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A New Variable for Maximizing the Superconductive Transition Temperature in Oxide Systems

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The maximum transition temperature in superconductive oxides appears to occur when the oxygen sublattice is completely filled. Variation of the conditions of preparation may open an additional path to establish this condition.

In a recent letter to the editor of this journal, Lin *et al.* (*1*) describe the development of a new family of superconductive oxides with the composition $Tl_{0.5}^{3+}\ Pb_{0.5}^{4+}\ Cu_{1-y}^{2+}\ Y_y^{3+}\ Sr_2^{2+}\ Cu_{2-x}^{2+}\ Cu_x^{3+}\ O_{7-\sigma}^{2-}$ with a maximum of the superconductive transition temperature $T_{c(zero)} = 107$ K at $y = 0.2$. The authors also determined the percentage of Cu^{3+}, $100x/2 = 50x$, which was found to vary from 17.33% at $y = 0$ to 11.5% at $y = 1$.

Consideration of the charge balance for the composition indicated above shows that

$$x = 0.5 - y - 2\sigma. \qquad (1)$$

Using Eq. (1) with the values determined for percentage Cu^{3+} shows that $\sigma = 0.077$ at $y = 0$ but $\sigma = -0.35$ at $y = 1$, indicating a change from oxygen deficiency at $y = 0$ to oxygen excess at $y = 1$, with a crossover with $\sigma = 0$ at $y = 0.21$—almost exactly the composition at which $T_{c(zero)}$ is maximum. This suggests that a completely filled oxygen sublattice is favorable for a high transition temperature.

The nonstoichiometry parameter σ depends not only on the composition of the oxide, but also on the conditions under which it is prepared, i.e., the oxygen pressure and the temperature. The compounds reported on were prepared at 950°C under $P_{O_2} = 10^5$ Pa (= 1 atm). It should be possible to make $\sigma = 0$ at other compositions, decreasing the oxygen deficiency for $y < 0.2$ by working at a higher oxygen pressure or decreasing the oxygen excess for $y > 0.2$ by working under reduced oxygen pressure. Alternatively, the temperature of preparation could be changed keeping P_{O_2} unchanged. In any case, it appears that we have found a new variable in the search for materials with a maximum transition temperature.

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References

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