Crystal chemistry of Ruddlesden–Popper type structures in high T_c ceramic superconductors

ANURAG DWIVEDI and A N CORMACK

NYS College of Ceramics, Alfred University, Alfred, NY 14802, USA.

Abstract. Similar structural patterns have been noticed in the systems La–Cu–O, La–Ni–O and Bi and Tl-containing superconducting oxides. The formation of Ruddlesden–Popper type layers (alternating slabs of rocksalt and perovskite structures) is seen in these oxides which is similar in many respects to what is seen in the system Sr–Ti–O. However, there are some significant differences, for example the rocksalt and perovskite blocks in new superconducting compounds are not necessarily electrically neutral, unlike in the Sr–Ti–O system. It, thus, becomes necessary to create oxygen vacancies in the basic perovskite (figure 1) structure of Bi-containing compounds, when the width of the perovskite slab changes on addition of extra Cu–O planes. Results of our atomistic simulations suggest that these missing oxygen ions allow the Cu–O planes to buckle in Bi-series of compounds. This is also supported by the absence of buckling in the Sr–Ti–O series of compounds and the first member of Bi-containing compounds in which there are no missing oxygen ions. We present additional results on the phase stability of polytypoid structures in La–Cu–O system and defect chemistry of compounds of La–Ni–O system.

Keywords. Defect chemistry; Ruddlesden–Popper; buckling; energetics; superstructures.

1. Introduction

Several high temperature superconductors have been studied recently and the number of high temperature oxide superconductor compositions has increased enormously. In addition to the original $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, and the subsequently discovered $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, there have been added Bi-containing and Tl-containing compounds. All these compounds contained Cu and thus it was considered an essential requirement for high T_c superconductivity. However the discovery of superconductivity at reasonably high temperature (30 K) in the non-copper containing compound $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ ($x = 0.4$) by Cava *et al* (1988) clearly indicates that the presence of copper is not always an essential condition for high T_c superconductivity. Subsequently Kakol *et al* (1989a, b), Spalek *et al* (1989) reported the superconductivity in $\text{La}_{1.8}\text{Sr}_{0.2}\text{NiO}_4$ and even in undoped La_2NiO_4 . This further confirmed the possibility of obtaining superconductivity without copper.

It is, in fact, noteworthy that all the known superconductors, irrespective of whether or not they contain copper, show similar structural features. It is, thus, important to understand better the crystal and defect chemistry of these new ceramic superconducting compounds.

2. Summary of work

This work is concerned with developing our understanding of the crystal and defect chemistry of these systems. An atomistic computer simulation study is performed; the details of computational techniques are given elsewhere (Dwivedi and Cormack 1989).

Figures 1-4. 1. Ideal perovskite blocks showing angles O(1)-O(2)-Cu; overestimation of buckling in Bi-O plane. Idealised structures of 2. $\text{Bi}_2\text{Sr}_2\text{CuO}_6$; 3. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$; 4. $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$.

Results of our studies on Bi-containing compounds, La–Cu–O system, and La–Ni–O systems are reported below.

2.1 Studies on Bi-containing compounds

The stoichiometry of Bi-containing compounds is of the form $m\text{AO} \cdot n\text{A}'\text{BO}_3$ (table 1); the structures of these materials can be related to a generalized form of the Ruddlesden–Popper (R–P) series of structures, in which two-dimensional perovskite-like slabs are separated by layers of the large-cation (e.g. Bi) oxide having NaCl structure. There are minor distortions and displacements in the actual systems which produce slight deviations from regular patterns.

The literature reports only the first three members, corresponding to $n = 1, 2$ and 3 , of the homologous series; higher members can also be modelled for theoretical investigations. We produced model structures of the next two members of the series. These are reported in figures 2–6. Matheis *et al* (1989) used this information to calculate XRD patterns of these ideal model compounds.

In our model structures the interplanar distances were assumed the same in both perovskite and rocksalt blocks and the planes were not buckled. We expected significant distortions, after relaxation, and we do see these, producing the buckling in the Cu–O planes, as seen in those structures which have been solved so far.

So far, energy minimization has only been possible with a rigid ion potential model which does not account for polarizability of the ions. In addition to showing a large relaxation energy, the relaxed structures overestimate the buckling in Bi–O planes, possibly because we have ignored superlattice effects.

Table 1. Some members of R–P homologous series of Bi-containing compounds.

Compound	Ideal prototype $m\text{AO} \cdot n\text{A}'\text{BO}_3$	$m:n$	% Missing oxygen	T_c
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	$3\text{AO} \cdot \text{A}'\text{BO}_3$ $3\text{A} = \text{Bi}_2\text{Sr}$ $\text{A}' = \text{Sr}$	3:1	0	12 K
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	$3\text{AO} \cdot 2\text{A}'\text{BO}_3$ $3\text{A} = \text{Bi}_2\text{Sr}$ $2\text{A}' = \text{SrCa}$	3:2	11	85 K
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	$3\text{AO} \cdot 3\text{A}'\text{BO}_3$ $3\text{A} = \text{Bi}_2\text{Sr}$ $3\text{A}' = \text{SrCa}_2$	3:3	17	110 K
$\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$	$3\text{AO} \cdot 4\text{A}'\text{BO}_3$ $3\text{A} = \text{Bi}_2\text{Sr}$ $4\text{A}' = \text{SrCa}_3$	3:4	20	90 K?
$\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_{14}$	$3\text{AO} \cdot 5\text{A}'\text{BO}_3$ $3\text{A} = \text{Bi}_2\text{Sr}$ $5\text{A}' = \text{SrCa}_4$	3:5	22	?

Figures 5–6. Idealised structures of 5. $\text{Bi}_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_{12}$; 6. $\text{Bi}_2\text{Sr}_2\text{Ca}_4\text{Cu}_5\text{O}_{14}$.

2.2 La–Cu–O system

Recent investigations of Davies and Tilley (1987) have shown that a series of phases belonging to a Ruddlesden–Popper homologous series exist in the system La–Cu–O, similar to what has been found in the systems Sr–Ti–O, and suggested for La–Ni–O. The generic formula for the stoichiometry of this family of compounds is $\text{La}_{n+1}\text{Cu}_n\text{O}_{3n+1}$. We developed the model structures of members up to $n = 10$, in the same manner employed by Udayakumar and Cormack (1988) for the system Sr–Ti–O. In this system only the structure of the first member, i.e. La_2CuO_4 , has been reported in detail.

Model structures were generated by adding a Cu–O layer to the next lowest member. However, some of the copper ions have to change their valence state from +2 to +3, in order to maintain the charge neutrality. In all of the model structures the distance between the planes normal to c axis was initially kept the same ($= 2.208 \text{ \AA}$). However, the atoms were allowed to relax during the equilibration process. The stoichiometries of these compounds are reported in table 2.

The lattice energies of the relaxed structures are given in table 3. A three-body potential model was used for these energy minimization calculations. The lattice energies of binary compounds La_2O_3 and CuO were also calculated keeping the potential model consistent; these energies are also reported in table 3.

Table 2. Few members of R–P homologous series of La–M–O compounds (M = Cu or Ni):
Generic Formula: $\text{La}_{n+1}\text{M}_n\text{O}_{3n+1}$

<i>n</i> in formula	Compound M = Cu or Ni	$\text{M}^{+3}/\text{M}^{+2}$ ratio	No. of atoms per unit cell	(Å)	
				M = Cu	M = Ni
1	La_2MO_4	NONE/1	28	13.2487	12.640
2	$\text{La}_3\text{M}_2\text{O}_7$	1/1	48	22.0812	21.067
3	$\text{La}_4\text{M}_3\text{O}_{10}$	2/1	68	30.9136	29.493
4	$\text{La}_5\text{M}_4\text{O}_{13}$	3/1	88	39.7461	37.920
5	$\text{La}_6\text{M}_5\text{O}_{16}$	4/1	108	48.5786	46.347
6	$\text{La}_7\text{M}_6\text{O}_{19}$	5/1	128	57.4110	54.773
7	$\text{La}_8\text{M}_7\text{O}_{22}$	6/1	148	66.2435	63.200
8	$\text{La}_9\text{M}_8\text{O}_{25}$	7/1	168	75.0760	71.627
9	$\text{La}_{10}\text{M}_9\text{O}_{28}$	8/1	188	83.9084	80.053
10	$\text{La}_{11}\text{M}_{10}\text{O}_{31}$	9/1	208	92.7409	88.480
∞	LaMO_3	1/none	5	$a = b = c = 3.7817$	$a = b = c = 3.88$

Note: M^{2+} was kept at sites (0,0,0) and (0.5,0.5,0.5); rest of the M sites were occupied by M^{3+} . This was decided after doing energy minimization for several possible combinations in the first few members of the series. Energy for all the combinations was more or less the same.

Table 3. Energetics of the binary compounds and the first few members of the R–P homologous series in the La–Cu–O system:

<i>n</i> in formula	Compound	Lattice energy (eV)	ΔE Reaction 1 (eV)	ΔE React. 2 (eV)	ΔE React. 3 (eV)
—	La_2O_3	–126.15	—	—	—
—	CuO	–37.84	—	—	—
∞	LaCuO_3	–143.01	—	—	—
1	La_2CuO_4	–164.70	—	–0.71	0.00
2	$\text{La}_3\text{Cu}_2\text{O}_7$	–307.34	0.37	–0.34	0.37
3	$\text{La}_4\text{Cu}_3\text{O}_{10}$	–450.19	0.17	–0.18	0.53
4	$\text{La}_5\text{Cu}_4\text{O}_{13}$	–593.29	–0.09	–0.27	0.44
5	$\text{La}_6\text{Cu}_5\text{O}_{16}$	–736.22	0.08	–0.19	0.52
6	$\text{La}_7\text{Cu}_6\text{O}_{19}$	–879.16	0.07	–0.12	0.60

Reaction 1: $\text{LaCuO}_3 + \text{La}_n\text{Cu}_{n-1}\text{O}_{3(n-1)+1} \rightarrow \text{La}_{n+1}\text{Cu}_n\text{O}_{3n+1}$

Reaction 2: $(n-1)\text{LaCuO}_3 + \text{La}_2\text{O}_3 + \text{CuO} \rightarrow \text{La}_{n+1}\text{Cu}_n\text{O}_{3n+1}$

Reaction 3: $(n-1)\text{LaCuO}_3 + \text{La}_2\text{CuO}_4 \rightarrow \text{La}_{n+1}\text{Cu}_n\text{O}_{3n+1}$

Knowledge of these energies allowed us to calculate the energies of the reactions denoting the formation of homologous series compounds. These reactions along with their energies are reported in table 3.

2.3 La–Ni–O system

Oxides in this system show a large range of oxygen non-stoichiometry. The nature of accommodation of excess oxygen in the lattice is not clearly known. In a very recent

report, Jorgensen *et al* (1989) suggested that the stoichiometric La_2NiO_4 does not show superconductivity and it is, in fact, the oxygen-rich non-stoichiometric phase $\text{La}_2\text{NiO}_{4+\delta}$ which is responsible for the superconducting properties. They suggest that the formation of an oxygen interstitial is equivalent to two substitutional Sr^{2+} defects at the La^{3+} site in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor.

Several studies have been done to understand the way excess oxygen goes into the structure, producing several schools of thought: (i) Variable valence of the Ni ion has been proposed. But X-ray photo-electron spectra and X-ray absorption edge studies of Buttrey *et al* (1988) provide no evidence of Ni^{+3} in these excess oxygen nickelates. (ii) Other possible mechanisms are metal vacancies or oxygen interstitials. Density measurement techniques of Buttrey *et al* (1988) indicate that oxygen interstitials are dominant defect type. (iii) Buttrey *et al* (1988) also suggested the existence of a peroxide species (O_2^{-2}) in La_2NiO_4 structure. Recent neutron diffraction studies of Jorgensen *et al* (1989) however, show the presence of O^{-2} ion in interstitial sites of oxygen excess La_2NiO_4 , but no evidence of a peroxide species. (iv) In addition to the above suggestions, Drennan *et al* (1982) have shown by electron microscopy studies that a homologous series ($\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$) in the system La-Ni-O does exist. They characterized first four members of the series. The topotactic nature of the structure gives rise to intergrowths. HREM imaging studies of Mohan Ram *et al* (1986) have also suggested the existence of such homologous series. Since the oxygen:metal ratio increases as n in the homologous series increases, formation of higher order members has also been suggested as a means of accommodating excess oxygen.

The compound LaNiO_3 , which has distorted perovskite structure, is assumed to be the $n = \infty$ end member of the series ($\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$). Drennan *et al* (1982) suggested well-defined stages of decomposition of LaNiO_3 on heating, through the formation of lower order members, NiO and O_2 , following the reaction:

On the other hand, Buttrey *et al* (1988) argue that large values of δ in $\text{La}_2\text{NiO}_{4+\delta}$ cannot be attributed to the presence of intergrowth phases or deviations in the metal atom ratio (La/Ni) which means the creation of metal vacancies. Because of this controversy, it is important to understand better the defect and crystal chemistry of these compounds. A computer-based atomistic simulation study is in progress on the present system.

A standard unit cell of La_2NiO_4 was set up with the lattice parameters suggested by Rao *et al* (1984) initially, using a simple tetragonal model. Model structures of higher members of the R-P homologous series $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$ were also developed (table 2) which were similar to their cuprate analogs (see figure 7). The exact location of these Ni^{3+} ions is not reported in the literature. We, based on our calculations, found that the Ni^{2+} ions prefer to occupy (0.0, 0.0, 0.0) and (0.5, 0.5, 0.5) sites, leaving the rest of the sites for Ni^{3+} ions in all these compounds.

The lattice energies of some of these compounds have been determined by relaxing the structure to a minimum energy configuration. These energies along with the lattice energies of LaNiO_3 , La_2O_3 and NiO are reported in table 4. We calculated the energies of the reactions listed in table 4.

Figure 7. Schematic diagram of Ruddlesden–Popper type phases in La–M–O (M = Cu, Ni) systems.

Table 4. Energetics of binary compounds and first few members of R–P homologous series in La–Ni–O system.

n in formula	Compound	Lattice energy (eV)	ΔE Reaction 1 (eV)	ΔE Reaction 2 (eV)	Reaction 3 (eV)
—	La ₂ O ₃	– 126.15	—	—	—
—	NiO	– 41.85	—	—	—
∞	LaNiO ₃	– 146.45	—	—	—
1	La ₂ NiO ₄	– 167.19	—	0.81	—
2	La ₃ Ni ₂ O ₇	– 313.05	0.59	1.40	0.59
3	La ₄ Ni ₃ O ₁₀	– 459.31	0.20	1.60	0.79
4	La ₅ Ni ₄ O ₁₃	– 605.83	– 0.07	1.53	0.72
5	La ₆ Ni ₅ O ₁₆	– 752.09	0.20	1.72	0.91

Note: Ni²⁺ was kept at sites (0, 0, 0) and (0.5, 0.5, 0.5); remaining nickel sites were occupied by Ni³⁺.

Reaction 1: LaNiO₃ + La _{n} Ni _{$n-1$} O_{3($n-1$)+1} → La _{$n+1$} Ni _{n} O_{3 $n+1$}

Reaction 2: ($n-1$)LaNiO₃ + La₂O₃ + NiO → La _{$n+1$} Ni _{n} O_{3 $n+1$}

Reaction 3: La₂NiO₄ + ($n-1$)LaNiO₃ → La _{$n+1$} Ni _{n} O_{3 $n+1$}

Apart from these lattice energy calculations we have also done some defect energy calculations. A position for the oxygen interstitial (O_i') has been suggested by Jorgensen *et al* (1989), their neutron data, to be at (0.5, 0.0, 0.25) in the type of lattice we have chosen. They have determined the structure around the interstitial oxygen ion and have reported a non-equivalent environment of oxygen and lanthanum ions around the interstitial ion. Our potential model, however, relaxed the structure symmetrically around the interstitial ion with a distance approximately equal to the average of the bond lengths determined by Jorgensen *et al* (1989). Moreover, during the calculations, the lattice oxygen ions close to the interstitial, initially in the O(2) position of Jorgensen *et al* (1989) displaced to an equilibrated relaxed position which could be identified as their O(4) position. Thus one concludes that these O(4) oxygens are really an integral part of the oxygen interstitial defect structure. Other defect energy calculations show that defect $Ni_{Ni^{2+}}^{3+}$ is bound to O_i' by a small amount.

3. Discussion of results

3.1 Bi–Sr–Ca–Cu–O system

We have used various types of Cu–O potentials to investigate the energetics and relaxed structures of the first five members of the series. Results of three-body potentials were almost the same as those using pair potentials. After relaxing the structure we found that Bi ions moved substantially from their initial position. The Cu–O planes also showed buckling, except in the first member $Bi_2Sr_2CuO_6$ (figure 2).

As mentioned earlier rocksalt and perovskite blocks in these superconducting compounds are not electrically neutral, unlike in the Sr–Ti–O system. The rocksalt block has a net positive charge which remains constant throughout the homologous series. When additional Cu–O planes are inserted, increasing the size of the perovskite blocks of the higher order members, it becomes necessary to create oxygen vacancies in the basic perovskite structure in order to maintain the electrical neutrality. Our calculations suggest that these missing oxygen ions allow the Cu–O planes to buckle. This is also supported by the absence of buckling in the first member of Bi-containing compound in which there are no missing oxygen ions, and in the Sr–Ti–O series of compounds (figures 2 and 3). Thus one of the major differences between the Cu-containing superconductors and the strontium titanates, the buckling of Cu–O planes (and “non-buckling” of the comparable Ti–O planes) can be explained in terms of the stoichiometry and crystal chemistry.

There are still some remaining problems, the main one being the apparent overestimation of lattice relaxation. This problem appears to be associated with the extent of Bi ion relaxation and the buckling of the Bi–O layers. Whilst the difficulty probably lies with the Bi–O interatomic potential, it may reflect the constraints imposed on the model structures during the calculations. We used the basic unit cell, although there are indications that the true structure is a modulated structure with a superlattice cell parameters of the order of 5 times the $\bar{a}$ parameters we used. The origin of this superlattice ordering is apparently related to the structure of the Bi–O planes, although this has not been demonstrated conclusively. Our results may be reflecting this desire of the Bi ions not to be constrained to the smaller periodicity. Further work is needed to clarify this.

3.2 System La–Cu–O

In the La–Cu–O system, the energies of reaction for R–P member formation suggest that all higher order members will decompose to La_2CuO_4 and LaCuO_3 after long times, following reaction-3. The high stability of the compound La_2CuO_4 seems to be the reason for this. However, starting with a stoichiometric mixture of binary compounds one may form higher members because of kinetic reasons; energies of reaction-2 suggest the formation of the R–P superstructure from the oxides CuO , La_2O_3 and LaCuO_3 . However, ultimately a reaction to form La_2CuO_4 will occur leading to the decomposition of the superstructure phase. This is in part due to the low stability of the Cu^{3+} ion under most conditions. More work on the cation mobility in such compounds is needed to predict the ease of cation site rearrangement.

3.3 System La–Ni–O

The energies of various possible reactions (1, 2 and 3) are given in table 3 which determine the stability of products with respect to starting components.

The question of the nature of accommodation of oxygen non-stoichiometry in the lattice may be approached by considering the appropriate defect reactions. We have formulated the following reactions:

(i) *Oxygen interstitial model*:

This model assumes the accommodation of an excess oxygen ion at interstitial position; the charge is compensated by the substitution of a Ni^{3+} at Ni^{2+} site. This follows Jorgensen *et al* (1989). The energy of this defect reaction is estimated to be -3.25 eV . Detailed calculations are given elsewhere (1989).

(ii) *Metal vacancy model*: This model assumes the formation of a higher order member of the R–P series, along with a vacancy of Ni^{2+} which is needed to maintain La and Ni site conservation.

Defect equation (2) involves the formation of V_{Ni} which may either be in La_2NiO_4 lattice or in $\text{La}_3\text{Ni}_2\text{O}_7$ lattice.

The net energy of defect equation (2) when V_{Ni} is in La_2NiO_4 , $\Delta E_2^{\text{La}_2\text{NiO}_4} = -3.39 \text{ eV}$ and the energy of the defect equation (2) when V_{Ni} is in $\text{La}_3\text{Ni}_2\text{O}_7$, $\Delta E_2^{\text{La}_3\text{Ni}_2\text{O}_7} = -2.71 \text{ eV}$. Detailed calculations are reported elsewhere (Dwivedi and Cormack 1989).

Interestingly, these energies are all negative and their similarity suggests that either reaction (1 or 2) mechanism may be operative. However, there are sufficient uncertainties in some of the component energies, notably the third ionization energy of Ni and the second electron affinity of oxygen, to rule out any conclusive statements about which of the two mechanisms should be preferred.

Note that the question of whether or not one should see different R–P layer formation depends to a large extent on the methods of preparation. Thus it is reasonable in the case of Drennan *et al* (1982) who made up specimens with different La/Ni ratios as required by the stoichiometries of the homologous series. Simple

oxidation on the other hand means that the La/Ni ratio is maintained, so the formation of crystallographic planar defects may be expected to be more difficult.

References

- Buttrey D J *et al* 1988 *J. Solid State Chem.* **74** 233
Cava R J, Batlogg B, Krajewski J J, Farrow R, Rupp A W Jr., White A E, Short K, Peck W F and Kometani T 1988 *Nature (London)* **332** 814
Davies A H and Tilley J D 1987 *Nature (London)* **326** 859
Drenan J, Tavares C P and Steele B C H 1982 *Mater. Res. Bull.* **17** 621
Dwivedi A and Cormack A N 1990 in *Ceramic transactions*, (eds) K M Nair and E A Giess (American Ceramic Soc. Inc.) Vol. **13**, pp 149–192
Dwivedi A and Cormack A N 1989b *J. Solid State Chem.* **79** 218
Jorgensen J D *et al* 1989 *Phys. Rev.* **B40** 2187
Kakol Z, Spalek J and Honig J M 1989a *J. Solid State Chem.* **79** 288
Kakol Z, Spalek J and Honig J M 1989b *Solid State Commun.* **71** 283
Matheis D P, McIntyre P and Snyder R L 1989 in *91st Annual Meeting of the American Ceramic Society, Indianapolis*
Mohan Ram R A *et al* 1986 *J. Solid State Chem.* **63** 139
Rao C N R *et al* 1984 *J. Solid State Chem.* **51** 266
Spalek J, Kakol Z and Honig J M 1989 *Phys. Rev. Lett.* (to be published)
Udaykumar K R and Cormack A N 1988 *J. Am. Ceram. Soc.* **71** C469