

Oxygen Vacancy Ordering in Superlattices of the Two Novel Oxides, $\text{La}_2\text{Ni}_2\text{O}_5$ and $\text{La}_2\text{Co}_2\text{O}_5$, prepared by Low Temperature Reduction of the Parent Perovskites

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Controlled reduction of LaBO_3 ($B = \text{Co}$ or Ni) perovskites gives rise to ordered structures of composition $\text{La}_2\text{B}_2\text{O}_5$, belonging to the homologous series $\text{La}_n\text{B}_n\text{O}_{3n-1}$, which retain the original features of the perovskite; the co-ordination of the transition metal ions differ, with Ni^{2+} ions showing octahedral and square-planar co-ordination and the Co^{2+} ions showing octahedral and tetrahedral co-ordination.

Superstructures resulting from the ordering of anion vacancies in metal oxides,¹ particularly those of perovskite structure,² have attracted considerable attention in the last few years. The best known example of such an oxide is $\text{Ca}_2\text{Fe}_2\text{O}_5$ possessing the brownmillerite structure with alternate sheets of octahedra and tetrahedra³ along the b -axis of an orthorhombic unit cell; $\text{Ca}_2\text{Mn}_2\text{O}_5$ and $\text{Ca}_2\text{Co}_2\text{O}_5$, on the other hand, possess sheets of square-pyramids^{4,5} along the c -axis of an orthorhombic unit cell (Figure 1). We have investigated two novel oxides of the formula $\text{La}_2\text{B}_2\text{O}_5$ ($B = \text{Co}$ or Ni), prepared by low temperature reduction⁶ of the parent perovskites, LaBO_3 , and representing the $n = 2$ members of the homologous series $\text{La}_n\text{B}_n\text{O}_{3n-1}$. This homologous series was first proposed by Gai and Rao⁷ on the basis of a thermogravimetric study of LaNiO_3 in air which showed the presence of members with $n \geq 7$. While $\text{La}_2\text{Ni}_2\text{O}_5$ can be prepared by the reduction of LaNiO_3 at 600 K in pure or dilute (10% H_2 -90% N_2 by volume) hydrogen, $\text{La}_2\text{Co}_2\text{O}_5$ can only be prepared by the reduction of LaCoO_3 in dilute hydrogen at 670 K. Neither $\text{La}_2\text{Co}_2\text{O}_5$ nor $\text{La}_2\text{Ni}_2\text{O}_5$ can be made by the solid state reaction of La_2O_3 and the transition metal oxide. Reduction of LaBO_3 gives rise to these oxides because of the topotactic nature of the reaction; $\text{La}_2\text{B}_2\text{O}_5$ so formed can be oxidized back to the parent LaBO_3 at low temperature as seen from the typical thermogravimetric curves shown in Figure 2.

X-Ray powder diffraction data of $\text{La}_2\text{Co}_2\text{O}_5$ could be indexed on an orthorhombic unit cell ($a = 5.460$, $b = 15.908$, and $c = 5.700$ Å) with a brownmillerite structure involving alternate sheets of octahedra and tetrahedra along the b -axis (Figure 1). The electron diffraction pattern also confirms this structure, although some streaking is noticed owing to some disorder. The topotactic relationship between the orthorhombic $\text{La}_2\text{Co}_2\text{O}_5$ and the cubic perovskite can be expressed as $(100)_0 \parallel (110)_c$ and $(040)_0 \parallel (001)_c$ and $(001)_0 \parallel (1\bar{1}0)_c$.

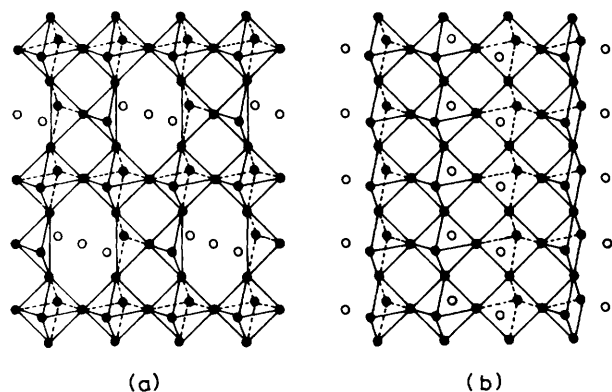


Figure 1. Schematic representations of the structures of (a) $\text{Ca}_2\text{Fe}_2\text{O}_5$ with alternate sheets of octahedra and tetrahedra along the b -axis and (b) $\text{Ca}_2\text{Mn}_2\text{O}_5$ with sheets of square pyramids along the c -axis (●: oxygen; ○: oxygen vacancy).

The X-ray powder diffraction pattern of $\text{La}_2\text{Ni}_2\text{O}_5$ is quite different from that of brownmillerite or that of the parent LaNiO_3 and could be indexed on a tetragonal cell ($a = 7.816$ and $c = 7.468$ Å), the relationship with the cubic perovskite being $a \approx c \approx 2a_c$. Electron diffraction studies confirm these unit cell dimensions. In Figure 3, the electron diffraction pattern of $\text{La}_2\text{Ni}_2\text{O}_5$ in the $[001]$ zone-axis is shown, along with the projection of the proposed structure and the expected

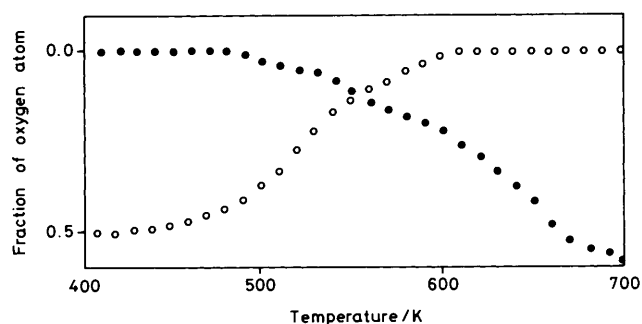


Figure 2. Thermogravimetric curves showing reduction of LaNiO_3 to $\text{La}_2\text{Ni}_2\text{O}_5$ in pure hydrogen (●) and reoxidation of $\text{La}_2\text{Ni}_2\text{O}_5$ to LaNiO_3 in oxygen (○). A similar behaviour was found in the LaCoO_3 - $\text{La}_2\text{Co}_2\text{O}_5$ system.

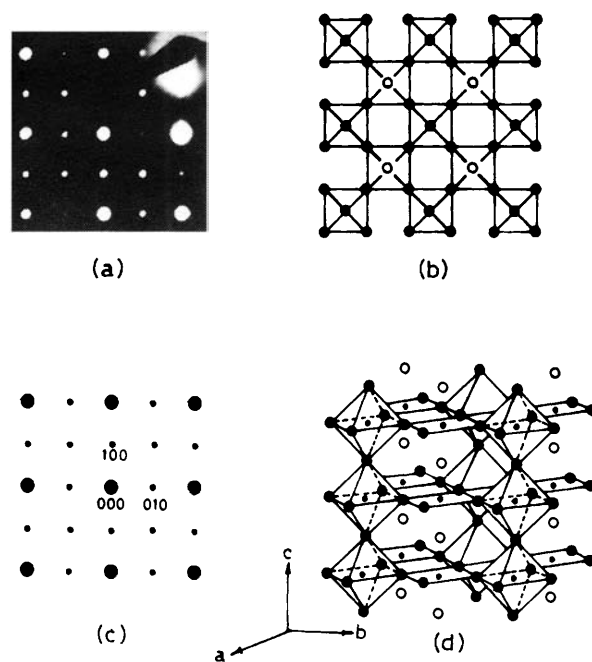


Figure 3. (a) $[001]$ Zone-axis electron diffraction pattern of $\text{La}_2\text{Ni}_2\text{O}_5$. (b) Projection along $[001]$ of the proposed structure of $\text{La}_2\text{Ni}_2\text{O}_5$. (c) Expected electron diffraction pattern in the same direction. (d) Proposed 3-D structure for $\text{La}_2\text{Ni}_2\text{O}_5$ (●: oxygen; ○: oxygen vacancy; ●: nickel; lanthanum ions are not shown).

electron diffraction pattern. The most likely structure of this oxide is one involving the ordering of oxygen vacancies along the [110] direction in the (001) LaO planes of the perovskite lattice as depicted in Figure 3. Such an arrangement of oxygen vacancies results in planes of $\text{LaO}_{0.5}\square_{0.5}$ and NiO_2 stacked alternately parallel to the c -axis giving rise to square planar and octahedral co-ordination for Ni^{2+} . The topotactic relationship between the tetragonal $\text{La}_2\text{Ni}_2\text{O}_5$ and the cubic perovskite may be expressed as: $(200)_t \parallel (100)_c$ and $(002)_t \parallel (001)_c$. This tetragonal cell is different from that of La_2NiO_4 which bears the relationship with the cubic perovskite cell, $a \approx a_c$ and $c \approx 3a_c$. The difference between the structures of $\text{La}_2\text{Co}_2\text{O}_5$ and $\text{La}_2\text{Ni}_2\text{O}_5$ can also be understood in terms of the site preference energies of Co^{2+} and Ni^{2+} ions. It appears that Ni^{2+} , which has lower tetrahedral site preference energy than Co^{2+} , prefers a square planar co-ordination; both Ni^{2+} and Co^{2+} however have relatively high octahedral vs. tetrahedral site preference energies.

Both $\text{La}_2\text{Co}_2\text{O}_5$ and $\text{La}_2\text{Ni}_2\text{O}_5$ exhibit high electrical resistivity and show i.r. bands in the $1000\text{--}200\text{ cm}^{-1}$ region, characteristic of perovskite related structures; metallic LaNiO_3 does not show any i.r. bands. Both these oxides exhibit a large magnetic susceptibility, especially at low

temperatures. The origin of this magnetic behaviour is not clear.

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