

REFINEMENT OF THE CHRYSOBERYL STRUCTURE¹E. F. FARRELL, J. H. FANG AND R. E. NEWNHAM, *Laboratory for Insulation Research, M.I.T.*

ABSTRACT

Chrysoberyl, Al_2BeO_4 , is isomorphous with olivine; the space group is $Pnma$, orthorhombic, with $a=9.404$, $b=5.476$ and $c=4.427$ Å. The oxygen positions approximate hexagonal close-packing with aluminum cations occupying octahedral interstices and beryllium in tetrahedral sites. Accurate atomic coordinates were obtained by least-squares analysis of three-dimensional x-ray diffraction data. Both the octahedra and tetrahedra are distorted, showing significant deviations from their mean bond lengths: Al—O 1.91 Å and Be—O 1.63 Å.

The mineral chrysoberyl is a hard, dense gemstone with interesting optical properties. The color of yellow chrysoberyl, a relatively common mineral, is due to iron substitution. Alexandrite, the chromium-bearing variety, is extremely rare and highly prized as a gemstone because of its unique coloring. It is green by daylight and red under ordinary incandescent illumination; it is also strongly pleochroic. These properties, together with the hardness and chemical stability of the Al_2BeO_4 host lattice, recommend the crystal as a promising solid-state maser material. The magnetic properties and crystal field absorption spectra of $(\text{Al,Cr})_2\text{BeO}_4$ and $(\text{Al,Fe})_2\text{BeO}_4$ are currently under investigation (Santoro and Newnham, 1962), and will be reported elsewhere. Refinement of the crystal structure has been undertaken to assist in the interpretation of these data.

Single crystals of undoped chrysoberyl up to $4.0 \times 1.5 \times 0.5$ mm³ have been grown by a flux melt method. Using a seed crystal of the natural mineral, an oriented overgrowth of $10.0 \times 5.0 \times 0.5$ mm³ was obtained by the same technique. These results were achieved with a PbO—PbF_2 flux in 1:1 molar ratio, a soak time of 4 hours at 1250° C., and a cooling rate of 12.5° C./hour. The experiments were carried out in a 50-ml platinum crucible using a Global furnace and a saturable reactor controller. Efforts to obtain chromium-doped chrysoberyl by the same method were unsuccessful because of the preferential crystallization of lead chromate. Other firing conditions and fluxes proved less satisfactory. Small Al_2BeO_4 crystals were obtained in PbO but the flux evaporation rate was excessive. Na_2CO_3 failed to dissolve either BeO or Al_2O_3 . The results with boric acid and calcium carbonate were also disappointing, although previous work (Palache *et al.*, 1944) indicates that both seed-pulling and doping should be possible with a $\text{H}_3\text{BO}_3 + \text{CaCO}_3$ flux.

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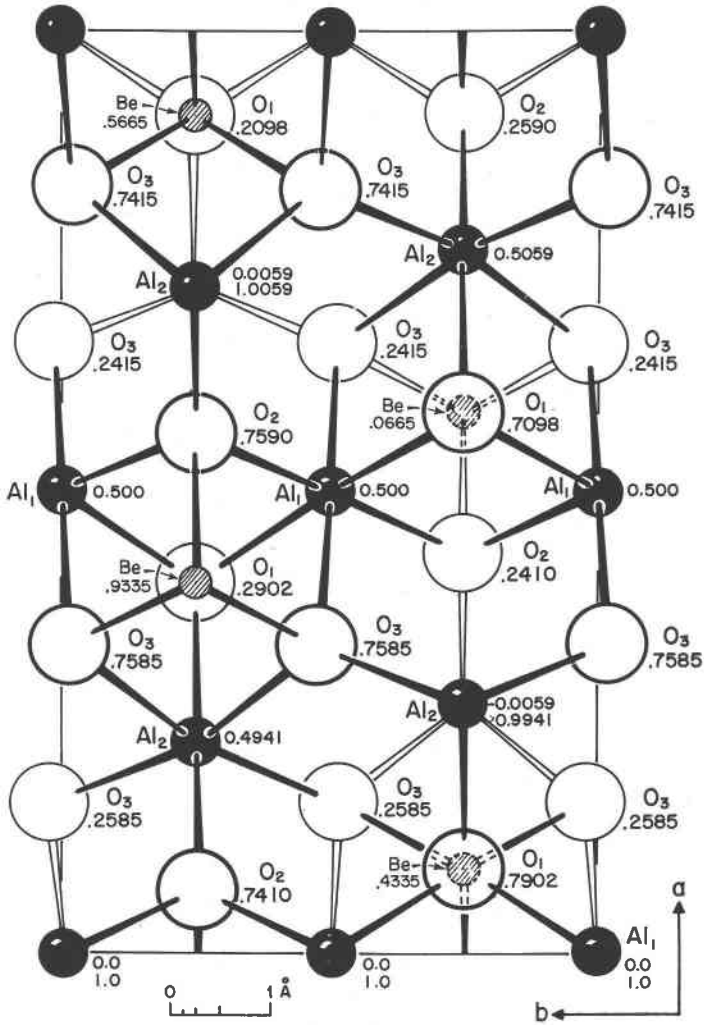


FIG. 1. The refined chrysoberyl structure projected on (001). Heights of the atoms are expressed in cell fractions.

Chrysoberyl is a hexagonal close-packed analog to the cubic close-packed spinel structure. Its structure is isomorphous with olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, and is illustrated in Fig. 1. The oxygens form a distorted hexagonal close-packed array in which one eighth of the tetrahedral interstices are occupied by beryllium, and half the octahedral sites are filled by aluminum. Bragg and Brown (1926) first analyzed the chrysoberyl structure; the space group is $Pnma$, orthorhombic, with four

TABLE 1. CHRYSOBERYL COORDINATES AND TEMPERATURE FACTORS AT SEVERAL STAGES OF THE LEAST-SQUARES REFINEMENT. THE FINAL COORDINATES (IN CELL FRACTIONS) ARE GIVEN IN COLUMN (d)

| Parameter | | (a) | (b) | (c) | (d) | (e) | (f) |
|------------------|---|------|---------|---------|---------|--------|--------|
| Al _I | B | — | .100 | .100 | .073 | .011 | .005 |
| Al _{II} | x | .278 | .27426 | .27327 | .27319 | .00015 | .00000 |
| | z | .000 | -.01037 | -.00643 | -.00595 | .00034 | .00003 |
| Be | B | — | .100 | .100 | .103 | .013 | .005 |
| | x | .083 | .09603 | .09310 | .09294 | .00065 | .00002 |
| | z | .375 | .43897 | .43489 | .43347 | .00138 | .00042 |
| O _I | B | — | .100 | .100 | .151 | .055 | .008 |
| | x | .083 | .09061 | .09056 | .09051 | .00027 | .00001 |
| | z | .750 | .79093 | .79020 | .79016 | .00057 | .00010 |
| O _{II} | B | — | .200 | .200 | .061 | .020 | .014 |
| | x | .417 | .43366 | .43371 | .43343 | .00030 | .00002 |
| | z | .250 | .24065 | .24028 | .24097 | .00071 | .00005 |
| O _{III} | B | — | .200 | .200 | .226 | .024 | .006 |
| | x | .167 | .16333 | .16317 | .16318 | .00019 | .00000 |
| | y | .000 | .01809 | .01860 | .01718 | .00055 | .00025 |
| | z | .250 | .25795 | .25856 | .25850 | .00043 | .00004 |
| | B | — | .200 | .200 | .140 | .014 | .002 |

- (a) Bragg and Brown¹ coordinates
 (b) Two dimensional data, *B*'s constant
 (c) Three dimensional data, *B*'s constant
 (d) Three dimensional data, *B*'s varied
 (e) Standard deviation for (d)
 (f) Last recorded change

molecules per unit cell. The lattice parameters, redetermined at NBS, (Swanson *et al.*, 1960) are $a=9.404$, $b=5.476$, and $c=4.427$ Å. The aluminum ions are all octahedrally coordinated but occupy sites of two different symmetries. Al_I occupies a set of inversion centers at $(0, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the Al_{II} sites at $\pm(x, \frac{1}{4}, z; \frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$ possess mirror symmetry. Be, O_I, and O_{II} also lie on mirror plane sites. O_{III} is located in general position at $\pm(x, y, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z; x, \frac{1}{2}-y, z; \frac{1}{2}+x, y, \frac{1}{2}-z)$. Table 1 lists the coordinates proposed by Bragg and Brown; these were used in the initial stages of the structure refinement.

The intensities of approximately 900 reflections were used to determine accurate values of the eleven atomic coordinates. Zero-layer intensity data were collected about the [010]-, [001]-, and [011]-zone axes using a Weissenberg camera and MoK α radiation. The first and second layers about [010] were also recorded. Intensities were estimated visually by comparison with a calibrated scale. Pure Al₂BeO₄ crystals were used;

they are about 0.2 mm on edge and were grown from the PbO—PbF₂ flux. The small size of the crystals made absorption corrections unnecessary.

Least-squares analysis of the x-ray data was carried out at the M.I.T. Computation Center using the Busing-Levy OR FLS program. Lorentz-polarization corrections were applied to the observed intensities from the five layers: hk0, hkk, h0l, h1l, and h2l. An approximately uniform intensity scale as obtained by comparing reflections common to two or more layers. Separate scale factors for the five sets of data were included as variables in the early stages of refinement. The scattering factors of Berghuis *et al.* (1955), slightly modified for 50% ionization, were used in the calculations, and approximate temperature factors were chosen by plotting $\ln (F_o/F_c)$ against $\sin^2 \theta/\lambda^2$.

The refinement is complicated by strong interaction between the scale factors and thermal parameters and by the presence of extinction. Extinction reduces the intensity of the strong low-angle reflections, thereby lowering the calculated temperature factors. These in turn interact with the scale factors during the least-squares analysis. The B values of several atoms became negative when they were adjusted simultaneously to the scale factors. Geller and Durand (1960) also observed substantial interdependence of these parameters in his refinement of isomorphous LiMnPO₄. To avoid this difficulty, the temperature factors were held constant during the initial stages of refinement, and the scale factors were kept fixed during the final few cycles. Fortunately the structure determination is little affected, since neither the scale factors nor the thermal-vibration parameters interact significantly with the atomic coordinates.

Beginning with the Bragg and Brown coordinates (Table 1, column *a*), several refinement cycles were carried out with the h0l and hk0 data. As a result, the R factor was decreased from 0.35 to 0.21 and the coordinates in column *b* were obtained. Only the scale factors and eleven atomic coordinates were adjusted in the analysis; the temperature factors were held constant at the initial values, $B_{A1} = B_{Bc} = 0.1$ and $B_o = 0.2 \text{ \AA}^2$. At this stage, several mistakes were corrected and the hkk, h1l, and h2l data were introduced. The coordinates and scaling factors were then refined through two more least-squares cycles, giving the coordinates in column *c* and an R factor of 0.15. The accompanying matrix showed only one correlation coefficient greater than 0.1: the x coordinate of Be interacts with that of O₁ giving -0.26 . None of the five scale factors interacted appreciably with the coordinates nor with each other.

Four further cycles were performed holding the scale factors fixed and allowing the coordinates and temperature factors to vary. The effect of

TABLE 2. BOND LENGTHS AND OXYGEN DISTANCES IN CHRYSOBERYL
SHARED EDGES ARE DENOTED BY AN ASTERISK (*)

| Al _I (i) Octahedron | | Al _{II} (m) Octahedron | | Be Tetrahedron | |
|--|---------|---|---------|---|---------|
| Al _I —O ² _I | 1.861 Å | Al _{II} —O _I ¹ | 1.940 Å | Be—O _I ¹ | 1.579 Å |
| Al _I —O _{II} ² | 1.892 | Al _{II} —O _{II} ¹ | 1.862 | Be—O _{II} ¹ | 1.687 |
| Al _I —O _{III} ² | 1.917 | Al _{II} —O _{III} ² | 2.017 | Be—O _{III} ² | 1.631 |
| O _I —O _{II} ² | 2.756 | Al _{II} —O _{III} ² | 1.895 | O _I —O _{II} ¹ | 2.777 |
| O _I —O _{II} ² | 2.548* | O _I —O _{III} ² | 2.743 | O _I —O _{III} ² | 2.763 |
| O _I —O _{III} ² | 2.807 | O _I —O _{III} ² | 2.528* | O _{II} —O _{III} ² | 2.509* |
| O _I —O _{III} ² | 2.528* | O _{II} —O _{III} ² | 2.845 | O _{III} —O _{III} ¹ | 2.550* |
| O _{II} —O _{III} ² | 2.509* | O _{II} —O _{III} ² | 2.744 | | |
| O _{II} —O _{III} ² | 2.866 | O _{III} —O _{III} ¹ | 2.550* | | |
| | | O _{III} —O _{III} ¹ | 2.926 | | |
| | | O _{III} —O _{III} ² | 2.757 | | |

Standard deviations

$\sigma(\text{Al—O}) = 0.003 \text{ \AA}$

$\sigma(\text{O—O}) = 0.005 \text{ \AA}$

$\sigma(\text{Be—O}) = 0.007 \text{ \AA}$

Average values

| | |
|---------------------|---------|
| Al _I —O | 1.890 Å |
| Al _{II} —O | 1.938 |
| Al—O | 1.914 |
| Be—O | 1.632 |

| | |
|----------------------|---------|
| O—O | 2.731 Å |
| O—O (shared edges) | 2.529 |
| O—O (unshared edges) | 2.799 |

extinction was empirically tested by omitting a group of intense reflections in the final two least-squares cycles. The changes in atomic coordinates were less than the standard deviations, averaging only 0.0016 Å. Column *d* of Table 1 lists the final coordinates and temperature parameters; these values were used in calculating the structure factors and the interatomic distances in Table 2. The structure factors¹ give an *R* factor of 0.18 with all reflections included, and 0.15 omitting those below the observational limit. The latter were not included in the least-squares analysis. A correlation matrix evaluated after the final cycle showed two interaction coefficients with magnitudes in excess of 0.1. The *x* coordinates of

¹ A table of structure factors is available upon request from the authors.

Be and O_{II} are negatively correlated (-0.27), as noted previously, and the temperature factors of Be and O_{II} possess a similar interaction of -0.22 . Both values are small compared with the interaction coefficients found in grossularite garnet and tetragonal $BaTiO_3$ (Geller, 1961). The cross correlations between temperature factors and atomic coordinates in chrysoberyl were negligible.

Standard deviations of the final coordinates are listed in Table 1, column *e*. The last recorded changes in the parameters (column *f*) are smaller than the standard deviations, showing that the refinement has converged satisfactorily. When multiplied by the appropriate lattice parameter and averaged over direction and atoms of the same element, the standard deviations are $\sigma(Al)$ 0.0015, $\sigma(Be)$ 0.0061, and $\sigma(O)$ 0.0025 Å. These values give a rough estimate of the accuracy but are probably somewhat optimistic since the effect of systematic errors is not included.

The refined temperature factors in column *d*, Table 1, are very small, ranging from 0.06 to 0.23 Å². For comparison, the room-temperature value for diamond is near 0.20 Å² (Gottlicher and Wölfel, 1959). Chrysoberyl is very hard (8.5 on Mohs' scale), but the *B* values seem unreasonably low. Much of the discrepancy is due to extinction, as mentioned earlier.

Some of the important interatomic distances are listed in Table 2, along with their standard deviations and arithmetic means. Differences in bond lengths greater than 2.3σ are probably significant. The average Al—O length of 1.914 Å is almost identical with the value of 1.915 observed in corundum, $\alpha-Al_2O_3$ (Newnham and deHaan, 1962). One feature of interest is the fact that the Al_{II} octahedron is appreciably larger than that of Al_I . Fe or Cr substituted for Al might therefore prefer one site to the other. Differences in the crystal fields are also to be expected, thus influencing the optical absorption spectra.

Another surprising feature is the irregularity of the BeO_4 tetrahedron: the Be—O distances range from 1.58 to 1.69 with a mean value of 1.632 Å. The average Be—O distance in beryllium oxide is 1.649 Å (Smith *et al.*, 1962). The deviations from ideal close-packing in the chrysoberyl structure (see Fig. 1) are explicable in terms of cation-cation coulomb repulsion. Without exception the equilibrium cation positions are shifted away from their nearest cation neighbors. The oxygen-oxygen distances fall into two well-defined groups: shared edges 2.51–2.55 Å in length, and unshared edges, 2.74 Å or greater.

The good agreement between observed and calculated structure factors precludes any extensive disorder among the octahedral and tetrahedral cations, as observed in the spinel family. There is, however, some uncertainty regarding the disposition of beryllium because of its small scatter-

ing factor. Confirmation of the Be coordinates must await the results of a neutron-diffraction analysis of isomorphous Cr_2BeO_4 , presently under way.

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