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REFINEMENT OF THE CRYSTAL STRUCTURE OF A
CHROME PYROPE GARNET: AN INCLUSION
IN NATURAL DIAMOND

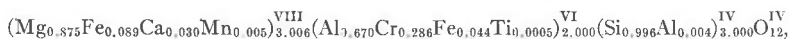
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ABSTRACT

The crystal structure of a chrome pyrope garnet, $a = 11.526(1) \text{ \AA}$,

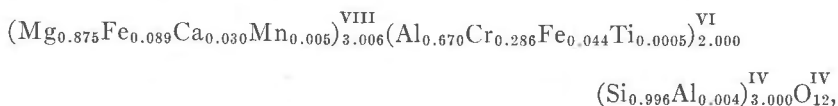


has been refined to $R = 0.038$ using 3-dimensional data. The Si–O bond length is $1.639(1) \text{ \AA}$ and the $\text{M}^{\text{VI}}\text{–O}$ bond is $1.905(1) \text{ \AA}$. The structural data are similar to those of synthetic pyrope (Gibbs and Smith, 1965).

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EXPERIMENTAL RESULTS

Two fragments of claret colored garnet, which together formed a single crystalline inclusion in a Venezuelan diamond, were obtained by oxidizing the diamond in air at 850°C for several hours. Electron microprobe analysis of one of the fragments resulted in the following structural formula,



when normalized to 12 oxygen atoms per formula unit. The formula conforms to the general garnet structural formula $\text{X}_3^{\text{VIII}}\text{Y}_2^{\text{VI}}\text{Z}_3^{\text{IV}}\text{O}_{12}^{\text{IV}}$. In terms of garnet end members this analysis is equivalent to approximately 59 percent pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and 28 percent chrome pyrope (or knorringite- $\text{Mg}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$), with almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), predominant in the remaining minor end members.

The other fragment, mounted in finger nail polish and "shaved" with a razor blade until it was essentially equidimensional and approximately 0.12 mm in diameter, was used in the single crystal X-ray diffraction study. Zero, first, and second level precession photographs displayed Laue and diffraction symmetry consistent with space group $Ia3d$. The room temperature cell edge ($a=11.526(1)$ Å) was refined from back-reflection Weissenburg data using Burnham's (1962) LCLSQ program. The calculated cell edge based on stoichiometry is 11.535 Å (McConnell, 1966).

Three each of 200 nonequivalent, observable reflections were collected with a scintillation-counter equi-inclination Weissenburg diffractometer using Nb-filtered $\text{MoK}\alpha$ radiation. A full anisotropic least squares refinement¹ using Busing, Martin and Levy's (1962) ORFLS program was carried out, resulting in a final unweighted R -factor of 0.038. Symmetrically equivalent F_{obs} were statistically identical. Weights were assigned following Hanson (1965) with

$$w = 1.0 / \sqrt{\{1.0 + [(F_{\text{obs}} - PA \times FT) / (XX \times FT)]^2\}}$$

where the constants $PA=7.0$, $FT=6.0$ and $XX=2.3$ were chosen so as to yield essentially constant values of $\langle w\Delta^2 \rangle$ in groups of increasing F_{obs} . The positional parameters of the oxygen atom are $x=0.03346(9)$, $y=0.0507(1)$, and $z=0.65366(9)$. Pertinent bond distances and angles

¹ A listing of the observed and calculated structural amplitudes may be ordered as NAPS Document #01113 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022: remitting \$2.00 for microfiche or \$5.00 for photocopies in advance payable to CCMIC-NAPS.

TABLE 1. INTERATOMIC DISTANCES AND ANGLES

SiO ₄ Tetrahedron	Si-O	1.639(1) Å ^a
	O-O	2.510(2), 2.757(2)
	O-Si-O	99.88(8) ^o , 114.47(5) ^o
YO ₆ Octahedron	Y-O	1.905(1) Å
	O-O	2.646(2), 2.740(2)
	O-Y-O	88.00(5) ^o , 92.00(5) ^o
XO ₈ Triangular Dodecahedron	X ₍₁₎ -O	2.216(1) Å
	X ₍₂₎ -O	2.353(1)
	O-O	2.510(1), 2.757(2), 2.722(2)
		2.728(2), 3.327(1)
	O-X-O	68.98(5) ^o , 70.71(5) ^o , 73.08(5) ^o 93.41(3) ^o , 109.88(5) ^o
M-M	Si-Y	3.222 Å
	Si-X(1)	3.529
	Si-X(2)	2.882
	Y-X(1, 2)	3.222
	X(1)-X(2)	3.529
	Si-Si	3.529
	Y-Y	4.991
Angles About Oxygen	X(1)-O-Si	95.79(9) ^o
	X(2)-O-Si	122.47(8)
	X(1)-O-X(2)	100.25(5)
	X(1)-O-Y	102.78(6)
	X(2)-O-(Y)	97.23(5)
	Y-O-Si	132.10(8)
	Mean	108.35

^a Numbers in parenthesis are the estimated standard errors.

(Table 1), r.m.s. displacements, and the orientations of the apparent thermal vibration ellipsoids with respect to the crystallographic axes (Table 2) were calculated with Busing, Martin and Levy's (1964) ORFEE program.

With only minor differences, the structure of chrome pyrope is similar to that of synthetic pyrope (Gibbs and Smith, 1965). The Y-O and X-O distances in chrome pyrope are slightly, and significantly longer than those of pyrope and can be related to the mean size of the Y and X cations, respectively. The Si-O bond length in both pyrope and chrome pyrope are statistically identical reflecting the constant coordination number of the oxygen atoms (Brown and Gibbs, 1969). The relationship of chrome pyrope to the crystal chemistry of other silicate garnets is discussed by Novak and Gibbs (in press).

TABLE 2. ANISOTROPIC TEMPERATURE FACTORS, R.M.S. DISPLACEMENTS AND ORIENTATIONS OF THE THERMAL VIBRATION ELLIPSOIDS

Atom	ij	B_{ij}	r^a	$u(r)$	(r, x)	(r, y)	(r, z)
O	11	.00130(7)	1	.0802(23) Å	144(27)°	82(7)°	55(7)°
	22	.00142(6)	2	.0825(21)	118(16)	134(42)	121(34)
	33	.00115(6)	3	.1061(19)	109(21)	46(40)	129(28)
	12	.00006(4)					
	13	— .00019(5)					
	23	.00002(5)					
X ^b	11	.00095(5)	1	.0826(27)	90.0	90.0	0.0
	22	.00134(4)	2	.0970(26)	45.0	45.0	90.0
	23	.00033(5)	3	.0994(25)	135.0	45.0	90.0
Y ^c	11	.00058(1)	e				
	12	— .00003(2)					
Si ^d	11	.00068(4)	e				
	33	.00055(8)					

^a r_1, r_2, r_3 are the ellipsoid axes, and x, y, z the crystallographic axes.

^b Symmetry constraints require $\beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = 0.0$.

^c $\beta_{11} = \beta_{22} = \beta_{33}, \beta_{12} = \beta_{13} = \beta_{23}$.

^d $\beta_{11} = \beta_{22}, \beta_{12} = \beta_{13} = \beta_{23} = 0.0$.

^e Thermal vibration ellipsoid is isotropic and indeterminate.

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