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ORDERING OF Fe AND Cr IN CHRYSOBERYL¹

R. NEWNHAM, R. SANTORO, J. PEARSON AND C. JANSEN, *Laboratory for Insulation Research, M.I.T.*

Refinement of the chrysoberyl structure (Farrell *et al.*, 1963) showed that the two aluminum octahedral sites differ significantly in size. Half of the aluminum atoms occupy Al_I sites with inversion symmetry, and the remainder are in Al_{II} mirror-plane positions. The average nearest-neighbor distances are Al_I—O = 1.890 and Al_{II}—O = 1.934 Å. Because of the differences in size and symmetry, trivalent cations substituted for Al might prefer one site to the other. Experimental evidence for selective substitution in Al_{2-x}Fe_xBeO₄ and Al_{2-x}Cr_xBeO₄ solid solutions is presented.

Polycrystalline ceramic specimens of Al-Cr, Al-Fe, and Cr-Fe chrysoberyl were prepared by firing the coprecipitated metal-ion hydroxides between 900° and 1300° C. X-ray diffractometer patterns were used to determine the lattice parameters and cation ordering. Al₂BeO₄ and Cr₂BeO₄ form a complete solid-solution series and our lattice-parameter measurements agree with those published by Weir and Van Valkenburg (1960). About 50 atomic per cent iron can be substituted in Al₂BeO₄ or Cr₂BeO₄; unit-cell dimensions for the Al_{2-x}Fe_xBeO₄ and Cr_{2-x}Fe_xBeO₄ solid solutions are shown in Fig. 1. Iron substitution causes both structures to expand, as expected from the Goldschmidt ionic radii (Al³⁺ 0.57, Cr³⁺ 0.65, Fe³⁺ 0.67 Å). Three phases were identified in specimens containing more than 50% iron: chrysoberyl solid solution, corundum solid solution and beryllia.

The intensities of five prominent low-angle reflections especially sensitive to cation distribution were used to determine ordering in Al-Cr and Al-Fe chrysoberyl. The difference between the atomic scattering factors of Fe and Cr is too small to permit study of the Fe-Cr system. Data for two of the samples are given in Table 1. The calculated structure factors were computed for several values of the ordering parameter *M* using the refined Al₂BeO₄ atomic coordinates (Farrell *et al.*, 1963). *M* is defined as

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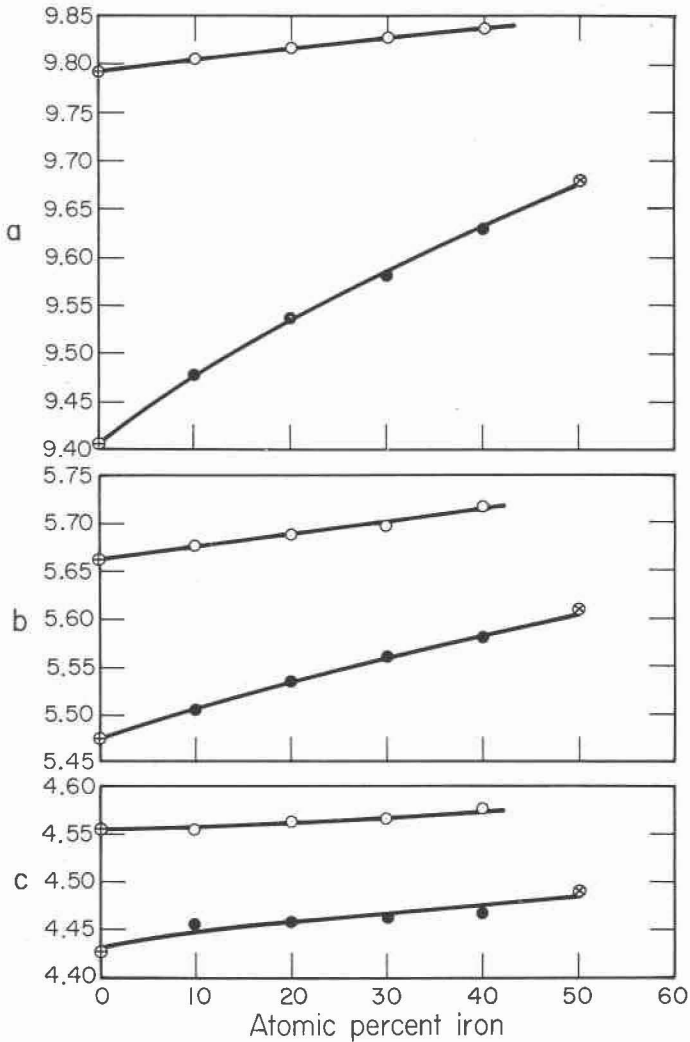


FIG. 1. Lattice parameters of $\text{Al}_{2-x}\text{Fe}_x\text{BeO}_4$ (●) and $\text{Cr}_{2-x}\text{Fe}_x\text{BeO}_4$ (○) chrysoberyl. Data from Swanson *et al.*, 1960, (⊕) and Major *et al.*, 1942. (⊗), are also shown.

the fraction of Fe or Cr atoms occupying the mirror-symmetry site (Al_{II}). For compositions with less than 50% substitution, M lies between the limits 0 and 1. If the transition-metal ions populate the two different crystallographic sites equally, $M = \frac{1}{2}$. An estimate of the experimental precision in determining M was obtained from the root-mean-square deviation of $M(hkl)$, the ordering parameter calculated for reflection hkl .

TABLE 1. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TWO CHRYSOBERYL COMPOSITIONS. THE OPTIMUM VALUE OF M IS GIVEN IN THE THIRD COLUMN; CALCULATIONS FOR THREE OTHER VALUES ARE ALSO LISTED

Al _{1.4} Fe _{0.6} BeO ₄ fired at 1300° C. for 13 hours					
h k l	$ F_0 ^1$	$F_c (M=0.85)$	$F_c (M=0)$	$F_c (M=\frac{1}{2})$	$F_c (M=1)$
1 0 1	48.8	47.7	83.9	62.9	40.1
1 1 1	89.5	-91.2	-53.5	-75.7	-99.4
3 0 1	100.0	102.6	114.9	107.9	100.3
3 1 1	81.0	77.5	46.2	64.6	84.5
1 2 1	74.0	73.1	94.5	82.2	68.7
R	—	3%	36%	15%	7%
Al _{1.4} Cr _{0.6} BeO ₄ fired at 1300° C. for 24 hours					
h k l	$ F_0 $	$F_c (M=0.70)$	$F_c (M=0)$	$F_c (M=\frac{1}{2})$	$F_c (M=1)$
1 0 1	56.9	53.5	80.3	61.9	42.2
1 1 1	81.4	-82.1	-56.2	-74.6	-94.8
3 0 1	100.0	102.5	111.6	105.7	99.3
3 1 1	72.8	69.6	47.9	63.5	80.1
1 2 1	75.1	75.8	90.9	80.7	69.6
R	—	3%	26%	8%	11%

¹ Lorentz-polarization and multiplicity factors are included in $|F_0|$.

The experimental values for M (Table 2) range between 0.60 and 0.91, showing that about three quarters of the transition-metal atoms occupy mirror-plane sites. The chromium samples show more disorder than the iron ones; no other significant variations with composition or firing con-

TABLE 2. EXPERIMENTAL ORDERING PARAMETERS AND THEIR STANDARD DEVIATION

Composition	Firing Conditions	M
Al _{1.8} Fe _{0.2} BeO ₄	1300° C., 13 hours	0.76 ± 0.10
Al _{1.6} Fe _{0.4} BeO ₄	1300° C., 13 hours	0.90 ± 0.16
Al _{1.4} Fe _{0.6} BeO ₄	1300° C., 13 hours	0.84 ± 0.07
Al _{1.4} Fe _{0.6} BeO ₄	1100° C., 72 hours	0.85 ± 0.14
Al _{1.4} Fe _{0.6} BeO ₄	1100° C., 24 hours	0.81 ± 0.11
Al _{1.4} Fe _{0.6} BeO ₄	900° C., 72 hours	0.87 ± 0.12
Al _{1.4} Fe _{0.6} BeO ₄	900° C., 24 hours	0.87 ± 0.13
Al _{1.2} Fe _{0.8} BeO ₄	1300° C., 13 hours	0.91 ± 0.14
Al _{1.6} Cr _{0.4} BeO ₄	1300° C., 24 hours	0.74 ± 0.18
Al _{1.4} Cr _{0.6} BeO ₄	1300° C., 24 hours	0.71 ± 0.09
Al _{1.0} Cr _{1.0} BeO ₄	1300° C., 24 hours	0.60 ± 0.10

ditions were noted. Thus Fe and Cr preferentially populate the larger Al_{II} sites, consistent with size considerations. This result is contrary to the assumption of Vinokurov *et al.* (1960). In explaining the electron paramagnetic resonance (EPR) spectrum of natural chrysoberyl, they hypothesize that Fe occupies only the inversion symmetry sites. Their interpretation of the EPR data has been questioned by Germanier *et al.* (1962).

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NOTES ON WESTERN MINERAL OCCURRENCES¹

E. WM. HEINRICH, *Department of Geology and Mineralogy,
The University of Michigan, Ann Arbor, Michigan.*

3. THULITE FROM CAMP CREEK, RUBY MOUNTAINS, MONTANA

Unusually fine specimens of thulite occur at the Camp Creek corundum deposit in the NE $\frac{1}{4}$, sec. 36, T. 8 S., R. 8 W., about $\frac{1}{3}$ mile southwest of the Crystal Graphite mine and about 11 miles southeast of Dillon in southwestern Montana. The occurrence is at an elevation of about 7000 feet near the southwestern corner of the southern Ruby Range. The thulite occurs in a lens of impure marble, 280 feet long and as much as 100 feet thick, which is enclosed in a northeast-trending layer of biotite schist, both forming part of the Prebeltian Cherry Creek Group (Heinrich, 1950; Heinrich and Rabbitt, 1960).

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