Redox and crystal chemistry of complex alkaline earth transition-metal oxides: Stabilization of unusual oxidation states

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All known high-T_c superconductive copper oxides, expressed as $M_mA_2Q_{n-1}Cu_nO_{m+2+2n\pm\delta}$ or M-$m^{(A)}2^{(Q)}(n-1)n$:P/RS (P/RS stands for perovskite/rock-salt type charge reservoir) [1], involve at least one alkaline earth element. The larger Ba^{II} and Sr^{II} ions tend to sit at the A-cation site with a coordination number (CN) ranging from 8 up to 10, while the smaller Ca^{II} ion prefers the Q-cation site with CN = 8 in the oxygen-depleted layer sandwiched by two CuO_2 planes. Here Pauling's first rule thus seems to work, though this is not always the case; More elaborated concepts such as the "bond-valence-sum" rule need to be considered to explain *e.g.* the effects of "the smaller Sr^{II}"-for-"the larger Ba^{II}" substitution in M-$m^{(A)}2^{(Q)}(n-1)n$. The alkaline earths, Ba, Sr and Ca, are constituent elements to various other functional layered oxides of transition metals (T) as well. In general, the role of these elements in supporting the desired (*i.e.* superconductivity, magnetic, transport, catalytic, *etc.*) properties is usually based on their (*i*) basicity that helps the T atoms to reach the highest oxidation state(s), and (*ii*) suitable size that puts the T-O layers under proper compression/tension. Furthermore, for alkaline earth ions with s-orbital bonding spherical coordination sphere is favoured, and in layered structures such as those of the $M_mA_2Q_{n-1}Cu_nO_{m+2+2n\pm\delta}$ phases the AO layer therefore tends to be buckled (especially in the case of $CN \approx 8$, *i.e.* $1 \pm \delta \approx 0$). This is for instance the reason why the distance from the in-plane copper atom to the apical oxygen atom (*i.e.* oxygen atom in the buckled BaO layer) becomes unusually large for the Hg-$1^{(Ba)}2^{(Ca)}(n-1)n$ phases.

In the present contribution, representative examples taken from the authors' own research are discussed the purpose being to illustrate some of the afore-mentioned characteristic features and functions of alkaline earths in layered transition metal oxides. Among the selected topics are: (*i*) the unusual oxidation states of high-pressure-synthesized "zero" (m = 0) 126-K superconductor, $0^{(Ba)}2^{(Ca)}23$, and its c-axis expanded, water-containing 90-K derivative [2,3], (*ii*) the fundamental difference between the effects of mechanical pressure and "chemical pressure" as generated by means of smaller-for-larger cation substitution [4], (*iii*) isovalent Sr^{II}-for-Ba^{II} substitution effects [4] and functioning of the "hole-doping routes" [5] in the Cu-$1^{(Ba,Sr)}2^{(RE)}12$ (*RE* stands for rare earth element) and (Hg,Pb)-$1^{(Ba,Sr)}2^{(Ca)}23$ systems, and (*iv*) the degree of iron valence fluctuation [6] in the $(Ca,Sr,Ba)_2FeMoO_{6.0}$ double perovskite possessing tunneling-type magnetoresistance (TMR).

Representative references

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