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DIFFUSE REFLECTIONS AND THE SYMMETRY OF VESUVIANITE

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Vesuvianite is a common rock-forming silicate mineral with the general chemical formula $X_{19}Y_{13}Z_{18}T_{0-5}O_{68}W_{10}$, where X = Ca, Na, Ln, Pb, Sb; Y = Al, Mg, Fe, Ti, Mn, Cu, Zn; Z = Si; T = B; W = (O, OH, F). Vesuvianite is ideally tetragonal with space group *P*4/*nnc*, but many samples show physical properties that indicate deviations from this symmetry. Many vesuvianite samples are optically biaxial; a sector-zoned crystal from Quebec shows {100}, {010} and {001} sectors with low (0° to 5°), intermediate (approximately 36°) and high (approximately 60°) 2*V* values, respectively. X-ray precession photographs of fragments from each of the sectors show that the number and intensity of glide-violating reflections increase in the sequence {101} → {001} → {100}; in addition, deviations from 4/*mmm* Laue symmetry were also apparent. Diffuse streaking is associated with the violating reflections. A combination of the optical and X-ray evidence indicates that vesuvianite is monoclinic. However, attempts to refine the crystal structure in monoclinic space groups have been inconclusive.

Keywords: Vesuvianite; Symmetry; Optics; Diffuse reflections

INTRODUCTION

Vesuvianite is a common rock-forming silicate mineral with the general chemical formula $X_{19}Y_{13}Z_{18}T_{0-5}O_{68}W_{10}$, where X = Ca, Na, Ln, Pb^{2+}, Sb^{3+}; Y = Al, Mg, Fe^{2+}, Fe^{3+}, Ti, Mn, Cu, Zn; Z = Si; T = B; W = (O, OH, F) (Groat, 1988; Groat *et al.*, 1992a). It is ideally tetragonal ($a \sim 15.5$ Å, $c \sim 11.8$ Å) with space group symmetry *P*4/*nnc*. The crystal structure is closely related to that of garnet, but with additional

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atoms occupying channels down the fourfold axes (Fig. 1). Numerous refinements of the structure have been published (Coda *et al.*, 1970; Rucklidge *et al.*, 1975; Allen and Burnham, 1983a; Valley *et al.*, 1985; Yoshiasa and Matsumoto, 1986; Fitzgerald *et al.*, 1986a; Groat *et al.*, 1994a,b, 1996). In addition, several studies (Giuseppetti and Mazzi, 1983; Allen and Burnham, 1983b; Allen, 1985; Fitzgerald *et al.*, 1986b, 1987) have shown that cation ordering at the sites on the fourfold axes can reduce the symmetry of the structure to *P*4/*n*.

Many vesuvianite crystals show physical properties that indicate deviations from tetragonal symmetry. In particular, samples from

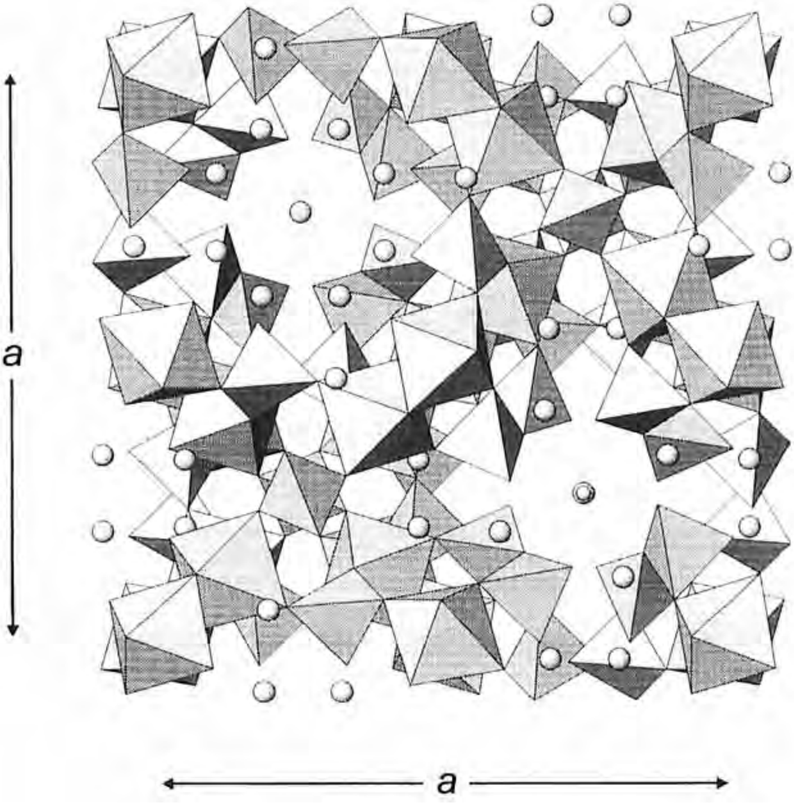

FIGURE 1 Projection of the vesuvianite structure down [001] showing the framework of *Y* octahedra and *Z* tetrahedra. The spheres primarily represent *X* cations. Note the prominent channels along the fourfold axes and parallel to *Z*.

low-temperature environments often show biaxial optical behaviour. Groat *et al.* (1993) used optical and diffraction evidence to show that the true symmetry of biaxial vesuvianite crystals is monoclinic, and suggested that vesuvianite undergoes a phase transition from tetragonal to monoclinic symmetry. Groat *et al.* (1995a) used birefringence measurements to show that the phase transition takes place at approximately 780 K. However, because the true symmetry of the low-temperature phase remains unknown, it was not possible to determine the physical mechanism associated with the structural transition. In this paper, we review the evidence, which includes diffuse X-ray reflections, for the non-tetragonal symmetry of the low-temperature phase.

The sample used in this and previous studies (Groat *et al.*, 1993, 1995a) is V12, a sector-zoned vesuvianite from the Jeffrey mine, Quebec, Canada. Crystals are pale brown, translucent, and occur as {100} prisms (confirmed by precession photography) singly terminated by the {101} pyramid and the {001} pinacoid (forms indexed as tetragonal). Electron-microprobe analysis shows that the average composition of these crystals is $X = \mathrm{Ca}$ and $Y = (\mathrm{Al}_{10}\mathrm{Mg}_{1.5}\mathrm{Fe}_{1.5})$. In this paper, we consider only the symmetry of low-temperature vesuvianite; the origin of the sector zoning will be considered in a future contribution.

OPTICAL EVIDENCE

As described previously (Groat *et al.*, 1993), a crystal of V12 was serial sectioned parallel to (001). One of the sections is shown in polarized light in Fig. 2. Each zone is associated with a face of the crystal, and may be denoted by the corresponding face- or form-symbol. In the core, the {001} sector, $2V$ varies from 0° to 5° (measured both by the methods of Kamb and Tobi, described in Bloss (1961), and with a spindle stage), and the birefringence is low. In the intermediate {101} sector, $2V$ is approximately 36° with intermediate birefringence. In the rim {100} sector, $2V$ is approximately 60° and the birefringence is high (approximately 0.003). Some V12 crystals show a narrow (low $2V$) {110} sector extending from the corners of the core sector to the corners of the crystal (Fig. 3). For each sector, the optic axial plane is parallel or perpendicular to the axes of the corresponding tetragonal crystal. None of the sectors is truly uniaxial, and hence none are truly tetragonal.

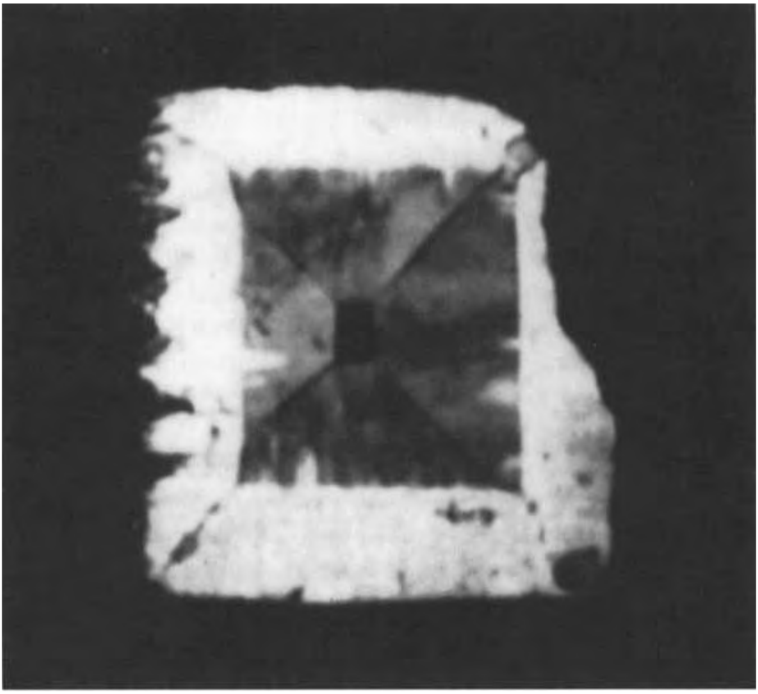

FIGURE 2 Photograph of a thick (001) section of vesuvianite V12 in polarized light. The edges of the crystal are approximately 3 mm long.

Backscattered-electron images show slight compositional differences between the sectors (on the order of 0.2 in the average atomic number). Electron-microprobe analysis shows that the core has slightly more Al (and less Fe, Mg) than the outer two sectors. There was no detectable chemical difference between the intermediate and rim sectors. Bulk-chemical analysis shows no detectable Li, Be or B in this sample. All H in vesuvianite is present as OH (Groat *et al.*, 1995b); as the OH content varies in response to cation substitution, it is unlikely that variation in H content is responsible for the optical differences between the sectors.

PRECESSION PHOTOGRAPHY

Following initial optical and electron-microprobe work, crystal fragments were carefully removed from each sector of a (001) section of a

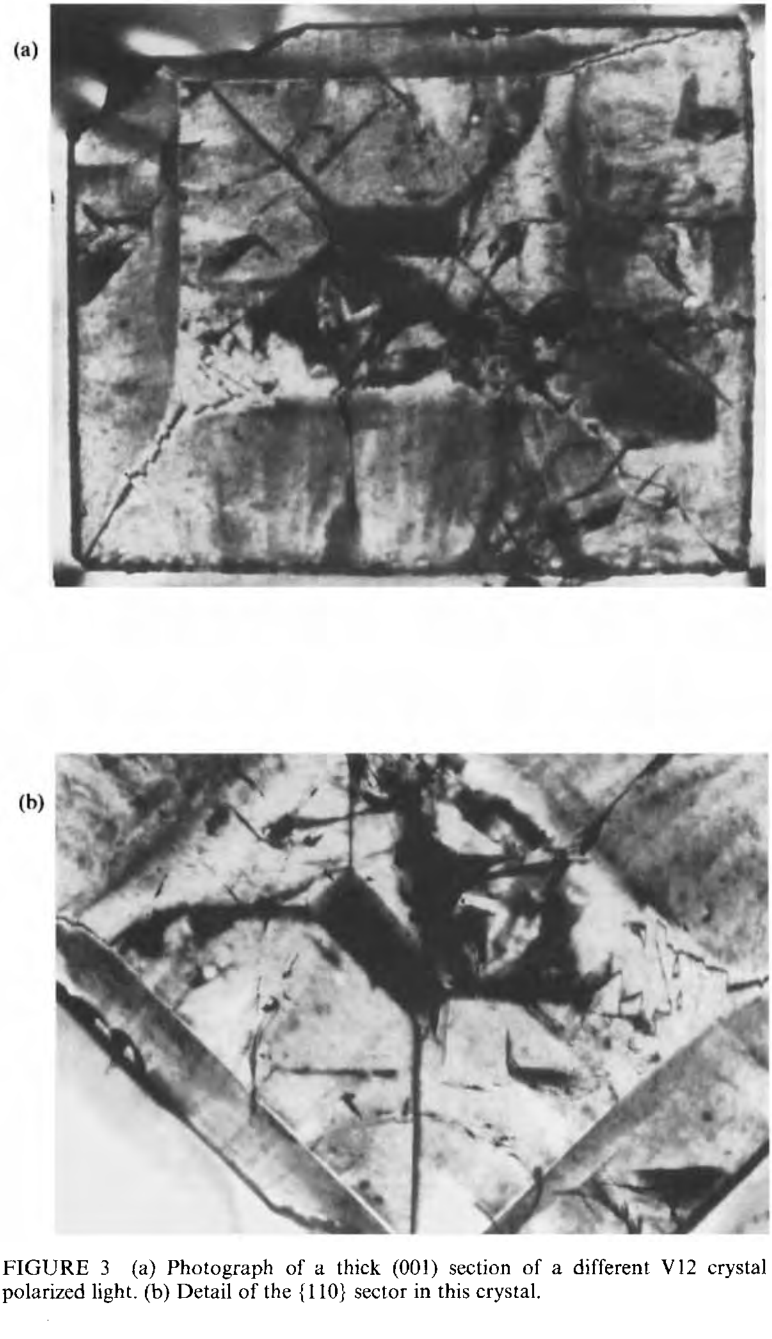

FIGURE 3 (a) Photograph of a thick (001) section of a different V12 crystal in polarized light. (b) Detail of the {110} sector in this crystal.

V12 crystal. The fragments were ground into spheres and mounted on glass fibers. Zero- and upper-level photographs were taken with a Buerger precession camera using Ni-foil filtered Mo$K\alpha$ X-radiation. Exposure times were approximately 80 to 100 h. All photographs were taken at two different precession angles to identify double-diffraction (Renninger) effects. The precession photographs were examined carefully for violations of the standard $4/mmm$ Laue symmetry and violations of systematic absences due to translational symmetry elements. These elements and corresponding violating conditions are listed in Table I. Note that there are three types of violating reflections, designated a', b', and c' (after Allen, 1985).

Precession photographs for the V12C crystal are shown in Fig. 4(a) and (b). The photographs show a significant number of b'-type violating reflections. Although some b' reflections are quite intense, most are relatively weak and show streaking in the a^* direction. Streaking is also associated with non-violating reflections, and is especially noticeable around (004) and (008), and along the (h03) and (h06) rows. The (hk0) zero-level photograph (Fig. 4(b)) shows faint diagonal streaking (parallel to [110]) around (440) and (480). All reflections related by 90° rotations about Z appear to have equal intensities. However, this is not the case for reflections related by vertical mirror planes; weak high-index reflections (such as 7 11 0 and 11 7 0) show notable differences in intensity, a feature that is also apparent on upper-level (hk1) and (hk3) photographs. Violating reflections of type c' are also observed in these upper levels, which is consistent with the loss of the diagonal vertical mirror planes in the Laue symmetry. Corresponding precession photographs of the V12I crystal (not shown) show most of the features present in V12C, although the violating reflections are considerably weaker in intensity.

An (hk0) precession photograph of the V12R crystal is shown in Fig. 4(c). Inspection of this and other photographs reveals many more

TABLE I $P4/nnc$ extinction conditions and classes of violating reflections

Symbol	*Glide plane*	*Violating conditions*
a'	n glide perpendicular to c	$hk0$, $h+k$ odd
b'	n glide perpendicular to a	$h0l$, $h+l$ odd $0kl$, $k+l$ odd
c'	c glide perpendicular to [110]	hhl, l odd

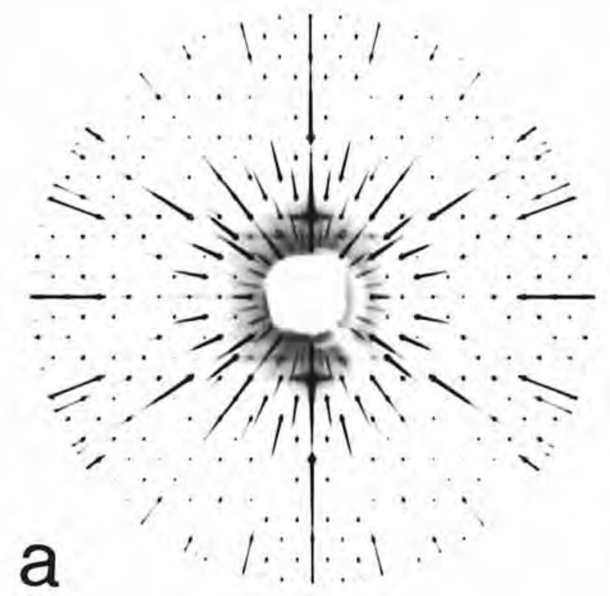

FIGURE 4(a)

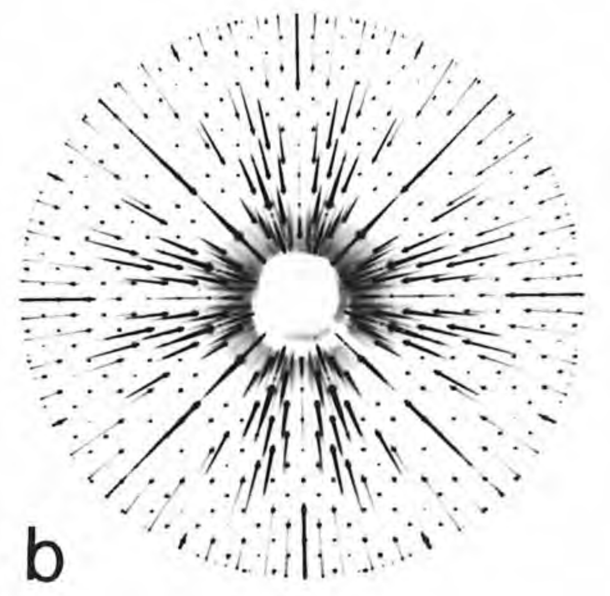

FIGURE 4(b)

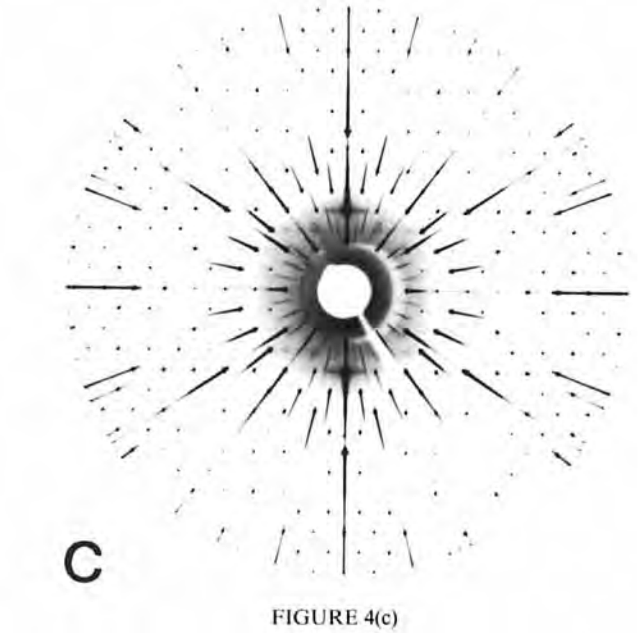

FIGURE 4(c)

FIGURE 4 Precession photographs, sample V12: (a) an ($h0l$) zero-level photograph of V12C; (b) an ($hk0$) zero-level photograph of V12C; (c) an ($h0l$) photograph of V12R.

violating reflections than for crystals V12C and V12I. The violating reflections are more intense and much less diffuse than is the case for analogous reflections in the core and intermediate sectors. Very little streaking is apparent in the photographs. The same Laue group symmetry is observed; the fourfold axis is retained, but there is non-equivalence across the vertical mirrors.

In summary, all sectors of V12 show b'- and c'-type violating reflections, together with loss of vertical mirror-plane Laue symmetry; however, no a'-type reflections were observed, and the horizontal mirror symmetry of the Laue group is retained. There is also no diffraction evidence for the loss of fourfold rotational symmetry parallel to Z. The precession photographs thus indicate that the maximum symmetry of V12 is $P4/n$, and show no evidence of departure from tetragonal symmetry.

SINGLE-CRYSTAL INTENSITY DATA

Single-crystal intensity data were collected using a Nicolet *R*3*m* automated four-circle diffractometer equipped with a molybdenum-target X-ray tube (operated at 50 kV, 35 mA) and a graphite-crystal monochromator mounted with equatorial geometry. Twenty-five reflections were centered using an automated search routine, and least-squares refinement produced the cell dimensions and an orientation matrix relating the crystal axes to the diffractometer axes. Intensity data were collected in the θ–2θ scan mode according to the procedure of Groat *et al.* (1992b). Complete sets of selected equivalent reflections (in 4/*mmm* Laue symmetry) were collected from each V12 crystal.

In the original data collections (Groat, 1988), the cell dimensions were constrained to tetragonal symmetry ($a = b$). However, the cell dimensions reported here (and in Groat *et al.*, 1993) have no metric constraints (Table II). The cell dimensions for crystals V12C and V12I show no deviation from tetragonal symmetry. However, the cell dimensions for crystal V12R show a large deviation (0.026 Å) between *a* and *b*; this difference corresponds to a spontaneous strain of approximately 0.001, which was initially thought to be too small to have any effect on the optical properties of the crystal (see below).

In Groat (1988) and Groat *et al.* (1993), we reported intensity data for the {346} set of reflections (equivalent in Laue group 4/*mmm*) from each V12 crystal; the data are reproduced here (Table III). The various zones of V12 show significant differences in the intensities of potentially equivalent reflections. This is particularly noticeable for crystal V12R, in which the reflections split up into two non-equivalent sets with mean intensities of 295(4) and 261(3) cps, respectively. The

TABLE II Unconstrained cell dimensions for crystals of vesuvianite V12

	V12C	V12I	V12R
a (Å)	15.516(2)	15.518(2)	15.522(2)
b (Å)	15.521(1)	15.519(2)	15.548(2)
c (Å)	11.800(2)	11.810(1)	11.816(2)
α (°)	90.00(1)	89.99(1)	89.96(1)
β (°)	90.05(1)	90.05(9)	90.05(1)
γ (°)	89.97(1)	90.02(1)	90.07(1)
V (Å^3)	2841.9(7)	2844.1(6)	2851.6(7)
Δa (Å)	0.005	0.001	0.026

TABLE III Intensities (counts per second × 10^{-3}) for 346 and equivalent reflections (*P*4/*nnc*)

	V12C	V12I	V12R
$\bar{4}\,3\,\bar{6}$	499(4)	235(3)	290(3)
$\bar{4}\,3\,6$	496(4)	223(3)	293(3)
Mean	498	229	292
$3\,4\,\bar{6}$	484(4)	225(3)	298(3)
$3\,4\,6$	476(4)	228(3)	299(3)
Mean	480	227	299
$\bar{3}\,4\,\bar{6}$	490(4)	228(3)	263(3)
$\bar{3}\,4\,6$	495(4)	233(3)	257(3)
Mean	493	231	260
$4\,3\,\bar{6}$	482(4)	227(3)	260(3)
$4\,3\,6$	484(4)	223(3)	264(3)
Mean	483	225	262

TABLE IV Reflections violating extinction conditions for *P*4/*nnc* from X-ray intensity datasets ($F/\sigma F > 5$)

Class	V12C	V12I	V12R
a′	0	0	0
b′	15	5	24
c′	4	2	14

difference (34) can be compared with the pooled standard deviation (4.6) to show that it is highly significant. Similar results are obtained for other sets of reflections, most notably {124}, {126}, {133} and {137}; the reflections split into the same groups as {346}, indicating that fourfold rotational symmetry is preserved. The glide-violating reflections do not show this same relationship, in that they seem to obey 4/*mmm* Laue symmetry. Thus for V12R, all vertical mirror planes are lost from Laue group 4/*mmm*, resulting in 4/*m* Laue symmetry.

In all single-crystal data collections, the reflections systematically absent in *P*4/*nnc* were collected and processed in the same way as all allowed Bragg reflections. The number of violating reflections exceeding 5σ (based on counting statistics) are shown in Table IV. Note that for crystals V12C and V12R, there are many observed violating reflections. Psi-scans (rotation of the crystal about its diffraction vector) were used to confirm that these numbers represent valid Bragg reflections rather than double-diffraction effects. Results of subsequent crystal-structure refinement studies are presented below.

HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

As described by Groat *et al.* (1993), a (001) section of V12 was examined using a Hitachi 100 kV transmission electron microscope equipped with a tilting stage. A hole was milled through the sample in such a way that all three sectors could be examined. A careful search of each sector showed no evidence of domain structure or variable intensity. However, in moving from one sector to another, it was necessary to tilt the stage in order to recenter the image of (001). Further investigation showed that in the rim and intermediate sectors, the *Z* axis tilts inward (toward the center of the crystal) by as much as 3°.

The only study to report domain structure in vesuvianite is Veblen and Weichmann (1991). They showed that a vesuvianite crystal from California is made up of domains 10 to 50 nm wide and elongated parallel to [001]. The sample showed selected-area diffraction (SAD) patterns consistent with *P*4/*n* symmetry, but was weakly biaxial. The authors suggested that the true symmetry of their sample is *P*2/*n* or lower.

OTHER EVIDENCE

Polarized single-crystal infrared measurements (Groat, 1988) show slight deviations from tetragonal symmetry in (001) sections of V12 crystals. Single-crystal Raman spectra (Groat *et al.*, 1995a) show bands that are assigned to the Si tetrahedra in the vesuvianite structure, and comparison of peak intensities of the *xx*, *yy*, and *zz* spectra indicate that the deviation from tetragonal symmetry at room temperature is very slight.

TWINNING

Several investigators have suggested that the deviations from *P*4/*nnc* symmetry in vesuvianite are due to twinning. Twinning is definitely possible in vesuvianite. Indeed, if vesuvianite does undergo a second-order (or near second-order) transition on cooling as suggested by Groat *et al.* (1993), twinning is very probable. However, twinning cannot be responsible for the observed deviations from *P4/nnc* symmetry. Any (merohedral) twin plane must correspond to a potential mirror- or glide-plane in the maximal symmetry possible for a specific unit cell. Thus merohedral twinning will tend to *increase* the apparent symmetry of the crystal, not decrease it. If a vesuvianite crystal is twinned, the apparent symmetry of the twinned crystal is greater (i.e., shows less deviation from higher symmetry) than the symmetry of one member of the twin.

POSSIBLE SPACE GROUPS

The basic structure of vesuvianite has space-group symmetry *P4/nnc*, and thus any simple structural modification of this can occur only in a space group that is a subgroup or a supergroup of this basic symmetry. There are no space groups that are supergroups of *P4/nnc*. Possible subgroups (from Stokes and Hatch, 1988) are given in Table V. Combination of the evidence presented above (primarily the biaxial character, orientation of the optic-axial plane, and the diffuse reflections) with the list of possible subgroups limits the possible space groups of low-symmetry vesuvianite to *P2/n* or its subgroups. For *P2/n* symmetry, the unique axis is *Z* (tetragonal) and all subgroups (*Pn*, *P2*, $P\bar{1}$, *P1*) are possible with this orientation. However, the space group *P2* is also possible with the unique axis corresponding to *X* or *Y* (tetragonal).

As we have seen, there have been several refinements of the structure of vesuvianite in space group *P4/n*, and these have shown significant ordering of cations over sites that are equivalent in *P4/nnc*. There have been several suggestions that lowering of symmetry in vesuvianite primarily involves ordering of cations over sites along the fourfold axes. However, the basic problem in vesuvianite involves breaking

TABLE V Subgroups of *P4/nnc*

Tetragonal	$P4/n$	$P4$	$P\bar{4}$	$P422$	$P4nc$	$P\bar{4}n2$	$P\bar{4}2c$	
Orthorhombic	$Pnnn$	$P222$	$Pnn2$	$Pn2n$	$P2nn$	$Pncn$*	$P2_122$*	$Pnc2$*
	$Pn2n$*	$P2_1cn$*	$Pcnn$	$P22_12$	$Pcn2$	$Pc2_1n$	$P2nn$	
Monoclinic†	$P2^x/n$	Pn	$P2^x$	$P2^y$	$P2^{[110]}$	$P2_1^{[110]}$		
Triclinic	$P\bar{1}$	$P1$						

*Principal axes at 45° to the tetragonal *a* axes.

†Superscripts for the monoclinic space groups indicate the orientation of the principal axis relative to the ideal tetragonal axes.

of tetragonal symmetry (as indicated by the biaxial optics of some crystals), and such channel ordering cannot be the cause of this (Groat *et al.*, 1993) unless the symmetry is *P*2 rather than *P*2/*n*, in which case the loss of symmetry could be due to ordering over quartets of sites along the fourfold axes.

STRUCTURE REFINEMENT

Many refinements in different space groups were attempted using the approximately 18,000 reflections collected from each of the V12C, I and R crystals. Full details are presented in Groat (1988). Initial refinements of all three crystals were done in space group *P*4/*nnc*. Full-matrix least-squares refinement for anisotropic-displacement models resulted in convergence at *R* values of 3.5, 4.3 and 5.5% for V12C, I and R, respectively, correlating with the increase in 2*V* from core to rim (see Table VI). V12C was also refined in space group *P*4/*nnc* using an input dataset that includes reflections that violate *P*4/*nnc* extinction criteria; the resulting *R* value was 4.2% (anisotropic-displacement model). In addition, V12C was refined in space groups $P\bar{4}$ and *P*4. Neither refinement converged satisfactorily, primarily because of the high

TABLE VI Crystal-structure refinement results for anisotropic models in different space groups

Refinement	*R*(%)	*Rw*(%)	*Rg*(%)	*Number of unique refs*
V13C *P*4/*nnc*	3.5	2.5	2.8	2085
*P*4/*n*	4.3	3.0	3.2	4008
$P\bar{4}$	3.4*	2.7	2.8	7429
*P*4 (isotropic)	12.2*	10.9	11.8	7416
V13I *P*4/*nnc*	4.3	3.0	3.0	2070
V13R *P*4/*nnc*	5.5	4.3	3.9	2094
*P*4/*n*	6.0	4.3	4.1	4030
*P*2/*n*	5.4	3.9	3.7	7580
Pn	4.2*	3.2	3.0	7758

*Did not converge.

$$R = \sum(|[F(\text{obs}) - F(\text{calc})]|)/\sum(F(\text{obs})),$$

$$Rw = \sum[|[F(\text{obs}) - F(\text{calc})]| \cdot w^{0.5}]/\sum[F(\text{obs}) \cdot w^{0.5}],$$

$$Rg = wR = \left[\sum(w \cdot |[F(\text{obs}) - F(\text{calc})]|)^2/\sum\left(w \cdot F(\text{obs})^2\right)\right]^{0.5},$$

$$w = \left[\sigma^2 F \cdot (\text{obs})\right]^{0.5}.$$

correlations between atoms that are equivalent in *P*4/*nnc*. V12C and V12R were also refined in space group *P*4/*n* as suggested by the diffraction evidence. However, there was no significant improvement in the *R* indices.

Since the evidence presented previously suggests that V12R is the most non-tetragonal, it was also refined in space groups *P*2/*n* and *Pn*. The *P*2/*n* refinement (anisotropic model) converged to an *R* index of 5.4%, almost identical to that of *P*4/*nnc*. Displacement factors, however, varied considerably for *P*4/*nnc*-equivalent atoms. The *Pn* refinement (isotropic model) converged to an *R* index of 6.2%, lower than that of the other refinements. The anisotropic model, with ~1200 parameters, failed to converge, even after ~50 cycles. Once again, the high degree of correlation between pseudo-equivalent atoms resulted in unrealistic displacement factors, and in some case, non-positive definite behaviour.

These results suggest that the deviation from tetragonal symmetry must be very slight. It is likely that the necessary and most important information is carried by very weak reflections and/or in slight differences between intensities of reflections that are equivalent in *P*4/*nnc*. In order to try and obtain better data, we used synchrotron X-ray radiation to collect weak symmetry-equivalent reflections from crystal V12R. A total of 3738 reflections were collected at HASYLAB, using the beamline F1. Intensity variations show that all glide planes parallel to [001] in *P*4/*nnc* are strongly violated. The *n*-glide perpendicular to [001] in the *P*4/*nnc* model, and the fourfold axis itself, are also violated, although to a much lesser degree. The evidence seems to confirm that the space group is *P*2/*n* or a subgroup. In addition to the synchrotron data, we have collected a total of 16,295 reflections for V12R using a conventional instrument (CAD-4, Ag radiation). The data were combined with the data from the synchrotron, and refinements in different space groups are continuing.

Acknowledgements

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