The crystal structure of ganomalite, $Pb_9Ca_{5.44}Mn_{0.56}Si_9O_{33}$

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Abstract. A redetermination of the crystal structure of ganomalite, with composition $Pb_9Ca_{5.44(1)}Mn_{0.56(1)}Si_9O_{33}$, using new single crystal X-ray diffraction data is reported. Hexagonal space group symmetry $P\bar{6}$, with $Z = 1$ and unit cell parameters $a = 9.8456(3)$ Å and $c = 10.1438(4)$ Å. The refinement of a structural model based on the $Pb_5Ge_3O_{11}$ structure, with a partially occupied manganese position, resulted in an R-value of 0.031. The arrangement of the SiO_4 tetrahedra in ganomalite is an intermediate between the nasonite and pyromorphite structure, and the structure can be described as containing "lead tunnels" based on Pb_9O_{21} units extending through the structure.

Introduction

Ganomalite, from Greek *γανωμα* ("brilliance", in allusion to its high lustre), was first described by Nordenskiöld [1, 2] from Långban, Filipstad, Sweden. It was for a long time erroneously considered as the hydroxyl analogue of nasonite, $Pb_6Ca_4Si_6O_{21}Cl_2$. Ganomalite has subsequently been redefined as $Pb_9Ca_5MnSi_9O_{33}$ by Dunn et al. [3], who obtained new chemical data on materials from Jakobsberg, Filipstad and from Franklin, New Jersey. A preliminary crystal structure analysis was also undertaken by them, indicating hexagonal symmetry for the mineral, space group $P\bar{6}$ or possibly $P3$, with unit cell parameters $a = 9.82(5)$ Å, $c = 10.13(5)$ Å and $Z = 1$. Because of experimental problems no relevant structural details as interatomic bond distances were reported. In the present study a structure model based on new single crystal X-ray diffraction data is given.

Experimental

Crystal fragments were isolated from a matrix specimen originating from Jakobsberg (Swedish Museum of Natural History cat. no. 333052), in which the mineral occurs associated with calcite, phlogopite, native copper and nasonite. An energy dispersive microanalysis of this ganomalite showed 36.8 Pb, 24.6 Ca, 1.7 Mn and 36.9 Si (all in mol.%), suggesting a sample deficient in Mn but otherwise in reasonable agreement (metal composition $Pb_9Ca_{6.02}Mn_{0.41}Si_{0.02}$) with the expected composition $Pb_9Ca_5MnSi_9O_{33}$. The unusually low manganese content, and the fact that Charalamptides [4] prepared synthetic ganomalite in the pure Pb–Ca–Si–O system, indicate that manganese may in fact not be an essential component of the mineral. From the specimen, a white transparent single crystal with approximative trigonal prismatic shape was selected and investigated by conventional single crystal X-ray diffractometry techniques. The unit cell dimensions (cf. Table 1) and the $6/m$ Laue symmetry observed, were similar to those published by Dunn et al. [3] for the mineral. Single crystal X-ray diffraction data were collected on a Philips PW1100 diffractometer. The diffraction data were corrected for background, Lorentz, polarisation and absorption effects [5]. The cell parameters, $a = 9.8456(3)$ Å and $c = 10.1438(4)$ Å, were determined by least squares fitting of the setting angles of eleven accurately centred reflections distributed randomly in reciprocal space ($\theta < 21°$). Further experimental conditions are listed in Table 1.

The initial model for the least squares refinement of the structural parameters was that of the study by Newnham, Wolfe and Darlington [6] on the structure of $Pb_5Ge_3O_{11}$ which is isostructural to ganomalite. Intensity statistics including cumulative [7] distributions of intensities using the program ENORM [8] suggest a non-centric electron distribution in the unit cell. The average of the derived estimated normalised structure factor amplitudes became 0.840, which is in between the value 0.886 expected for a

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Table 1. Experimental details of the structure determination of ganomalite.

Formula	$Pb_9Ca_{5.44(12)}Mn_{0.56(12)}Si_9O_{33}$
Formula weight	2894.34
Space group; Z	$P\bar{6}$ (no. 174); 1
Unit cell dimensions, $T = 293$ K	$a = 9.8456(3)$ Å and $c = 10.1438(4)$ Å
Unit cell volume, V	$851.56(4)$ Å^3
Density (calcd.), D_x	5.657 g $\cdot$ cm^3
Radiation; λ	MoK_α; 0.71073 Å
Crystal shape	Trigonal prism
Crystal size	$0.10 \times 0.10 \times 0.05$ mm^3
Diffractometer	Philips PW1100
Intensity data collection:	$\omega/2\theta$ scan
Maximum sin $(\theta)/\lambda$	0.70 Å^{-1}
Range of h, k and l	$-12 \le h \le 12$, $-11 \le k \le 11$ and $-14 \le l \le 14$
Internal R	0.037
Collected reflections	8088
Unique reflections	952
Observed reflections	830
Criterion for significance	$I \ge 3 \cdot \sigma(I)$
Absorption correction:	Numerical integration
Linear absorption coefficient	457.5 cm^{-1}
Transmission factor range	0.095–0.292
Structure refinement:	Full-matrix least squares
Minimised function	$\Sigma w \cdot (\Delta F)^2$
Anisotropic thermal parameters for	Lead and calcium
Number of refined parameters	58
Weighting scheme	$(\sigma_F^2 + 0.0005 \cdot F^2)^{-1}$
R for observed reflections	0.031
wR for observed reflections	0.038
Max. of $\lvert\Delta\rvert/\sigma$	<0.001
Max. and min. of $\Delta\varrho$	2.9 e $\cdot$ Å^{-3} and -3.2 e $\cdot$ Å^{-3}

non-centric distribution and 0.798 for a centric distribution. For a compound with such a high lead content as the present one the intensity distribution might be expected to give a value less than the normal non-centric value. The possible space groups consistent with the observations would thus be $P\bar{6}$ or $P3$.

The chosen initial structure model was refined with the space group symmetry $P\bar{6}$, with the silicon and oxygen atoms vibrating isotropic and only the heavier atoms (Pb, Ca and Mn) anisotropic. The refinement converged smoothly and gave a satisfactory R-value of 0.032 for the 58 parameters used. In view of the chemical composition, $Pb_9Ca_{6.02}Mn_{0.41}Si_{9.02}$, obtained by the microanalysis, a simple substitutional disorder model for the manganese position was included in the refinement to reduce the manganese content of the refined model ($Pb_9Ca_5MnSi_9$). Thus, manganese and one calcium were allowed to occupy the same position, i.e. a compositional parameter was assigned to this position. To avoid severe correlation problems, the thermal vibrations of this position was also kept isotropic.

The final R-value decreased slightly to 0.031 ($wR = 0.038$) and the metal composition calculated from the model became $Pb_9Ca_{5.44(12)}Mn_{0.56(12)}Si_9$, in reasonable agreement with the analysis ($Pb_9Ca_{6.02}Mn_{0.41}Si_{9.02}$). When allowing all atoms but those at the mixed (Mn, Ca) positions to vibrate anisotropically, several of the thermal parameters of the lighter atoms became non-positive definite. It is therefore likely that the diffraction data do not contain enough information to allow refinement of a model with a more extented vibrational description.

Previously, Dunn et al. [3] refined the structure model of ganomalite with space group symmetry $P\bar{6}$, but encountered problems with several physically non-realistic thermal parameters (cf. above). The authors suggested that this was a strong indication that the space group symmetry ought to be lowered from $P\bar{6}$ to $P3$ symmetry. The lower symmetry has previously been assigned by Kay et al. [9] and Iwata et al. [10] for the related $Pb_5Ge_3O_{11}$ structure. However, when lowering the symmetry of the present model to $P3$, the refinements gave no improvement of the R values ($R = 0.036$ and $wR = 0.045$) despite the increased number of parameters (from 58 to 101). Thus, it can be concluded that the diffraction data does not contain any information that supports a deviation from the higher space group symmetry $P\bar{6}$.

Further details on the final least squares refinement and the obtained atomic coordinates are given in Tables 1 and 2. Selected bond distances and bond angles are listed in Tables 3 and 4. The atomic scattering factors used, were those for neutral atoms as given in the International Tables for X-ray Crystallography [11]. The SHELXTL PC^{TM} [12] and the PLATON [13] program packages were used for the crystallographic calculations and the program ATOMS [14] for the structure packing diagrams.

Table 2. Fractional atomic coordinates and isotropic thermal parameters (Å^2) with esd's for the ganomalite structure. The atomic position labelled Mn is substitutionally disordered and contains 56(1)% Mn and 44(1)% Ca. The equivalent isotropic thermal parameters of the anisotropically refined atoms, were estimated as $1/3 \cdot \mathrm{trace}(\mathbf{U})$.

Site symmetry	Atom	x	y	z	U_{eq}
1	Pb(1)	0.26780(9)	0.26951(9)	0.17827(6)	0.0132(4)
m . .	Pb(2)	0.98852(14)	0.25428(13)	1/2	0.0176(5)
$\bar{6}$ . .	Mn	2/3	1/3	0	0.011(3)
3 . .	Ca(1)	1/3	2/3	0.3367(6)	0.010(18)
$\bar{6}$ . .	Ca(2)	1/3	2/3	0	0.009(3)
3 . .	Ca(3)	2/3	1/3	0.3229(6)	0.0095(19)
$\bar{6}$ . .	Ca(4)	2/3	1/3	0	0.011(3)
m . .	Si(1)	0.4090(8)	0.3850(8)	1/2	0.0035(14)
1	Si(2)	0.0232(7)	0.4068(7)	0.1486(7)	0.0076(10)
1	O(1)	0.5129(18)	0.1558(18)	0.1514(12)	0.019(3)
m . .	O(2)	0.0745(18)	0.3751(19)	0	0.007(4)
1	O(3)	0.1342(15)	0.5973(18)	0.1655(12)	0.012(3)
m . .	O(4)	0.1540(23)	0.6566(27)	1/2	0.024(5)
1	O(5)	0.3508(16)	0.2658(16)	0.3763(14)	0.013(3)
1	O(6)	0.0779(14)	0.3191(15)	0.2546(12)	0.016(3)
m . .	O(7)	0.5987(26)	0.4749(23)	1/2	0.017(5)

Table 3. Distances (<3.5 Å) in the ganomalite structure. Bond valence sums, bvs, are given for the metal atoms using the Brown-Altermatt parameters [17].

Bonds	Multiplicity	Distance (Å)	Bvs
Pb(1)–O(5)	1	2.176(15)	2.3
O(3)	1	2.284(17)	
O(6)	1	2.290(16)	
O(1)	1	3.139(19)	
O(2)	1	3.154(19)	
O(1)	1	3.22(3)	
O(6)	1	3.386(14)	
Pb(2)–O(7)	1	2.22(2)	2.0
O(5)	2	2.539(14)	
O(6)	2	2.611(12)	
O(4)	1	3.09(3)	
O(4)	1	3.45(4)	
Mn–O(1)	2	2.249(14)	1.7
O(1)	2	2.249(18)	
O(1)	2	2.250(19)	
Ca(1)–O(4)	1	2.39(4)	1.9
O(4)	2	2.39(3)	
O(3)	1	2.446(18)	
O(3)	1	2.447(13)	
O(3)	1	2.45(2)	
O(6)	1	3.18(2)	
O(6)	1	3.182(17)	
O(6)	1	3.183(17)	
Ca(2)–O(3)	2	2.406(13)	2.2
O(3)	1	2.406(16)	
O(3)	1	2.406(18)	
O(3)	2	2.41(2)	
O(2)	1	2.72(2)	
O(2)	1	2.72(3)	
O(2)	1	2.73(3)	
Ca(3)–O(1)	1	2.393(15)	1.8
O(1)	1	2.393(18)	
O(1)	1	2.393(19)	
O(7)	1	2.558(19)	
O(7)	1	2.559(19)	
O(7)	1	2.56(2)	
O(5)	1	2.888(15)	
O(5)	1	2.888(17)	
O(5)	1	2.888(18)	
Si(1)–O(4)	1	1.53(4)	4.3
O(5)	2	1.615(15)	
O(7)	1	1.62(3)	
Si(2)–O(1)	1	1.576(17)	4.0
O(6)	1	1.631(19)	
O(3)	1	1.64(2)	
O(2)	1	1.667(13)	

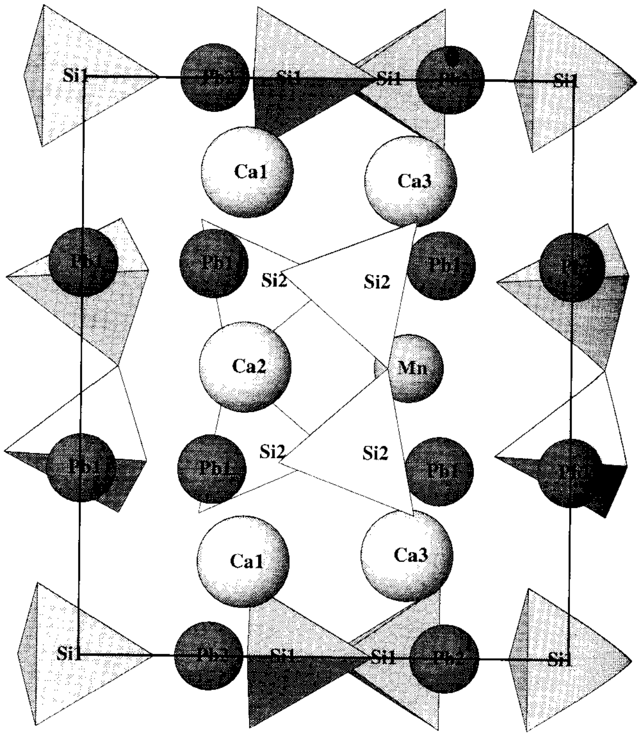

Fig. 1. The arrangement of the SiO_4 and Si_2O_7 units viewed along [010]. The lead atoms are shown as dark spheres, manganese as small light spheres and calcium atoms as big light spheres. The labels of the metal atomic positions are indicated.

Discussion

The structural model obtained in the present study is in general agreement with that obtained by Dunn, et al. [3]. Thus, the structure is composed of both isolated SiO_4 tetrahedra and linked tetrahedra of Si_2O_7 units, similar to the arrangements of the GeO_4 and Ge_2O_7 units in the $Pb_5Ge_3O_{11}$ structure. Fig. 1 shows the arrangement of the SiO_4 and Si_2O_7 units viewed along the *b*-axis. As previously shown by Engel [15], this arrangement of the SiO_4 tetrahedra is an intermediate between that found in nasonite und pyromorphite.

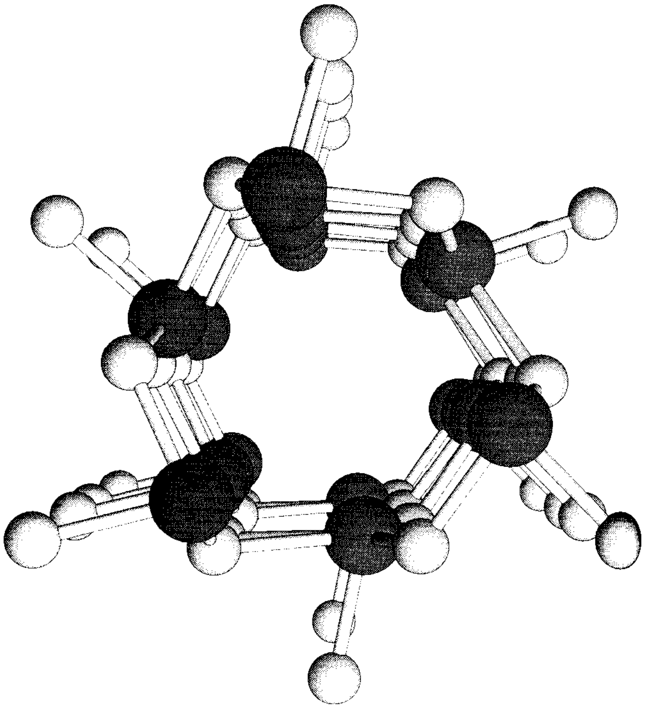

Fig. 2. 'Lead tunnel' through a section of the structure viewed along [001]. Lead atoms are shown as dark spheres and oxygen atoms as light ones.

Fig. 2 shows a section of the structure viewed along the [001] direction, in which lead atoms are arranged so that tunnels are formed through the structure. In Fig. 3 one can see a part of a 'lead tunnel' formed by Pb_9O_{21} units, extending through the structure in the [001] direction. Due to the site symmetry *m* . . for Pb(2), the number of Pb(2) atoms in the [001] directions is half of that of Pb(1) (site symmetry 1). Considering only distances less than 2.3 Å, Pb(1) is coordinated by three oxygen atoms in a triangular pyramid fashion, with the shortest bonding distance of

Table 4. Bond angles (°) in the ganomalite structure. The symmetry codes are:
a, b, k: $x, y, -z$; c, d, m: $-y, x-y, z$; e, f, n: $-y, x-y, -z$; h: $-x+y, -x, z$; i: $-x+y, -x, -z$

Atoms	Multiplicity	Angle
O(5)–Pb(1)–O(3^{h})	1	93.7(5)
O(6^{c})	1	92.6(6)
O(3^{h})–Pb(1)–O(6^{c})	1	80.9(9)
O(5)–Pb(2)–O(7^{d})	2	77.2(7)
O(6)	2	77.9(4)
O(6^{b})	2	137.1(4)
O(5^{b})	1	59.42(5)
O(6)–Pb(2)–O(7^{d})	2	93.4(5)
O(6^{b})	1	144.9(4)
O(1)–Mn–O(1^{d})	2	78.5(7)
O(1^{h})	2	78.5(6)
O(1^{a})	1	86.1(5)
O(1^{d})–Mn–O(1^{h})	2	78.5(9)
O(1^{e})	1	86.1(7)
O(1^{h})–Mn–O(1^{i})	1	86.1(6)
O(4)–Ca(1)–O(4^{m})	2	77.2(11)
O(6^{h})	1	88.2(9)
O(6^{c})	1	73.5(8)
O(6^{k})	1	149.5(7)
O(3^{h})	1	90.4(7)
O(4^{m})–Ca(1)–O(4^{n})	1	77.2(12)
O(3^{c})–Ca(1)–O(3^{h})	1	75.2(8)
O(3^{k})	1	75.2(7)
O(3^{h})–Ca(1)–O(3^{k})	1	75.2(5)
O(6^{c})	1	62.0
O(6^{h})	1	54.6(7)
O(6^{k})	1	119.5(5)
O(6^{h})–Ca(1)–O(6^{c})	2	113.4(4)
O(3^{c})–Ca(2)–O(3^{h})	2	76.7(8)
O(3^{k})	1	76.7(7)
O(3^{n})	1	88.5(6)
O(2^{c})	1	60.0(6)
O(2^{k})	1	78.9(7)
O(2^{h})	1	133.9(4)
O(3^{h})–Ca(2)–O(3^{k})	2	76.7(5)
O(3^{m})–Ca(2)–O(3^{n})	1	76.7(6)
O(2^{k})	1	60.0(5)
O(2^{h})	1	78.8(6)
O(2^{c})–Ca(2)–O(2^{h})	2	119.9(7)
O(1)–Ca(3)–O(1^{d})	1	73.0(7)
O(1^{h})	1	73.0(5)
O(7^{d})	1	91.8(5)
O(5)	1	75.7(5)
O(5^{d})	1	81.2(5)
O(1^{d})–Ca(3)–O(1^{h})	1	73.0(8)
O(7)–Ca(3)–O(7^{d})	1	76.1(6)
O(7^{h})	1	76.1(8)
O(5)	1	56.6(7)
O(5^{h})	1	65.9(6)
O(5)–Ca(3)–O(5^{d})	3	116.6(5)
O(7)–Si(1)–O(5)	2	106.9(8)
O(4)	1	113.3(15)
O(3)–Si(2)–O(1)	1	110.8(11)
O(6)	1	109.2(8)
O(2)	1	102.4(10)

2.18 Å for Pb(1)–O(5). Pb(2) has five Pb–O bonds (within 2.6 Å) in a pentagonal pyramid coordination. Notably here is also one short Pb(2)–O(7) distance 2.22 Å. When including Pb–O distances up to 3.5 Å, both of the symmetry independent lead atoms, Pb(1) and Pb(2), become seven-coordinated. Figure 2 indicates that the lead atomic positions are moved from the coordination centroid towards the O(3), O(5), O(6) and O(7) atoms. This type of displacement of the lead atom, away from the lone pair electrons, is apparently due to the well-known stereoactive lone-pair effect of divalent lead (see e.g. Hyde and Andersson [16] and Moore et al. [17]). From Figs. 2 and 3 it can be seen that Pb(2) has its lone pair regions directed into the 'lead tunnels', while Pb(1) has its lone pairs directed toward a neighbouring Pb_9O_{21} unit. In between the Pb_9O_{21} units one oxygen atom (O(2)) is bonded to Pb(1) of adjacent units at a distance of 3.154 Å, thus connecting the Pb_9O_{21} units in the [001] direction. The shortest Pb–Pb distance in the ganomalite structure is 3.6167(9) Å.

The manganese atoms are coordinated by six oxygen atoms at an average distance of 2.249 Å, forming distorted trigonal prisms. The calcium atoms can also be considered to be coordinated by six oxygen atoms in trigonal prisms with an average Ca–O distance of 2.39 Å. The trigonal prisms of the calcium and manganese coordination polyhedra share faces and thus forms strings extending in the [001]

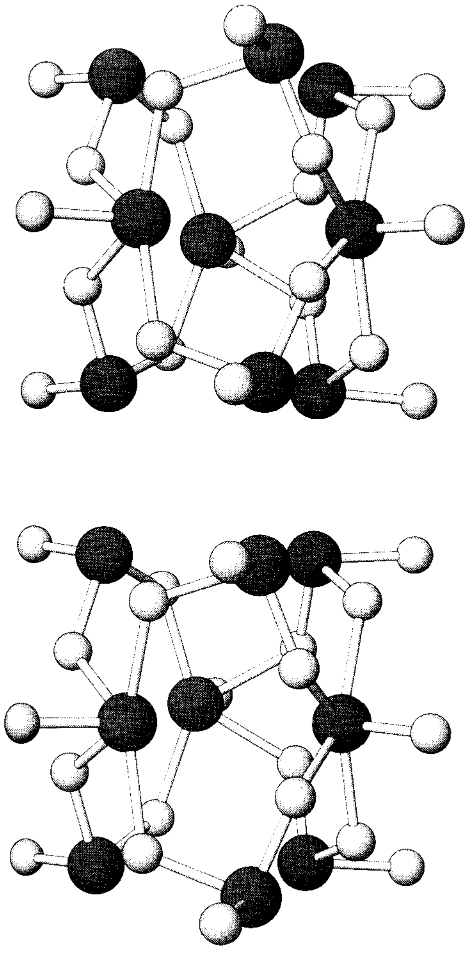

Fig. 3. Part of 'lead tunnel' in the structure, showing the Pb_9O_{21} units, viewed perpendicular to [001]. Lead atoms are shown as dark spheres and oxygen atoms as light ones.

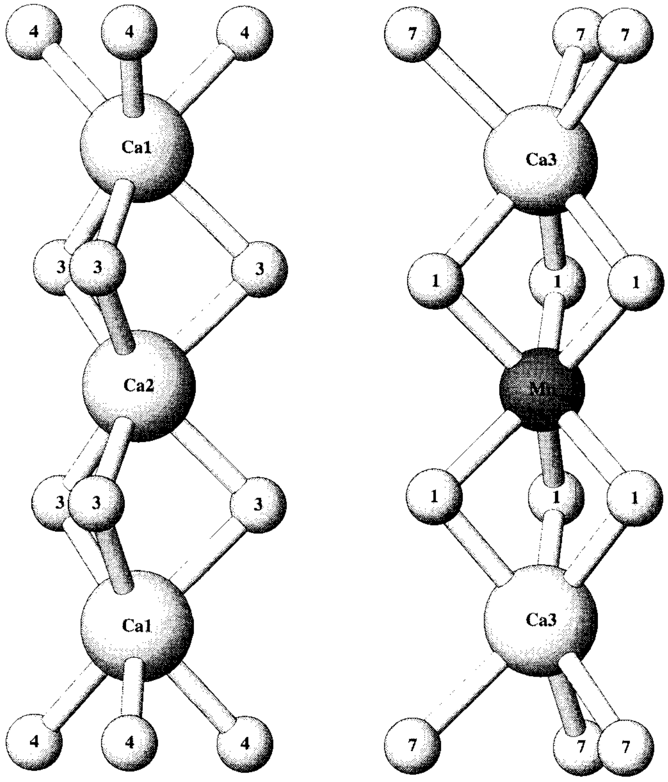

Fig. 4. Two manganese and calcium strings in the structure viewed along the [110] direction. Calcium atoms are drawn as light spheres, manganese atoms as dark spheres and oxygen atoms as small light spheres. Labels of the unique calcium, manganese and oxygen positions are indicated.

direction of the structure. Fig. 4 shows two manganese and calcium strings in the structure viewed along [110] direction. Along the strings, the substitutionally disordered Mn/Ca positions ($z = 0$) and the Ca(3) positions ($z \approx 0.32$) are stacked with the sequence ...MnCa(3)Ca(3).... By including Ca–O bonds distances up to 3.18 Å, the obtained oxygen nine-coordination polyhedron can be described as capped square anti-prisms.

Estimates of empirical bond valence sums (see Table 3) calculated with the Brown-Altermatt parameters [18] are consistent with the expected values 2, 2, 2 and 4 for lead, manganese, calcium and silicon atoms. For the oxygen atoms the bond valence sums are in the range 1.7 to 2.2.

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