Oxygen Vacancy Ordering in Superlattices of the Two Novel Oxides, La₂Ni₂O₅ and La₂Co₂O₅, prepared by Low Temperature Reduction of the Parent Perovskites

Kanamaluru Vidyasagar, Armin Reller, Jagannatha Gopalakrishnan, and C. N. Ramachandra Rao*
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Controlled reduction of LaBO₃ (B = Co or Ni) perovskites gives rise to ordered structures of composition La₂B₂O₅, belonging to the homologous series La_nB_nO_{3n-1}, which retain the original features of the perovskite; the co-ordination of the transition metal ions differ, with Ni²⁺ ions showing octahedral and square-planar co-ordination and the Co²⁺ ions showing octahedral and tetrahedral co-ordination.

Superstructures resulting from the ordering of anion vacancies in metal oxides, particularly those of perovskite structure, 2 have attracted considerable attention in the last few years. The best known example of such an oxide is Ca₂Fe₂O₅ possessing the brownmillerite structure with alternate sheets of octahedra and tetrahedra along the b-axis of an orthorhombic unit cell; Ca₂Mn₂O₅ and Ca₂Co₂O₅, 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 $La_2B_2O_5$ (B = Co or Ni), prepared by low temperature reduction⁶ of the parent perovskites, LaBO₃, and representing the n = 2 members of the homologous series $La_nB_nO_{3n-1}$. This homologous series was first proposed by Gai and Rao⁷ on the basis of a thermogravimetric study of LaNiO₃ in air which showed the presence of members with $n \ge 7$. While La₂Ni₂O₅ can be prepared by the reduction of LaNiO₃ at 600 K in pure or dilute (10% H₂-90% N₂ by volume) hydrogen, La₂Co₂O₅ can only be prepared by the reduction of LaCoO₃ in dilute hydrogen at 670 K. Neither La₂Co₂O₅ nor La₂Ni₂O₅ can be made by the solid state reaction of La₂O₃ and the transition metal oxide. Reduction of LaBO₃ gives rise to these oxides because of the topotactic nature of the reaction; La₂B₂O₅ so formed can be oxidized back to the parent LaBO₃ at low temperature as seen from the typical thermogravimetric curves shown in Figure 2.

X-Ray powder diffraction data of La₂Co₂O₅ 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 La₂Co₂O₅ and the cubic perovskite can be expressed as $(100)_0 \parallel (110)_c$ and $(040)_0 \parallel (001)_c$ and $(001)_0 \parallel (1\overline{10})_c$.

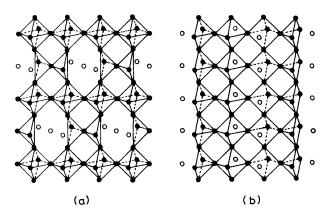


Figure 1. Schematic representations of the structures of (a) $Ca_2Fe_2O_5$ with alternate sheets of octahedra and tetrahedra along the *b*-axis and (b) $Ca_2Mn_2O_5$ with sheets of square pyramids along the *c*-axis (\bullet : oxygen; \circ : oxygen vacancy).

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 La_3Ni_3 and could be indexed on a tetragonal cell (a=7.816 and c=7.468 Å), the relationship with the cubic perovskite being $a=c=2a_c$. 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

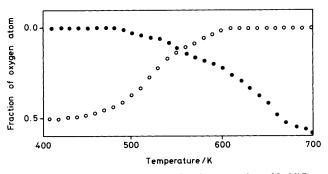


Figure 2. Thermogravimetric curves showing reduction of LaNiO₃ to La₂Ni₂O₅ in pure hydrogen (\bullet) and reoxidation of La₂Ni₂O₅ to LaNiO₃ in oxygen (\circ). A similar behaviour was found in the LaCoO₃-La₂Co₂O₅ system.

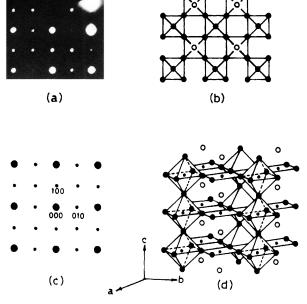


Figure 3. (a) [001] Zone-axis electron diffraction pattern of $La_2Ni_2O_5$. (b) Projection along [001] of the proposed structure of $La_2Ni_2O_5$. (c) Expected electron diffraction pattern in the same direction. (d) Proposed 3-D structure for $La_2Ni_2O_5$ (\bullet : oxygen; \circ : oxygen vacancy; \bullet : 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 $LaO_{0.5}\square_{0.5}$ and NiO_2 stacked alternately parallel to the c-axis giving rise to square planar and octahedral co-ordination for Ni2+. The topotactic relationship between the tetragonal La2Ni2O5 and the cubic perovskite may be expressed as: (200), $\|(100)$ _c and $(002)_t \parallel (001)_c$. This tetragonal cell is different from that of La₂NiO₄ which bears the relationship with the cubic perovskite cell, $a \approx a_c$ and $c \approx 3a_c$. The difference between the structures of La₂Co₂O₅ and La₂Ni₂O₅ can also be understood in terms of the site preference energies of Co²⁺ and Ni²⁺ ions. It appears that Ni2+, which has lower tetrahedral site preference energy than Co2+, prefers a square planar coordination; both Ni2+ and Co2+ however have relatively high octahedral vs. tetrahedral site preference energies.

Both La₂Co₂O₅ and La₂Ni₂O₅ exhibit high electrical resistivity and show i.r. bands in the 1000—200 cm⁻¹ region, characteristic of perovskite related structures; metallic LaNiO₃ does not show any i.r. bands. Both these oxides exhibit a large magnetic susceptibility, expecially at low

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

The authors thank the Department of Science and Technology, Government of India and the University Grants Commission for support of this research.

Received, 3rd September 1984; Com. 1248

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