Crystal chemistry of kimzeyite from Stromboli, Aeolian Islands, Italy

Rosalba Munno

Istituto di Mineralogia dell'Università
Via Mezzocannone 8, Naples

Giuseppe Rossi and Carla Tadini

C.N.R. Centro di Studio per la Cristallografia Strutturale
Via Bassi 4, Pavia, Italy

Abstract

Kimzeyite, a zirconium-rich garnet, found in a shoshonitic basalt from Stromboli has been submitted to chemical and X-ray structure analysis. The cell edge, determined with single-crystal diffractometry, is 12.365A. Three points on the crystal used for the X-ray structure refinement were analyzed with the electron microprobe. The chemical formula assigned on the basis of the chemical analysis, the site occupancy refinement, and the known spectral data is: $(Ca_{2.94}Mg_{0.06})(Zr_{1.21}Ti_{0.47}Mg_{0.32})Si_{1.51}Al_{1.00}Fe^{3+}_{0.49})O_{12}$. The bond distances are: T–O 1.725, Y–O 2.055, X–O 2.472A.

Introduction

The name kimzeyite is applied to the calcium garnets with zirconium as dominant cation in the six-coordinated position and containing Al and Fe^{3+} as compensating ions in the tetrahedral position (Ito and Frondel, 1967). The only example of kimzeyite known till now is that from Magnet Cove, Arkansas (Milton *et al.*, 1961), since the calcium garnets high in zirconium described by Borodin and Bykova (1961; quoted from Ito and Frondel, 1967) and by Koritnig *et al.* (1978) can be considered as Zr-schorlomites, their kimzeyitic component being less than 50 percent.

Previous works (Ito and Frondel, 1967; Dowty, 1971; Huggins *et al.*, 1977a,b) have utilized Mössbauer, optical and infrared spectroscopy, but no crystal-chemical study on natural Zr,Ti-bearing garnets based on X-ray structural determination is available at present. We aim to fill this gap with the determination of the crystal structure of kimzeyite found in a lava sample from Stromboli, Aeolian Islands.

Description of the sample and chemical analysis

A mineralogical and petrographic study was carried out on lava flow and scoria samples collected from the last effusive activity (November 1975) of Stromboli Island. The analyzed samples are shosho-nitic basalts (Capaldi *et al.*, 1979). Minerals were separated from the lava sample with heavy liquids. The light fraction contains zoned plagioclase and some grains of saccharoidal azure quartz. The heavy fraction contains dark green salitic pyroxene, olivine, dark green spinel, monticellite, and some brown garnets with a cell edge ($a = 12.365$A) similar to that of kimzeyite. The unit cell of the Stromboli garnet is also similar to that of some Zr and Ti garnets synthesized in the ternary system $Ca_3Fe_2Si_3O_{12}$ (andradite)–$Ca_3Zr_2Fe_2SiO_{12}$ (kimzeyite)–$Ca_3Ti_2Fe_2SiO_{12}$ (schorlomite) (Ito and Frondel, 1967).

The same crystal was used for the electron microprobe analysis and for the X-ray data collection. In Table 1 the microprobe chemical analyses of three points in a crystal of the Stromboli kimzeyite are compared with the analysis of the Magnet Cove kimzeyite. The analyses were carried out in the wavelength dispersive mode on a fully automated ARL-SEMQ instrument operated at 15 kV, 0.2μA beam current and a defocused beam. On-line data reduction was based on the Ziebold and Ogilvie (1964) method by the use of Albee and Ray (1970) correction factors. The following standard were used: hornblende, Wilberforce, Ontario, for Fe; $Di_{85}Jd_{15}$ pyroxene for Ca; A 128 ilmenite for Ti and Mg; zircon for Zr and Si; Amelia albite for Al.

Table 1. Chemical analyses of kimzeyite

	1	2	3	4	5		6	7
SiO_2	16.14	16.18	17.56	16.63	9.6	Si	1.51	0.94
Al_2O_3	9.52	9.58	9.00	9.37	11.0	Al	1.00	1.26
TiO_2	6.51	6.79	7.54	6.95	5.6	Ti	0.47	0.40
FeO	6.31	6.48	6.49	6.43	0.8	Fe^{2+}	-	0.07
Fe_2O_3	-	-	-	-	13.4	Fe^{3+}	0.49	0.98
ZrO_2	28.07	28.13	25.93	27.38	29.9	Zr	1.21	1.42
MgO	3.20	3.06	3.71	3.32	0.5	Mg	0.45	0.07
CaO	29.86	30.22	30.67	30.25	29.8	Ca	2.94	3.11
Nb_2O_5	-	-	-	-	1.0	Nb	-	0.05
Total	99.61	100.44	100.90	100.33	101.0			

1,2,3 : analyzed spots (see fig. 1) of Stromboli kimzeyite. All Fe as FeO.
  Analist M.G. Vezzalini, Istituto di Mineralogia della Università di Modena, Italy.
4 : Stromboli kimzeyite, average analysis.
5 : Magnet Cove kimzeyite (Milton et al., 1961).
6 : cations per 12 oxygen atoms, Stromboli (average).
7 : cations per 12 oxygen atoms, Magnet Cove.

The comparison of the chemical analyses of the three points shows some inhomogeneity of composition. Significant chemical differences exist between the Magnet Cove and the Stromboli kimzeyite, the latter having a higher silicon and magnesium and a lower iron content.

X-ray data collection and structure refinement

A crystal fragment approximately spherical in shape (mean radius 0.08 mm) was used for the X-ray data collection. The intensities of 3130 reflections were measured by means of a Philips PW 1100 four-circle automatic diffractometer, using $MoK\alpha$ radiation monochromatized by a flat graphite crystal. The equivalent reflections *hkl, hlk, khl, lhk, lkh, klh* were scanned and their intensities were averaged to obtain 236 independent reflections, 168 of which had $I > \sigma(I)$ and were considered as observed in the refinement.

The symmetrically-equivalent reflections were statistically identical, the mean deviation from the average being less than 4 percent. The intensities were corrected for absorption, assuming a spherical shape. No extinction correction was applied. The X-ray data were processed with a locally modified version of a program specifically written for the PW 1100 diffractometer by Hornstra and Stubbe (1972).

The room-temperature cell edge ($a = 12.365\pm0.002A$) was obtained with the diffractometer routine LAT: the rows $(h00)$, $(0h0)$, and $(00h)$

were investigated in the range $3° < \theta < 50°$ ($MoK\alpha$); by using the circle with highest precision (ω with coupled 2θ), the profiles of the four most intense reflections (as weighted by $\tan \theta$) in each row were scanned in the positive and in the negative region of θ. The centers of gravity of these eight profiles were used in a least-squares refinement of λ/d. The d spacing of the three investigated equivalent rows were used to obtain the cell edge a.

The least-squares structure refinement was carried out by using a locally re-written version of the program ORFLS (Busing *et al.,* 1962). This program allows assignment of two atomic scattering factors, *f1* and *f2*, to each site, and refinement of the occupancy factor X(f) with the constraint that X($f1$) + X($f2$) = 1. The scattering curves for neutral atoms given by the *International Tables for X-ray Crystallography* (1974, p. 99–101) were used: for the dodecahedral site the curves of Ca and Mg, for the octahedral site the curve of Mg, and a computed curve 0.7 Zr + 0.3 Ti and those of Si and Fe for the tetrahedral site were used. The initial atomic parameters were those of andradite refined by Novak and Gibbs (1971). A sequence of refinement steps was devised in such a way as to avoid correlation effect among variables. The observed reflections were introduced in the refinement with weights $w = 1/\sigma (Fo)$. No need for a secondary extinction correction was observed. At the end of the anisotropic refinement the discrepancy factors were: $R_w = 0.022$, $R_{obs} = 0.028$, $R_{all} = 0.045$.

The refined atomic parameters and the most relevant bond distances and angles are given in Tables 2 and 3; the observed and calculated structure factors are listed in Table 4.[1]

Conclusions

On the basis of the bond distances and of the refined site population, the following remarks can be made:

A—Dodecahedral site. Both chemical analysis and structure refinement suggest that only Ca (with small amounts of Mg) occupies this site. It must be pointed out that the average X–O distance is significantly longer than that of the Ca-bearing silicate garnets.

B—Octahedral site. The site population of the octahedra is formed by Zr, Ti, and Mg; the results of the site occupancy refinement (0.543 Zr, 0.233 Ti, 0.224

[1]To receive a copy of this material, order Document AM-80-124 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

Mg) suggest a slightly lower Zr content than that given by the chemical analysis (0.605 Zr). The possibility that some Ti is present also in the tetrahedral site (and conversely, that some Fe^{3+} occurs in the octahedra) cannot be excluded. As a matter of fact, the observed Y–O distance is shorter than the corresponding value (2.073A) computed on the basis of the ionic radii of Shannon and Prewitt (1969).

C—Tetrahedral site. Si, Al, and Fe^{3+} occupy this site; the corresponding T–O distance (1.721A) computed on the basis of the T–O distances of end-member garnets andradite (Novak and Gibbs, 1971), Y–Al (Euler and Bruce, 1965), and Y–Fe^{3+} (Bonnet et al., 1975) garnets, is very close to the observed one.

The X-ray structure data cannot determine uniquely the cation distribution in this case where at least four cations (Ti^{4+}, Mg, Al, Fe^{3+}) can be distrib-

Table 2. Atomic parameters of Stromboli kimzeyite. Standard deviations in parentheses

A – Occupancy factors*, atomic coordinates and equivalent isotropic temperature factors.

Atom	Occupancy factors	x/a	y/b	z/c	$B(Å^2)$
O		0.0365(2)	0.0497(2)	0.6543(2)	0.96
X	0.965(4) Ca, 0.035 Mg	0.125	0.	0.25	0.80
Y	0.776(1) ZT**, 0.224 Mg	0.	0.	0.	0.65
T	0.870(3) Si, 0.130 Fe	0.375	0.	0.25	0.74

B – Anisotropic temperature factors ($\times 10^5$) in the form:

$$\exp-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23}).$$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O	211(14)	152(14)	110(13)	-38(12)	25(12)	6(12)
X	63(9)	164(6)	–	0	0	62(9)
Y	107(2)	–	–	2(4)	–	–
T	105(11)	128(7)	–	0	0	0

C – R.m.s. displacements (Å) along the ellipsoid axes and angles (°) between the crystallographic axes and the principal axes of the vibration ellipsoid.

Atom	J	r.m.s.	Uj.a	Uj.b	Uj.c
O	1	0.087(6)	72(7)	71(14)	153(14)
	2	0.105(5)	72(8)	32(12)	65(15)
	3	0.134(4)	153(6)	66(7)	99(6)
X	1	0.070(5)	0	90	90
	2	0.089(4)	90	45	45
	3	0.132(3)	90	45	135
Y		Isotropic and indeterminate			
T	1	0.090(5)			
	2	0.099(3)	uniaxial (indeterminate)ellipsoid		
	3	0.099(3)			

* The occupancy factors and the symbols of the elements corresponding to the scattering curves f1 and f2 used in the refinement are given.

** ZT corresponds to a computed scattering curve composed by 0.7 Zr and 0.3 Ti.

Table 3. Bond distances (A) and angles (°). Standard deviations in parentheses

TO_4 tetrahedron			YO_6 octahedron	
T – O	1.725(2)		Y – O	2.055(2)
O – O	2.666(4), 2.889(4)		O – O	2.894(4), 2.917(4)
O – T – O	101.2(1), 113.7(1)		O – Y – O	89.5(1), 90.5(1)

XO_8 triangular dodecahedron				
X – O	2.401(2)			
	2.544(2)			
mean	2.472			
O – O	2.666(4)		O – X – O	67.5(1)
	2.894 "			71.0 "
	2.955 "			71.6 "
	2.969 "			73.7 "
	3.572 "			92.5 "

Metal-metal distances			Angles about oxygen	
T – Y	3.456		X(1) – O – T	95.7(1)
T – X(1)	3.786		X(2) – O – T	123.8 "
T – X(2)	3.091		X(1) – O –X(2)	99.9 "
Y – X	3.456		X(1) – O – Y	101.5 "
X(1)–X(2)	3.786		X(2) – O – Y	96.9 "
T – T	3.786		Y – O – T	132.1 "
Y – Y	5.354		mean	108.3

uted over two sites. This fact can explain the discrepancies between the observed and calculated values mentioned above. However, the following crystal-chemical formula can be assigned taking into account the microprobe analysis, the X-ray structure refinement, and the known spectral data (Dowty, 1971):

$$(Ca_{2.94}Mg_{0.06})(Zr_{1.21}Ti_{0.47}Mg_{0.32})(Si_{1.51}Al_{1.00}Fe^{3+}_{0.49})O_{12}$$

Further X-ray structure refinements of Ti- and Zr-bearing natural garnets seem to be necessary; the known relationships (Novak and Gibbs, 1971) between cell edge and composition and between composition and atomic coordinates of oxygen are not applicable to natural garnets containing tetrahedral cations other than silicon. On the other hand, some Mössbauer interpretations (Koritnig et al., 1978) assigning most of Fe^{2+} to the tetrahedral site need a structural check. This work will continue in this direction.

Acknowledgments

References

Albee, A. L. and L. Ray (1970) Correction factors for electron probe microanalysis of silicates, oxides, carbonates, phosphates and sulphates. *Anal. Chem., 42,* 1408–1414.

Bonnet, M., A. Delapalme, H. Fuess and M. Thomas (1975) Refinement of the structure of yttrium iron garnet (YIG). A case of severe extinction and absorption. *Acta Crystallogr., B31,* 2233–2240.

Busing, W. R., K. O. Martin and H. A. Levy (1962) ORFLS, a Fortran crystallographic least-squares program. *U.S. Natl. Tech. Inform. Serv., ORNL-TM-305.*

Capaldi, G., E. Del Pezzo, M. R. Ghiara, I. Guerra, L. La Volpe, L. Lirer, A. Lo Bascio, G. Luongo, M. Martini, R. Munno, R. Pece, A. Rampolla and R. Scarpa (1979) Stromboli and its 1975 eruption. *Bull. Volcanol.,* in press.

Dowty, E. (1971) Crystal chemistry of titanian and zirconian garnet: I. Review and spectral studies. *Am. Mineral., 56,* 1983–2009.

Euler, F. and J. E. Bruce (1965) Oxygen coordinates of compounds with the garnet structure. *Acta Crystallogr., 19,* 971–978.

Hornstra, J. and B. Stubbe (1972) PW 1100 data processing program. *Philips Research Laboratory, Eindhoven, Holland.*

Huggins, F. E., D. Virgo and G. Huckenholz (1977a) Titanium-containing silicate garnets. I. The distribution of Al, Fe^{3+} and Ti^{4+} between octahedral and tetrahedral sites. *Am. Mineral., 62,* 475–490.

———, ——— and ——— (1977b) Titanium-containing silicate garnets. II. The crystal chemistry of melanites and schorlomites. *Am. Mineral., 62,* 646–665.

International Tables for X-ray Crystallography, Vol. IV. (1974) Kynoch Press, Birmingham, Great Britain.

Ito, J., and C. Frondel (1967) Synthetic zirconium and titanium garnets. *Am. Mineral., 52,* 773–781.

Koritnig, S., H. Rösch, A. Schneider and F. Seifert (1978) Der Titan–Zirkon–Granat aus den Kalksilikatfels-Einschlüssen des Gabbro in Radautal, Harz, Bundesrepublik Deutschland. *Tschermaks Minerol. Petrogr. Mitt., 25,* 305–313.

Milton, C., B. L. Ingram and L. V. Blade (1961) Kimzeyite, a zirconium garnet from Magnet Cove, Arkansas. *Am. Mineral., 46,* 533–548.

Novak, G. A. and G. V. Gibbs (1971) The crystal chemistry of the silicate garnets. *Am. Mineral., 56,* 791–825.

Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr., B25,* 925–946.

Ziebold, T. O. and R. E. Ogilvie (1964) An empirical method for electron microanalysis. *Anal. Chem., 36,* 322–327.