The Synthesis and Crystal Structure of $CaCu_3Mn_4O_{12}$: A New Ferromagnetic–Perovskite-like Compound

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Single crystals of $CaCu_3Mn_4O_{12}$, a new ferromagnetic perovskite-like compound ($T_c \simeq 160°C$), have been synthesized at 50 kbar and 1000°C. By X-ray analysis it was found to be cubic ($a = 7.241$ Å), space group $Im3$ with two molecules per unit cell. The two Ca^{2+} and six Cu^{2+} cations occupy the A sites of the ideal perovskite structure, while the eight Mn^{4+} cations occupy the B sites. In the $Im3$ space group the sites occupied by the calcium and copper cations have different point symmetry and therefore the 12-oxygen polyhedra have different distortions. The Ca cations are surrounded by slightly distorted icosahedra, the Ca–O distance is 2.562 Å. The twelve oxygens around the copper cations are arranged as three mutually perpendicular rectangles of different size, the smallest and the largest of which are almost squares. The three sets of Cu–O distances are 1.942, 2.707, and 3.181 Å, respectively. The octahedral Mn–O distance is 1.915 Å. This arrangement is similar to that found in $NaMn_3Mn_4O_{12}$. A comparison between the two structures and a discussion of their thermal data are given.

Introduction

In a previous paper we reported the synthesis and crystal structure of $[NaMn_3^{3+}](Mn_2^{3+}Mn_2^{4+})O_{12}$ (*1*). This compound is cubic ($a = 7.308$ Å),[1] space group $Im3$ with two molecules per unit cell, and it has a perovskite-like arrangement. The cations between brackets and those between parentheses occupy the A and B sites of the ideal perovskite structure. As a consequence of the complete order among the cations occupying the A sites and of the distortion of the oxygen lattice, the cell parameter of $NaMn_3Mn_4O_{12}$ is twice that of the cubic ideal perovskite. In the ordered structure the two sodium cations, having $m3$ point symmetry, are surrounded by 12 equidistant oxygen ions arranged as three equal rectangles perpendicular to each other. These three rectangles form a slightly distorted icosahedron. In the ideal perovskite the 12 equidistant oxygen ions around the A cations are arranged as three equal squares. The point symmetry of the Mn^{3+} cations occupying the other six A sites, is mmm, and the 12-oxygen polyhedron is formed by three unequal rectangles, the smallest and the largest of which are nearly square. The three sets of Mn^{3+}–O distances of these sites are 1.909, 2.688, and 3.256 Å, respectively. It is difficult to determine the cation coordination number when the cation–oxygen distances vary over such large range. Nevertheless, it is clear

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[1] This new value has been obtained by using KCl as an interval standard.

that the four oxygens at 3.256 Å are second-nearest neighbors and therefore the coordination number should be taken as $4 + 4$. This arrangement is a new Jahn–Teller configuration for the Mn^{3+} cations. Usually, in oxide compounds these cations have a $4 + 2$ coordination (an apically elongated octahedron). In $NaMn_3Mn_4O_{12}$ they assume a higher Jahn–Teller coordination because the synthesis is done under high pressure.

The Mn^{3+} and Mn^{4+} cations occupying the B sites are surrounded by slightly distorted oxygen octahedra. At room temperature these cations are completely disordered. Recent X-ray powder data taken at lower temperatures indicate that at ~180 K $NaMn_3Mn_4O_{12}$ undergoes a crystallographic phase transition. The symmetry lowers from cubic to monoclinic, which seems to be the result of an ordering taking place over the B sites between the Mn^{3+} and the Mn^{4+} cations (2).

Recently, we reported the synthesis of the CMn_7O_{12} compounds (C = Ca, Cd, Sr, La, and Nd) (3). All the structures of these compounds can be derived from that of $NaMn_3Mn_4O_{12}$. The symmetry lowers to trigonal if C is a divalent cation, whereas it becomes monoclinic if C is a trivalent one. The lower symmetry is due to a cooperative Jahn–Teller effect which takes place on the B sites because of the increasing amount of Mn^{3+} cations compensating the higher charge of the C cations.

This structure type can be stabilized with many other cations. In general, one needs a relatively large cation, a Jahn–Teller one, and a relatively small cation. This paper reports the synthesis and crystal structure of a new member of this series: $[CaCu_3^{2+}](Mn_4^{4+})O_{12}$. This compound has been found to be a cubic ferromagnet ($T_c \simeq 160°C$), and it can be considered the prototype of a new series of cubic ferromagnetic oxide compounds. The magnetic properties of several members of this series—Curie temperatures, saturation curves as a function of temperature, hysteresis loops, ferromagnetic resonance, and magnetic structures investigated by neutron diffraction—will be published later.

Experimental

The apparatus and the procedure of the high-pressure experiments have been des-

TABLE I

POWDER DATA[a]

	CaCu₃Mn₄O₁₂			NaMn₃Mn₄O₁₂		
$h\ k\ l$	I_{obsd}	d_{obsd}	d_{calcd}	I_{obsd}	d_{obsd}	d_{calcd}
1 1 0	w	5.122	5.120	M	5.166	5.168
2 0 0	vw	3.620	3.621	w	3.652	3.654
2 1 1[b]	M	2.956	2.956	M	2.983	2.984
2 2 0[b]	VS	2.559	2.559	VS	2.586	2.584
3 1 0[b]	M	2.288	2.289	S	2.311	2.311
2 2 2[b]	M	2.090	2.090	w	2.110	2.110
3 2 1[b]	M	1.9358	1.9351	M	1.953	1.953
4 0 0[b]	S	1.8095	1.8102	S	1.827	1.827
4 1 1 } 3 3 0 }	vw	1.7075	1.7067	vw	1.723	1.723
4 2 0	—		1.6191	—		1.634
3 3 2	vw	1.5434	1.5438	vw	1.558	1.558
4 2 2[b]	VS	1.4785	1.4781	vw	1.492	1.492

[a] vw, very weak; w, weak; M, medium; S, strong; VS, very strong.
[b] Reflections used for the least-squares refinements.

cribed elsewhere (4). The samples were prepared by thoroughly mixing Ca(OH)$_2$, 3CuO, and 4MnO$_2$. These mixtures were subjected to 50 kbar and 1000°C for 1 hr. The quenched materials consisted of well-crystallized black powders which contained small brilliant single crystals. X-ray powder photographs of these samples proved that a new compound had been synthesized. All the lines of the diffraction pattern were indexed on an I-cubic cell. From the similarity between the powder data shown in Table I and those of NaMn$_7$O$_{12}$ it was deduced that the newly synthesized compound could possibly be CaCu$_3$Mn$_4$O$_{12}$. This formula was confirmed later by single-crystal X-ray analysis. Powder photographs showed that the final products consisted mainly of CaCu$_3$Mn$_4$O$_{12}$ with traces of CuMn$_2$O$_4$ (spinel) and CuO. Pure CaCu$_3$Mn$_4$O$_{12}$ was obtained by making the synthesis in the presence of KClO$_3$, which prevents the partial reduction of Mn^{4+} to Mn^{3+}. The crystals are small but have well-developed {100} faces. On the average, these cubes have a 0.15-mm edge. Precession photographs confirmed that the crystals were single and isostructural with NaMn$_3$Mn$_4$O$_{12}$.

A Guinier powder photograph taken with monochromatic FeKα radiation and KCl as an internal standard was used to determine the powder data reported in Table I. The lattice parameter, 7.241 ± 0.001 Å, was ob-

tained by least-squares refinement on the seven strongest reflections. Exactly the same value was obtained from the single crystal mounted on the automatic diffractometer for the intensity data collection. The least-squares refinement was applied on 12 reflections chosen in the region where a complete α_1/α_2 separation occurred. The zero of the ω circle was obtained by measuring the ω and $-\omega$ values for each reflection.

The intensity measurements were taken with a computer-controlled, automatic, Philips four-circle diffractometer, equipped with a fine focus Mo tube (take-off angle = 6°) and a scintillation counter. The (002) reflection from a graphite monochromator was used as the incident beam. The specimen was a small cube whose edge measured 0.005 cm. All possible reflections in the region $2\theta < 80°$ were measured by the ω-scan technique with a speed of 0.04°/sec. The intervals of integration were $(0.84° + 0.15° \tan\theta)$, where θ is the Bragg angle. The background was measured at each end of the interval, and the counting time was (scan time/2)$(I_{bg}/I_{int})^{1/2}$. Three standard reflections were monitored so as to keep a running check on the crystal orientation. In sequential fashion the intensities of equivalent reflections were first averaged and then the Lorentz and polarization corrections were made. No absorption correction was applied since the dimensions of

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS[a]

	Ca	Cu	Mn	O
x	0	0	0.25	0.3033(4)
y	0	0.5	0.25	0.1822(4)
z	0	0.5	0.25	0
β_{11}[b]	0.0023(3)	0.0023(2)	0.00098(8)	0.0021(3)
β_{22}	0.0023	0.0021(2)	0.00098	0.0025(4)
β_{33}	0.0023	0.0032(3)	0.00098	0.0014(3)
β_{12}	0	0	−0.0002(1)	0.0003(4)
β_{13}	0	0	−0.0002	0
β_{23}	0	0	−0.0002	0

[a] $R = (\sum |\Delta F|/\sum |F_0|) = 2.0\%$; $wR = 1.3\%$.
[b] By symmetry $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$ for Ca; $\beta_{12} = \beta_{13} = \beta_{23} = 0$ for Cu, $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23}$ for Mn, and $\beta_{13} = \beta_{23} = 0$ for O.

TABLE III

COMPARISON BETWEEN OBSERVED AND CALCULATED STRUCTURE FACTORS

h	k	l	F_0	$|F_c|$	h	k	l	F_0	$|F_c|$
0	1	1	1.43	1.58	0	8	0	10.10	10.08
0	2	0	1.19	0.54	5	5	4	1.28	1.15
1	2	1	1.97	2.13	1	7	4	0.64	0.58
0	2	2	17.48	17.54	0	8	2	1.12	1.08
0	3	1	3.84	3.91	6	5	3	1.45	1.49
3	0	1	3.58	3.29	5	6	3	0.82	1.06
2	2	2	4.75	5.13	6	6	0	11.72	11.63
1	3	2	2.57	2.66	2	8	2	11.94	11.87
2	3	1	2.44	2.18	7	4	3	1.05	1.05
0	0	4	19.83	19.84	4	7	3	1.31	1.26
0	3	3	3.11	3.21	7	0	5	1.24	1.18
1	4	1	0.92	1.09	8	3	1	1.02	1.02
0	4	2	1.84	1.51	3	8	1	1.22	1.24
2	3	3	2.22	2.26	5	7	2	1.43	1.51
2	2	4	17.06	16.94	8	4	0	9.06	9.10
4	3	1	0.66	0,64	4	8	0	8.52	8.53
5	0	1	2.55	2.65	3	8	3	1.22	1.11
1	5	2	0.98	0.92	0	9	1	1.31	1.28
2	5	1	2.16	2.29	5	5	6	1.53	1.49
0	4	4	14.74	14.81	6	6	4	9.66	9.56
3	4	3	2.55	2.67	8	5	1	1.14	1.07
0	5	3	3.23	3.30	3	9	0	1.93	1.85
5	0	3	2.80	2.85	4	8	4	8.61	8.57
0	0	6	3.69	3.88	5	8	3	1.70	1.72
2	5	3	1.15	1.25	0	10	0	1.91	1.75
5	2	3	2.18	2.16	8	6	2	8.09	8.08
1	6	1	0.95	1.13	6	8	2	7.09	7.93
2	0	6	13.03	13.15	0	10	2	7.53	7.49
0	2	6	12.23	12.34	2	10	0	8.31	8.26
5	4	1	1.01	0.92	9	4	3	0.97	0.92
4	5	1	0.97	1.00	9	5	0	1.68	1.72
6	3	1	1.03	1.10	10	4	2	7.27	7.22
3	6	1	0.80	0.79	4	10	2	7.36	7.33
4	4	4	12.39	12.30	9	6	3	1.33	1.13
0	5	5	1.83	1.98	8	8	0	6.66	6.64
0	7	1	0.99	0.85	11	3	0	1.28	1.37
0	6	4	1.40	1.48	8	8	2	1.15	1.07
2	5	5	1.57	1.57	10	5	3	1.29	1.26
3	6	3	1.25	1.22	8	6	6	6.58	6.57
7	2	1	1.59	1.64	10	6	0	8.14	8.17
2	6	4	10.74	10.69	6	10	0	8.38	8.43
4	6	2	11.64	11.62	8	8	4	7.30	7.33
3	7	0	1.27	1.22	0	12	0	7.31	7.38
6	5	1	1.01	0.86	6	10	4	6.80	6.82
5	6	1	1.40	1.58	2	12	2	7.02	7.07
2	7	3	1.63	1.70	4	12	0	5.98	6.03

the crystal were such that the absorption effect was negligible ($\mu = 160$ cm^{-1}). The total number of independent reflections with $I > 0$ was 92. As a first approximation it was assumed that the composition of the crystal corresponded to $CaCu_3Mn_4O_{12}$. Therefore, the two Ca cations were placed in the $2a$ (000) positions of the $Im3$ space group, the six Cu in the $6b$ $(0, \frac{1}{2}, \frac{1}{2})$, the eight Mn in the $8c$ $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the 24 O in the $24g$ $(x, y, 0)$. The LINUS least-squares refinement program was used together with the f curves for neutral atoms given by Doyle and Turner (5). The real and imaginary anomalous-dispersion coefficients were those given by Cromer and Liberman (6). The starting positional and thermal parameters were those reported for $NaMn_7O_{12}$. The weighting scheme was

$$w = 1/\sigma^2(F), \text{ where } \sigma(F) = (1/2F) \times$$
$$\{(LP)^{-1} A^* [N_P + N_B + \alpha(N_P - N_B)^2]^{1/2}\},$$

where N_P is the number of counts of the integrated intensity, N_B of the background, and α an empirical factor which was taken as 0.02. The scale factor, two positional parameters, 10 anisotropic thermal parameters, and the isotropic extinction coefficient were varied. Convergence was attained after four cycles of full matrix refinement. The R and wR factors were 0.020 and 0.013, respectively. The final positional and thermal parameters are reported in Table II. Although the final R and wR factors were very small, which indicated that the formula $CaCu_3Mn_4O_{12}$ was indeed correct, another two cycles of refinement were carried out, during which the occupancy factors of the sites at $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ were varied. They remained equal to their initial values, well within their standard deviations. A comparison between observed and calculated structure factors is shown in Table III, where $14.33F_c$ represents the scattering power per unit cell.

Discussion

The interatomic distances and the angles with their standard deviations are reported in Table IV. These values were calculated by the ORFFE program. The corresponding distances in $NaMn_3Mn_4O_{12}$ are included in the table for comparison. These distances were recalculated by using the new value of the lattice parameter. It is readily seen that the two structures are essentially the same. As all the perovskite-like structures, they consist of a tri-dimensional network of oxygen octahedra sharing corners. These octahedra are tilted with respect to each other in the X, Y, and Z directions. In $CaCu_3Mn_4O_{12}$ the tilt angle is 19°, while it is 20.2° in $NaMn_3Mn_4O_{12}$. The coordination polyhedra of the three cations and the way they join together are shown in Fig. 1.

The Jahn–Teller cations, Cu^{2+} for $CaCu_3Mn_4O_{12}$ and Mn^{3+} for $NaMn_3Mn_4O_{12}$, seem to be responsible for the stability of the structure. By assuming the square coordination, they stabilize the octahedral tilting of the oxygen network and, consequently, the structure. These cations are surrounded by 12 oxygen ions arranged as three unequal mutually perpendicular rectangles, the smallest and the largest of which are nearly square. The three sets of Cu–O distances are 1.942, 2.707, and 3.181 Å while the Mn–O ones are 1.910, 2.690, and 3.258 Å. From these values it is clear that the four oxygen ions at 3.181 and 3.258 Å are not first nearest neighbors. In fact, although the first set of Cu^{2+}–O distances are larger than the corresponding distances of Mn^{3+}–O the third set of cation–oxygen distances increase on going from $CaCu_3Mn_4O_{12}$ to $NaMn_3Mn_4O_{12}$. Such behavior is typical of second nearest neighbors (7). Also, the four oxygen ions at 2.707 and 2.690 Å cannot be considered as true first nearest neighbors as the four closest oxygen ions. The difference between the shortest Cu–O distance and the corresponding Mn–O one is 0.032 Å, whereas it is only 0.017 Å for the 2.707 and 2.690 Å distances.

In these compounds calcium or sodium cations are needed mainly to balance the electrostatic charge. The size of the 12-oxygen polyhedra occupied by these cations depends mainly upon the size of the octahedra. On the contrary, it does not depend much upon the ionic radii of Ca or Na cations and very little upon the tilting of the octahedra. In

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TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)

		Corresponding distances and angles in $NaMn_7O_{12}$
Ca polyhedron		
Ca–O × 12	2.562(3)	2.651
O(XXI)–O(XVII) × 24	2.708(4)	2.817
O(XXI)–O(XVIII) × 6)	2.639(7)	2.672
O(XV)–Ca(II)–O(XVIII) × 6	118.0(1)	119.5
O(XXI)–Ca(II)–O(XVIII) × 6	62.0(1)	60.5
O(XVI)–Ca(II)–O(XVIII) × 24	63.8(1)	64.2
Cu Polyhedron		
Cu(I)–O(XXII) × 4	1.942(3)	1.910
Cu(I)–O(V) × 4	2.707(3)	2.690
Cu(I)–O(XXI) × 4	3.181(3)	3.258
O(XIX)–O(XXII) × 2	2.639(7)	2.672
O(XIII)–O(XXII) × 4	2.849(7)	2.731
O(V)–O(XXII) × 8	2.709(4)	2.691
O(XI)–Cu(I)–O(V) × 2	116.5(1)	119.0
O(VIII)–Cu(I)–O(V) × 2	63.5(1)	61.0
O(XIX)–Cu(I)–O(XXII) × 2	85.6(1)	88.8
O(XIII)–Cu(I)–O(XXII) × 2	94.4(1)	91.2
O(V)–Cu(I)–O(XXII) × 8	69.0(1)	69.2
Mn Octahedron		
Mn–O × 6	1.915(1)	1.947
O(V)–O(XXII) × 6	2.709(4)	2.691
O(XXI)–O(XVII) × 6	2.708(4)	2.817
O(XXI)–Mn(I)–O(XVII) × 6	90.0(1)	92.6
O(V)–Mn(I)–O(XXII) × 6	90.0(1)	87.4
Important angles		
Cu(I)–O(XIX)–Mn(I)	108.7(1)	110.2
Cu(I)–O(II)–Mn(I)	83.6(1)	84.7
Cu(I)–O(XXI)–Mn(I)	71.1(1)	69.8
Cu(I)–O(XIX)–Ca(I)	106.2(1)	105.4
Cu(I)–O(II)–Ca(I)	152.8(1)	150.8
Cu(I)–O(XXI)–Ca(II)	77.3(1)	75.6
Mn(I)–O(I)–Ca(I)	87.7(1)	85.5
Cu(I)–O(XIX)–Cu(II)	101.0(1)	103.9
Cu(I)–O(XIX)–Cu(IV)	176.5(1)	179.0
Cu(I)–O(VIII)–Cu(II)	75.4(1)	75.1
Mn(I)–O(XXI)–Mn(II)	141.9(1)	139.5

$CaCu_3Mn_4O_{12}$ the Mn^{4+}–O distance is 1.915 Å, whereas the corresponding octahedral distance in $NaMn_3Mn_4O_{12}$ is 1.947 Å. As a consequence, the Ca–O distance (2.562 Å) is appreciably smaller than the Na–O one (2.651 Å), which is contrary to what one would expect from the reported ionic radii of Ca^{2+} and Na^+. The fact that the Ca cations are more tightly bonded than the sodium cations to the surrounding oxygen ions makes the square around Cu^{2+} more rectangular than the corresponding square in $NaMn_3Mn_4O_{12}$. The angles between the diagonals are 85.6° in $CaCu_3Mn_4O_{12}$ and 88.8° in $NaMn_3Mn_4O_{12}$.

The octahedra around Mn^{4+} in $CaCu_3Mn_4O_{12}$ are almost undistorted as the

TABLE V

THERMAL DATA IN $CaCu_3Mn_4O_{12}$ AND $NaMn_3Mn_4O_{12}$

		R.M.S.	Angles with				R.M.S.	Angles with		
			x	y	z			x	y	z
Ca		0.078(4)				Na	0.127(2)			
Cu	1	0.075(4)	90	0	90	Mn	0.072(2)	90	0	90
	2	0.078(4)	180	90	90		0.074(4)	180	90	90
	3	0.093(4)	90	90	0		0.127(2)	90	90	0
Mn	1	0.038(4)	55(6)	55	55	Mn	0.076(2)	55(1)	55	55
	2	0.057(4)	45	135	90		0.070(2)	45	135	90
	3	0.057(4)	114	114	35		0.070(2)	114	114	35
O	1	0.061(7)	90	90	0	O	0.070(4)	90	90	0
	2	0.071(8)	155(25)	65	90		0.103(3)	135(2)	45	90
	3	0.084(8)	65	25	90		0.121(3)	45	45	90

12 O–O distances are either 2.708 or 2.709 Å and the 12 O–Mn–O angles are all equal to 90°. The corresponding octahedra in $NaMn_3Mn_4O_{12}$ are more distorted. This is perhaps due to the fact that in the latter compound the octahedral sites accommodate at random Mn^{3+} and Mn^{4+} cations, whereas in $CaCu_3Mn_4O_{12}$ the octahedra are occupied only by Mn^{4+} cations. From the two octahedra distances $Mn^{3.5+}–O = 1.947$ Å and $Mn^{4+}–O = 1.915$ Å, one can deduce a value

Center of the oxygen atoms

○ Mn^{4+}

◯ Cu^{2+}

◯ Ca^{2+}

FIG. 1. Coordination polyhedra of cations in $CaCu_3Mn_4O_{12}$.

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of 1.979 Å for the octahedral $Mn^{3+}–O$ distance, which is appreciably smaller than the average value found in Mn_2O_3 (2.027 Å) (8). In this compound the oxygen octahedra are apically elongated. Since the average $Mn^{3+}–O$ distance varies considerably with the distortion of the oxygen octahedra (8), it seems plausible that a smaller distance is observed in $NaMn_3Mn_4O_{12}$ because the oxygen octahedra have only a small trigonal distortion.

The thermal data for $CaCu_3Mn_4O_{12}$ and for $NaMn_3Mn_4O_{12}$ are reported in Table V. It can be seen that, while the Ca cations have a normal thermal vibration (0.078 Å), the Na cations have an anomalously large one (0.127 Å). This is a consequence of the fact that the oxygen polyhedron around the Na cation is larger than what its ionic radius would require, which corroborates the conjecture that these cations, Ca or Na, do not contribute much to the stability of this type of structure. A similar case was found for the Ca cations in the structure of the high-pressure phase of $CaB_2O_4(IV)$ (9). This structure contains a tridimensional array of oxygen tetrahedra occupied by the boron cations. There are large holes in the tetrahedral array, and these holes are occupied by the calcium cations. There are two independent Ca atoms in this structure, one of which is surrounded by 12 oxygens arranged as the oxygen polyhedron around the A cations of the perovskite structure. For these cations,
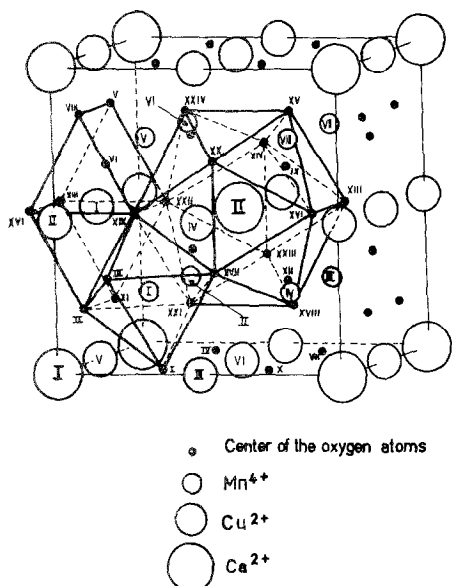
a large average Ca–O distance was found (2.728 Å). The other calcium cations have nine oxygens as first neighbors, the average distance between which is 2.489 Å, and a normal thermal vibration (rms $= 0.085$ Å) was observed.

The thermal vibration of the Jahn–Teller cations, Cu^{2+} or Mn^{3+}, is quite anisotropic; the long component is perpendicular to the small square. The oxygen rectangle perpendicular to this square is larger in $CaCu_3Mn_4O_{12}$ than in $NaMn_3Mn_4O_{12}$ but not as much as the difference in size between Cu^{2+} and Mn^{3+} would require. This is why the thermal vibration of the Mn^{3+} cations in $NaMn_3Mn_4O_{12}$ have a larger component perpendicular to the square (rms $= 0.127$ Å) than the Cu^{2+} cations (rms $= 0.093$ Å).

The thermal vibrations of the octahedrally coordinated Mn^{4+} cations are also anisotropic with a small component (rms $= 0.038$ Å) along the [111] direction—that is, toward the large Ca cations. The corresponding octahedral cations in $NaMn_3Mn_4O_{12}$ have isotropic thermal vibrations. The Na cations are not as close to the octahedral sites as their Ca counterparts, and therefore the component along the [111] of the octahedral cations in $NaMn_3Mn_4O_{12}$ does not have to be small.

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