P4/n and *P4nc* long-range ordering in low-temperature vesuvianites

THOMAS ARMBRUSTER[1,*] AND EDWIN GNOS[2]

[1]Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
[2]Mineralogisch-Petrographisches Institut, Universität Bern, Baltzerstrasse1, CH-3012 Bern, Switzerland

ABSTRACT

Low-temperature vesuvianites crystallize in the two space groups *P4/n* or *P4nc* due to different arrangements of Ca-dodecahedra and $M^{2+,3+}$ square pyramids that form strings along the fourfold axes. Long-range ordered vesuvianites of acentric *P4nc* symmetry may have the same diffraction symmetry as centrosymmetric disordered *P4/nnc* vesuvianites. In contrast, *P4/n* long-range ordered vesuvianites exhibit glide plane violating reflections and can easily be identified. We report the first successful X-ray single-crystal structure refinement of a *P4nc* vesuvianite, $a = 15.487(2)$, $c = 11.764(2)$ Å from the N'chwaning II mine of the Kalahari manganese fields (RSA). This untwinned crystal has Cu^{2+} and Mn^{2+}, Mn^{3+} forming the square pyramid and exhibits an acentric ordering pattern with 85% string A and 15% string B. This is compared to a reinvestigation of the structure of a *P4/n* vesuvianite from Asbestos Quebec (Canada), $a = 15.531(2)$, $c = 11.817(2)$ Å. The crystal is composed of a merohedral (110) twin with a close to 1:1 twin ratio and has mainly Fe^{3+} in square pyramidal coordination. In this centric structure, string A is 84% and string B is 16% occupied. Criteria to determine the symmetry of low-temperature vesuvianites, studied by diffraction experiments, are discussed.

INTRODUCTION

A simplified formula of tetragonal vesuvianite ($a \sim 15.5$, $c \sim 11.8$ Å, $Z = 2$), taking into account the various cation coordinations and its domain structure, may be written as $X_{18}X'Y_{12}Y' Z_{18}O_{69}(OH,F)_9$ where X and X' are seven to ninefold-coordinated, Y has octahedral coordination, Y' has square pyramidal coordination, 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 and 2 Mg) and Z is mainly occupied by Si. X' and Y' occupy strings along the fourfold axes. In space group *P4/nnc*, these strings have the sequence Y'X'X'Y' but due to short X'X' and Y'X' distances occupied sites always alternate with vacancies (□). Thus, a string along a fourfold axis has locally either Y'□X'□ or □X'□Y' arrangement. Each string itself is fully ordered (short range ordering), however, adjacent strings are either long-range disordered (space group *P4/nnc*) or they follow some specific ordering patterns leading to decreased symmetry (Giuseppetti and Mazzi 1983; Fitzgerald et al. 1986b; Allen and Burnham 1992; Pavese et al. 1998). Subgroups of space group *P4/nnc* allowing for long-range string ordering are *P4/n*, centric, and *P4nc*, acentric (Giuseppetti and Mazzi 1983, Fitzgerald et al. 1986b, and Allen and Burnham 1992). Allen and Burnham (1992) argue that the long-range ordered space groups are characteristic of low temperature (<300 °C) vesuvianites whereas high-temperature (400–800 °C) vesuvianites are long-range disordered in agreement with *P4/nnc* diffraction symmetry.

String ordering takes place during crystal growth rather than by an ordering transformation on cooling.

Recent structural and chemical studies on long-range disordered *P4/nnc* vesuvianites (Yoshiasa and Matsumoto 1986; Fitzgerald et al. 1986a, Ohkawa et al. 1992; Groat et al. 1992a, 1992b, 1993, 1994a, 1994b, 1995, 1996) addressed various substitution mechanisms like boron incorporation and F → OH replacement and provided information on the local configuration of cations and OH,F sites. A boron-rich vesuvianite group mineral named wiluite has recently been defined (Groat et al. 1998).

Deviations from *P4/nnc* symmetry were either analyzed in terms of glide plane violating reflections in single-crystal diffraction patterns or by the presence of a slight piezoelectric or SHG (second harmonic generation) effect (Arem and Burnham 1969; Giuseppetti and Mazzi 1983; Fitzgerald et al. 1986b; Allen and Burnham 1992; Groat et al. 1993). Three types of glide violating reflections were distinguished (1) $hk0$ with $h + k = 2n + 1$; (2a) $0kl$ with $k + l = 2n + 1$; (2b) hhl with $l = 2n + 1$. Type 1 violates the *n* glide plane perpendicular to the fourfold axis, type 2a violates the *n* glide plane in (100), and type 2b violates the *c* glide plane in (110). Occurrence of type 1 reflections excludes space groups *P4/n* and *P4/nnc* and suggests *P4nc*. Observation of reflections of type 2a,b excludes *P4nc* and *P4/nnc* leading to space group *P4/n*. The piezoelectric or SHG effect is only possible in the acentric space group *P4nc*. Frequently all three types of weak glide violating reflections were observed or only type 2a,b were present but the piezoelectric effect was also observed thus it had to be assumed that such vesuvianites have a complex domain structure assembled of individual *P4nc* and *P4/n* domains (e.g., Valley et al. 1985; Fitzgerald et al. 1986b; Allen and Burnham 1992).

*E-mail: armbruster@krist.unibe.ch

Electron microscopic evidence (Veblen and Wiechmann 1991; Groat et al. 1993) indicates that the symmetry of some vesuvianites is non-tetragonal but monoclinic $P2/n$ leading to pseudomerohedral twins. Non-tetragonal symmetry may also be the cause for deviations from uniaxial optical behavior found in many vesuvianites (e.g., Groat et al. 1993). The latter authors also suggest that there is a continuous ferroelastic phase transition between a high-temperature $P4/nnc$ structure and a low-temperature $P2/n$ or Pn structure.

DIFFERENCES BETWEEN LONG-RANGE $P4nc$ AND $P4/n$ ORDERING

In space group $P4/n$ and a setting (choice 2) with the origin at the inversion center, the site coordinates on the fourfold axes are 1/4, 1/4, z and 3/4, 3/4, –z. Thus the string Y'□X'□ occurs at 1/4, 1/4 and the string □X'□Y' occurs at 3/4, 3/4, or □X'□Y' at 1/4, 1/4 and Y'□X'□ at 3/4, 3/4. Another way to visualize the string arrangement is that the apex of the square pyramid around Y' points to opposite directions along the two fourfold axes (Fig. 1).

In space group $P4nc$ the site coordinates on the fourfold axes are 0, 0, z and 1/2, 1/2, 1/2 +z. Either □Y'□X' occurs at x = 0, y = 0 and □X'□Y' at 1/2, 1/2 or Y'□X'□ occurs at 0, 0 and X'□Y'□ at 1/2, 1/2. The apex of the square pyramid around Y' points to the same direction on both fourfold axes, indicating the acentric character of this arrangement (Fig. 1).

Although many recent structure refinements exist on various vesuvianites (Ohkawa et al 1992; Groat et al. 1992b, 1994a, 1994b, 1996; Lager et al. 1999), very few were performed in space group $P4/n$ (Giuseppetti and Mazzi 1983; Fitzgerald et al. 1986b, 1987; Pavese et al. 1998) and none were published in space group $P4nc$. Yet, the piezoelectric or SHG effect was observed in various vesuvianites (Arem and Burnham 1969; Fitzgerald et al. 1986b; Allen and Burnham 1992). This discrepancy initiated the present study. There are either energetic reasons why $P4/n$ symmetry is more frequent than $P4nc$ (con-
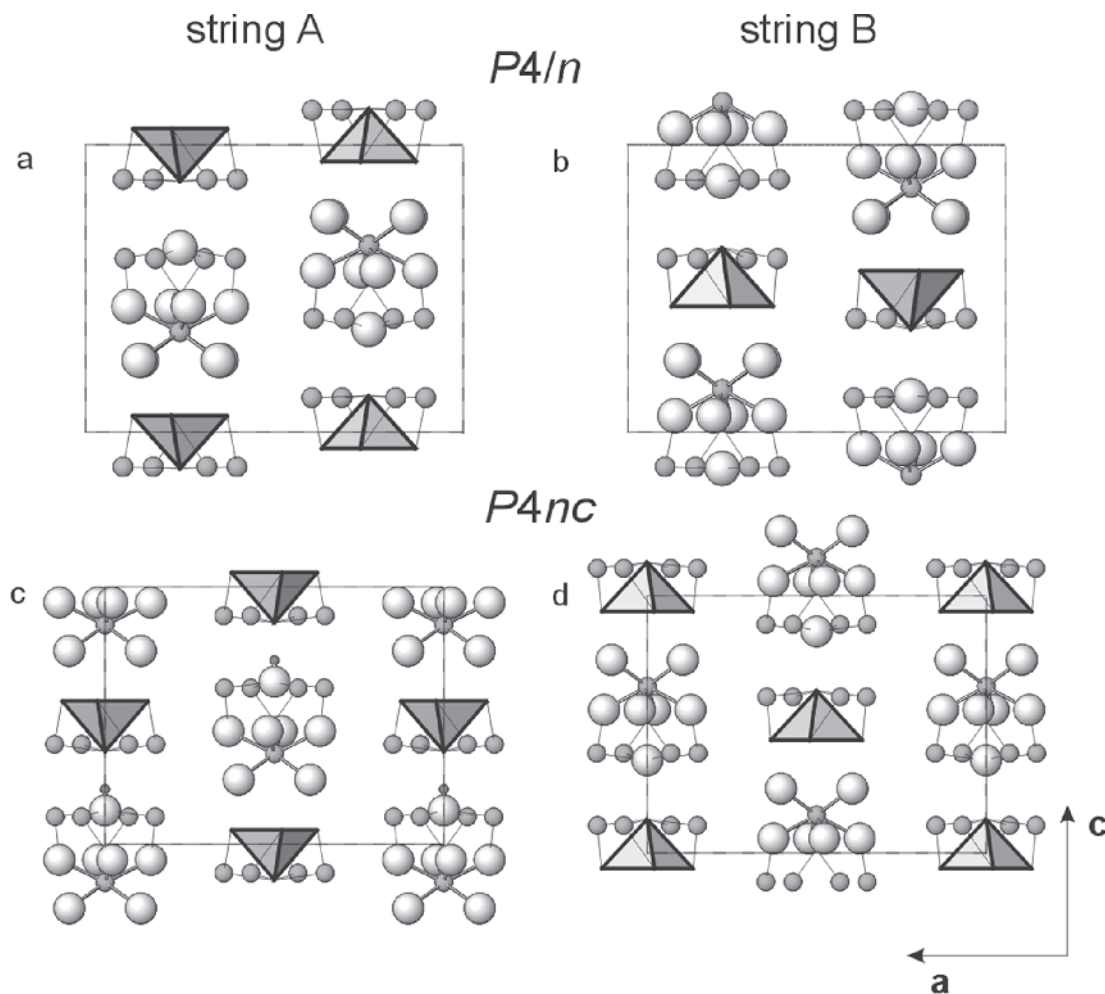
FIGURE 1. String arrangements along the fourfold axes in long-range ordered vesuvianites. Large spheres represent O atoms, intermediate spheres are Ca, small spheres are hydrogen. For clarity the oxygen square pyramids around Y' positions are shown as polyhedra. (**a,b**) In space group $P4/n$ (origin at $\bar{1}$) the fourfold axes pass through x = 1/4, y = 1/4 and 3/4, 3/4. The two possible string arrangements have the apices of the square pyramids pointing in opposite directions along the two fourfold axes. (**c,d**) In space group $P4nc$ the fourfold axes pass through the origin and 1/2, 1/2. Each string type is characterized by apices of square pyramids pointing in the same direction.

tradicting the observation of acentricity in vesuvianite) or other not yet recognized effects are responsible for the unsuccessful attempts to refine a $P4nc$ vesuvianite structure (Giuseppetti and Mazzi 1983).

Allen and Burnham (1992) provide a list (their Table 2) showing that glide violating reflections (type 2a,b) leading to the subgroup $P4/n$ are much stronger than those of type 1 violating the n glide plane in (001). This is the key for understanding why successful $P4nc$ refinements are missing. Consultation of the International Tables Volume A (1983) shows that the Wyckoff position of Y' and X' string sites in space group $P4nc$ is 2a with the special reflection condition $h + k + l = 2n$. In other words, a string arrangement according to space group $P4nc$ (apices of the square pyramids pointing in the same direction) does not lead to glide violating reflections ($hk0$ with $h + k = 2n + 1$) which were commonly used to distinguish space group $P4/nnc$ from $P4nc$. Therefore, disordered vesuvianites of $P4/nnc$ average symmetry and long-range ordered $P4nc$ vesuvianites may reveal the same diffraction symmetry. Observation of weak reflections of type 1: $hk0$ with $h + k = 2n + 1$ indicates that the acentric string arrangement leads also to relaxation of the entire structure to $P4nc$ symmetry.

The situation differs for space group $P4/n$. A correspondingly ordered string arrangement leads to glide violating reflections (type 2a,b) without the necessity that low symmetry relaxation of the structure must be considered. Thus long-range ordered $P4/n$ and long-range disordered $P4/nnc$ vesuvianites show different diffraction symmetry.

HOW CAN $P4nc$ ORDERING IN VESUVIANITES BE INVESTIGATED BY DIFFRACTION METHODS?

Potential candidates for $P4nc$ symmetry are vesuvianites from rodingites showing $P4/nnc$ pseudo diffraction-symmetry and possibly a significant effect of acentricity such as SHG or piezoelectricity (Allen and Burnham 1992). The fact that such crystals show only very weak or no reflections of the type $hk0$ with $h + k = 2n + 1$ indicates that, except the string arrangement, the remaining structure reveals $P4/nnc$ pseudosymmetry. Thus, routine structure-refinements in space group $P4nc$ will lead to extreme parameter correlations imposed by the pseudosymmetry as evidenced by Giuseppetti and Mazzi (1983). As a compromise, the structure refinement in space group $P4nc$ has to be conducted with all atoms, except the string cations, constrained to their pseudosymmetric $P4/nnc$ analogues. Such constraints for positional and displacement parameters can be set up by FVAR parameters within the program SHELX-97 (Sheldrick 1997). This approach leads to approximately 50% of the variables necessary for an unconstrained $P4nc$ refinement and removes the disturbing correlation problems. As a starting model, a disordered string arrangement may be entered where two possible Y' and X' sites in the string are considered with the corresponding population factors kept as variables. In the following text, this refinement type will be designated the position constrained model. If the diffraction data of such a constrained model contain information on string ordering, it will converge to a long-range ordered string arrangement leading to a significantly lower agreement factor than a corresponding refinement with $P4/nnc$ symmetry (ran-

dom string distribution) based on exactly the same number of reflections. In addition, merohedral twinning by the center of symmetry must be considered, this is possible in SHELX-97 by Flack's (1983) x parameter. The same parameter also indicates whether the absolute structure is correct or whether the structure must be inverted. As discussed by Allen and Burnham (1992) special care must be taken in recording and weighting weak reflection intensities because out of 256 total atoms per unit cell of vesuvianite only 4 atoms contribute to the string arrangement.

EXPERIMENTAL METHODS

An unusual purple to lilac fissure or pocket filling reaction rock from the N'chwaning II mine of the Kalahari manganese field (Republic of South Africa) was investigated using polarized optical microscopy and electron microprobe analyses. The rock was composed of pink Mn-bearing grossular, calcite, xonotlite, henritermierite, strontiopiemontite and strongly zoned lilac vesuvianite with Mn_2O_3 and/or MnO concentrations between less than 1 wt% and up to 5 wt%. The zoned mangoan vesuvianites were commonly short prismatic with striations on the prism faces. In addition, we found colorless fibrous vesuvianite without any striations embedded in calcite and xonotlite. Such a vesuvianite crystal, only $0.02 \times 0.02 \times 0.20$ mm^3 in dimension, with a composition determined by electron microprobe (Table 1), was extracted after dissolving the calcite with hydrochloric acid. The crystal was subsequently studied on a Siemens three-circle SMART X-ray diffractometer (Mo$K\alpha$ X-radiation) equipped with a CCD type area detector. Preliminary X-ray data collection yielded $P4/nnc$ diffraction symmetry and a structure refinement in space group $P4/nnc$ led to a rather poor $R1$ value of about 8% and to residual positive and negative electron density peaks (± 2 electrons/Å^3) along the fourfold axes which could not be removed in the $P4/nnc$ refinement model.

Cell dimensions were determined with an ENRAF NONIUS CAD4 diffractometer (Mo$K\alpha$ X-radiation) on reflections with $\theta > 15°$ yielding $a = 15.487(2)$, $c = 11.764(2)$ Å. In a subsequent more precise data collection (SMART system) each frame was collected for 300 seconds with ω-step width of 0.15° (Table 2). Thus if a single reflection was covered by four subsequent frames the measuring procedure corresponds to a scan time of twenty minutes for each reflection on a conventional diffractometer equipped with a point detector. The data set comprising 12972 reflections revealed glide violating reflections (Table 3) of type 1 and type 2a,b. However, the glide violations of type 2a,b were slightly weaker than those of type 1.

As example for a typical $P4/n$ vesuvianite, a light apple-green crystal, $0.15 \times 0.08 \times 0.03$ mm^3 in dimension, from the Asbestos mine (Quebec) was reinvestigated. In the original study on a sample from the same locality (Fitzgerald et al. 1986b) possible string disorder was not refined and possible merohedral twinning was not considered. Furthermore, our Asbestos sample is more Fe-rich (Table 1) than that of Fitzgerald et al. (1986b). Cell dimensions on reflections with $\theta > 15°$ were measured with a CAD4 diffractometer (Mo$K\alpha$ X-radiation) applying various crystal orientations. In each case the cell dimensions were clearly non-tetragonal $a = 15.532(2)$, $b = 15.546(2)$, $c = 11.817(2)$ Å with all angles at 90.00(1)°. A sub-

TABLE 1. Electron microprobe analyses of vesuvianites from N'chwaning mine (NC) and Asbestos mine (AS)

	NC1-4	NC1-5	NC1-8	NC1-9	AS-6	AS-9	AS-17	AS-33
SiO_2	36.93	36.71	36.46	36.98	37.84	36.56	36.61	36.64
TiO_2	–	–	–	–	0.60	0.54	0.49	0.00
Al_2O3	20.12	20.05	20.76	20.10	18.79	17.03	17.28	17.67
Cr_2O_3	–	–	–	–	0.04	0.00	0.00	0.02
FeO	0.00	0.00	0.02	0.00	2.30	2.25	2.40	1.74
MnO	1.97	1.88	0.53	1.92	0.48	0.37	0.35	0.40
MgO	0.23	0.24	0.35	0.19	0.98	2.48	2.53	2.61
CuO	0.77	0.69	2.39	0.82	0.06	0.06	0.01	0.05
CaO	35.73	35.53	35.16	35.58	34.95	35.69	35.68	35.94
SrO	0.07	0.01	0.00	0.00	–	–	–	–
BaO	0.00	0.13	0.00	0.03	–	–	–	–
Na_2O	0.63	0.63	0.72	0.62	0.06	0.08	0.05	0.05
K_2O	0.00	0.00	0.00	0.00	0.02	0.02	0.05	0.01
F	0.41	0.18	0.31	0.31	0.00	0.00	0.00	0.00
Cl	0.00	0.00	0.01	0.01	0.10	0.07	0.03	0.03
Si	18.00	18.00	18.00	18.00	18.00	18.00	18.00	18.00
Ti	–	–	–	–	0.214	0.200	0.181	0.00
Al	11.560	11.587	12.079	11.529	10.535	9.882	10.013	10.231
Cr	–	–	–	–	0.015	0.000	0.000	0.008
Fe	0.000	0.000	0.008	0.000	0.913	0.926	0.986	0.715
Mn	0.811	0.781	0.222	0.792	0.191	0.154	0.167	0.166
Mg	0.164	0.175	0.258	0.138	0.629	1.820	1.854	1.911
Cu	0.282	0.256	0.891	0.302	0.020	0.022	0.004	0.019
Ca	18.661	18.660	18.598	18.555	17.817	18.827	18.749	18.917
Sr	0.019	0.003	0.000	0.000	–	–	–	–
Ba	0.000	0.025	0.000	0.006	–	–	–	–
Na	0.596	0.599	0.689	0.585	0.051	0.072	0.048	0.048
K	0.000	0.000	0.000	0.000	0.013	0.011	0.031	0.006
F	0.627	0.279	0.484	0.471	0.000	0.000	0.000	0.000
Cl	0.000	0.000	0.008	0.000	0.077	0.058	0.025	0.025

Notes: Vesuvianite formula calculated on the basis of 18 Si. Ti and Cr in the N'chwaning sample were below detection limit. Sr and Ba in the Asbestos sample were below detection limit.

TABLE 2. CCD data collection and refinement of vesuvianites from N'chwaning (NC) and Asbestos (AS)

Diffractometer	Siemens SMART CCD system
X-ray radiation	sealed tube MoKa
X-ray power	50 kV, 40 mA
Temperature	293 K
Detector to sample distance	5.18 cm
Detector 2θ angle	27°
Resolution	0.77 Å
Rotation axis	ω
Rotation width	0.15° (NC); 0.3° (AS)
Total number of frames	2542 (NC); 1271 (AS)
Frame size	512 × 512 pixels
Data collection time per frame	300 s (NC); 60 s (AS)
Collection mode	hemisphere
Reflections measured	12972 (NC); 15978 (AS)
max. 2θ	56.03; −20 ≤ h ≤ 6, −19 ≤ k ≤ 20, −15 ≤ l ≤ 15 (NC)
	55.61; −20 ≤ h ≤ 14, −17 ≤ k ≤ 19, −15 ≤ l ≤ 15 (AS)
Unique reflections	3156 (NC); 3197 (AS)
Reflections > 2σ(I)	3029 (NC); 2833 (AS)
Space group, cell dimensions	$P4nc$, a = 15.487(2), c = 11.764(2) Å (NC)
	$P4/n$, a = 15.538(2), c = 11.817(2) Å (AS)
R(int)	3.25% (NC); 4.41% (AS)
R(σ)	2.37% (NC); 3.07% (AS)
Number of l.s. parameters	206 (NC); 309 (AS)
GooF	1.750 (NC); 1.148 (AS)
$R1$, $Fo > 4σ(Fo)$	3.44% (NC); 3.11% (AS)
$R1$, all data	3.70% (NC); 4.01% (AS)
$wR2$ (on F^2)	8.31% (NC); 7.14% (AS)

$$R1 = \left(\Sigma\|F_o|-|F_c\|\right)/\left(\Sigma|F_o|\right)$$

$$wR2 = \sqrt{\left[\Sigma\left(F_o^2 - F_c^2\right)^2\right]\Big/\left[\Sigma w\left(F_o^2\right)^2\right]}$$

$$GooF = \sqrt{\left[\Sigma\left(F_o^2 - F_c^2\right)^2\right]\Big/(n - p)}$$

sequent data collection (Table 2) with the SMART system (MoKα X-radiation) did not indicate any intensity distribution (no inconsistent equivalents) different from tetragonal symmetry. Thus tetragonal symmetry with a = 15.538, c = 11.817 Å was assumed for subsequent structure solution and refinement (SHELX-97; Sheldrick 1997). The diffraction pattern (15978 reflections) showed clearly $P4/n$ symmetry (Table 3).

$P4nc$ N'chwaning vesuvianite

The position constrained refinement (165 parameters), described above, yielded lower standard deviations for atomic positions and displacement parameters but converged to an higher $R1$ = 4.94% than the unconstrained $P4nc$ model (302 parameters) with $R1$ = 3.42%. Both refinement models confirmed that string A (Fig. 1) is 85% populated and string B 15%. There was no twinning by the inversion operation. Both models have their individual advantages. The constrained model

TABLE 3. Systematic absence exceptions of X-ray single-crystal reflections of long-range ordered vesuvianites from N'chwaning (space group $P4nc$) and Asbestos mine (space group $P4/n$)

	N'chwaning			Asbestos		
Symmetry type	n— 1	—n— 2a	—c 2b	n— 1	—n— 2a	—c 2b
N	333	422	268	405	664	426
N I>3σ	140	125	68	5	270	177
<I>	1.1	0.7	0.7	0.2	1.5	1.5
<I/σ>	3.0	2.1	2.1	0.9	4.1	4.6

yielded all hydrogen positions. Such detailed information could not be extracted from the unconstrained model. However, the latter refinement type provided information on the $P4nc$ relaxation of the entire structure. As compromise between the position constrained and the unconstrained model, an U_{ij} constrained model has been executed (only displacement parameters of $P4/nnc$ pseudo-symmetric sites are constrained to each other). This model had only 206 parameters, converged at $R1 = 3.44\%$ and provided the same detailed structural information as the unconstrained model. In the final least-square cycles H positions were restrained to have a distance of 0.90(5) Å to the neighboring O site. Populations of string positions were allowed to vary. Tetrahedral sites were refined with isotropic displacement parameters to reduce the number of variables. Previous tests indicated isotropic behavior of Si positions. Corresponding

atomic coordinates, displacement parameters, and interatomic distances are given in Tables 4, 5[1], and 6[1].

In contrast to the analyses of Fitzgerald et al. (1992) and Groat et al. (1992a), the N'chwaning vesuvianite has less than two divalent Y-type cations pfu [$\Sigma(Cu^{2+} + Fe^{2+} + Mn^{2+} + Mg^{2+}) = 1.3$]. For charge balance the crystal has 0.6 Na pfu. Na mainly substitutes for Ca with 0.3 Na pfu located on the Ca1 site. The Y'3b position (population 15%) is occupied by light elements and it seems probable that Na and/or Mg prefer this site.

The square pyramidal Y'3a site (string A), occupied by Mn and Cu, displays a characteristic 4+1 coordination (4 × Y'3a-O6a of 2.002(3) and 1 × Y'3a-O10a of 2.327(8) Å). In contrast Y'3b is more regular (string B) with 4 × Y'3b-O6b of 2.125(4) and 1 × Y'3b-O10b of 2.14(1) Å. This difference may indicate that Y'3a is preferentially occupied by Jahn-Teller ions like Cu^{2+} and Mn^{3+} (Fitzgerald et al. 1986b, Fitzgerald et al. 1992; Hålenius and Annersten 1994) whereas Y'3b is preferred by Na and Mg. The different bonding of O6a and O6b to Y'3a and Y'3b is balanced by variable bond lengths of O6a and O6b to Ca2a, Ca2b, X'4a and X'4b (Table 6). Preferred occupation of string A determines also the favorable orientation of the OH vector at O10. If O10a is part of the square pyramid, the OH group is at O10b and forms a hydrogen bond to O10a (Fig. 1c). The H11a and H11b positions (Fig. 2) are similar to the ones determined by Groat et al. (1996) and Lager et al. (1999) for $P4/nnc$ vesuvianites.

The result indicating 85% string A and 15% string B is slightly simplified. The diffraction pattern of this N'chwaning vesuvianite also revealed significant glide violating reflections of the type 2a,b (Table 3). Thus there are domains (although in minor concentrations) of $P4/n$ symmetry which are neglected in the present model. A subsequent test refinement with a position constrained $P4/n$ model led to a 1:1 merohedral (110) twin with string A 60% occupied and string B 40% converging at $R1 = 7.1\%$. Furthermore, the list of the 50 most disagreeable reflections showed the typical characteristics of a wrong space group assignment. All F_o^2 of mainly weak reflections were larger than F_c^2. An unconstrained $P4/n$ model led to several non-positive definite displacement parameters. These tests clearly suggest that the dominant domain types follow the $P4nc$ string arrangement (Fig. 1).

$P4/n$ Asbestos vesuvianite

All refinements were carried out with an unconstrained model. Populations of string cations were allowed to vary and H positions were restrained to have a distance of 0.90(5) Å to the neighboring O site forming the OH group. Corresponding atomic coordinates, displacement parameters and interatomic distances are given in Tables 7, 8[1], and 9[1]. Merohedral (110) twinning led to a 0.52:0.48 twin ratio. The string sites X'4a (Ca) and Y'3a are 84% occupied (string A in Fig. 1) with X'4b and Y'3b (string B in Fig. 1) hosting the remaining 16%. Twinning

TABLE 4. Positional parameters and B_{eq} values of $P4nc$ vesuvianite from N'chwaning

atom	x/a	y/b	z/c	B_{eq} (Å²)
Si1	½	0	0.0002(2)	0.66(2)*
Si2a	0.56994(8)	0.20863(8)	−0.1293(1)	0.53(1)*
Si2b	−0.70928(8)	0.06815(8)	0.1292(1)	0.53(1)*
Si3a	0.40063(8)	0.33032(8)	−0.6340(1)	0.55(1)*
Si3b	0.33580(8)	0.40100(9)	0.1360(1)	0.55(1)*
Al1	0.2502(1)	0.2482(1)	0.5008(2)	0.61(1)
Al2a	0.36212(9)	0.12802(9)	−0.6263(2)	0.57(1)
Al2b	−0.36191(9)	0.13014(9)	0.1269(2)	0.57(1)
Ca1†	½	0	0.2507(2)	0.80(2)
Ca2a	0.43951(7)	0.20435(7)	0.12082(8)	0.740(8)
Ca2b	−0.43939(6)	0.20737(7)	−0.62028(9)	0.740(8)
Ca3a	−0.56939(7)	0.35056(7)	−0.1111(1)	1.137(8)
Ca3b	0.85241(7)	0.06941(7)	0.1081(1)	1.137(8)
O1a	0.5320(2)	0.0779(2)	0.0860(3)	0.67(2)
O1b	−0.5320	0.0777(2)	−0.5853(3)	0.67(2)
O2a	0.5927(2)	0.1325(2)	−0.2215(4)	0.73(2)
O2b	−0.6336(2)	0.0891(2)	0.2233(3)	0.73(2)
O3a	0.4720(2)	0.2003(2)	−0.0772(3)	0.67(2)
O3b	−0.4705(2)	0.2006(2)	−0.4229(3)	0.67(2)
O4a	0.6884(2)	0.1439(2)	−0.5280(3)	0.64(2)
O4b	−0.6866(2)	0.1422(2)	0.0299(3)	0.64(2)
O5a	−0.4208(2)	0.2368(2)	0.1776(3)	0.75(2)
O5b	0.4187(2)	0.2322(2)	−0.6783(3)	0.75(2)
O6a	0.5222(2)	0.3727(2)	0.0573(3)	1.04(3)
O6b	−0.5209(2)	0.3647(2)	−0.5596(3)	1.04(3)
O7a	0.1938(2)	0.0770(2)	0.1782(3)	1.10(3)
O7b	−0.6939(2)	−0.5776(2)	−0.1785(3)	1.10(3)
O8a	0.6603(2)	0.3110(2)	−0.5663(4)	0.68(2)
O8b	−0.6578(2)	0.3099(2)	0.0664(3)	0.68(2)
O9	0.3953(3)	0.3939(3)	0.2524(3)	0.80(3)
O10b	0	0	0.1336(6)	1.20(4)
H10b	0	0	0.220(4)	2.37*
O10a	0	0	−0.6373(6)	1.20(4)
O11a	0.2553(2)	0.1866(2)	−0.6346(3)	0.64(2)
H11a	0.211(3)	0.191(3)	−0.706(4)	2.37*
O11b	−0.2555(2)	0.1887(2)	0.1376(3)	0.64(2)
H11b	−0.259(3)	0.220(3)	0.201(4)	2.37*
Y'3a‡	½	½	0.0605(1)	0.60(2)
X'4a§	½	½	0.3522(2)	0.97(3)
Y'3b‖	0	0	−0.048(1)	0.39*
X'4b#	½	½	0.148(1)	0.98*

Notes: Anisotropic displacement parameters of sites related by $P4/nnc$ pseudo-symmetry were constrained to each other.
* Starred atoms were refined isotropically.
† 0.88 Ca + 0.12 Na.
‡ 0.852(5) (Mn + Cu).
§ 0.852(5) Ca.
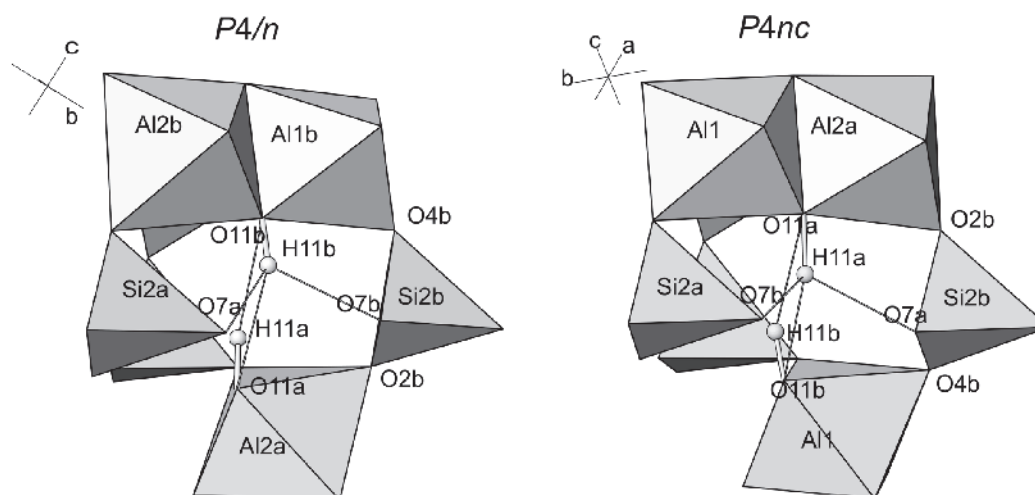‖ 0.148(5) (Mg + Na).
0.148(5) Ca.

FIGURE 2. Hydrogen bonding in low-temperature vesuvianites of space group *P4/n* (Asbestos) and *P4nc* (N'chwaning). In the Asbestos sample H11b has tri-furcated hydrogen bonds to O7a, O7b, and O11a. H11a has its shortest hydrogen bond to O11b. In the N'chwaning sample H11a is trifurcated and H11b is hydrogen bonded to O11a.

and long-range ordering are thus very similar to the Val d'Ala (Piemonte, Italy) sample (Pavese et al. 1998). The fivefold-co-ordinated Y'3a site is occupied by atoms with an average number of 23 electrons (e.g., Fe, Mn, Ti, and minor Mg) leading to 4 × Y'3a-O6a of 1.994(4) Å and 1 × Y'3a-O10a of 1.884(6) Å. *P4/n* relaxation of the structure yields 4 × Y'3b-O6b of 2.148(4) Å and 1 × Y'3b-O10b of 2.14(1) Å. The Ca string site X'4a has 4 × X'4a-O6a of 2.375(4) and 4 × X'4a-O9a of 2.593(3) Å, whereas the low occupied X'4b site has 4 × X4b-O6b of 2.251(7) and 4 × X'4b-O9b of 2.599(7) Å. In *P4/nnc* symmetry a- and b-labeled sites are equivalent and have the same interatomic distances.

It is striking that each of the individual Al2a-Oa distances is significantly longer than the corresponding Al2b-Ob distances leading to an average octahedral Al2a-Oa distance of 1.976 versus 1.935 Å for Al2b-Ob. This may indicate that the slightly larger Mg is preferentially occupying Al2a. A corresponding site preference was found by Giuseppetti and Mazzi (1983) and Pavese et al. (1998). The hydrogen positions forming the OH groups at O11a and O11b (Fig. 2) are similar to the ones determined by Pavese et al. (1998) using more H sensitive neutron diffraction. Acceptors of the weak hydrogen bonds are O7a, O7b, O11a, and O11b. The hydrogen atom close to O10 occurs only as a weak peak in the difference Fourier map at 1/4, 1/4, 1/4 halfway between O10a and O10b. Also this result conforms findings of Pavese et al. (1998) who located two strongly smeared (parallel to *c*) hydrogen positions between O10a and O10b.

The same simplifications concerning the variable string occupation as mentioned above for the *P4nc* N'chwaning vesuvianite also hold for the *P4/n* Asbestos sample. Fitzgerald et al. (1986b) and Allen and Burnham (1992) determined a medium SHG effect for Asbestos vesuvianite. Thus there are definitely acentric structural blocks which may be related to *P4nc* domains. A subsequent test refinement with a position constrained *P4nc* model led to $R1 = 7.7\%$ and to a disordered string arrangement 50% type A and 50% type B (equivalent to *P4/nnc* symmetry). Furthermore, the list of the 50 most disagree-

able reflections showed the typical characteristics of a wrong space group assignment. All F_o^2 of mainly weak reflections were larger than F_c^2. An unconstrained *P4nc* model led to several non-positive definite displacement parameters. These tests clearly suggest that the dominant domain types follow the *P4/n* string arrangement (Fig. 1).

Quality check for vesuvianite structure refinements from diffraction data

Allen and Burnham (1992) showed that the intensity of glide violating reflections of type 2a,b is below 1% with the strongest reflection, 004, normalized to 100%. The intensity of type 1 glide violating reflections (e.g., 290, 470, 160) is even below 0.02%. If a structure of a long-range ordered vesuvianite of true space group *P4nc* is erroneously refined in space group *P4/nnc* a characteristic pattern in the list of the 50 most disagreeable reflections arises: F_o^2 is always larger than F_c^2. This effect is especially pronounced for weak reflections of the type: 147, 013, 057, 143, 077. Notice that the glide violating reflections of type 1 play only a minor role in this list. If a constrained *P4nc* refinement is carried out, where except the string sites all other positions are constrained to their *P4/nnc* pseudo-symmetric counterparts, a different pattern in the list of the most disagreeable reflections arises. Now the glide violating reflections of type 1 (e.g., 470, 290, 7.12.0, 160, 8.11.0, 7.14.0, 450) appear at the top of the list with F_o^2 of low intensity but with $F_c^2 = 0$. The intensity distribution among the most disagreeable reflections show that (a) information on *P4nc* string ordering is contained in weak reflections like 147, 013, 057, etc.; (b) information on the relaxation of the structure to *P4nc* symmetry is mainly contained in the glide violating reflections of type 1.

Another useful test can be performed on the basis of the *K* values grouped into ten categories with ascending $F_c/F_{c(max)}$ where *K* for each group of reflections is defined as $K = \text{mean}(F_o^2)/\text{mean}(F_c^2)$. A wrong model or space group increases the *K* values of the weakest vesuvianite reflections up to a value

TABLE 7. Positional parameters and B_{eq} values of $P4/n$ (origin at $\bar{1}$) vesuvianite from Asbestos

atom	x/a	y/b	z/c	B_{eq} (Å^2)
Si1a	$-\frac{1}{4}$	$\frac{1}{4}$	0	0.53(3)
Si1b	$-\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	0.67(3)
Si2a	−0.0404(1)	0.3187(1)	0.1300(1)	0.55(2)
Si2b	−0.0417(1)	0.1801(1)	0.3727(1)	0.48(3)
Si3a	0.08662(9)	0.3490(1)	−0.1339(1)	0.56(2)
Si3b	0.0804(1)	0.15049(9)	0.6367(1)	0.53(2)
Al1a	0	0	0	0.55(4)
Al1b	$-\frac{1}{2}$	0	$\frac{1}{2}$	0.48(4)
Al2a†	−0.1135(1)	0.1201(1)	0.1254(1)	0.62(3)
Al2b	−0.3887(1)	0.1225(1)	0.3733(1)	0.51(3)
Ca1	$-\frac{1}{4}$	$\frac{1}{4}$	0.2501(1)	0.63(1)
Ca2a	−0.04524(8)	0.18824(8)	−0.11935(8)	0.64(2)
Ca2b	0.19023(8)	−0.04298(8)	0.62120(8)	0.65(2)
Ca3a	0.09914(8)	0.17886(8)	0.12047(8)	1.02(2)
Ca3b	−0.39629(8)	−0.18512(8)	−0.39542(8)	0.98(2)
O1a	−0.2213(2)	0.1723(2)	0.0863(3)	0.61(6)
O1b	−0.2816(2)	0.1724(2)	0.4144(3)	0.70(6)
O2a	−0.1173(3)	0.3386(3)	0.2235(3)	0.62(6)
O2b	−0.1175(3)	0.1581(2)	0.2813(3)	0.79(6)
O3a	−0.0478(2)	0.2216(2)	0.0762(3)	0.66(6)
O3b	−0.0489(2)	0.2775(2)	0.4246(3)	0.68(6)
O4a	−0.0618(2)	0.3936(2)	0.0324(3)	0.66(6)
O4b	−0.0624(2)	0.1062(2)	0.4723(3)	0.66(6)
O5a	−0.0107(2)	0.3274(2)	−0.1768(3)	0.91(6)
O5b	−0.0178(2)	0.1682(2)	0.6801(3)	0.73(6)
O6a	0.1249(2)	0.2720(2)	−0.0570(3)	1.02(6)
O6b	0.1146(2)	0.2284(2)	0.5621(3)	0.96(6)
O7a	0.0559(2)	0.3255(2)	0.1824(3)	0.91(6)
O7b	0.0556(2)	0.1708(2)	0.3266(3)	0.82(6)
O8a	0.0924(2)	0.4389(2)	−0.0647(3)	0.67(7)
O8b	0.0899(2)	0.0609(2)	0.5687(3)	0.76(6)
O9	0.1484(3)	0.3585(3)	−0.2495(3)	0.77(7)
O10a	$\frac{1}{4}$	$\frac{1}{4}$	0.1265(5)	0.92(9)
O10b	$-\frac{1}{4}$	$-\frac{1}{4}$	−0.3579(6)	1.3(1)
O11a	−0.0046(2)	0.0603(2)	0.1361(3)	0.84(6)
H11a	−0.018(3)	0.027(3)	0.203(4)	2.37*
O11b	−0.4954(2)	0.0627(2)	0.3659(3)	0.81(6)
H11b	−0.528(3)	0.054(4)	0.312(4)	2.37*
X'4a‡	$\frac{1}{4}$	$\frac{1}{4}$	0.6507(2)	0.73(3)
Y'3a§	$\frac{1}{4}$	$\frac{1}{4}$	−0.0329(2)	0.69(3)
X'4b#	$\frac{1}{4}$	$\frac{1}{4}$	−0.149(1)	0.79*
X'3b‖	$\frac{1}{4}$	$\frac{1}{4}$	0.5388(8)	0.79*

* Starred atoms were refined isotropically.
† 0.5 Mg + 0.5 Al.
‡ 0.840(7) Ca.
§ 0.840(7) (Fe + Ti + Mn).
#0.160(7) Ca.
‖ 0.160(7) (Fe + Ti + Mn).

of 10. In the refinements of $P4/n$ Asbestos and $P4nc$ N'chwaning vesuvianites this K value of the weakest reflection was close to 2. Considering the possibility of other minor string arrangements and taking into account that the CCD data were not corrected for $\lambda/2$ diffraction (no energy dispersion of the detector) this result must be rated good.

The fact that long-range ordered $P4nc$ vesuvianites and long-range disordered $P4/nnc$ vesuvianites may exhibit the same diffraction symmetry could initiate speculations that many vesuvianites refined in space group $P4/nnc$ are actually long-range ordered and that the wrong space group was selected. However, such speculations can be ruled out. Allen and Burnham (1992) have demonstrated that high-temperature vesuvianites lack any indication of acentricity thus the choice of the centric space group ($P4/nnc$) is correct. Valley at al. (1985) intentionally refined a low-temperature vesuvianite in the long-range disordered space group $P4/nnc$ and yielded an R value of 10%, which is similar to the high R value of 8%

obtained for the N'chwaning vesuvianite if refined with $P4/nnc$ symmetry.

For low-temperature vesuvianites, type 1 glide violating reflections are between one and two orders of magnitude weaker than those of type 2a,b. Thus, even if the diffraction symmetry of a low-temperature vesuvianite clearly suggests $P4/n$ symmetry, $P4nc$ might still be the more appropriate model.

REFERENCES CITED

Allen, F.M. and Burnham, C.W. (1992) A comprehensive structure-model for vesuvianite: Symmetry variations and crystal growth. Canadian Mineralogist, 30, 1–18.

Arem, J.E. and Burnham, C.W. (1969) Structural variations in idocrase. American Mineralogist, 54, 1546–1550.

Fitzgerald, S., Rheingold, A.L., and Leavens, P.B. (1986a) Crystal structure of a Cu-bearing vesuvianite. American Mineralogist, 71, 1011–1014.

——(1986b) Crystal structure of a non-P4/nnc vesuvianite from Asbestos, Quebec. American Mineralogist, 71, 1483–1488.

Fitzgerald, S., Leavens, P.B., Rheingold, A.L., and Nelen, J.A. (1987) Crystal structure of a REE-bearing vesuvianite from San Benito County, California. American Mineralogist, 72, 625–628.

Fitzgerald, S., Leavens, P.B., and Nelen, J.A. (1992) Chemical variation of vesuvianite. Mineralogy and Petrology, 46, 163–178.

Flack, H.D. (1983) On enantiomorph-polarity estimation. Acta Crystallographica, A39, 876–881.

Giuseppetti, G. and Mazzi, F. (1983) The crystal structure of a vesuvianite with P4/n symmetry. Tschermaks Mineralogische und Petrographische Mitteilungen, 31, 277–288.

Groat, L.A., Hawthorne, F.C., and Ercit, T.S. (1992a) The chemistry of vesuvianite. Canadian Mineralogist, 30, 19–48.

——(1992b) The role of fluorine in vesuvianite: A crystal-structure study. Canadian Mineralogist, 30, 1065–1075.

Groat, L.A., Hawthorne, F.C., Ercit, T.S., and Putnis, A. (1993) The symmetry of vesuvianite. Canadian Mineralogist, 31, 617–635.

Groat, L.A., Hawthorne, F.C., and Ercit, T.S. (1994a) Excess Y-group cations in the crystal structure of vesuvianite. Canadian Mineralogist, 32, 497–504.

——(1994b) The incorporation of boron into the vesuvianite structure. Canadian Mineralogist, 32, 505–523.

Groat, L.A., Hawthorne, F.C., Rossman, G.R., and Ercit, T.S. (1995) The infrared spectroscopy of vesuvianite in the OH region. Canadian Mineralogist, 33, 609–626.

Groat, L.A., Hawthorne, F.C., Lager, G.A., Schultz, A.J., and Ercit, T.S. (1996) X-ray and neutron crystal structure refinements of a boron-bearing vesuvianite. Canadian Mineralogist, 34, 1059–1070.

Groat, L.A., Hawthorne, F.C. Ercit, T.S., and Grice, J.D. (1998) Wiluite, $Ca_{19}(Al,Mg,Fe,Ti)_{13}(B,Al)_5Si_{18}O_{68}(O,OH)_{10}$, a new mineral species isostructural with vesuvianite, from the Sakha Republic, Russian Federation. Canadian Mineralogist, 36, 1301–1304.

Hålenius, U. and Annersten, H. (1994). Five-coordinated trivalent manganese in vesuvianite: A spectroscopic study. International Mineralogical Association, 16th General Meeting, Pisa, Italy, 162–163.

International Tables for X-ray Crystallography (1983) Space-Group Symmetry, Vol. A, In T. Hahn, Ed., International Union of Crystallography, 854 p. Reidel, Dordrecht, Holland.

Lager, G.A., Xie, Q., Ross, F.K., Rossman, G.R., Armbruster, Th., Rotella, F.J., and Schultz, A.J. (1999) Hydrogen-atom positions in P4/nnc vesuvianite. Canadian Mineralogist, in press.

Ohkawa, M., Yoshiasa, A., and Takeno, S. (1992) Crystal chemistry of vesuvianite: Site preferences of square-pyramidal coordinated sites. American Mineralogist, 77, 945–953.

Pavese, A., Prencipe, M., Tribaudino, M., and Aagaard, St.S. (1998) X-ray and neutron single-crystal study of P4/n vesuvianite. Canadian Mineralogist, 36, 1029–1037.

Sheldrick, G.M. (1997) SHELX-97, program for crystal structure determination, University of Göttingen, Germany.

Valley, J.W., Peacor, D.R., Bowman, J.R., Essene, E.J., and Allard, M.J. (1985) Crystal chemistry of a Mg-vesuvianite and implications of phase equilibria in the system CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2. Journal of Metamorphic Geology, 3, 137–153.

Veblen, D.R. and Wiechmann, M.J. (1991) Domain structure of low-symmetry vesuvianite from Crestmore, California. American Mineralogist, 76, 397–404.

Yoshiasa, A. and Matsumoto, T. (1986) The crystal structure of vesuvianite from Nakatatsu mine: reinvestigation of the cation site-populations and of the hydroxyl groups. Mineralogical Journal, 13, 1–12.