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"Rod" polytypism in vesuvianite: crystal structure of a low-temperature *P4nc* vesuvianite with pronounced octahedral cation ordering

by *Thomas Armbruster*[1] and *Edwin Gnos*[2]

Abstract

Vesuvianites are known to crystallize in three different tetragonal space-groups, *P4/nnc*, *P4/n*, and *P4nc*. These different varieties are interpreted as "rod" polytypes. Positional cation disorder on strings parallel to the 4-fold axes, characteristic of vesuvianites crystallized between 400 and 800 °C, leads to *P4/nnc* symmetry. Low temperature (< 300 °C) vesuvianites have long-range ordered strings leading to either *P4/n* (centrosymmetric) or *P4nc* symmetry (non-centrosymmetric).

The crystal structure of a low-temperature vesuvianite ($a = 15.569(2), c = 11.841(1)$ Å) of $Ca_{19}Al_{9.0}Mg_{2.2}Fe^{3+}_{1.8}Si_{18}O_{69}(OH)_9$ composition, from a rodingitized dolerite dike of the Bela Ophiolite in Pakistan, was refined from single-crystal X-ray data in *P4nc* symmetry to $R = 2.92\%$. The refinement showed that ca. 84% of the strings have a non-centrosymmetric arrangement where the apices of the five-fold coordinated Fe^{3+} square pyramids point in the same direction. In addition, the entire structure relaxes to *P4nc* symmetry leading to pronounced cation ordering on the octahedral Y sites. Y1 hosts only Al, whereas Y2a and Y2b (symmetry equivalent in *P4/nnc* symmetry) show strongly different bond lengths indicating different occupation by Al, Mg, and Fe^{3+}.

Keywords: vesuvianite, polytypism, long-range ordering, single-crystal X-ray structure refinement, cation ordering, Pakistan, rodingite.

Introduction

Conventionally, a compound is defined as polytypic if it occurs in several different structural modifications, each of which may be regarded as built up by stacking of layers of (nearly) identical structure and composition, where the modifications differ only in their stacking sequence (GUINIER et al., 1984). The same nomenclature paper also remarks: "a more general definition of polytypism that includes 'rod' and 'block' polytypes may be become necessary in the future". The major reason for the omission of "rods" and "blocks" is the fact that well defined examples of these types were missing at that time. A subsequent extension of the definition suggested by ANGEL (1986) also includes "rod" polytypes.

The structure of vesuvianite is composed of a polyhedral framework enclosing structural channels. These channels have potential cation positions with the sequence Y'X'X'Y', where X' is eight- and Y' is five-coordinated (Fig. 1). Due to short X'X' and Y'X' distances occupied sites always alternate with vacancies (□). Thus a string or "rod" along a 4-fold axis has locally either a Y'□X'□ or □X'□Y' arrangement (Fig. 2). If we assume for electrostatic reasons that two adjacent vacancies do not occur, each string itself is fully ordered. However, adjacent strings are either long-range disordered (space group *P4/nnc*) or they follow some specific ordering patterns leading to decreased symmetry (*P4/n* or *P4nc*). An easy way to visualize the string arrangement in space group *P4/n* is that the apex of the square pyramid around Y' points to opposite directions along the two adjacent 4-fold axes. In space group *P4nc* apices of square pyramids point in the same direction (Fig. 2). The various arrangements of or-

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dered strings may be described in terms of "rod" polytypism. String ordering is frozen in during growth and does not alter with heat treatment of the crystal (ALLEN and BURNHAM, 1992).

The aspect of polytypism in vesuvianite has mostly been overlooked or ignored. The reasons are that in contrast to conventional polytypes composed of stacked layers, the "rod" polytypes of vesuvianite have the same cell dimensions and the observed space groups have similar symbols (*P4/nnc*, *P4/n*, and *P4nc*). The space groups (*P4/n*, *P4nc*) of the ordered polytypes are actually subgroups of the disordered polytype (*P4/nnc*). Furthermore, the systematic extinctions of X-ray diffractions which enable distinction of the various

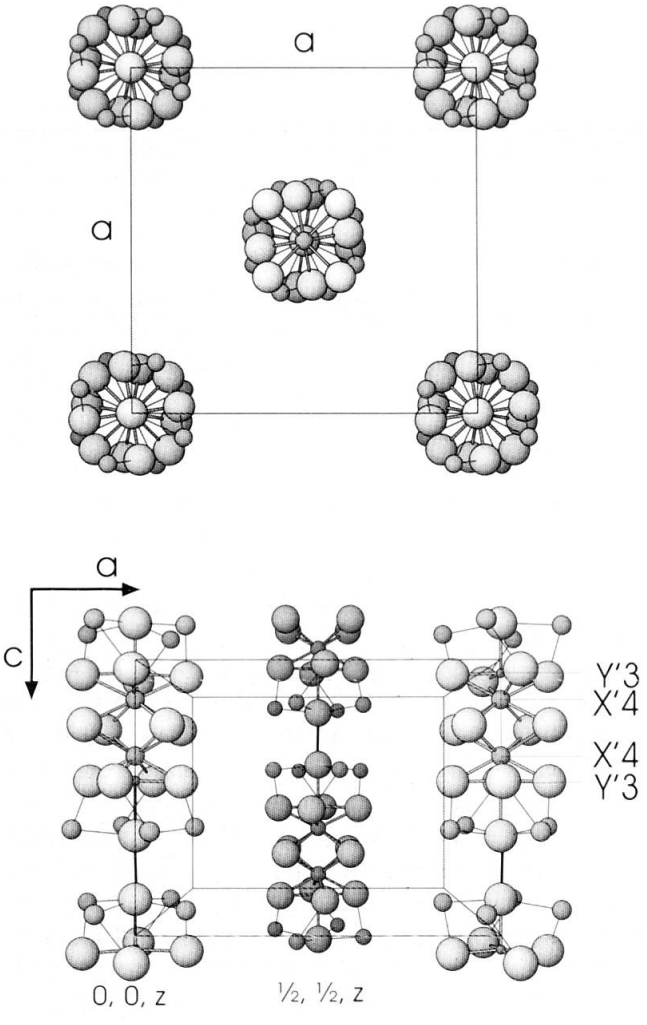

Fig. 1 Large, medium, and small sized spheres represent oxygen, Ca, and five-coordinated cations in square pyramidal coordination (Y'3 sites), respectively. Upper part: Projection of vesuvianite rods along the *c*-axis. Lower part: Perspective view of the vesuvianite rods. For clarity, the two rods on the back of the unit cell have been removed. Notice that the close spacing of two adjacent X'4 or X'4 and Y'3 sites does not allow for simultaneous occupation. Thick dashed lines indicate hydrogen bonding connecting two modules within a string.

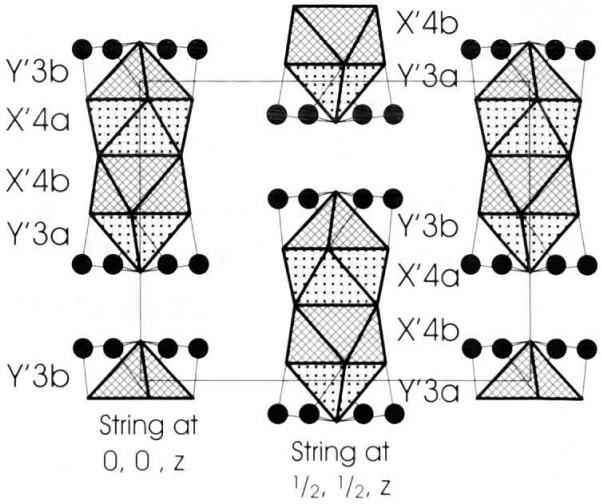

Fig. 2 Arrangement of potential X'4 and Y'3 sites forming strings parallel to the 4-fold axes. The Y'3 site is a five-coordinated square pyramid where the tip may point up or down. The X'4 site possesses dodecahedral coordination. Due to short distances of adjacent Y'3, X'4 and X'4, X'4 polyhedra, only two of the available sites are occupied. In space group *P4nc* the crosshatched polyhedra form a type A string and the polyhedra with the weaving pattern form an alternative type B string. The black circles are Ca atoms bonding to the oxygen atoms of the string sites.

space groups are not very pronounced. In other words the decisive reflections are either very weak or absent. Thus powder diffraction methods are not suitable for a distinction of the stacking variants (AREM and BURNHAM, 1969).

Polytypism in vesuvianite is of great importance also from a petrological point of view because polytypes with long-range string ordering (space groups *P4/n* and *P4nc*) are characteristic of low crystallization temperature (< 300 °C) whereas high-temperature (>> 300 °C) vesuvianites have long-range disordered strings leading to *P4/nnc* diffraction symmetry (ALLEN and BURNHAM, 1992). A consequence of symmetry lowering from *P4/nnc* to *P4/n* or *P4nc* is splitting of various tetrahedral, octahedral, and seven- to nine-coordinated sites. As an example, in space group *P4/nnc* (high-temperature vesuvianites) there are only two octahedral positions (Y1 and Y2). In space group *P4nc* (low-temperature vesuvianites) there are three symmetry independent octahedral sites (Y1, Y2a, and Y2b) and in space group *P4/n* (low-temperature vesuvianites) there are four symmetry independent octahedral sites (Y1a, Y1b, Y2a, and Y2b). Thus in addition to string ordering, low-temperature vesuvianites exhibit a more complex pattern for possible cation ordering. Unfortunately all experimental studies dealing with vesuvianite stability have either ignored "rod" polytypism in vesuvianite or were carried out at temperatures

above 400 °C where the disordered *P*4/*nnc* variant has to be expected (e.g. VALLEY et al., 1985).

A simplified formula of vesuvianite, taking into account the various cation coordinations, may be written as $X_{18}X'Y_{12}Y'Z_{18}O_{69}(OH,F)_9$, where X and X' are seven to nine-coordinated, Y has octahedral coordination, Y' has square pyramidal coordination (five-fold), and Z represents tetrahedral coordination. X and X' are commonly occupied by Ca. Y and Y' host elements with an average valence of 2.85 (e.g. 11 (Al, Fe^{3+}) and 2 (Mg, Fe^{2+})). Another important Y-type cation is Ti^{4+} thus the concentration of octahedral divalent cations may increase above 2. The fact that for stoichiometric reasons vesuvianites with homovalent octahedral cations are very rare underlines the importance of octahedral cation ordering in the various stacking variants. There are two different types of tetrahedral Z sites, those of the orthosilicate units (10 per formula unit), and those of the disilicate unit (8 p.f.u.).

The existence of vesuvianites of lower symmetry than *P*4/*nnc* was first recognized by AREM and BURNHAM (1969) who noticed glide-plane violating reflections in single-crystal X-ray photographs. A subsequent piezoelectric test indicated that some specimens were non-centrosymmetric. CODA et al. (1970) suggested that string ordering could be responsible for lower symmetry vesuvianites. GIUSEPPETTI and MAZZI (1983) performed the first successful structure refinement of a string ordered *P*4/*n* (centrosymmetric) vesuvianite and also noticed that a vesuvianite from Canzocoli (contact aureole of the Preddazzo-Monzoni area) crystallized in the non-centrosymmetric space group *P*4*nc*. However, they were not successful in refining the structure because of correlation problems due to *P*4/*nnc* pseudo-symmetry. The idea of string ordering in vesuvianite was elaborated by ALLEN and BURNHAM (1992) who also applied second harmonic generation tests (SHG) to screen for non-centrosymmetric samples. The crystal chemical variability of the string disordered *P*4/*nnc* high-temperature polytype is well documented (e.g. YOSHIASA and MATSUMOTO, 1986; FITZGERALD et al., 1986a; OHKAWA et al., 1992; GROAT et al., 1992a,b; 1993; 1994a,b; 1995; 1996; 1998). Structure refinements of low-temperature vesuvianites with *P*4/*n* symmetry were reported for samples from six localities: from a rodingite at Val d'Ala, Piemonte, Italy (GIUSEPPETTI and MAZZI, 1983; PAVESE et al., 1998), from the Jeffrey Asbestos mine, Quebec, Canada (FITZGERALD et al., 1986b; ARMBRUSTER and GNOS, 2000a), from veins in greenstones in San Benito County, California, USA (FITZGERALD et al., 1987), from Ogose, Saitama Prefecture, Japan, from Muslimbagh, Pakistan (OHKAWA et al., 1994), and from hydrothermal pocket fillings of the N'chwaning II mine in the Kalahari manganese fields, South Africa (ARMBRUSTER and GNOS, 2000b). There are only two structure refinement of a non-centrosymmetric *P*4*nc* vesuvianite, one from Saueseter, Drammen, Norway (OHKAWA et al., 1994) and one from the N'chwaning II mine (ARMBRUSTER and GNOS, 2000a).

ARMBRUSTER and GNOS (2000a) defined criteria how a successful structure refinement of vesuvianite in the non-centrosymmetric space group *P*4*nc* can be performed. The most important findings of their study are: (1) String ordering according to *P*4*nc* symmetry does not lead to glide-plane violating reflections different to *P*4/*nnc* symmetry. (2) Only if string ordering according to *P*4*nc* symmetry leads to low symmetry relaxation of the entire vesuvianite structure, glide-plane violating reflections of type 1, *hk*0 with $h + k = 2n + 1$, become evident. This is in contrast to *P*4/*n* vesuvianites where glide-plane violating reflections of type 2a, *hhl* with $l = 2n + 1$, and type 2b, 0*kl* with $k + l = 2n + 1$, are caused by both the string arrangement and structural relaxation. As a consequence, type 2a, b reflections in *P*4/*n* vesuvianites are about one order of magnitude stronger than type 1 reflections in *P*4*nc* vesuvianites. (3) To reduce correlation effects due to strong *P*4/*nnc* pseudo-symmetry in single-crystal X-ray structure refinements, atomic displacement parameters of pseudo-symmetry related positions have to be constrained to each other.

The observation that the entire structure may relax to *P*4*nc* symmetry (ARMBRUSTER and GNOS, 2000a) has also bearing on the interpretation of the intensity of the piezoelectric or SHG effect. A weak effect could either mean that a crystal is composed of centrosymmetric *P*4/*n* (or even *P*4/*nnc*) and non-centrosymmetric *P*4*nc* domains or it could indicate that the structure is completely *P*4*nc* ordered but the low symmetry relaxation of the entire structure is only weakly developed. One possible cause of enhanced low symmetry structure-relaxation could be cation ordering on the non-symmetry related octahedral sites.

The colorless low-temperature *P*4*nc* vesuvianite from the N'chwaning II mine of the Kalahari manganese field (ARMBRUSTER and GNOS, 2000a) had only a low concentration of transition metals and Mg on the octahedral Y sites. Thus pronounced octahedral cation ordering could not be expected for chemical reasons. For the present study we have selected an olive green low-temperature vesuvianite which seemed to be more promising to study cation ordering.

Sample origin

The studied vesuvianites form coatings on open fissures in slightly boudinaged and partially rodingitized dolerite dikes in serpentinized harzburgite of the Bela Ophiolite, Pakistan (GNOS et al., 1998a; 1998b). The rodingitization, formation of open fissures, and hydrothermal activity are related to faulting parallel to the large Chaman, Ornach-Nal and Ghazaband fault systems. The faults are the result of southward extrusion of the Afghanistan continental blocks due to the Himalayan contraction. Rodingites are abundant in the Hazarganji area and dikes metasomatized towards rodingite are weathering white. The green vesuvianite crystals are associated with green, < 1 mm sized andradite (variety demantoid), abundant natrolite, calcite, and xonotlite. Based on other natrolite occurrences and experimental work GNOS et al. (1998b) estimated 150–285 °C for the hydrothermal formation of the minerals.

When studied with a polarizing microscope, the vesuvianite shows anomalous interference colors and undulatory extinction. The optical character is positive.

Experimental

Single-crystal X-ray data collection on a prismatic, 0.30 × 0.25 × 0.20 mm, olive green vesuvianite from the Bela Ophiolite was performed with an ENRAF NONIUS CAD4 single-crystal X-ray diffractometer with graphite monochromated Mo$K\alpha$ X-radiation. Cell dimensions were refined from the angular settings of 18 reflections with $18 < \theta < 29°$ yielding tetragonal symmetry with a = 15.569(2), c = 11.841(1) Å. Diffraction data were collected up to θ = 30°, yielding 2373 unique reflections of which 2254 had $F > 4\sigma(F)$ used for structure solution and refinement. Experimental details are given in table 1. Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (ENRAF NONIUS, 1983). An empirical absorption correction using the Ψ-scan technique was applied. Systematic absences indicated $P4$ as a possible space group. However, $0kl$ reflections with $k + l = 2n + 1$ (type 2a) and hhl reflections with $l = 2n + 1$ (type 2b) were very weak (Tab. 2), thus the space group $P4nc$ was chosen for structure solution and refinement using the program SHELX-97 (SHELDRICK, 1997). The weak but observed forbidden reflections are due to minor concentrations of domains with $P4/n$ symmetry. The strongest of the forbidden reflections were 0 15 0 , 0 1 4, 0 1 6, and 0 0 11 with approximately $F^2 = 10\ \sigma(F^2)$. Reflections of corresponding indices were also found to be the strongest reflections of the type 2a, b, hhl with $l = 2n + 1$, and $0kl$ with $k + l = 2n + 1$, for a $P4/n$ vesuvianite studied by ARMBRUSTER and GNOS (2000a). Notice that type 1 reflections (Tab. 2) were about four-times stronger than those of type 2a, b thus choice of $P4nc$ space group symmetry was justified (ARMBRUSTER and GNOS, 2000a). Cation assignment was based on interatomic distances and scattering power. Least squares refinements, where anisotropic displacement parameters of all atoms were constrained to their $P4/nnc$ pseudo-symmetric equivalents (ARMBRUSTER and GNOS, 2000a), converged at R = 2.92% with 262 variables for 2254 observations > 4$\sigma(F)$. The absolute configuration was evaluated using the FLACK (1983) x parameter which was 0.02(2) thus twinning or an inverted absolute structure could be excluded. H atoms were restrained to have a distance of 1.00(5) Å to the oxygen atom forming the OH group. Final atomic coordinates, populations and B_{eq} val-

Tab. 1 Single-crystal X-ray data collection and refinement of vesuvianite from the Bela Ophiolite.

space group	$P4nc$, No. 104
a, c (Å)	15.569(2), 11.841(1)
X-radiation	Mo$K\alpha$
upper θ limit	30°
h, k, l limit	$21 \geq h \geq -1$, $21 \geq k \geq -1$, $16 \geq l \geq -1$
reflections measured	5278
unique reflections	2372
reflections > 4σ (F)	2254
absorption corr.	empirical: Ψ scans
R_{int}, R_σ (%)	3.7, 3.1
absolute configuration	no enantiomorph twinning
number of parameters	262; U_{ij} constraint to $P4/nnc$ symmetry
R (on F) %	2.91
wR (on F^2) %	7.62

$$R = \left(\Sigma\left\|F_o\right| - \left|F_c\right\|\right) / \left(\Sigma\left|F_o\right|\right) \qquad wR = \sqrt{\left(\Sigma\left(F_o^2 - F_c^2\right)^2\right) / \left(\Sigma w\left(F_o^2\right)^2\right)}$$

Tab. 2 Systematic absence exceptions of X-ray single-crystal reflections of long-range ordered vesuvianite from the Bela Ophiolite (space group $P4nc$).

symmetry type	n-- 1	-n- 2a	--c 2b
N	218	343	148
$NF^2 > 3\sigma$	136	86	45
$\langle F^2 \rangle$	0.6	0.1	0.1
$\langle F^2/\sigma \rangle$	8.1	2.0	2.3

Notice $F^2_{400} > 1 \times 10^6$

Tab. 3 Atomic coordinates, B_{eq}(Å^2) values, and population for green vesuvianite from the Bela Ophiolite.

atom	x/a	y/b	z/c	B_{eq}	population
Si1	1/2	0	–0.0001(2)	0.57(2)*	
Si2a	0.56886(7)	0.20984(7)	–0.1287(1)	0.45(1)*	
Si2b	–0.70883(7)	0.06940(6)	0.1281(1)	0.45(1)*	
Si3a	0.40055(7)	0.33026(7)	–0.6348(1)	0.46(1)*	
Si3b	0.33706(6)	0.40085(7)	0.1359(1)	0.46(1)*	
Y1	0.24955(9)	0.24791(9)	0.5014(2)	0.46(1)	1.0 Al
Y2a	0.36280(7)	0.12713(7)	–0.6251(1)	0.513(9)	0.906(4) Al + 0.094 Fe
Y2b	–0.36141(7)	0.13011(7)	0.1277(1)	0.513(9)	0.630(4) Al + 0.25 Mg + 0.12 Fe
Ca1	1/2	0	0.2494(1)	0.61(1)	
Ca2a	0.44021(5)	0.20539(5)	0.12123(8)	0.597(6)	
Ca2b	–0.43816(5)	0.20644(5)	–0.62034(8)	0.597(6)	
Ca3a	–0.57123(5)	0.34980(5)	–0.11875(9)	0.972(8)	
Ca3b	0.85373(6)	0.06447(5)	0.10427(9)	0.972(8)	
O1a	0.5296(2)	0.0779(2)	0.0862(3)	0.72(2)	
O1b	–0.5301(2)	0.0776(2)	–0.5857(3)	0.72(2)	
O2a	0.5893(2)	0.1327(2)	–0.2176(3)	0.69(2)	
O2b	–0.6334(2)	0.0899(2)	0.2225(3)	0.69(2)	
O3a	0.4709(2)	0.2016(2)	–0.0752(3)	0.64(2)	
O3b	–0.4730(2)	0.2030(2)	–0.4240(3)	0.64(2)	
O4a	0.6911(2)	0.1433(2)	–0.5306(3)	0.60(2)	
O4b	–0.6860(2)	0.1437(2)	0.0304(3)	0.60(2)	
O5a	–0.4219(2)	0.2405(2)	0.1795(3)	0.68(2)	
O5b	0.4190(2)	0.2317(2)	–0.6783(3)	0.68(2)	
O6a	0.5216(2)	0.3746(2)	0.0586(3)	0.87(2)	
O6b	–0.5228(2)	0.3658(2)	–0.5593(3)	0.87(2)	
O7a	0.1938(2)	0.0807(2)	0.1751(3)	0.82(2)	
O7b	–0.6942(2)	–0.5739(2)	–0.1813(3)	0.82(2)	
O8a	0.6610(2)	0.3099(2)	–0.5677(3)	0.68(2)	
O8b	–0.6562(2)	0.3116(2)	0.0659(3)	0.68(2)	
O9	0.3977(2)	0.3928(2)	0.2509(3)	0.74(2)	
O10a	0	0	–0.6255(6)	1.01(5)	
O10b	0	0	0.1414(6)	1.01(5)	
H10b	0	0	0.226(4)	2.37*	
O11a	0.2538(2)	0.1858(2)	–0.6340(3)	0.75(2)	
H11a	0.270(4)	0.219(4)	–0.703(5)	2.37*	
O11b	–0.2537(2)	0.1921(2)	0.1370(3)	0.75(2)	
H11b	–0.211(3)	0.214(4)	0.197(5)	2.37*	
Y'3a	1/2	1/2	0.0340(2)	0.52(2)	0.817(7) Fe
X'4a	1/2	1/2	0.3500(2)	0.51(3)	0.84(1) Ca
Y'3b	1/2	1/2	0.451(1)	2.2(3)*	0.148(7) Fe
X'4b	1/2	1/2	0.152(1)	1.6(3)*	0.16(1) Ca

* Starred atoms were refined isotropically.

ues are listed in table 3 and selected interatomic distances are summarized in table 4.

The same crystal as applied for the structure refinement was subsequently analyzed with a Cameca SX-50 microprobe using beam conditions of 15 kV and 20 nA, wavelength-dispersive spectrometers, and when possible, an enlarged spot size of ca. 10 µm. Natural and synthetic minerals were used as standards: orthoclase $Si_{K\alpha}$ (TAP) and $K_{K\alpha}$ (PET), anorthite $Al_{K\alpha}$ (TAP) and $Ca_{K\alpha}$ (PET), almandine $Fe_{K\alpha}$ (LiF), tephroite $Mn_{K\alpha}$ (LiF), spinel $Mg_{K\alpha}$ (TAP), covellite $Cu_{K\alpha}$ (LiF), ilmenite $Ti_{K\alpha}$ (LiF), albite $Na_{K\alpha}$ (TAP), fluor phlogopite $F_{K\alpha}$ (TAP), and scapolite $Cl_{K\alpha}$ (PET). Data for Ti, F, and Cl were collected for 30 seconds on peak and background, all other elements for 20 seconds. Pb, Ba, Sr, Zn and Cr concentrations were found below detection limit in qualitative wavelength-dispersive scans, and hence were not analyzed further.

Results

ALLEN and BURNHAM (1992) showed that the intensity of *-n-* and *--c* glide violating reflections characteristic of *P*4/*n* symmetry is below 1% with the strongest reflection, 0 0 4, normalized to 100%. The same authors report that the intensity of *P*4*nc* characteristic *n--* glide violating reflec-

tions is even below 0.02%. In the *P4nc* example (N'chwaning II mine) provided by ARMBRUSTER and GNOS (2000a) the intensity of the strongest *hk*0 reflections with $h + k = 2n + 1$ (e.g. 2 9 0, 4 7 0, 1 6 0) relative to 0 0 4 was below 0.06%. The vesuvianite from the Bela Ophiolite studied in this paper has the strongest *hk*0 reflections with $h + k = 2n + 1$ (e.g. 15 2 0, 11 18 0, 17 12 0, and 2 7 0) below 0.6% (relative to 0 0 4) violating the *n*-- glide plane. Though the average intensity of type 1 reflections is considerably lower (Tab. 2). It is also striking that the two *P4nc* vesuvianites have "strong" reflections with different Miller indices characteristic of the space group.

The *P4nc* refinement converged to ca. 84% of a polar string A arrangement. Notice that an unconstrained refinement was chosen to obtain the population of the string sites (Y'3a, Y'3b, X'4a, and X'4b). The most reliable information on the string arrangement is obtained from the X'4 sites because these positions are occupied by only Ca and vacancies. The occupation of the Y'3 sites is more complex. Not only vacancies and transition metals (e.g. Fe^{3+}) but also light elements (Mg, Al) may occupy the Y'3 sites. Light elements must be assumed if the Y'3a occupation (with Fe scattering factors) refines to a lower value than the X'4a occupation. It has also to be kept in mind that very weak reflections indicated the presence of domains with a centrosymmetric string arrangement which was neglected in the present refinement model. In addition, the whole structure distorts in a non-centrosymmetric fashion which is also seen in individual interatomic distances. The preferred position for Fe^{3+} is the square pyramid (Y3') on the four-fold axis. The mean Y2b–O distance (1.995 Å) is approximately 0.05 Å longer than the Y2a–O distance (1.942 Å) where Y2a and Y2b are related by pseudo-symmetry. The larger size of the Y2b site is mainly related to a preferred occupancy of this position by Mg. The Fe^{3+} concentrations on Y2b and Y2a are very similar, refining to 12.0(4)% and 9.4(4)%, respectively. The mean Y1–O distance is 1.899 Å which is characteristic of pure Al occupation.

Tab. 4 Interatomic distances of *P4nc* vesuvianite from Pakistan.

Si1-	O1b 2x	1.645(4)	Ca2b-	O8a	2.317(3)
	O1a 2x	1.651(4)		O5b	2.360(3)
	mean	1.648		O3b	2.388(4)
Si2a-	O7b	1.621(3)		O2a	2.422(3)
	O3a	1.657(3)		O5a	2.442(4)
	O2a	1.629(3)		O4a	2.479(4)
	O4a	1.667(3)		O1b	2.499(3)
	mean	1.644		O6b	2.901(4)
Si2b-	O7a	1.625(3)		mean	2.476
	O3b	1.626(3)	Ca3a-	O7b	2.372(3)
	O2b	1.652(4)		O6a	2.579(3)
	O4b	1.674(4)		O3a	2.454(3)
	mean	1.644		O11a	2.411(3)
Si3a-	O6b	1.591(3)		O7b	2.474(4)
	O8a	1.625(3)		O10a	2.589(1)
	O5b	1.644(3)		O8b	2.624(3)
	O9	1.667(3)		O7a	2.538(4)
	mean	1.632		O6a	3.022(3)
Si3b-	O6a	1.623(3)		mean	2.544
	O8b	1.621(3)	Ca3b-	O7a	2.408(3)
	O5a	1.622(3)		O6b	2.373(3)
	O9	1.662(3)		O3b	2.442(3)
	mean	1.632		O11b	2.626(3)
Y1-	O8b	1.878(3)		O7a	2.522(3)
	O8a	1.888(3)		O10b	2.527(2)
	O11a	1.874(3)		O8a	2.622(3)
	O11b	1.858(3)		O7b	2.651(4)
	O4b	1.952(3)		O6b	2.937(3)
	O4a	1.944(3)		mean	2.568
	mean	1.899	X'4a-	O6b 4x	2.375(3)
Y2a-	O2b	1.897(4)		O9 4x	2.588(3)
	O11a	1.930(3)		mean	2.482
	O1b	1.895(3)	X'4b-	O6a 4x	2.272(8)
	O3a	1.919(3)		O9 4x	2.585(7)
	O5b	1.953(3)		mean	2.429
	O4b	2.059(4)	Y'3a-	O6a 4x	2.003(3)
	mean	1.942		O10a	1.888(8)
Y2b-	O2a	1.940(4)		mean	1.980
	O11b	1.938(3)	Y'3b-	O6b 4x	2.123(3)
	O1a	1.946(3)		O10b	2.25(1)
	O3b	1.989(3)		mean	2.148
	O5a	2.054(3)			
	O4a	2.103(4)	O11a-	H11a	1.00(6)
	mean	1.995	H11a-	H11b	1.48(8)
Ca1a-	O1a 2x	2.327(4)	H11a-	O5b	2.35(6)
	O1b 2x	2.344(4)	H11a	O11b	2.31(6)
	O2a 2x	2.521(3)	O11b-	H11b	1.00(6)
	O2b 2x	2.524(3)	H11b-	O11a	2.13(5)
	mean	2.429	H11b-	O7a	2.06(5)
Ca2a-	O8b	2.328(3)			
	O5a	2.321(3)			
	O3a	2.376(3)			
	O2b	2.446(3)			
	O5b	2.431(4)			
	O4b	2.437(3)			
	O1a	2.459(3)			
	O6a	3.016(3)			
	mean	2.477			

Tab. 5 Average of 25 electron-microprobe point analyses on vesuvianite from the Bela Ophiolite, Pakistan. Formula normalized to 19 (Ca + Na + K).

oxides	wt%	stand. dev.	atoms	p.f.u.	stand. dev.
SiO_2	36.65	0.17	Si	17.98	0.11
TiO_2	0.01	0.01	Ti	0.00	0.00
Al_2O_3	15.59	0.14	Al	9.02	0.09
Fe_2O_3	4.96	0.18	Fe^{3+}	1.83	0.07
Mn_2O_3	0.14	0.04	Mn^{3+}	0.06	0.02
MgO	3.00	0.05	Mg	2.19	0.03
CaO	36.14	0.11	Ca	19.00	0.01
CuO	0.01	0.02	Cu	0.00	0.01
Na_2O	0.00	0.01	Na	0.00	0.00
K_2O	0.00	0.00	K	0.00	0.00
F	0.03	0.04	F	0.00	0.00
Cl	0.01	0.01	Cl	0.00	0.00
Sum	96.54	0.22			

The average chemical composition, evaluated on the basis of 25 point analyses is shown in table 5. The chemical formula was normalized to 19 (Ca + Na + K). Because vesuvianites from the Bela Ophiolite do not exhibit excess Y ions (GROAT et al., 1994a) normalization to a total of 50 cations leads within one standard deviation to the same results. The crystal was chemically homogeneous and the measured Fe + Mn concentration of 1.89(8) p.f.u. is in excellent agreement with 1.86(3) obtained from the structure refinement. Stoichiometry considerations indicate that Fe is of the ferric type. Due to the low concentration of Mn its valence could not be evaluated and was treated as Mn^{3+}.

Discussion

The string arrangement in low-temperature vesuvianites was hitherto refined for six *P*4/*n* crystals: two from Val d'Ala, Piemonte (PAVESE et al., 1998), one from Asbestos mine (ARMBRUSTER and GNOS, 2000a), one from Ogose, Japan, and from Muslimbagh, Pakistan (OHKAWA et al., 1994), and one from N'chwaning mine, South Africa (ARMBRUSTER and GNOS, 2000b). These refinements have in common that string A was 62–85% occupied. In addition, in some structures (PAVESE et al., 1998; ARMBRUSTER and GNOS, 2000a) the octahedral Y2a site was significantly larger than the pseudosymmetric Y2b site. Thus Y2b accepts preferentially trivalent cations like Al^{3+}, Fe^{3+}, and Mn^{3+} whereas the larger divalent cations like Mg, Fe^{2+}, and Mn^{2+} occupy together with trivalent ions the Y2a site. However, in the less ordered structures by OHKAWA et al. (1994) the opposite trend was observed (Y2b > Y2a). In all refinements on Al-rich vesuvianites only Al was found on Y1a and Y1b. Exceptions are the Mn^{3+}-rich vesuvianites (ARMBRUSTER and GNOS, 2000b) which have the Y1a site partly occupied by Mn^{3+}.

In the three non-centrosymmetric *P*4*nc* refinements (OHKAWA et al., 1994; ARMBRUSTER and GNOS, 2000a and this study) string A is 84–92% occupied. Notice that string A in space groups *P*4/*n* and *P*4*nc* has a different arrangement (ARMBRUSTER and GNOS, 2000a). In the N'chwaning sample studied by ARMBRUSTER and GNOS (2000a) the five-fold coordinated Y'3a was mainly occupied by Cu^{2+} and $Mn^{2+,3+}$ whereas in the vesuvianites from Saueseter (OHKAWA et al., 1994) and the Bela Ophiolite mainly Fe^{3+} was found on Y'3a. This difference has a strong bearing on the distortion of the square pyramid (Y'3a). The Jahn-Teller ions Cu^{2+} and Mn^{3+} lead to a stretched (parallel to *c*) pyramid whereas Fe^{3+} has no electronic effect enhancing polyhedral distortion. Because divalent cations in the N'chwaning sample were enriched on Y'3a and the concentration of Fe^{3+} and Mn^{3+} was very low, the octahedral sites Y1, Y2a, and Y2b did not display a pronounced selectivity but were mainly occupied by Al. In contrast, the Bela Ophiolite sample (this study) exhibits octahedral selectivity. Y1 is a pure Al site, Y2a and Y2b have 9 and 12% Fe^{3+}, respectively. Furthermore, Mg is concentrated on Y2b (ca. 25% Mg, equivalent to 2 Mg p.f.u.) increasing the bond distance to ca. 2 Å. A corresponding Mg ordering pattern was also found by OHKAWA et al. (1994) for the Saueseter vesuvianite. The similarity of X-ray scattering power of Al and Mg does not allow a direct determination of the Mg population but the larger size of Mg compared to Al leads to increased Y2b–O distances. The octahedral site preference in the Bela Ophiolite sample enhances the *P*4*nc* structure relaxation and causes the relatively strong intensity of *hk*0 reflections with $h + k = 2n + 1$.

It is striking that all hitherto studied *P*4/*n* and *P*4*nc* low-temperature vesuvianites have a string A preference (62–92%) and pure end-members have not yet been detected. Our results on the Bela vesuvianite allow various interpretations of the actual string arrangement: (1) 84% of an A string and 16% of a B string could indicate that the crystal is predominantly built by A strings but within the crystal small domains (less than ca. 100 unit cells large) possess B strings. The size of the B domains must be small otherwise a twin model would have been successful. (2) It could also indicate that the crystal is composed of 68% *P*4*nc* polytype (with A strings) and 32% *P*4/*nnc* polytype (with disordered A and B strings). (3) An alternative interpretation would be 68% *P*4*nc* and 32% *P*4/*n* polytype (with ordered A and B strings). As mentioned above, very weak reflections (type 2a, b) were detected in the diffraction pattern of the Bela vesuvianite which are characteristic of a *P*4/*n* polytype. If we compare F^2 of the type 2a, b reflections (normalized to F^2_{004}) with corresponding reflections from a vesuvianite which consisted to more than 92% of the *P*4/*n* polytype (GNOS and ARMBRUSTER in prep.) it can be shown that the portion of the *P*4/*n* polytype in the Bela vesuvianite is below 5%.

The simultaneous occurrence of various polytypes within the same single crystal could mean that the energetic differences between the polytypes are very low. It is not understood as yet whether crystallization conditions or very minor chemical differences are responsible for formation of the two possible low-temperature polytypes.

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