

Solid state chemistry of Ruddlesden–Popper type complex oxides

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Abstract. Various criteria of formation of perovskites and K_2NiF_4 -type compounds, which are the end members of homologous Ruddlesden–Popper series of phases, have been discussed. RP-phases show some general trends in their physical properties. Literature survey of the formation of these phases, their properties, and effect of oxygen stoichiometry and doping is presented. Some conditions for their synthesis are also described.

Keywords. RP-type complex oxides; synthesis; crystal structure; physical properties.

1. Introduction

Complex oxides of composition ABO_3 generally take up perovskite structure provided a tolerance factor (t), which is defined by the relation $t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$, has value between 0.75 and 1, where r_s are the ionic radii (Geller and Wood 1956; Katz and Ward 1964; Glasco 1969; Ganguly and Rao 1984; Rao and Gopalakrishnan 1986). Another study shows that perovskite and related compounds usually crystallize if $1.0 < r_A < 1.9 \text{ \AA}$ and $0.5 < r_B < 1.2 \text{ \AA}$ (Kafalas and Longo 1972). The complex oxides of general formula A_2BO_4 crystallize in K_2NiF_4 -type structure, which could be said as consisting of perovskite slabs of unit thickness stacked one over the other along the c -axis such that adjacent slabs are displaced relative to one another by $1/2 \ 1/2 \ 1/2$ (Wells 1978). Crystal chemical considerations suggest that for K_2NiF_4 -type structure to be stable, r_A/r_B ratio should lie between 1.7 and 2.4 (Ganguli 1979; Rao *et al* 1984). According to the literature survey, of all the known compounds, hardly 5% have r_A/r_B values lying outside the prescribed range. By using invariant method, Poix (1980) has given the following relation between the average cation–oxygen distances associated to the 9 and 6 coordinated sites (ψ_A and β_B) and volume V of the unit cell in K_2NiF_4 structure:

$$0.99615 V^{1/3} = \beta_B + \psi_A 2^{1/2}.$$

K_2NiF_4 -type structure is two-dimensional in the sense that only equatorial anions of BO_6 octahedra are linked through the corners. The perovskite and K_2NiF_4 -type structures are shown in figure 1. Recently, on the basis of a geometrical matching between the bond distances, a new tolerance factor, $t_t = [3\sqrt{2}r_O + 2\sqrt{6}(r_A + r_O)] / 9(r_B + r_O)$, has been formulated for the Nd_2CuO_4 -type structure,

where r_A , r_B and r_O are the radii of the A, B and O ions, respectively (Chen 1996). T' phases occur for $t_t < 1.00$, while T phases form for $t_t > 1.00$. The T^* phase exists in a very narrow region between the stability boundaries of the other two structure-types.

The perovskites and K_2NiF_4 -type compounds are the end members of homologous series of the phases given by the general formula $A_{n+1}B_nO_{3n+1}$. This formula could also be written as $AO(ABO_3)_n$, where n perovskite layers are stacked between rock-salt AO layers along the crystallographic c -axis (Ruddlesden and Popper 1957, 1958). Such compounds, also known as Ruddlesden–Popper (RP) type phases, exhibit interesting physical properties as one moves to higher members of the family. The three-dimensional character increases in higher members of the family because of presence of increased numbers of the ABO_3 slabs. A schematic presentation of RP-type phases is given in figure 2. In these structures, the BO_6 octahedral corners share each other, extending infinitely in the ab plane, and the n units of such planes stack in the c -direction to form the perovskite slab. In case A is a rare earth and/or alkaline earth ion, and B is a transition metal ion in such compounds, the electric transport and magnetic properties of these phases within a given series are governed by the identity and valence state of the ions, width of n perovskite slabs, B–O–B bond angle and the oxygen content (Singh *et al* 1984; Buttrey *et al* 1986; Zhang and Greenblatt 1994).

2. General trends in properties

It is interesting to note that in many RP-type compounds, magnetic properties reflect itinerant electron behaviour, while the electric transport properties do not; although both insulating and metallic behaviour are observed, the

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former is predominant. The lowest electric resistivity observed in an $n=1$ phase of any RP family is of the order of 10^{-2} ohm cm. Resistivity generally decreases further in higher members of the family because of the increasing three-dimensional character (Rao *et al* 1988). Sr_2FeO_4 has resistivity of several orders of magnitude higher than the corresponding $n=2$ member (Adler 1994). In the $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ family, the room temperature resistivity (ρ_{300}) decreases from ~ 250 m ohm cm for the $n=2$ member to ~ 1.8 m ohm cm for the $n=\infty$ member (Sreedhar *et al* 1994). The K_2NiF_4 -type oxides, if metallic, do not show metallic phenomenon over wide range of temperature. However, higher members of the analogous series could be exception; Sr_2VO_4 is an insulator, while

$\text{Sr}_4\text{V}_3\text{O}_{9.7}$ is metallic down to 4.2 K (Rey *et al* 1990; Gong *et al* 1991; Takeno *et al* 1991; Ohashi *et al* 1992). Moving upwards from $n=1$ to higher members of the family, an evolution in metallic conductivity is observed.

K_2NiF_4 , which is paradigm of the RP phases when $n=1$, has magnetic cell with dimensions $a_M = \sqrt{2}a_{CM}$ and $c_M = c_{CM}$, where subscripts refer to magnetic (M) and chemical (CM) cells (Greedan *et al* 1992). The magnetic interactions are essentially antiferromagnetic; intralayer magnetic interactions are strongly antiferromagnetic due to nearest neighbour 180° Ni-F-Ni superexchange, while interlayer interactions are much weaker as the pathways, Ni-F-K-F-Ni, are more convoluted. Stoichiometric two-dimensional phases, having either K_2NiF_4 type structure or the one derived from the tetragonal K_2NiF_4 cell by an orthorhombic distortion, possess essentially the same magnetic structure as K_2NiF_4 except that moment direction may be along a different axes. Only a few compounds are known, namely, LaSrFeO_4 and $\beta\text{-Sr}_2\text{MnO}_4$, which require a magnetic cell different from that of K_2NiF_4 ($a_M = a_{CM}$) (Soubeyroux *et al* 1980; Bouloux *et al* 1981).

Flem *et al* (1982) have shown that it is possible to predict the electronic configuration of various cations in

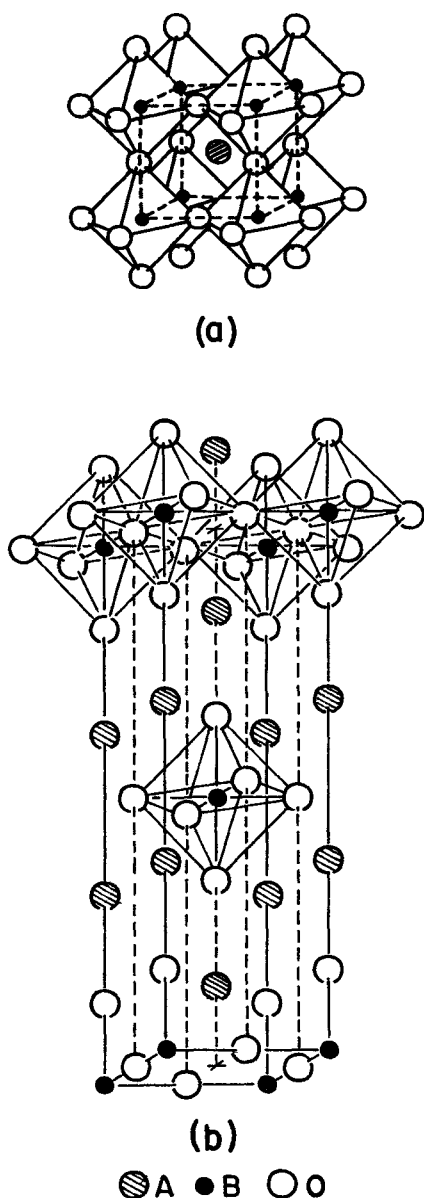


Figure 1. (a) Perovskite structure; and (b) K_2NiF_4 structure.

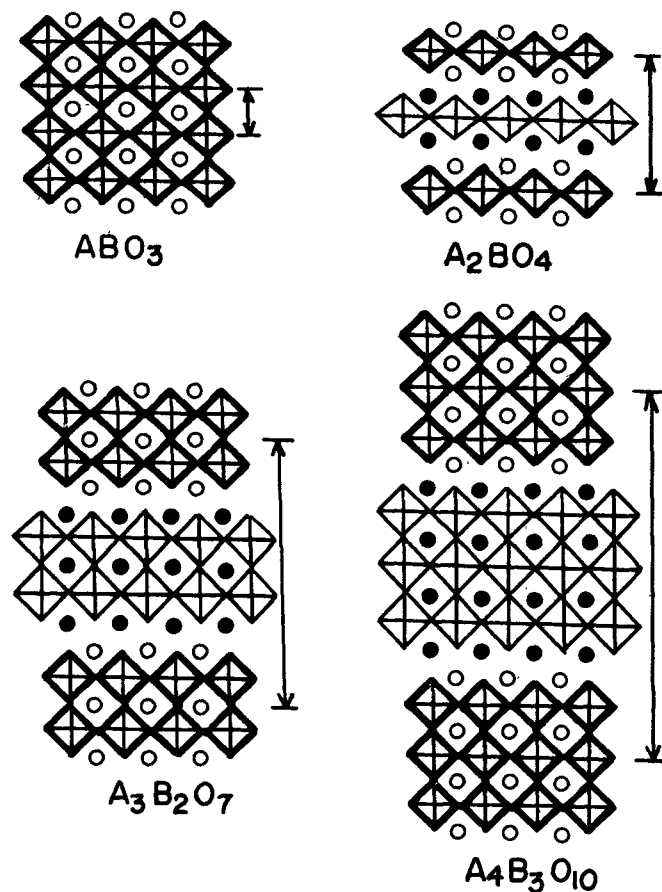


Figure 2. Schematic illustration of the members of $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ series.

K_2NiF_4 -type oxides on the basis of elementary structural and boundary considerations. $CaLaFeO_4$ and $SrLaFeO_4$ ferrites have a prevailing 2D behaviour, while for La_2MnO_4 and $CaYCrO_4$, in the absence of e_g electrons and $e_g-p_g-e_g$ bonds, the competition between $\pi(Mn, Cr)-O$ and $(Ca, Ln)-O$ bonds alters the 2D character of magnetic interactions and leads to 3D behaviour. Such deviations could be as a result of two factors: (i) decreasing distance between the magnetic $(MnO_4)_n$ or $(CrO_4)_n$ layers due to substitution of one ion by a smaller one in the 9-coordinated site, and (ii) decreasing the covalent character of Mn–O or Cr–O bonds.

Nature and size of the cations at the sites A and B influence the structure and properties of these layer-structured phases significantly. The size of A-site ion at the 9-coordinated position affects the cell parameters and consequently, the structure of these compounds. The larger cations at site A elongate the interlayer distance, hence increase in c , while smaller ions shorten it. The size of the ion at site A is expected to affect the lattice constant c more prominently than a . In the system $Ln_2SrFe_2O_7$ ($Ln = La, Nd, Gd$ and Dy), there is drastic change in c as a result of the heavier rare-earth ions substitution, and in these quasi two-dimensional phases interlayer magnetic interactions become more dominant with decrease in c (Sharma *et al* 1998). Because B–O interactions occur only along ab plane, the cation at site B is expected to influence the cell parameter a more predominantly.

Acidity of the ions at the A and B sites influences the structure and property. According to Goodenough (1971), more basic the cation at the position A higher is the covalency of the $\pi(B-O)$ bond which competes with the $\sigma(A-O)$ bond. The metallic character of $LaSrNiO_4$ is due to strong covalency of the Ni–O bonding. Another factor which influences the behaviour of these phases is the John–Teller effect, which comes into existence due to difference in the electronic population in the e_g orbitals. For example, high spin Fe^{4+} ion in $t_{2g}^4 e_g^1$ electronic state undergoes John–Teller distortion due to anisotropic electronic configuration, affecting both structure and properties (Tresse *et al* 1993).

2.1 Importance

The intergrowth structures based on perovskite blocks in inorganic systems have provided a fertile field of solid state chemical research for many years for the rich variety of their structural and physical properties. The epoch making discovery of superconductivity in the $La_{2-x}Ba_xCuO_4$ system, derived from La_2CuO_4 , has added additional dimension to the investigation of these phases (Bednorz and Muller 1986; Cava *et al* 1987; Mohan Ram *et al* 1987). However, there has been much interest in the physical properties and structural chemistry of

perovskite-related compounds even before the discovery of superconductivity for their wide range of applications such as ideal semiconductors, magnetic materials, high temperature superconductors, catalysts, electrode materials etc (Longo and McCauley 1986).

2.2 Range of studies

One of the extensively studied systems in RP series of phases is rare-earth copper oxides (RE_2CuO_4). The rare-earth copper oxides are known to exist in five different structural modifications, T' , T^* , T'' , and tetragonal and orthorhombic T structures (Manthiram and Goodenough 1990; Chen and Eichhorn 1992). The specific structural modifications correlate exceedingly well with the value of the tolerance factor t . When a reasonable match between the A–O and B–O layers exists ($0.99 \geq t \geq 0.88$), the T phase is tetragonal with $I4/mmm$ crystal symmetry. The tolerance factor in the range $0.88 \geq t \geq 0.87$ leads to orthorhombic distortion, while $t \leq 0.865$ results into T' (or T^*) structure. La_2CuO_4 crystallizes in a slightly distorted K_2NiF_4 T -tetragonal structure at high temperature and undergoes a displacive transition to orthorhombic symmetry below transition temperature. Unlike La_2CuO_4 , Nd_2CuO_4 has a T' -tetragonal structure, consisting of planer $(CuO_2)_2$ anionic layers cross linked by $(Nd_2O_2)_2$ layers. The A-site atoms are 8-coordinated in this case against 9-coordinated in the K_2NiF_4 structure. The mixed lanthanide system $La_{2-x}Ln_xCuO_4$ ($Ln = Sm, Dy$), takes up hybrid T^* tetragonal structure. Here the inactive Ln–O layers alternate between the (001) rocksalt LaO layers of the T structure and the fluorite-type layers of the T' structure. The T'' structure suggests cation ordering within a Ln–O layer. The T , T' and T^* structures are shown in figure 3 (James *et al* 1989; Tokura *et al* 1989; Bringley *et al* 1990).

The properties of $La_2CuO_{4+\delta}$ are extremely sensitive to change in oxygen stoichiometry. For a slightly negative value of δ , $La_2CuO_{4+\delta}$ is an antiferromagnetic semi-

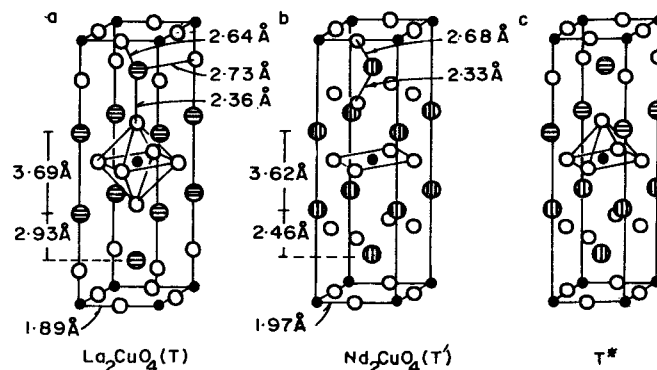


Figure 3. Illustration of the T , T' and T^* structures.

conductor. Antiferromagnetism disappears with change in oxygen stoichiometry as small as 1%. As δ become positive, holes are introduced into the structure and metallic behaviour is observed (Bringley *et al* 1990). La_2CuO_4 when doped with holes either by introducing excess oxygen into the structure or partial replacement of La by alkaline earth metal ions, containing Cu nominally in mixed valent state (2+, 3+), shows superconductivity (Cava *et al* 1987; Mohan Ram *et al* 1987). The compounds with *T* structure become superconducting only when electron doped, which is possible by partial substitution of Ce at RE-site or partial replacement of oxygen by fluorine. $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ ($T_c = 24$ K) and $\text{Nd}_2\text{CuO}_{3.6}\text{F}_{0.4}$ ($T_c = 27$ K) are examples of this category of superconductors (James *et al* 1989; Tokura *et al* 1989).

$\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ ($n = 1, 2$ and 3) series is one of the widely studied systems (Poix 1980; Drenan *et al* 1982; Mohan Ram *et al* 1986; Bassat *et al* 1987; Buttrey and Honig 1988; Arbuckle *et al* 1990; Nanjundaswamy *et al* 1990; Sreedhar and Honig 1994; Sreedhar *et al* 1994; Zhang and Greenblatt 1994; Zhang *et al* 1994). The crystal structure of La_2NiO_4 is reported to be tetragonal with space group *I4/mmm*; electron diffraction studies, however, show it having monoclinic distortion. The unit cells of $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$ are orthorhombic; the former in the space group *Fmmm*. Electric transport and magnetic properties suggest an interesting 3-dimensional character across the homologous series with increase in n , and this trend is suggested to be related to the percolation threshold. La_2NiO_4 exhibits a semiconductor-metal transition at around 550 K, while $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ is reported to be superconducting down to 70 K (Kakol *et al* 1989; Rao *et al* 1989). Samples of La_2NiO_4 , annealed in CO_2 at 1400 K, show evidence for long range antiferromagnetic ordering. The magnetic susceptibility seems to be simply the sum of the susceptibilities of $(n-1)$ LaNiO_3 and La_2NiO_4 , as if Ni^{3+} and Ni^{2+} are segregated in different layers (Mohan Ram *et al* 1986). Results of another study suggest cross over from fluctuating valence to a Fermi-liquid-like behaviour with increase in n (Bassat *et al* 1987). Fully reduced $\text{La}_3\text{Ni}_2\text{O}_{6.35}$ shows linear dependence of $\ln \rho$ vs $T^{-1/4}$, suggesting a variable range hopping mechanism for electrical conductance (Zhang *et al* 1994). Discovery of diamagnetism in $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_{2-x}\text{M}_x\text{NiO}_4$ ($M = \text{Ca}, \text{Sr}$) compounds at low temperature is another reason for extensive studies on structure and properties of nickelates (Sreedhar and Honig 1994). In the series $\text{La}_{n+1}\text{CO}_n\text{O}_{3n+1}$, the $n = 1$ and 3 phases are reported to crystallize in orthorhombic unit cell in the space group *Fmmm* (Seppanen and Tikkanen 1976; Janecek and Wirtz 1978; Lehmann and Buschbaum 1980; Longo and McCauley 1986; Sharma and Singh 1995a). Some studies, however, suggest pseudo monoclinic/tetragonal structure for the $n = 1$ phase (Lehuede and Daire 1973; Kniga *et al* 1979).

The $n = 1$ and 2 phases in the series $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}$, Sr_2FeO_4 and $\text{Sr}_3\text{Fe}_2\text{O}_7$, are reported to crystallize in the tetragonal unit cell in the space group *I4/mmm* on the basis of X-ray and neutron diffraction (Dann *et al* 1992; Adler 1994). The $n = 1$ phase is Mott-type antiferromagnetic semiconductor undergoing magnetic ordering at about 60 K. $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$, its mixed Fe/Al analogue and the $\text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}$ ($n = 1$ and 3) phases are known to be iso-structural with the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ compounds (Ruddlesden and Popper 1957, 1958; Lees *et al* 1993). $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1-\delta}$ ($n = 2$ and 3) phases show electrical conduction which has little dependence on the stacking number of perovskite slabs (n), a phenomenon contrary to the belief that the properties of RP-phases are a function of n (Kim *et al* 1992).

If the size of cation at site A is too large relative to that at site B, the ABO_3 end members do not take up the perovskite or related structures at atmospheric pressure but form a hexagonal polytype, and to transform them to perovskite related structure higher pressures are needed. The phases of the systems $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ ($n = 1, 2$ and 3) and $\text{Sr}_{n+1}\text{Cr}_n\text{O}_{3n+1}$ ($n = 1$ and 2) have been synthesized by this process (Kafalas and Longo 1972). All the phases are known to have tetragonal unit cell dimensions. The synthesis under high pressure is achieved at faster pace.

The $n = 1, 2$ and 3 members in the series $\text{Sr}_{n+1}\text{V}_n\text{O}_{3n+1}$ are reported to crystallize in tetragonal unit cell in the space group *I4/mmm* (Feltz and Schmalfluss 1975; Cryot *et al* 1990; Itoh *et al* 1990; Rey *et al* 1990; Gong *et al* 1991; Suzuki *et al* 1991; Takeno *et al* 1991; Ohashi *et al* 1992). The $n = 2$ and 3 compounds exhibit metallic behaviour, while the $n = 1$ compound is an antiferromagnetic insulator. The electric and magnetic properties of these compounds indicate that localized t_{2g} orbitals of V^{4+} ions transform into the collective narrow π^* bands with increasing number of perovskite layers n .

A possible correlation exists between the observed electrical properties and the degree of distortion in the V-O polyhedra of $\text{Sr}_4\text{V}_3\text{O}_{10-\delta}$ (Takeno *et al* 1991; Ohashi *et al* 1992). This compound exists in two different polytypes. It is considered that because of their similarity of structural and physical properties with La-Cu-O superconductors, $\text{Sr}_{n+1}\text{V}_n\text{O}_{3n+1}$ ($n = 1, 2$ and 3) phases with 1/2 spin of V^{4+} ion—the property considered essential for high T_c superconductivity in the Cu-oxides—are the candidates for high T_c superconductivity with appropriate doping, although no such phase has as yet been discovered (Rey *et al* 1990; Gong *et al* 1991; Takeno *et al* 1991; Ohashi *et al* 1992).

La_2CuO_4 exhibits field-dependent ferromagnetism below 850 K and has nearly temperature-independent resistivity above 200 K except for small maximum near 530 K that is associated with a smooth O-T transition (Singh *et al* 1984), while its alkaline earth- and alkali-substituted analogues are superconductors (Bednorz and Muller 1986;

Mohan Ram *et al* 1987; Gunther and Schollhorn 1992). $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_{6+\delta}$ (212) and the related calcium doped compounds have been of considerable interest due to the discovery of superconducting behaviour in $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_{6+\delta}$ (Dann *et al* 1992).

In the system $\text{Sr}_{n-1}\text{Ru}_n\text{O}_{3n+1}$ ($n = 1$ and 2), both the known phases crystallize with tetragonal unit cell in the space group $I4/mmm$ (Muller-Buschbaum and Wilkens 1990; Huang *et al* 1994). When $n = 1$ and 2 , the phases are antiferromagnetic, while the $n = \infty$ phase is ferromagnetic conductor. Williams *et al* (1991) have shown that $n = 2$ phase is metallic down to 4 K, while we found that this phase follows variable range hopping mechanism in electric transport but the characteristic energy of hopping is much reduced (Sharma and Singh 1996). The recent discovery of superconductivity ($T_c \sim 1$ K) in Sr_2RuO_4 has generated new interest in the ruthenates (Maeno *et al* 1994). Strontium ruthenates SrRuO_3 and Sr_2RuO_4 , while well known materials for some time, have been subject of renewed interest due to their low metallic resistivities and chemical compatibility with $\text{YBa}_2\text{Cu}_3\text{O}_7$, suggesting that they might be useful as normal metal electrodes in superconducting thin film devices (Lichtenberg 1992; Cava *et al* 1995). The solid-solution $\text{Sr}_{3x}\text{La}_{2-3x}\text{Zn}_{1-x}\text{Ru}_x\text{O}_4$ also crystallizes in K_2NiF_4 structure with disordered arrangement of Zn^{2+} and Ru^{5+} over the octahedral sites (Kim and Battle 1994). Sr_2RhO_4 is reported to be orthorhombic with possible space group $Fmmm$ or $Cmca$ (Shimura *et al* 1992). The temperature coefficient of resistivity is positive down to 10 K, while magnetic measurements reveal a two-dimensional nature of the magnetic ordering. Another study shows that it crystallizes with the symmetry of space group $I4_1/acd$, isostructural with Sr_2IrO_4 (Itoh *et al* 1995).

In $\text{La}_2\text{MnO}_{4+\delta}$, the manganese ion is predominantly in 2+ oxidation state and it is not possible to stabilize this oxidation state in oxides at low temperature. Some workers have reported formation of this phase above 1653 K and stabilized it by very fast quenching of samples to room temperature (Borlera and Abbattista 1983). In the system $\text{Ca}_{n-1}\text{Mn}_n\text{O}_{3n+1}$, Ca_2MnO_4 is reported to crystallize in tetragonal unit cell in $I4_1/acd$ space group (Feltz and Schmalfluss *et al* 1975; Ganguli 1979; Takahashi and Kamegashira *et al* 1993). The purity of reaction product is affected by the heating rate. It has been observed that during the preparation of these compounds decomposition of solid-solution precursor does not always directly lead to desired products. For example, appropriate calcite precursors for $n = 2$ and 3 phases, when decomposed in oxygen, lead to mixed products which predominantly consist of CaMnO_3 and Ca_2MnO_4 (Longo and Horowitz 1981). It is preferred that the reactants be introduced in a furnace that has already been pre-heated to the required temperature to get single phase product.

The powder XRD pattern of La_2PdO_4 has been indexed on tetragonal unit cell with $a = 4.055 \text{ \AA}$ and $c = 12.624 \text{ \AA}$ in the space group $I4/mmm$ (Attfield and Ferey 1989). The data suggest that the structure of La_2PdO_4 is of Nd_2CuO_4 -type, rather than the K_2NiF_4 -type, as the c/a ratio is characteristic of the former structure, but too small to be consistent with the latter.

A large number of phases of the system $\text{Ln}_n\text{AM}_n\text{O}_{3n+1}$ ($\text{Ln} =$ rare earth ion, $\text{A} =$ alkaline earth ion and $\text{M} = \text{Co}, \text{Ni}, \text{Cr}, \text{Al}, \text{Fe}, \text{Mn}, \text{Ru}, \text{Rh}, \text{Ga}$) have been reported in the literature (Blasse 1965, 1968; Joubert *et al* 1970; Fava *et al* 1972; Daoudi and Flem 1973; Samaras *et al* 1973; Demazeau *et al* 1976a, b, 1979; Benabad *et al* 1977; Cheruy and Joubert 1981; Sharma and Singh 1995b, 1997). Most of these compounds, showing interesting electric transport and magnetic properties, crystallize either in the tetragonal or orthorhombic crystal symmetry in the space group $I4/mmm$, $Fmmm$ or $Cmca$. Magnetic studies suggest that Co^{3+} ions in LaSrCoO_4 are present in both high- and low-spin states in equal proportions, while the material undergoes spin state transition above 400 K. Some workers have, however, suggested intermediate spin state for the cobalt ion ($t_{2g}^5 e_g^1$) (Rao *et al* 1988). The iron containing phases are antiferromagnetic insulators. Electrical conduction in LaSrNiO_4 occurs via 2D variable range hopping, while Ni^{3+} ion is in low spin state. $\text{Ln}_2\text{Li}_{0.5}\text{Au}_{0.5}\text{O}_4$ ($\text{Ln} =$ rare earth) phases, having trivalent gold in square planar surroundings, also crystallize in tetragonal unit cell (Tresse *et al* 1993). X-ray diffraction study shows that c/a ratio is reduced to great extent (3.05 ± 0.06) as compared to that of isotropic electronic configuration in K_2NiF_4 structure (Glasso 1969). Demazeau *et al* (1984) have stabilized anisotropic electronic configuration of transition elements (high spin Fe^{4+} , low spin Co^{4+} , medium spin Co^{3+} , low spin Ni^{3+} and low spin Cu^{3+}) from matrix having K_2NiF_4 structure, which is the result of the elongation of MO_6 octahedra and is confirmed by c/a ratio of the tetragonal K_2NiF_4 -type cell of these phases. John-Teller distortion has also been propounded on this basis. Some other compounds, having Mn^{3+} -like ions, are also known to undergo John-Teller distortion, which leads to distortion in their structure and properties (Cheruy and Joubert 1981; Sharma and Singh 1995b).

Many manganites having perovskite-related structure such as $(\text{La}, \text{Sr})_{n-1}\text{Mn}_n\text{O}_{3n+1}$ ($n = 2$ and 3) and $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} =$ alkaline earth metal ion) exhibit ferromagnetism and insulator-metal transition at low temperature (Mahesh *et al* 1996; Sharma and Magotra 1998). These materials also show colossal magnetoresistance (CMR). The $\text{Mn}^{3+}/\text{Mn}^{4+}$ mixed valence state in the manganites creates mobile charge carriers and canting of Mn spins. These ionic states fluctuate due to electron transfer between them. As a result of this electron transfer, magnetization and metallic conductivity appear almost simultaneously

(Helmolt *et al* 1993; Verelst *et al* 1993; McCormack 1995). A distinct feature of such a barely metallic state in the manganese oxides is that there is a strong exchange interaction between the itinerant e_g electrons (or holes) and the local t_{2g} spins, which governs the electronic properties including the temperature and magnetic field dependent metal–non-metal phenomenon.

Many layered perovskites of titanium, and niobium and their mixed analogues have been studied recently because of their possible applications in catalysis and electrochemistry (Dion *et al* 1984; Gopalakrishnan and Bhat 1987; Sato *et al* 1992; Uma *et al* 1993; Richard *et al* 1994). There is growing interest in the proton exchange and subsequent dehydration of the layered alkali oxides. $K_2Nd_2Ti_3O_{10}$ and $Na_2Nd_2Ti_3O_{10}$ spontaneously intercalate water, and acid exchange of the compounds leads to formation of the protonated phases. In the mixed niobium and titanium phases, the variation of the Bronsted acidity across the series is probably due to an ordering of niobium–titanium atoms in the perovskite slabs (Gopalakrishnan *et al* 1993).

In recent years, there are reports of synthesis of some

Table 1. Some important RP-type phases with lattice type/symmetry.

Compound	Lattice type/symmetry
RE_2CuO_4 (RE = rare earth)	T, T', T'', T^*
$La_{n+1}Ni_nO_{3n+1}$ ($n = 1, 2, 3$)	tetragonal/monoclinic ($n = 1$), orthorhombic ($n = 2, 3$)
$La_{n+1}Co_nO_{3n+1}$	orthorhombic ($n = 1, 3$), pseudo monoclinic/tetragonal symmetry for $n = 1$ also suggested
$Sr_{n+1}Ti_nO_{3n+1}$	tetragonal
$Sr_{n+1}Fe_nO_{3n+1}$	tetragonal
$Sr_{n+1}Ir_nO_{3n+1}$	tetragonal
$Sr_{n+1}Cr_nO_{3n+1}$	tetragonal, $I4_1/acd$ ($n = 1$)
$Sr_{n+1}V_nO_{3n+1}$	tetragonal
$Sr_{n+1}Ru_nO_{3n+1}$ ($n = 1, 2$)	tetragonal
$LaSr_3Fe_3O_{10-\delta}$	tetragonal
$Ca_{n+1}Mn_nO_{3n+1}$	$I4_1/acd$ ($n = 1$)
$A_2Ln_2Ti_3O_{10}$ (A = Na, K)	tetragonal
$Sr_3MnM'O_7$ ($M' = Ru, Fe$)	tetragonal
$(A, A')_{n+1}M_nO_{3n+1}$ ($n = 1, 2, 3$)	tetragonal/orthorhombic
(A, A' = rare earth/alkaline earth M = Cr, Al, Ni, Fe, Mn, Ru, Ga)	
$Ln_2Li_{0.5}Au_{0.5}O_4$	tetragonal
La_2PdO_4	tetragonal
Sr_2RhO_4	$I4_1/acd$
Ba_2ZrS_4/Ba_2HfS_4	$I4/mmm$
$Ba_4Zr_3S_{10}$	$Fmmm$

RP-type sulphides. Ba_2ZrS_4 and Ba_2HfS_4 crystallized in the space group $I4/mmm$ with large unit cell, while $Ba_4Zr_3S_{10}$ and $Ba_4Hf_3S_{10}$ have orthorhombic cell symmetry; former in the space group $Fmmm$ (Chen and Eichhorn 1991; Saeki *et al* 1991; Chen *et al* 1993). Table 1 lists some of the important RP-type phases reported in the literature.

2.3 Effect of oxygen stoichiometry and doping

Wide range of oxygen stoichiometry in the RP-type phases, which occurs via completely reversible oxidation–reduction by oxygen gain/loss, is the source of varied change in their structure and properties. It has been shown that oxygen deficiency in RP-phases, when $n = 2$, is accounted for by systematic removal of oxygen from the site (2a;000) linking the BO_6 octahedra, while the other oxygen sites remain fully occupied (Dann *et al* 1992). Structurally, c -axis increases with decrease in oxygen content followed by continuous fall in c with further loss of oxygen. a continuously increases with decrease in oxygen stoichiometry. Figure 4 shows variation of cell parameters as function of oxygen content in $Sr_3Fe_2O_{7-\delta}$. $LaSr_3Fe_3O_{10-\delta}$ and $La_3Ni_2O_{7-\delta}$ also systematically follow this trend; the latter undergoing orthorhombic to tetragonal phase transition as δ changes

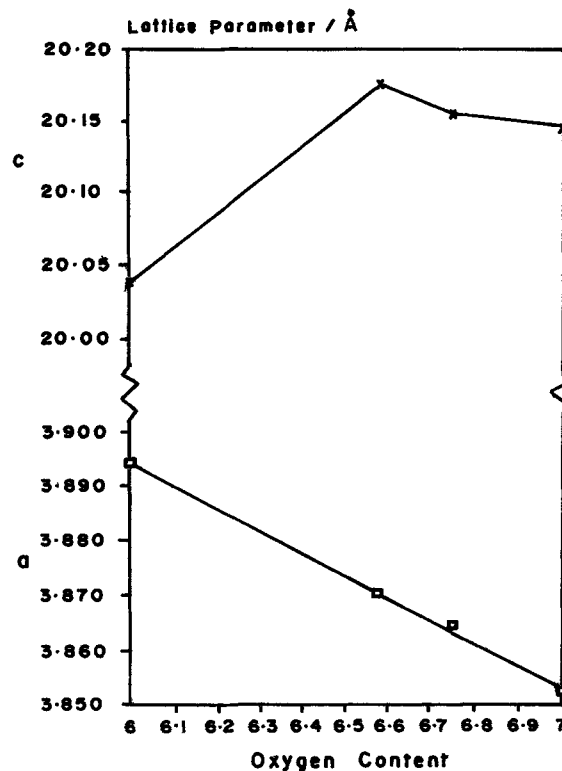


Figure 4. Change of the lattice constants a and c with variation in oxygen content in $Sr_3Fe_2O_{7-\delta}$.

from 0.08 to 0.65 (Dann *et al* 1992; Lees *et al* 1993; Sreedhar *et al* 1994). The change in lattice parameters with variation in oxygen content of the system $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ is given in table 2. The complete removal of oxygen in $\text{Sr}_3\text{Fe}_2\text{O}_{7-\delta}$ produced an unusual square-pyramidal coordination around Fe^{3+} ion and a stoichiometry of $\text{Sr}_3\text{Fe}_2\text{O}_6$ (Dann *et al* 1992). The effect of systematic removal of oxygen in $\text{La}_4\text{Ni}_3\text{O}_{10}$ on the structure and the nature of XRD pattern is shown in figures 5 and 6. Figure 5 shows removal of O(2) in the first step, which is followed by further loss of oxygen and shift of O(4) to $(4d; 0.5 \cdot 25)$ site. The stoichiometric $\text{La}_4\text{Ni}_3\text{O}_{10}$ is orthorhombic, while $\text{La}_4\text{Ni}_3\text{O}_9$ is tetragonal. Further loss of oxygen leads to shift in the (110) peak with formation of $\text{La}_4\text{Ni}_3\text{O}_8$. The structure of $\text{La}_4\text{Ni}_3\text{O}_9$ could be considered as the triple layer intermediate between *T* and the so-called infinite-layer structure. Contrary to these observations, the tetragonal $\text{Sr}_3\text{CO}_2\text{O}_{7-\delta}$ transforms to orthorhombic form in the space group *Immm* with increase in δ (Dann and Weller 1995). The ordering of oxygen vacancies in the RP-phase leads to a three-fold tripling along the b-axis. The lattice parameters and change in δ in the system $\text{Sr}_3\text{CO}_2\text{O}_{7-\delta}$ are also given in table 2.

Oxidation of insulating La_2CuO_4 (i) in oxygen atmosphere under high pressure at elevated temperature to $\text{La}_2\text{CuO}_{4+\delta}$ and (ii) by anodic oxidation in aqueous electrolytes at ambient temperatures converts it to superconducting mixed valent state (Beille *et al* 1987; Cava *et al* 1987; Mohan Ram *et al* 1987; Wattaux *et al* 1990). In the RP-phases, generally, gradual rise in room

temperature resistivity is observed with decrease in oxygen content. Absolute value of resistivity in Sr_2FeO_4 was three orders of magnitude large for the oxygen deficient sample than that of the one containing more oxygen (Adler 1994). Metallic $\text{La}_3\text{Ni}_2\text{O}_7$ transforms on reduction to insulating $\text{La}_3\text{Ni}_2\text{O}_{6.92}$ and $\text{La}_3\text{Ni}_2\text{O}_{6.33}$ (Sreedhar *et al* 1994). With an increase in δ in $\text{Sr}_4\text{V}_3\text{O}_{10-\delta}$, the carrier concentration decreases and electrical conduction changes from metallic to semiconducting, the effective magnetic moment increases and the material transforms from poly-paramagnetic to normal paramagnetic (Rey *et al* 1990; Gong *et al* 1991). The localization of carriers could be explained by the mobility edge formed by the random potential of V^{3+} ions and/or oxygen deficiencies. However, contrary to the general behaviour, the room temperature resistivity of the phases of the family $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1-\delta}$, decreases with increase in δ resulting in decreased characteristic energy of hopping (*B*). When the characteristic energy (*B*) becomes zero, the metallic $\text{Ca}_3\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Ca}_4\text{Ti}_3\text{O}_{10-\delta}$ are stabilized at all temperatures. In $\text{Pr}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ evidence of long-range magnetic order is observed as δ becomes small (Buttrey and Honig 1988).

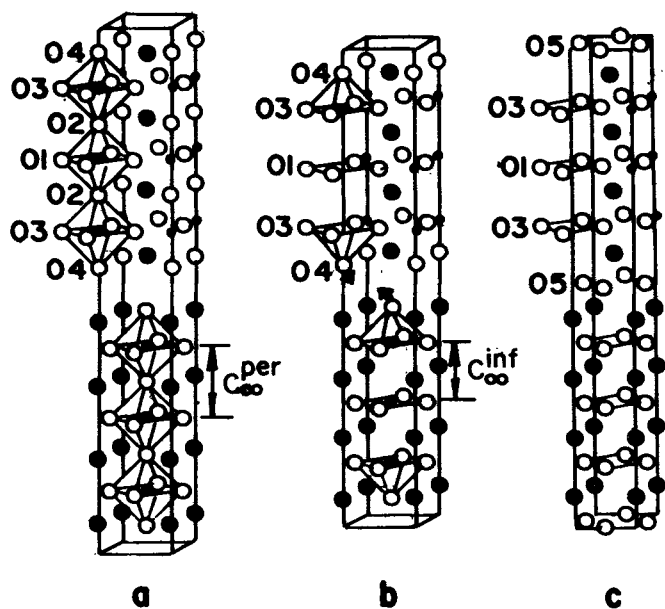


Figure 5. Crystal structure of a. $\text{La}_4\text{Ni}_3\text{O}_{10}$, b. reduced $\text{La}_4\text{Ni}_3\text{O}_8$ as expected and c. as effectively observed.

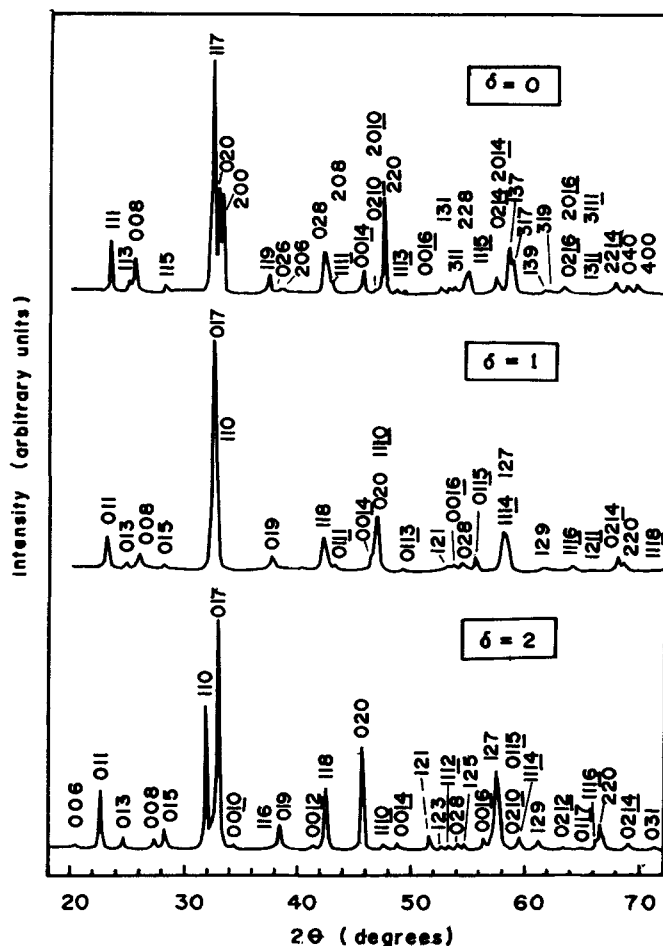


Figure 6. XRD patterns of $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ ($\delta = 0, 1, 2$).

Doping at A site by a suitable ion is one of the tools which could induce tremendous variation in the behaviour of the RP phases. The insulating La_2CuO_4 becomes superconducting when lanthanum is partially replaced by bivalent alkaline earth ion or basic monovalent cation with appropriate ionic size. Enthalpy of formation of $\text{La}_{2-x}\text{A}_x\text{CuO}_4$ ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$ and Pb) suggests that more basic A-site cations tend to energetically stabilize higher oxidation states of B-site cations, the phenomenon responsible for pronounced change in the electrical properties in the parent phase (Dicarlo *et al* 1992). $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ offers another interesting example describing change in properties as a function of doping at A-site (figure 7). The material behaves like an AF-insulator for x up to 0.1. When x lies between 0.1 and 0.95, it is non-metal showing variable range hopping mechanism for electrical conduction at low temperature and exponentially activated conduction at comparatively higher temperatures, while it turns to metallic form for concentration of x between 1.0 and 1.3. The resistivity data for the last phase in the temperature range up to 25 K follow $T^{1/2}$ dependence, where strong electron-electron interactions occur in the presence of disorder in a diffusive metallic phase (Sreedhar and Honig 1994). Orthorhombic $\text{Nd}_2\text{NiO}_{4+\delta}$ undergoes a phase transition to pseudo-tetragonal symmetry upon doping with Sr^{2+} at Nd-site (Arbuckle *et al* 1990). The increased magnetic moment in the system $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$ with increase in x is attributed to the frustration of AF pairing that originates from the mixed valence of $\text{Ni}^{2+}/\text{Ni}^{3+}$, while it showed a metal-semiconductor transition which is related to the onset of a charge density wave characteristic of half-filled conduction bands (Takeda *et al* 1992).

Both antiferromagnetic and ferromagnetic interactions are present in $\text{LaSr}_3\text{Fe}_3\text{O}_{10-\delta}$, the former predominates for large value of δ , while the latter when δ is small (Kim *et al* 1992). In $\text{Sr}_3\text{Fe}_2\text{O}_{6.0}$, which is antiferromagnetic at room temperature, increasing the oxygen content and hence Fe^{4+} level results in rapid decrease in T_c approaching 0 K for $\text{Sr}_3\text{Fe}_2\text{O}_{6.5}$. Further increase in oxygen content reverses the trend when $T_c \sim 130$ K is found for

Table 2. Variation of lattice parameters with change in oxygen content.

Phase	Space group	Lattice parameters
$\text{La}_3\text{Ni}_2\text{O}_{7.00}$	<i>Fmmm</i>	$a = 5.396; b = 5.449; c = 20.516 \text{ \AA}$
$\text{La}_3\text{Ni}_2\text{O}_{6.35}$	<i>I4/mmm</i>	$a = 3.8757; c = 20.062 \text{ \AA}$
$\text{Sr}_3\text{CO}_2\text{O}_{6.06}$	<i>I4/mmm</i>	$a = 3.8231; c = 20.0826 \text{ \AA}$
$\text{Sr}_3\text{CO}_2\text{O}_{5.94}$	<i>Immm</i>	$a = 3.8379; b = 11.4898;$ $c = 20.0812 \text{ \AA}$
$\text{Sr}_3\text{CO}_2\text{O}_{5.78}$	<i>Immm</i>	$a = 3.8631; b = 11.4319;$ $c = 20.2265 \text{ \AA}$

$\text{Sr}_3\text{Fe}_2\text{O}_{6.90}$. The phenomenon is attributed to a weak ferromagnetic $\text{Fe}^{4+}-\text{O}^{2-}-\text{Fe}^{4+}$ exchange interaction and a strong $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ interaction (Dann *et al* 1992). In $\text{Sr}_x\text{La}_{2-3x}\text{Zn}_{1-x}\text{Ru}_x\text{O}_4$, as the ruthenium concentration increases, short-range antiferromagnetic interactions between Ru^{5+} ions become more important (Kim and Battle 1994).

2.4 Preparative strategies

The ceramic method of preparation has been widely used for the preparation of these compounds. Appropriate atmosphere needs to be maintained during the course of synthesis to attain proper stoichiometry. Usually dry and oxygen free argon or nitrogen is used for creating an inert atmosphere, while hydrogen or a combination of hydrogen and some inert gas is needed for creating a reducing atmosphere. Occasionally evacuated silica ampules have also been used towards this end. If the required oxygen concentration is high, the atmosphere may be controlled by carefully maintaining the high oxygen pressure, while for low concentration of oxygen buffering mixtures such as CO/CO_2 or $\text{H}_2/\text{H}_2\text{O}$ are employed. Annealing of an oxide sample at low temperature under ordinary pressures of oxygen, leads to increased oxygen stoichiometry (Dann *et al* 1992; Zhang and Greenblatt 1994; Zhang *et al* 1994), while electrochemical oxidation procedure has also been used to control and extend oxygen stoichiometry of these phases (Demourgues *et al* 1993). In order to retain the high temperature structure, samples are some times quenched to various host-medium such as liquid nitrogen, water, water-methyl alcohol-ice or air, depending on the nature of the samples (Janecek and Wirtz 1978; Borlera and Abbattista 1983; Lees *et al* 1993).

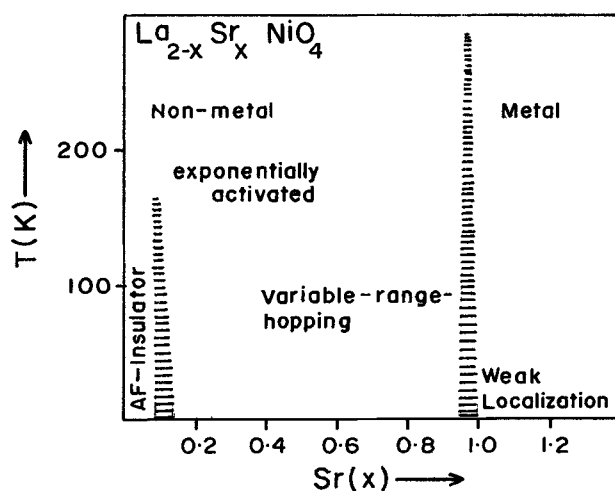


Figure 7. Schematic diagram describing changes in the electric transport as function of Sr doping in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$.

Since large diffusional distances of the order 10,000 unit cells are involved in a solid-state reaction, drastic conditions of temperature are required to overcome the diffusional limitations to get a single desired phase and still it may not be possible to achieve this in many cases. Application of high temperature in the ceramic technique to overcome diffusional limitations leads to the crystalline products of low surface area and limits the ability to stabilize the higher valence states of transition metal elements.

Ideally, in order to achieve complete reaction in shortest time span and at lowest possible temperature, one would have to achieve mixing of component cations on an atomic scale and a compound precursor is required. However, one of the limitations of this method is that it is not always possible to prepare a precursor compound with the desired composition. This limitation of a compound precursor could be overcome by preparation of solid solution precursors (Longo and Horowitz 1981). A solid-solution is the interpenetration on an atomic scale of two chemically different but structurally similar lattices. The method involves preparation of isostructural compounds of the component cations with a common ion such as oxalate, nitrate, hydroxide or cyanide, so that they form a solid-solution between two or more cations in the proper ratios. A complex oxide can be formed at low temperature by modification of the solid-solution. In a solid-solution precursor system, cations are already mixed on an atomic scale in a single phase precursor so that decomposition or reduction is rapid and complete at significantly low temperatures and shorter time; and the nature of solid-solution is such that it is possible

to continuously vary the cation composition in the structure and one is not limited to discrete compound precursor.

2.5 Characterization

Oxygen content generally determines the crystal symmetry and physical properties of these compounds and, therefore, its estimation is important. Iodometry is the most common method used for the estimation of oxygen content. Details of this method are available in the literature on analytical chemistry. Atomic absorption spectrometry, energy dispersive X-ray analysis and thermal gravimetric analysis are some of the other important techniques used for the purpose. Heating of a sample in continuous flow of either hydrogen or a mixture of H_2/Ar leads to its reduction to transition metal and alkaline earth/rare earth oxides, depending upon the species present in the sample. The study could lead to estimation of oxygen content (Lacorre 1992; Zhang and Greenblatt 1994; Zhang *et al* 1994).

Neutron and X-ray powder diffractometry are normally powerful and commonly used methods for crystal structure determination; the former being additionally successful for precise magnetic structure elucidation, especially in complex cases with multimagnetic sub-lattices. Rietveld profile analysis helps in precise determination of crystal structure in polycrystalline materials. Frequent co-existence of several members of homologous series and the presence of structural disorder and microdomains of different structures in individual crystals make the powder patterns complex and diffuse and difficult to interpret in detail. X-ray single crystal structural analysis is an

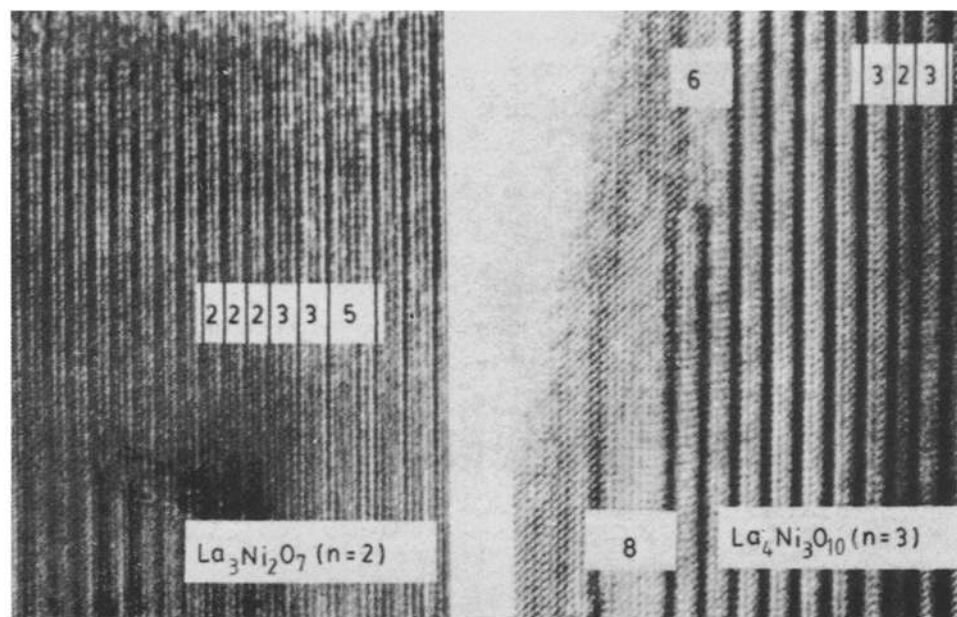


Figure 8. Lattice images of $La_3Ni_2O_7$ and $La_4Ni_3O_{10}$ showing the presence of other members of $La_{n+1}Ni_nO_{3n+1}$ series (from Rao 1985).

appropriate technique for identification of phases when good single crystals are available. This method is unsurpassed for getting precise structural information, but only average description of the atomic arrangement is obtained. Although the presence of disorder and defects can usually be detected when present frequently, study of intergrowth in RP-phases is rarely possible.

Transmission electron microscopy combined with selected area electron diffraction has proved to be the best technique for identification of phases of complex structure in inhomogeneous samples. HREM has unique advantage for the direct real-space study of interfaces. By direct lattice imaging, high resolution electron microscopy can be used to reveal inter-growth in RP-type phases. In these compounds, these studies show co-existence of lamellae with different n -values. Instead of ordered intergrowth of neighbouring members, disordered intergrowth of different members occurs, typical of them being Sr–Ti–O and La–Ni–O systems (Tilley 1977; Rao 1985; Rao and Thomas 1985). Figure 8 shows intergrowth of different phases in $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ family (Rao 1985).

3. Conclusions

Study of RP-type phases offers potential for synthesis and identification of phases which could be of theoretical and practical use in science and technology such as room temperature superconductors, ideal semiconductors, magnetic materials and materials with applications like catalysts, ferroelectrics, dielectrics, piezoelectrics, electrode material for batteries, fuel cells and so on. Every day there are continuous new reports of developments in this area. It is certain that some of the intergrowth structures have novel properties, thus intergrowth could be used as a tool for fashioning materials with desired properties in RP phases. As far as synthesis is concerned, quenching at rapid pace from very high to room temperature could lead to stabilization of materials with lower oxidation states and unique properties. 'Chimie douce' methods could prove ideal for development of materials with high surface area. When r_A/r_B ratios are not ideal for stabilizing structure of RP-type phases under normal conditions, high pressure techniques could lead to synthesis of novel phases. There are numerous oxides which absorb microwave energy and the strong absorption is reflected in heating effects when few grams of these samples could attain high temperatures within a minute or so. This property could be exploited to develop convenient and high yield synthesis of such solid-state materials (Baghurst and Mingos 1988). Doping at the cation sites and variation of oxygen stoichiometry could be ideal tools to cause novel changes in electric transport and magnetic properties in these materials.

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