Synthesis and Characterization of a New Double Perovskite: $LaCaMnCoO_6$

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A technique based on the formation of metallic complexes has been developed to synthesize a new mixed oxide of the perovskite structural type. Electron diffraction and microscopy of $LaCaMnCoO_6$ shows this phase to be cubic with a cell parameter $a = 7.666(1)$ Å, double that of a perovskite basic cell. The results are discussed in terms of ordering of both A and B sublattices of the perovskite structure.

Perovskite-related oxides, ABO_{3-x}, are now in the limelight since some of them have shown superconducting properties at temperatures much higher than those observed with other materials.[1,2] The aristotype of this structure family, $SrTiO_3$, is cubic with just the unit-cell dimension as an unique parameter.[3] Oxygens are placed so as to give corner-shared strings of TiO_6 octahedra, the Sr atoms being surrounded by twelve equidistant oxygens. Deviations from the ideal cubic symmetry frequently occur due to either different sizes of the A or B cations[4,5] or multiple occupation of the A or B sublattices.[6,7] However, some complex perovskites contain two or more octahedral cations in which the cubic symmetry is preserved. In such cases, an ordering takes place in the octahedral sites, leading to a double cubic cell.[8,9]

We present in this paper a study by electron diffraction and microscopy of a new ordered perovskite showing multiple occupation of both A and B sublattices. As is well known, the initial problem in the synthesis of powder mixed oxides, as in all the multicomponent systems, lies in the preparation of starting mixtures with a homogeneous and well controlled composition at the atomic level. For this reason, a synthetic method with which it is possible to obtain perovskite-type mixed oxides with multiple occupation of the cationic sublattices has been used.

Experimental

The compound $LaCaMnCoO_6$ was prepared by the so-called 'liquid mix' technique.[10] This technique is based on the formation of metallic complexes from concentrated solutions of polyfunctional organic acids and either salts or oxides of suitable cations for mixed oxide formation. Stoicheiometric amounts of $La(NO_3)_3$, $Co(NO_3)_2$, $MnCO_3$, and $CaCO_3$ of AnalaR quality were dissolved in citric acid until saturation, a transparent liquid solution being obtained. Individual solutions and starting compounds were analysed by means of atomic absorption and thermogravimetric analysis in order to estimate the concentration of the cations with an accuracy of 10 p.p.m. In order to solidify the liquid solution it is necessary to add a diol which increases the solution viscosity due to the formation of ester-type three-dimensional polymers. When the diol reacts with the citric solution a resin is formed, thus avoiding formation of partial segregations which could modify the homogeneity of the solution. In this way, ethylene glycol (3%, v/v) was added to the above citric solution. Evaporation of the solution obtained gave a vitreous intermediate polymer containing all the cations in the desired stoicheiometric amounts. To eliminate the organic resin, the sample was heated at 723 K for 16 h, a homogeneous cationic distribution being obtained. By heating this resin at 823 K in air, a solid showing the perovskite structure was obtained as deduced from the powder *X*-ray diffraction pattern. Several treatments were then carried out to improve the sample crystallinity: (*i*) at 1 273 K for 1 h and (*ii*) at 1 673 K for 1 h in air. The homogeneous dark powder obtained was quenched to room temperature.

Chemical analysis of the total amount of Ca, La, Co, and Mn was performed by means of atomic absorption by using a single-beam Perkin-Elmer 2280 spectrophotometer. Experimental results were in good agreement with the theoretical composition $LaCaMnCoO_6$.

The oxidation states of both Co and Mn were determined by thermogravimetric analysis using a Cahn balance equipped with a furnace and a two-channel register, thus allowing simultaneously recording of the weight loss and the reaction temperature. The sample (*ca.* 50 mg) was reduced by hydrogen at 673 K and 250 Torr (*ca.* 33 × 10^4 Pa). The experimental weight loss (2%) was in agreement with the theoretical loss corresponding to equation (1). An *X*-ray diffraction study of the

$$LaCaMn^{4+}Co^{3+}O_6 \xrightarrow{H_2} LaCaMn^{3+}Co^{2+}O_5 \quad (1)$$

reduced sample showed this material to be a mixture of $CaMnO_3$[11] and $La_2Co_2O_5$.[12]

Powder *X*-ray characterization was carried out on a Siemens D-500 diffractometer equipped with a graphite monochromator in the diffracted beam using Cu-K_α ($\lambda = 1.5418$ Å) radiation and silicon as an internal standard. Electron diffraction and microscopy were performed on a Siemens ELMISKOP 102 electron microscope fitted with a double tilting goniometer stage (±45%) operating at 100 kV. The sample was crushed in an agate mortar and suspended in n-butanol, then transferred to holey carbon-coated copper grids.

Results

Figure 1 shows the powder *X*-ray diffraction pattern corresponding to the $LaCaMnCoO_6$ phase. This pattern can be indexed on the basis of a single cubic perovskite (p) unit cell with $a_p = 3.833(1)$ Å. As no superstructure reflections were observed, an electron diffraction and microscopy study was carried out in order to look for superstructure spots corresponding to some kind of periodic ordering.

Figure 2 shows the electron diffraction pattern of this material along the $[001]_p$ zone axis. All the spots can be assigned, according to the *X*-ray diffraction data, to a single cubic perovskite cell. However, by tilting 45° around the b^* axis a somewhat more complex situation appears. Figure 3(*a*) shows the electron diffraction pattern corresponding to the $[10\bar{1}]_p$ zone axis. Superstructure maxima located at $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})_p$ and equivalent positions are observed, indicating that the three perovskite subcell axes are double. In the corresponding electron micrograph [Figure 3(*b*)] the doubling of the perovskite cell can clearly be seen since the periodicity of the

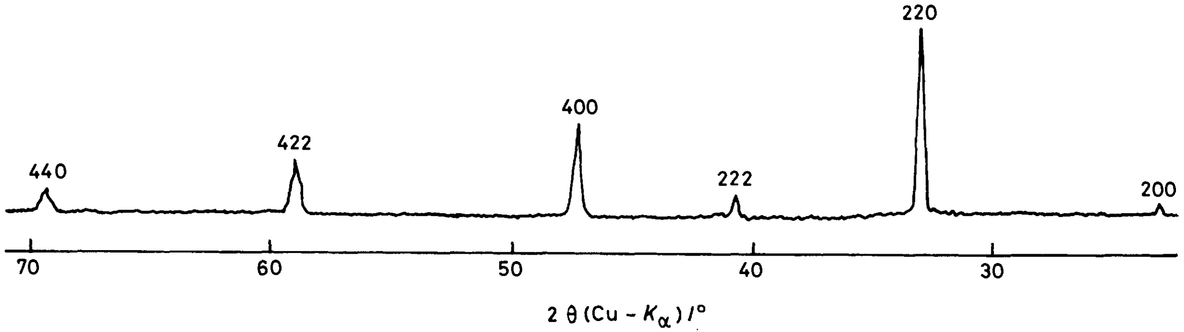

Figure 1. Powder *X*-ray diffraction pattern corresponding to $LaCaMnCoO_6$

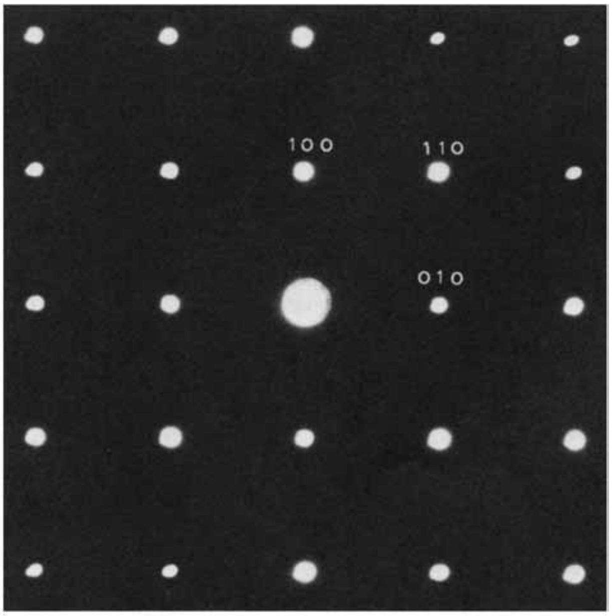

Figure 2. Electron diffraction pattern of $LaCaMnCoO_6$ along the $[001]_p$ zone axis indexed on the basis of a single perovskite unit cell

crystallographic planes along $(010)_p$ is 7.7 Å, *i.e.* twice the perovskite subcell parameter. Moreover, the distances measured along $(101)_p$ and $(111)_p$ are 5.4 and 4.4 Å, respectively, which correspond to the d_{101} and d_{111} spacings of a double perovskite unit cell with $2a_p \times 2a_p \times 2a_p$ parameters.

The electron diffraction pattern along $[1\bar{2}1]_p$ (Figure 4) confirms the existence of superstructure maxima along the $(111)_p$ direction doubling the unit cell. On the other hand, the pattern along the $[\bar{1}11]_p$ zone axis (Figure 5) shows ψ-$(110_p,101_p)$ and $\psi(101_p,0\bar{1}1_p)$ angles of 60° corresponding to a cubic unit cell.

On the basis of all this information, it can be concluded that (*hkl*) reflections are only allowed when $(h + k)$, $(k + l)$, $(l + h) = 2n$, the $LaCaMnCoO_6$ material being a face-centred cubic perovskite with $a = 7.666(1)$ Å, the *d* spacings of which are listed in the Table.

Discussion

As is well known, perovskite-related oxides with $A_2BB'O_6$ composition show a double cell due to ordering of cations in octahedral sites.[13] On the other hand, Glazer[14] has classified the different octahedral tilts in perovskites, describing the ratio between the tilt type and the symmetry of the unit cell. From this

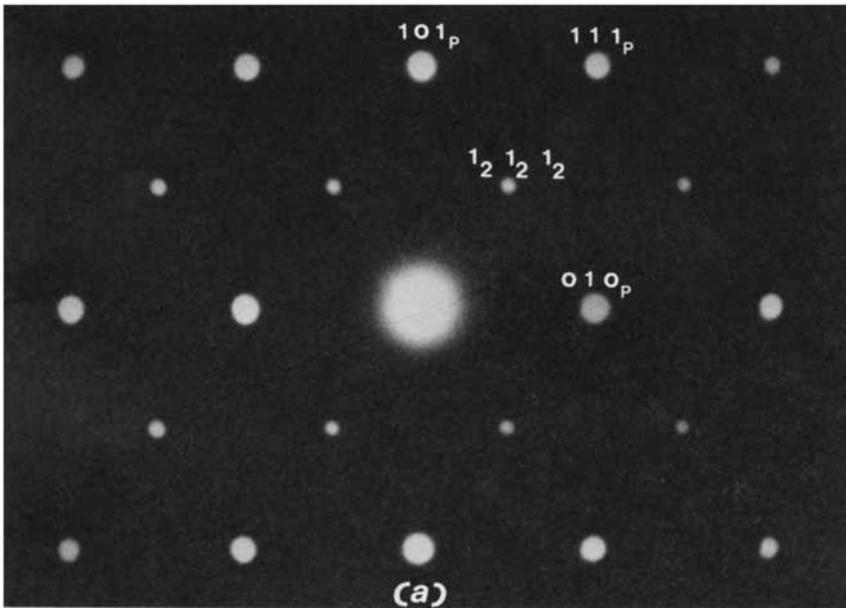

Figure 3. (*a*) Electron diffraction pattern along $[10\bar{1}]_p$. Superstructure spots are seen at $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})_p$ and equivalent positions

study it can be concluded that none of the 23 tilt systems proposed leads to a cubic symmetry of the F type.

However, when the A positions of the perovskite-type structure are occupied by various cations, as in our case, some distortions must occur because the CaO_{12} and LaO_{12} polyhedra are slightly different due to the different radii[15] and oxidation states of Ca^{2+} and La^{3+}. Since the symmetry of $LaCaMnCoO_6$ is cubic, some ordering in the B sublattice must be present in order to compensate for the above effect. If this is true, the most probable structural model should be that corresponding to a perovskite-type structure showing order in both A and B sublattices, as shown in Figure 6.

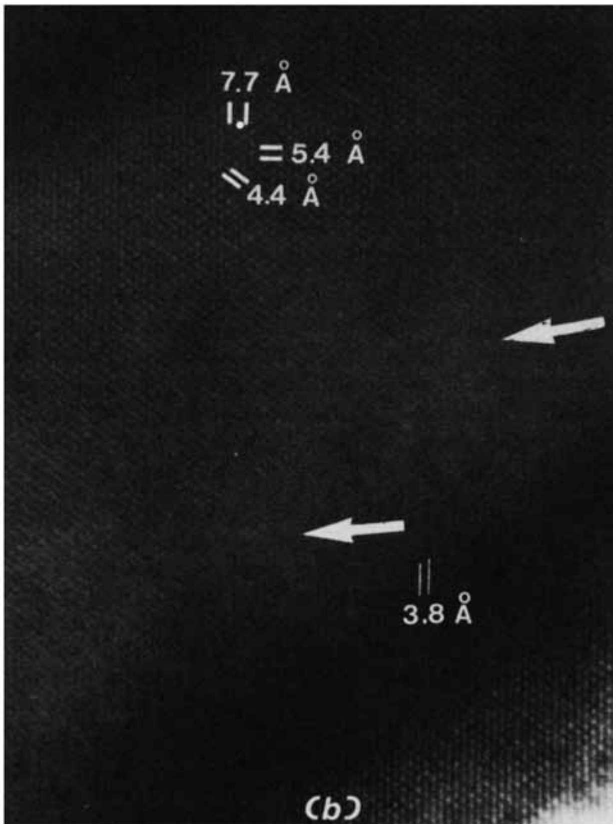

Figure 3. (*b*) Corresponding electron micrograph showing the stacking sequence corresponding to a double perovskite cell. Arrowed areas correspond to disordered domains

Nevertheless, the characteristic *X*-ray diffraction patterns of ordered double perovskites show all the reflections allowed by the space group. The fact that in $LaCaMnCoO_6$ ordering was only detected by a technique with a lower wavelength such as electron diffraction seems to suggest that the crystal shows only some ordered domains, while in other areas the cations will be distributed at random leading to a single cubic cell. This phenomenon is observed by means of high-resolution electron microscopy. All the crystals studied on the electron microscope showed some regions corresponding to a single cubic cell. The arrowed areas in Figure 3(*b*) show a different stacking sequence, where only fringes of 3.8 Å are seen.

On the other hand, it is worth mentioning that with the synthesis procedure developed a very precise control of the cation concentration has been possible in order to obtain a liquid solution whose homogeneity is retained in the solid state. Moreover, the diffusion process necessary to obtain the product from the starting materials is enormously favoured by means of

Table. Powder *X*-ray diffraction data, $\lambda(\text{Cu-}K_\alpha) = 1.5418$ Å, for the $LaCaMnCoO_6$ sample

d/Å			
obs.	calc.	*hkl*	I/I_0
3.840	3.833	200	5
2.710	2.711	220	100
2.212	2.213	222	13
1.919	1.916	400	50
1.563	1.565	422	27
1.355	1.355	440	13

$a = 7.666(1)$ Å, $U = 450.51(2)$ Å^3

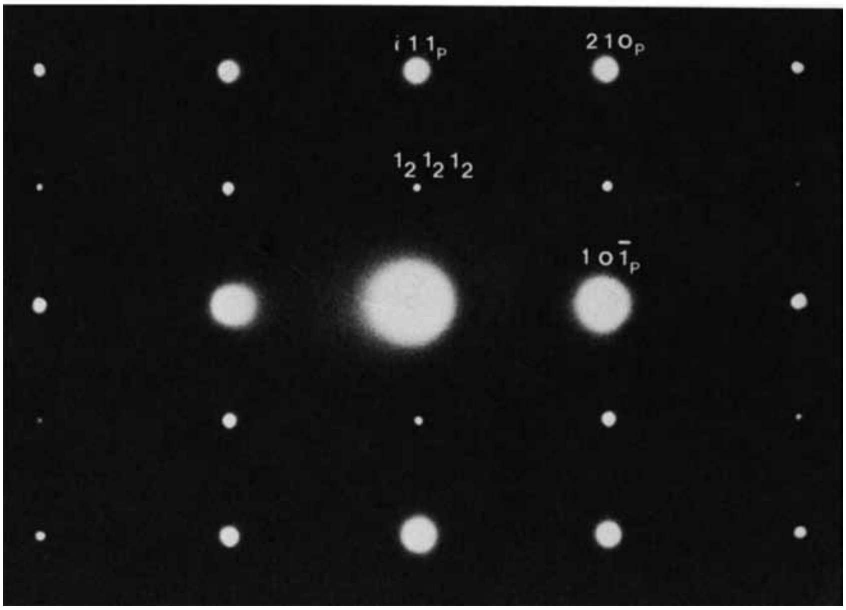

Figure 4. Electron diffraction pattern along the $[1\bar{2}1]_p$ zone axis

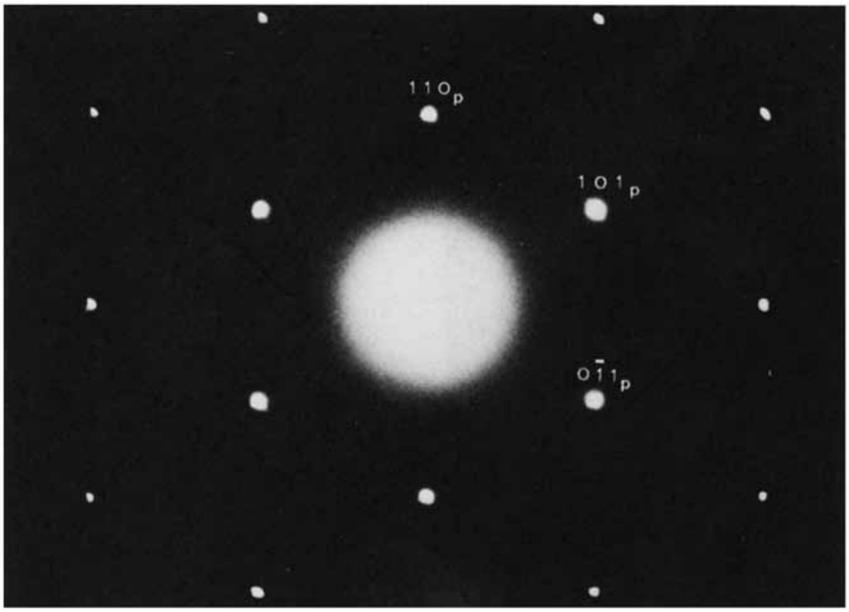

Figure 5. Electron diffraction pattern along $[\bar{1}11]_p$

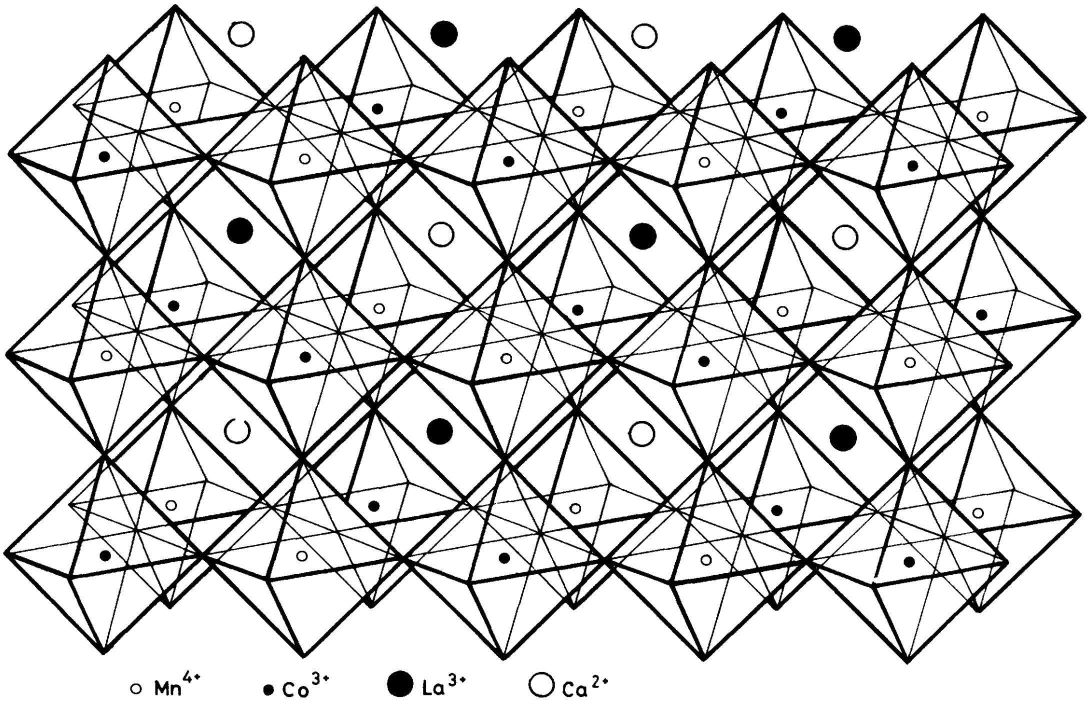

Figure 6. Tentative structural model for $LaCaMnCoO_6$

the liquid solution compared to other classical methods of synthesis of mixed oxides. For this reason, undoubtedly the synthesis temperature is considerably lower.

Acknowledgements

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