

Oxygen Bonding in High-Temperature Superconductors.

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Abstract. – Oxygen evolution experiments in low- and high- T_c ceramic superconductors are used to identify the desorption kinetics and activation energies. It is found that oxygen desorbs at 600 °C from Cu-O chains (where present) with an activation energy of 1.2 eV, whereas the desorption from other oxygen-containing planes occurs at 800 °C with a higher activation energy of 2.8 eV.

Because the oxygen content and ordering plays a crucial role in superconducting ceramics, their properties depend in a delicate fashion on the precise preparation method and history [1, 2]. Therefore, it is important to understand in detail the kinetics of oxygen evolution in high-temperature superconductors. Moreover, this type of experiments are useful in testing ideas related to high-temperature phase transitions and thermodynamics [3].

We present here a detailed study of the desorption kinetics in a large number of high-temperature superconductors. These measurements [4, 5] allow the estimation of oxygen binding energies and show the presence of structural features in agreement with those found from X-ray and neutron diffraction studies [1, 2]. The comparison of different types of superconductors indicates the absence of weakly bound oxygen in copper oxygen chains in the BiCaSrCuO systems [6], which is analogous with the La-based Cu-O superconductors.

In order to study the binding energy of the different oxygen sites in these materials we have performed evolution experiments from samples that are known to contain only Cu-O and La-O planes (La_2CuO_4 , $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$), samples that contain Cu-O planes and chains, Y or La and Ba-O planes ($\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{LaBa}_2\text{Cu}_3\text{O}_7$, $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_7$) and samples for which a more complex structure including Cu-O, Bi-O, Sr-O and Ca planes (BiCaSrCuO) are thought to be present.

All samples were prepared using standard powder metallurgy techniques and structural information was obtained using standard X-ray diffraction techniques. All these systems

were well characterized by critical temperature and resistivity measurements [1, 2, 7, 8]. Oxygen evolution was measured by placing the sample in an enclosed quartz tube and measuring the pressure and temperature as the sample was heated from room temperature to above 900°C [4]. In order to rule out spurious effects due to the evolution of impurity gases the evolved gas was analyzed using a mass spectrometer. The data are corrected for measured changes observed in the empty tube due to gas evolution from the walls of the vessel. All the corrections amounted to less than 5%. We should point out that the temperature rate decreased monotonically with increasing temperature, although over narrow ranges ($\approx 100^\circ\text{C} \div 150^\circ\text{C}$) it was constant. In any case, the qualitative conclusions obtained from the evolution experiments are independent of all these technical artifacts.

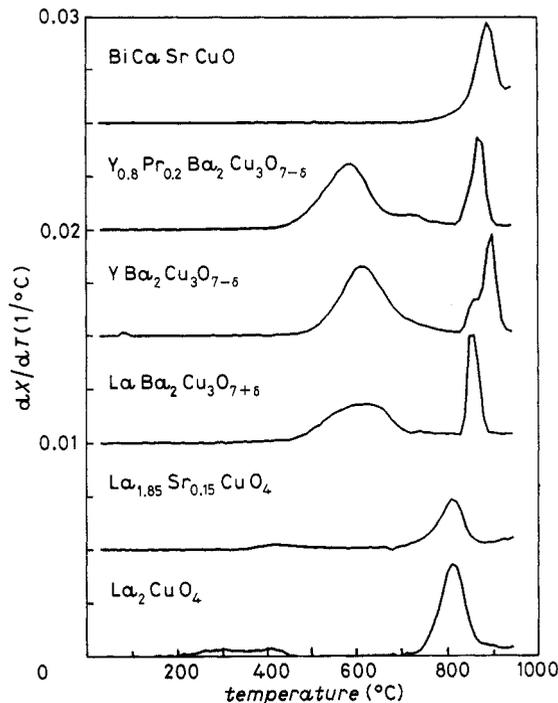


Fig. 1. - Temperature derivative of the number of oxygen atoms evolving from different ceramic superconductors.

Figure 1 shows a comparison of the oxygen evolution curves shifted for clarity along the y -axis, for representative samples of each category of superconductors. The y -axis is directly proportional to the temperature derivative of the number of oxygen atoms evolved from the sample. The spectra are characterized by sharp high-temperature peaks around 800°C in *all* samples and a broad low-temperature peak around 600°C in *some* of the samples. Only the samples that contain Cu-O chains ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{LaBa}_2\text{Cu}_3\text{O}_{7+\delta}$, $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$) exhibit the low-temperature peak. We identify therefore this peak with the oxygen evolution from the chains, commonly designated as the O1 site and the almost equivalent O5 sites [1]. A comparison of the evolution data with *in situ* neutron diffraction confirms this assignment [1, 4]. The fact that this peak is broad indicates the presence of oxygen with slightly different binding energies, perhaps due to oxygen vacancies together with oxygen-oxygen repulsion or presence of some oxygens in the O5 site which is commonly thought of

as unoccupied. The La_2CuO_4 and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples which are known not to contain Cu-O chains [9] also lack the low-temperature 600 °C evolution peak. Note that this peak is also absent in the BiCaSrCuO samples. Of course, the possibility of strongly bound Bi-O chains in BiCaSrCuO is not to be ruled out by the present experiments. The data are independent of dT/dt in the range $5^\circ\text{C}/\text{min} \leq dT/dt \leq 20^\circ\text{C}/\text{min}$. However, we stress that under very long time anneals oxygen can evolve even below 400 °C.

It is customary to fit first-order desorption experiments from a single site with the relation: $dN/dt = \mu (N_0 - N) \exp[-\Delta G/k_B T]$, where μ is a frequency factor, N_0 the initial oxygen content, N is the evolved oxygen per unit cell and ΔG a free-energy barrier for activation [10]. The low-temperature desorption curves fitted using the above formalism give a free energy $\Delta G \approx 1.2$ eV with an extremely low-frequency factor $\mu \approx 10^4$. We should stress, however, that the extremely low-frequency factor (which is mostly determined by the linewidth of the peaks in the evolution spectrum) should not be taken as an indication of some very low-frequency phenomenon. The broad line possibly arises from a distribution of inequivalent sites which give rise to a distribution of free energies, thereby producing the broad linewidth. Note that a slow diffusion process could also influence the experimental spectra.

The high-temperature peak (800 °C) looks quite similar among all samples with a splitting clearly observable in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples. The similarity of this evolution peak among different systems is a clear indication that this oxygen is evolving from the other oxygen-containing planes, the splitting being due to two slightly inequivalent sites, perhaps the O4 and O2-O3 sites. Our desorption experiment is also in agreement with neutron diffraction experiments in which the oxygen desorption from the planes was found to start at higher temperatures than from the chains [11]. It is interesting to note that when evolution starts to occur from the other planes (including the Cu-O plane), the $\text{YBa}_2\text{Cu}_3\text{SO}_{7-\delta}$ sample becomes unstable and decomposes. A fit of the high-temperature desorption using a single site activated model gives an activation energy $\Delta G \approx 2.8$ eV and a frequency factor $\mu \approx 10^{12}$. However, it is again difficult to assign physical significance to this desorption frequency because it is not clear whether the single site assumption is correct.

We envision that the surface barrier height is smaller than the activation energy required to remove an oxygen from the sample because the latter is given by the large chemical binding energy. However internally we expect to reach rapidly thermodynamic equilibrium between the different oxygen sites. We should stress that these later considerations do not affect in any way the main experimental result, namely the presence and origin of the evolution peaks. It is also important to note that our measurement is *local* in origin, *i.e.* it does not require long-range crystallographic coherence for the chains. Therefore, these measurements do not necessarily contradict the existence of *macroscopically* tetragonal [12] but *microscopically* (or locally) orthorhombic samples.

In summary, we have studied the evolution of oxygen from a number of high-temperature oxide systems. The results indicate the presence of two distinct evolution peaks, one related to the Cu-O chains (at low temperatures) and the other with all other oxygen-containing planes (at high temperatures). The activation energy obtained from these curves is ≈ 1.3 eV for the Cu-O chains and ≈ 2.8 eV for the other oxygen-containing planes. The linewidths are indicative of a distribution of inequivalent sites which is found to be more pronounced for the chains, indicating a higher degree of structural disorder in the chains.

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