JOURNAL OF SOLID STATE CHEMISTRY 10, 51–55 (1974)

X-Ray Diffraction Study of the Superstructure Deformation due to Pb Substitution in Ca_2MnO_4

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Received July 9, 1973

During the preparation of Ca_2MnO_4 single crystals with PbO flux, Pb atoms substitute for both Ca and Mn atoms. Analysis of single-crystal X-ray diffractometer data gives the formula $(Ca_{1.72}Pb_{0.28})(Mn_{0.77}Pb_{0.23})O_4$. Space group is $I4_1/acd$ with $a = 5.189$ Å, $c = 24.156$ Å, and $Z = 8$. As compared to pure Ca_2MnO_4, the oxygen octahedra surrounding the Mn (or Pb) atoms are enlarged and slightly rotated, and weak superstructure reflections result.

Introduction

The compound Ca_2MnO_4 was first synthetized in polycrystalline form by Ruddlesden and Popper (*1*). It is isostructural to the body-centered tetragonal K_2NiF_4 type (*2*). This structure can be described as a succession of planes stacked perpendicular to the 4-fold axis. The Mn atoms are situated in planes separated by 6 Å. As a result, the magnetic interactions between Mn atoms are stronger inside the basal plane than along the 4-fold direction, thus explaining the "quasi two-dimensional" magnetic ordering (*3*, *4*) observed by neutron diffraction experiments over a large range of temperatures above the Néel temperature ($T_N = 114$ K). A quantitative measurement of sublattice magnetization and critical exponent β (*5*) can be made from the analysis of magnetic intensities resulting from neutron diffraction. Unfortunately, these intensities become quite weak near the Néel temperature, and they may be superimposed on the nuclear intensities. A previous study (*6*) on polycrystalline samples showed the presence of one or two magnetic structures, depending upon the chemical preparation. Thus, it appeared that single-crystal experiments would be more reliable and that a precise knowledge of the atomic structure and chemical composition of the compound was needed.

The present paper describes the preparation of single-crystal specimens used for neutron diffraction experiments and the determination of the atomic structure of these crystals by X-ray diffraction experiments.

Experimental

Single crystals were prepared by the flux method. Polycrystalline samples of pure Ca_2MnO_4 were mixed up with PbO in order to lower the melting point of the compound. The mixture (Ca_2MnO_4 + 14 PbO) was heated in a sealed platinum crucible to 1400°C and then slowly cooled at a rate of 0.5°C/h. At

Printed in Great Britain

1000°C, the liquid part of the mixture was removed. Black single crystals of about 0.5 cm^3 volume were obtained.

The X-ray intensity data were collected at room temperature on a PW 1100 Philips computer-controlled four-circle diffractometer with a graphite monochromator, using Mo$K\alpha$ radiation and $\theta/2\theta$ scan. Three standard reflections were measured at regular intervals for crystal and electronic stability control. A total of 235 independent reflections with $\sin\theta/\lambda < 1$ Å^{-1} were recorded. Lorentz-polarization and absorption corrections were applied. The calculated linear absorption coefficient was 304.5 cm^{-1}. The crystal was approximately spherical with a radius of 0.032 mm.

Unit Cell and Space Group

The unit-cell dimensions were determined from precession photographs recorded with Cu$K\alpha$ radiation. Intense spots corresponding to the K_2NiF_4-type body-centered tetragonal cell ($a = 3.67$ Å, $c = 12.09$ Å) were recognized, but there were also weak superstructure reflections corresponding to a multiple tetragonal cell (a_s, c_s) defined by the following relation:

$$\begin{pmatrix} a_{1s} \\ a_{2s} \\ c_s \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ 1 & \bar{1} & 0 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ c \end{pmatrix}$$

Superstructure cell K_2NiF_4-type cell

The observed systematic extinctions were such that hkl was present only if $h + k + l = 2n$, $hk0$ only if $h, k = 2n$, $0kl$ only if $k, l = 2n$, and hhl only if $2h + l = 4n$. The space group is $I4_1/acd$. Accurate lattice parameters reported in Table I were determined by least-squares analysis of the θ and $-\theta$ values from the reflections ($h00$), ($hh0$), and ($00l$) recorded by the automatic diffractometer (λ Mo$K\alpha$ = 0.71069 Å).

TABLE I

CRYSTAL DATA

Crystal system space group	Tetragonal $I4_1/acd$
a	5.189 (1) Å
b	5.189 (1) Å
c	24.156 (8) Å
V	649.9 (3) (Å)^3
Z	8
μ(Mo$K\alpha$)	304 cm^{-1}

Refinement of the Structure

The refinement was carried out with the full matrix least-squares program OR-XFLS3 (*7*). The atomic scattering factors, used for the cations Ca^{2+}, Mn^{4+}, Pb^{2+}, and Pb^{4+}, were those calculated by Cromer and Waber (*8*). For oxygen we used the f values calculated by Hanson et al. (*9*). All cation scattering factors were corrected for $\Delta f'$ and $\Delta f''$ as reported by Cromer (*10*). A preliminary refinement based on the positions of pure polycrystalline samples of Ca_2MnO_4 as determined by Ollivier and Buisson (*6*) gave an R value of 25% ($R = \sum |F_o - F_c| / \sum F_o$). Thus, it seemed that the presence of Pb on Ca or Mn sites would be the only way to explain the difference between observed and calculated structure factors. A refinement of the occupancy factors of only the Ca and Mn sites immediately gave an R value of 15%

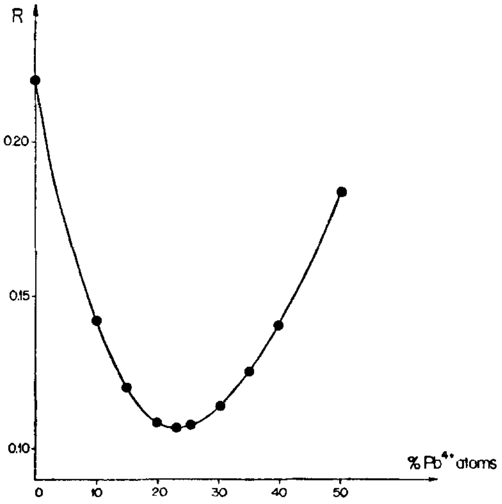

FIG. 1. Residual R as a function of Pb^{4+} at.% in the unit cell.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

2	0	0	1264.3	1192.0	2	1	5	92.1	55.9	4	4	12	517.6	527.4	7	1	18	215.1	220.9	8	2	28	236.2	236.2
2	2	0	1353.9	1263.1	4	1	5	78.1	57.8	6	6	12	314.5	310.0	9	3	18	155.7	143.9	6	0	28	307.1	311.8
4	4	0	654.1	670.5	6	1	5	49.4	43.8	8	6	12	222.5	234.9	9	1	18	155.3	129.5	8	0	28	226.1	206.2
6	6	0	372.9	380.0	7	7	6	174.1	155.7	6	4	12	371.6	389.6	2	2	20	125.6	117.3	1	1	30	66.1	94.1
8	6	0	272.9	294.7	5	5	6	292.7	312.2	4	2	12	578.2	595.3	4	4	20	106.4	105.4	3	1	30	77.2	95.5
6	4	0	452.0	484.8	3	3	6	521.2	577.4	2	0	12	835.5	813.0	6	6	20	43.8	88.8	5	3	30	90.6	89.8
4	2	0	772.7	789.1	1	1	6	918.3	924.8	4	0	12	729.0	724.9	6	4	20	97.2	95.1	7	5	30	84.3	65.2
4	0	0	999.0	962.4	3	1	6	746.3	773.8	6	2	12	440.3	456.3	4	2	20	186.1	169.2	7	1	30	71.5	56.0
6	2	0	553.2	574.8	5	3	6	478.0	503.7	8	4	12	275.3	274.7	2	0	20	307.8	265.6	4	2	32	87.0	61.9
8	4	0	332.1	337.4	7	5	6	308.0	304.6	10	4	12	216.3	215.8	4	0	20	126.1	117.2	2	0	32	130.4	93.5
10	4	0	252.7	259.0	9	5	6	182.0	143.0	8	2	12	329.1	344.8	6	2	20	104.0	108.7	5	5	34	219.5	191.0
8	2	0	397.4	418.8	7	3	6	273.4	293.1	6	0	12	457.7	483.6	8	4	20	66.1	85.6	3	3	34	321.0	305.4
6	0	0	588.9	612.2	5	1	6	466.5	514.6	8	0	12	306.0	313.2	6	0	20	112.9	113.3	1	1	34	406.8	401.8
8	0	0	377.9	391.9	7	1	6	361.5	376.4	10	2	12	199.7	194.3	8	0	20	86.8	109.8	3	1	34	375.1	373.6
10	2	0	238.5	242.8	9	3	6	239.0	235.5	10	0	12	258.4	271.3	7	7	22	146.6	125.3	5	3	34	313.8	304.9
10	0	0	307.8	321.8	9	1	6	236.7	228.5	2	1	13	56.3	48.4	5	5	22	241.4	232.9	7	3	34	212.6	181.5
2	1	1	96.3	59.8	11	1	6	181.8	143.4	4	1	13	90.7	48.3	3	3	22	377.1	394.6	5	1	34	297.7	288.6
3	2	1	42.2	29.2	2	1	7	77.5	52.5	5	5	14	86.6	75.3	1	1	22	544.1	555.5	7	1	34	251.7	240.0
4	1	1	34.4	59.7	4	1	7	74.2	55.9	3	3	14	89.8	91.7	3	1	22	479.9	496.0	2	2	36	103.7	114.7
4	3	1	50.7	35.1	4	3	7	48.6	33.3	1	1	14	63.0	74.9	5	3	22	363.7	374.9	4	4	36	78.3	75.3
6	1	1	44.2	44.5	6	1	7	51.6	43.1	7	3	14	56.9	55.5	7	5	22	255.7	252.1	4	0	36	97.4	96.3
3	3	2	46.2	45.8	2	2	8	60.4	65.2	5	1	14	53.2	61.4	7	3	22	228.8	222.8	6	2	36	77.2	61.1
1	1	2	130.9	147.9	4	4	8	46.9	72.0	2	2	16	525.5	526.1	5	1	22	349.0	364.6	5	5	38	44.4	37.8
3	1	2	175.9	144.3	6	4	8	79.6	67.0	4	4	16	300.4	315.6	7	1	22	289.7	289.0	3	3	38	73.7	73.2
5	3	2	133.4	114.3	4	2	8	169.3	143.2	6	6	16	192.6	178.4	9	3	22	205.0	197.7	1	1	38	102.9	107.3
7	5	2	99.7	89.6	4	0	8	65.8	77.0	8	6	16	141.2	128.6	9	1	22	195.9	187.5	3	1	38	100.9	111.6
5	1	2	67.9	57.9	6	2	8	75.2	73.5	6	4	16	219.6	227.6	2	2	24	403.1	394.3	5	3	38	109.7	114.8
7	1	2	78.4	69.9	6	0	8	84.5	93.2	4	2	16	305.3	333.2	4	4	24	260.0	260.3	7	3	38	54.0	44.2
9	3	2	56.7	62.0	8	0	8	72.3	84.4	2	0	16	362.9	409.5	6	6	24	171.0	164.2	5	1	38	92.1	79.4
11	1	2	73.0	35.1	2	1	9	61.6	43.6	4	0	16	414.0	427.1	6	4	24	200.9	198.8	7	1	38	90.7	85.4
2	1	3	93.9	58.5	4	1	9	72.7	53.5	6	2	16	256.9	266.9	4	2	24	254.3	264.2	2	2	40	348.9	335.3
4	1	3	84.4	59.0	7	7	10	88.4	92.0	8	4	16	171.5	151.8	2	0	24	292.2	306.4	4	4	40	265.4	242.9
6	1	3	67.5	44.3	5	5	10	145.6	154.3	8	2	16	213.7	206.8	4	0	24	330.4	335.2	4	2	40	273.6	245.5
2	2	4	313.5	277.5	3	3	10	277.4	296.6	6	0	16	267.8	284.1	6	2	24	230.6	225.2	2	0	40	300.9	274.8
4	4	4	132.3	125.4	1	1	10	542.0	537.0	8	0	16	173.7	172.5	8	4	24	145.0	142.3	4	0	40	309.9	297.9
6	6	4	77.3	61.1	3	1	10	441.7	428.5	10	2	16	122.6	92.8	8	2	24	185.1	189.4	6	2	40	232.8	211.8
8	6	4	64.3	42.1	5	3	10	300.1	293.2	10	0	16	172.3	163.8	6	0	24	226.7	236.4	6	0	40	236.0	222.4
6	4	4	69.4	81.0	7	5	10	204.4	196.9	7	7	18	98.7	75.6	8	0	24	156.8	154.6	1	1	42	76.3	49.8
4	2	4	66.7	98.2	9	5	10	100.0	83.2	5	5	18	153.3	163.3	2	2	28	487.5	497.3	2	2	44	80.8	88.5
2	0	4	197.1	40.3	7	3	10	140.8	150.4	3	3	18	265.7	304.5	4	4	28	342.3	330.7	4	4	44	63.5	47.0
4	0	4	201.6	196.5	5	1	10	260.8	273.0	1	1	18	408.6	450.8	6	6	28	234.0	208.8	4	0	44	73.9	70.5
6	2	4	87.3	96.6	7	1	10	218.1	217.3	3	1	18	371.5	405.4	6	4	28	271.5	268.1	3	3	46	184.4	149.2
8	4	4	63.9	43.9	9	3	10	161.0	151.8	5	3	18	290.9	301.7	4	2	28	347.1	359.1	1	1	46	233.7	203.8
10	4	4	67.1	49.2	9	1	10	145.3	133.1	7	5	18	209.1	192.6	2	0	28	405.0	427.3	3	1	46	220.8	195.9
8	2	4	34.5	85.2	2	1	11	48.7	44.5	9	5	18	185.8	73.4	4	0	28	416.7	429.8	5	1	46	182.2	144.8
6	0	4	39.1	103.3	4	1	11	73.6	50.9	7	3	18	164.7	155.5	6	2	28	300.8	297.1	1	1	50	176.4	153.4

[a] Reading from left to right the columns contain the values h, k, l, F_o, and $|F_c|$. $R = \sum |F_o - |F_c|| / \sum F_o = 0.068$. Isotropic extinction $G = 6.10^{-4}$.

with a significant increase of the occupancy factors above 1.0 on both the Ca and Mn sites. Contributions to the superstructure intensities (hkl with $l = 2n + 1$) come only from the oxygen atoms placed in the crystallographic site $16f$ and such that $x \neq 0.25$. A refinement of these oxygen positional parameters gave a value of $x = 0.20$. Successive independent refinements of occupancy factors and of positional and isotropic thermal parameters reduced R to 10%.

Figure 1 shows the variation of the residual R as a function of the Pb^{4+} concentration, the minimum of the curve indicating that 23% Pb^{+} atoms are substituted for Mn^{4+}. The corresponding amount of Pb^{2+} substituted

TABLE III

STRUCTURAL PARAMETERS FOR $(Ca_{1.72}Pb_{0.28})(Mn_{0.77}Pb_{0.23})O_4$[a]

Atom	Crystallographic site	Occupancy	x	y	z	B (Å)^2
Ca	$16d$	0.86	0	0.25	0.051 (1)	0.9 (0.3)
Pb	$16d$	0.14	0	0.25	0.051 (1)	0.5 (0.3)
Mn	$8a$	0.77	0	0.25	0.875	1.0 (0.4)
Pb	$8a$	0.23	0	0.25	0.875	0.5 (0.3)
O_1	$16f$	1.0	0.208 (1)	0.458 (1)	0.125	0.2 (0.5)
O_2	$16d$	1.0	0.0	0.25	0.955 (3)	0.2 (0.5)

[a] Space group $I4_1/acd$, symmetry center at origin. Standard error in parentheses.

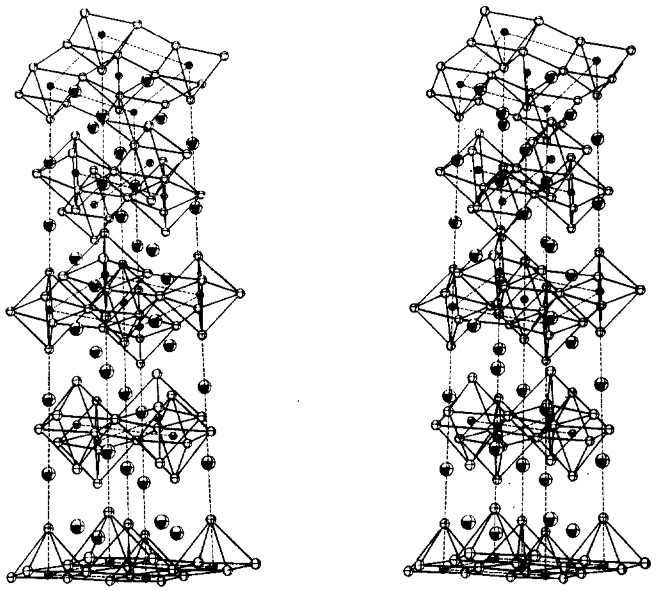

FIG. 2. A_2BO_4 structure with A = 0.86 Ca + 0.14 Pb, B = 0.77 Mn + 0.23 Pb. The B atoms are in the center of oxygen octahedra.

for Ca^{2+} as given by the refinement is 14% atoms. The final chemical composition is $(Ca_{1.72}Pb_{0.28})(Mn_{0.77}Pb_{0.23})O_4$. As has been observed previously (*11*) in the isotypical compounds $Ca_{2-x}Ln_xMnO_4$ (Ln = Pr, Nd, Sm, Eu, Gd), no ordering of the substituting atoms has been detected. At this stage, it was noticed that extinction effects were important, as all the strong reflections at low angle had observed intensities smaller than their calculated value. An isotropic extinction (*12*) correction was introduced in the refinement procedure and *R* reduced to 0.06. The observed and calculated structure factors are listed in Table II. Final values of all structural parameters are reported in Table III. A drawing of the structure is shown in Fig. 2.

Discussion and Conclusion

The substitution of Pb^{4+} for Mn^{4+} could be expected as the K_2NiF_4-type compound Ba_2PbO_4 (*13*) is known. As the ionic radius of Ca^{2+} is smaller than the radius of Ba^{2+}, the presence of a Pb^{2+} cation (with ionic radius intermediate between those of Ba^{2+} and Ca^{2+}) makes it possible for some Pb^{4+} to replace Mn^{4+}. As a consequence, the oxygen framework is slightly distorted. The oxygen atomic displacements from the ideal positions of the K_2NiF_4-type structure are shown in Fig. 3. The result is an enlargement of the oxygen octahedron due to the presence of Pb^{4+} at its center and also a slight rotation about the

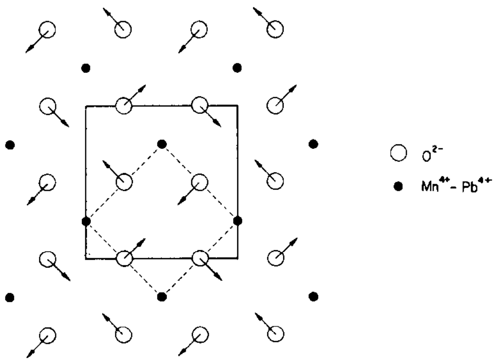

FIG. 3. Atomic plane (00*l*) at $z = \frac{1}{8}$. Arrows indicate the displacements of oxygen atoms into the plane due to substitution of Pb^{4+} by Mn^{4+}. Strong continuous line indicates the projection of the unit cell onto the plane. Light broken line indicates K_2NiF_4-type unit cell (subcell).

TABLE IV

INTERATOMIC DISTANCES IN A_2BO_4[a]

	Å		Å
A–1 O_2	2.308 (7)	Oxygen octahedra	
–2 O_1	2.352 (3)	O_1–2 O_1	2.631 (6)
–4 O_2	2.599 (1)	O_2–4 O_1	2.690 (6)
–2 O_1	2.790 (4)		
		B–4 O_1	1.860 (4)
		–2 O_2	1.943 (7)

[a] A = 0.86 Ca + 0.14 Pb, B = 0.77 Mn + 0.23 Pb. Standard error in parentheses.

4-fold axis. Interatomic distances are reported in Table IV. The oxygen octahedra remain almost regular. The bond lengths B–O represent the mean value between Pb^{4+}–O and Mn^{4+}–O, as it seems likely that the Pb^{4+}–O bond would be longer than the Mn^{4+}–O bond. The reported A–O distances of Table IV are the mean values between Ca^{2+}–O and Pb^{2+}–O.

As a consequence of the present work, the knowledge of the exact concentration of Mn in the crystal will be used to verify, by neutron diffraction, the hypothesis of Lines (*5*) concerning the reduction of magnetic moments when "two-dimensional" ordering occurs.

Acknowledgments

The authors thank Professor E. F. Bertaut for stimulating discussions and Professor E. Parthé for his continued help, guidance, and enthusiasm throughout the course of this work.

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