Mixed-Valent Perovskite Oxides

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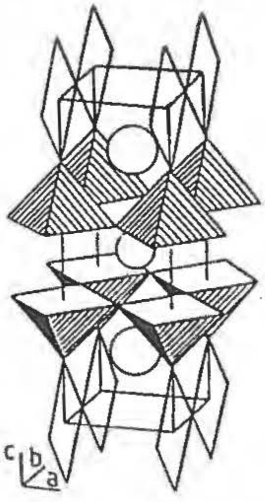
Many mixed-valent oxides with the general formula $A_2BB'O_6$ and $A_3B_2B'O_9$ exhibit perovskite or perovskite-like structures [1]. The electric and magnetic properties of these mixed-valent compounds are strongly dependent on the valency pair (B,B'). There are three ways of preparing these materials where B and B' are the same atoms with different oxidation states: (1) use of two A cations of different valency, (2) if little energy difference exists between the high-spin and low-spin states of the B cation, and (3) B^{m+} cations disproportionate into $B^{(m-1)+}$ and $B^{(m+1)+}$ cations.

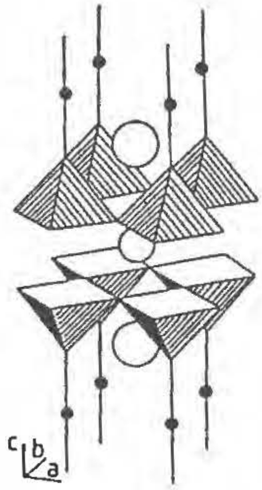
The oxidation state for Pb in semimetallic perovskite $BaPbO_3$ is consistently viewed as Pb(IV), both formulations $BaBi(IV)O_3$ and $Ba_2Bi(III)Bi(V)O_6$ have been proposed for the semiconductor $BaBiO_3$ [2]. Careful neutron diffraction studies [3] have shown that the unit cell of $BaBiO_3$ is monoclinic and contains four formula units. A striking feature of this structure is that Bi ions occupy two quite distinct sites with average nearest-neighbor oxygens at 2.28 and 2.12 A. This is consistent with the valence configuration $Ba_2Bi(III)Bi(V)O_6$. Interest in this area increased when it was shown [4] that phases of the $BaPb_{1-x}Bi_xO_3$ have perovskite related structures and superconductivity was observed over the range x = 0.05-0.3 with T_c = 13 K.

The report [5] by Bednorz and Muller of high-critical temperature superconductivity in the Ba-La-Cu-O system stimulated intensive studies of $La_{2-x}M_xCuO_{4-y}$ (M = Ba, Ca, Sr; $x<0.2$; $y = 0$). The parent compound, La_2CuO_4, is orthorhombic at room temperature with layered perovskite structure [6]. Doping La_2CuO_4 with an alkaline earth metal, M, affords a tetragonal phase at room temperature which superconducting at ca. 35 K. The single crystal structure analysis [7] showed that $La_{1.85}Sr_{0.15}CuO_4$ has the K_2NiF_4 structure, which contains layers of corner-sharing elongated CuO_6 octahedra(d[Cu-O(1)] = 1.898 A, d[Cu-O(2)] = 2.406 A). The lanthanum (and strontium) ions occupy cavities formed by 9 oxygen atoms. The substitution at the La site by Sr cause a charge redistribution at the Cu sites, possibly involving Cu(I) and Cu(III) cations randomly dispersed in copper sites.

It is worth noting that any attempt to replace La^{3+} in $La_{2-x}M_xCuO_4$ with other rare earth cations failed [8]. Although a nominal composition $Ln_{2-x}M_x$-CuO_{4-y} can be obtained, multiphase samples consisting of the 1-2-3 compound $LnBa_2Cu_3O_7$, $BaCuLn_2O_5$ and $Ln_2Cu_2O_5$ were produced. Among the rare earth phases, La_2CuO_4 is the only one to exhibit K_2NiF_4 structure. The other rare earths give ternary oxides with a different structure [9] featuring square planar coordination for Cu and square prism coordination for the smaller Ln ions. Because the coordination number of Cu(II) can be 4, 5, or 6, the rare earth ion is somehow important in determining the stoichiometry and structure types of Ln-Ba-Cu-O phases.



$YBa_2Cu_3O_7$



$YBa_2Cu_3O_6$

The structure of 1-2-3 phases $YBa_2Cu_3O_{7-y}$ can be described as oxygen deficient perovskites with tripled unit cells due to Ba-Y ordering along the c-axis [10]. The ordered oxygen vacancies in the structure result in a reduction in the coordination numbers of cations compared with ideal ABO_3 structure. For $YBa_2Cu_3O_7$, the Cu(1) atoms form linear chains of corner shared square planes oriented along the b axis and the Cu(2) atoms form two dimensional layers of corner shared square pyramids. It was found that the trivalent Ln ions, even if they are magnetic, do not affect the superconductivity. The tetragonal non-superconducting phase of $Ba_2YCu_3O_6$ [11] differs from that of $Ba_2YCu_3O_7$ by the removal of the oxygen atom from along the b axis as shown in Figure. This results in a linear two-fold coordination for Cu(1). This suggests that the Cu-O chains are crucial to superconductivity. The valence description of the Cu atoms could be: $(YBa_2)[Cu(I)Cu(II)_2]O_6$ and $(YBa_2)[Cu(II)_2Cu(III)]O_7$ for two end members respectively and $(YBa_2)[Cu(III)_{1-x}Cu(I)_xCu(II)_2]O_{7-x}$ for intermediate oxygen stoichiometries.

The mixed-valent perovskite, $Ba_2Bi(III)Bi(V)O_6$, is related to the disproportionation reaction of Bi(IV). On the other hand, mixed valent copper cations in the high-Tc copper oxides are a result of the solids having two different valent A cations, an oxygen deficit and possibly the disproportionation of Cu(II). It is no accident that Ba(II) is found in these systems. Highly electropositive Ba(II) stabilizes high oxidation states of Cu(III), Bi(V) and Pb(IV), and promotes high covalency of B-O bonds [12]. It has become evident that oxygen stoichiometry and mixed-valent copper cations related to oxygen content play a vital role in the structural dynamics and properties of these materials.

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