MANAGETTAM, J. W., *et al.* (1758) *Ludwigstorffisch Baad-Buch*, *2nd ed.* Vienna.
NICHOLAS, R. E. H., AND C. RIMINGTON (1951) *Biochem. J.* **50,** 194.
NIGGLI, P. (1940) *Die Mineralien der Schweizeralpen.* B. Wepf Basel.
ONISHI, H. (1955) *Anal. Chem.* **27,** 872.
PARKER, R. L. (1954) *Die Mineralfunde der Schweizer Alpen.* B. Wepf Basel, Switzerland.
PSCHORR, R., AND J. K. PFAFF (1920) *Chem. Ber.*, **53,** 2147–2162.
REILLY, J., AND J. A. EMLYN (1940) *Sci. Proc. Roy. Dublin Soc.* **22,** 267–272.
ROGINSKAYA, E. V. (1936) *Zhur. Prikl. Khim.* **9,** 108–111.
SCHAFFER, F. X. (1951) *Geologie von Osterreich, 2nd ed.*
SIGMUND, A. (1909) *Die Minerale Niederosterreichs.* Franz Deuticke, Vienna and Liepzig.
SUNDGREN, A., AND V. T. RAUHALA (1949) *Suomen Kremistilehti, B,* **22,** 24–32.
TOYAMA, Y. (1938) *J. Chem. Soc.* (*Japan*), **59,** 810.
TREIBS, A. (1934a) *Angew. Chem.*, **47,** 725.
——— (1934b) *Ann. Chem.* **510,** 42–62.
VETTERS, H. (1933) *Geologische Karte der Republik Osterreich. Geologische Bundesanstalt,* Vienna.
VOGEL, A. I. (1957) *Textbook of Practical Organic Chemistry 3rd ed.* Longmans, Green and Co., London, 682.
WEIBEL, M. (1966) *Guide to the Minerals of Switzerland* Interscience Publishers, London, New York, Sydney.
WILD, F. (1958) *Characterization of Organic Compounds, 2nd ed.* Cambridge University Press, Cambridge, 52.

THE AMERICAN MINERALOGIST, VOL. 55, NOVEMBER-DECEMBER, 1970

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

GARY A. NOVAK, *Department of Geological Sciences, Virginia Polytechnic Institute, Blacksburg, Virginia 24061*[1]

AND

HENRY O. A. MEYER, *Code 644, NASA, Goddard Space Flight Center, Greenbelt, Maryland 20771.*

ABSTRACT

The crystal structure of a chrome pyrope garnet, $a = 11.526(1)$ Å,

$$(Mg_{0.875}Fe_{0.089}Ca_{0.030}Mn_{0.005})^{VIII}_{3.006}(Al_{1.670}Cr_{0.286}Fe_{0.044}Ti_{0.0005})^{VI}_{2.000}(Si_{0.996}Al_{0.004})^{IV}_{3.000}O^{IV}_{12},$$

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

[1] Present address: Department of Geology, California State College at Los Angeles, Los Angeles, California 90032, U. S. A.

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,

$$(Mg_{0.875}Fe_{0.089}Ca_{0.030}Mn_{0.005})^{VIII}_{3.006}(Al_{0.670}Cr_{0.286}Fe_{0.044}Ti_{0.0005})^{VI}_{2.000}$$

$$(Si_{0.996}Al_{0.004})^{IV}_{3.000}O^{IV}_{12},$$

when normalized to 12 oxygen atoms per formula unit. The formula conforms to the general garnet structural formula $X_3^{VIII}Y_2^{VI}Z_3^{IV}O^{IV}_{12}$. In terms of garnet end members this analysis is equivalent to approximately 59 percent pyrope ($Mg_3Al_2Si_3O_{12}$) and 28 percent chrome pyrope (or knorringite-$Mg_3Cr_2Si_3O_{12}$), with almandine ($Fe_3Al_2Si_3O_{12}$), 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 MoKα radiation. A full anisotropic least squares refinement[1] 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

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

where the constants $PA=7.0$, $FT=6.0$ and $XX=2.3$ were chosen so as to yield essentially constant values of $<w\Delta^2>$ 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)°, 114.47(5)°
YO_6 Octahedron	Y–O	1.905(1) Å
	O–O	2.646(2), 2.740(2)
	O–Y–O	88.00(5)°, 92.00(5)°
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)°, 70.71(5)°, 73.08(5)°
		93.41(3)°, 109.88(5)°
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)°
	$X(2)$–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.

ACKNOWLEDGEMENTS

The authors wish to thank Professors G. V. Gibbs and F. D. Bloss of the Department of Geological Sciences, the Virginia Polytechnic Institute at Blacksburg, Virginia, and Dr. H. T. Evans of the U.S.G.S., Washington, D.C. for critically reviewing the manuscript. The National Science Foundation is gratefully acknowledged for supporting Grants GA-1133 and GA-12702 at VPI.

REFERENCES

BROWN, G. E., AND G. V. GIBBS (1969) Oxygen coordination and the Si–O bond. *Amer. Mineral.* **54,** 1528–1539.

BURNHAM, C. W. (1962) Lattice constant refinement. *Carnegie Inst. Wash. Year Book.* **61,** 132–135.

BUSING, W. R., K. O. MARTIN, AND H. A. LEVY (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Clearing house Fed. Sci. Tech. Info. Doc.* ORNL-TM-305,

———, ———, AND ——— (1964) ORFEE, a Fortran crystallographic function and error program. *U.S. Clearinghouse Fed. Sci. Tech. Info. Doc.* ORNL-TM-306,

GIBBS, G. V., AND J. V. SMITH (1965) Refinement of the crystal structure of synthetic pyrope. *Amer. Mineral* **50,** 2023–2039.

HANSON, A. W. (1965) The crystal structure of the azulene, S-trinitro-benzene complex. *Acta Crystallogr.* **19,** 19–26.

MCCONNELL, D. (1966) Propriétés physiques des grenats. Calcul de la dimension de la maille unité á partes de la composition chimique. *Bull. Soc. Fr. Mineral. Cristallogr.* **89,** 14–17.