data for $BeAl_2O_4$: (a) c-axis, (b) b-axis, and (c) a-axis.

TABLE IV Precise lattice parameters for orthorhombic $BeAl_2O_4$ as a function of temperature

Temperature (° C)	a_0		b_0		c_0	
	(Å)	(S.D.)	(Å)	(S. D.)	(Å)	(S. D.)
25	5.4753	(0.0003)	9.4031	(0.0010)	4.4257	(0.0004)
50	5.4759	(0.0007)	9.4047	(0.0014)	4.4270	(0.0006)
100	5.4779	(0.0004)	9.4075	(0.0013)	4.4280	(0.0005)
150	5.4790	(0.0006)	9.4101	(0.0014)	4.4296	(0.0008)
200	5.4810	(0.0005)	9.4137	(0.0013)	4.4311	(0.0009)
250	5.4821	(0.0005)	9.4159	(0.0013)	4.4324	(0.0009)
300	5.4846	(0.0005)	9.4197	(0.0010)	4.4339	(0.0006)

3.4. Precision lattice-constant determination of $BeAl_2O_4$ as a function of temperature

Precise orthorhombic unit-cell parameters determined for $BeAl_2O_4$ (chrysoberyl) in the temperature range 24 to 300° C are tabulated in Table IV. The following procedure was used to determine the lattice constants at seven temperatures from 24 to 300° C.

To obtain Debye–Scherrer ring-type diffraction, the specimen was powdered by light grinding in a mortar. The data were collected using a Norelco diffractometer with a specially designed, heated, sample holder. The diffractometer was run in parafocus geometry with copper radiation. Calibration at each temperature was accomplished by mixing an internal standard (silicon) with the specimen. The data (about 35 reflections per sample) were refined by use of a least-squares procedure. Fig. 2 shows the data from which the expansion coefficients were determined.

3.5. Vacuum ultra-violet transmission

The optical transmission of polished oriented discs of $BeAl_2O_4$ was determined on a MacPherson vacuum ultra-violet spectrometer. A ⟨1 0 0⟩ sapphire wafer was also run to have a basis for comparison. Fig. 3 illustrates the ultra-violet transmission of $BeAl_2O_4$ and Al_2O_3.

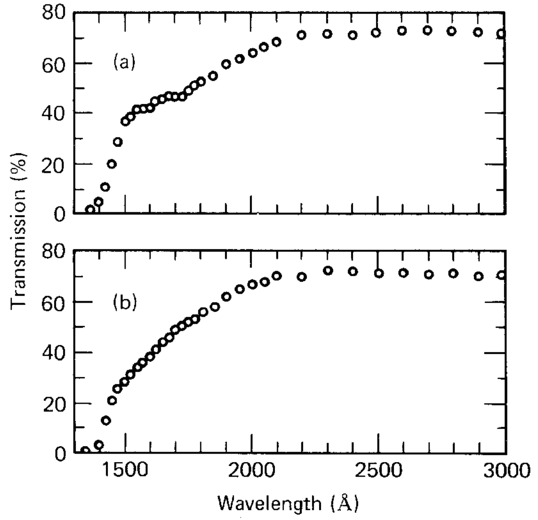

Figure 3 Optical transmission: (a) $BeAl_2O_4$ (0 0 1) 0.335 mm thick, and (b) Al_2O_3 (0 0 1), 0.508 mm thick.

4. Conclusions

Large single crystals of $BeAl_2O_4$ have been grown and a number of their physical properties measured. The data indicate that many properties, such as hardness, optical transmission, and elastic constants, are equivalent or superior to those of sapphire. The use of $BeAl_2O_4$ for structural applications appears promising, especially for structures such as transparent armour or windows requiring ultra-violet transmission.

The Cr^{3+}-doped $BeAl_2O_4$ has exhibited laser action [9] with properties distinctly different from those of ruby.

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