

## **THERMOGRAVIMETRIC DETERMINATION OF OXYGEN IN TRANSITION METAL OXIDES WITH A DERIVATOGRAPH**

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The thermal decompositions of a series of complex copper oxides and some other transition metal oxides were studied by simultaneous TG–DTA. The oxygen stoichiometry was determined by thermogravimetry. For the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , the electrical properties and some structural peculiarities depend on the oxygen content.

For simple and complex oxides of transition metals, some difficulties are involved in the direct determination of oxygen and the stoichiometry, because of the insolubility of the oxides in common solvents and acids or because of decomposition during dissolution. Oxygen analyses by a gas-volumetric technique or by reducing the oxide could not be carried out in many cases. Therefore, in this paper we describe oxygen determination by means of thermogravimetry, in which the mass loss is determined. The method is useful for oxides that decompose in air or an inert atmosphere. This paper describes experimental results on oxygen determination in different oxides.

For the method, it is obligatory to know the equation of the process of decomposition of the investigated compound. The advantages of the method are: i) the quickness of a determination (usual 60–150 min); ii) the good reproducibility of the results; iii) the opportunity to investigate the mechanism and kinetic data; iv) only small quantities of a substance are needed for an analysis (50–70 mg).

The described thermogravimetric method has already been used for oxygen determination in alkaline earth osmates (IV) with general formula  $\text{MOsO}_3$  [1–4]. The method has now been developed for determination of the oxygen deficit in double oxides with the pyrochlore structure,  $\text{Ln}_2\text{Os}_2\text{O}_7$ ,  $\text{Ln}_2\text{Ru}_2\text{O}_7$  and  $\text{Ln}_2\text{Ir}_2\text{O}_7$  (Ln is a rare earth or yttrium), which are insoluble in acids and aqua regia. Typical thermogravimetric curves and analytical data for some  $\text{Ln}_2\text{Os}_2\text{O}_7$  are given in Fig. 1. Neutron activation analyses for phases I–IV gave oxygen contents of 13.92, 13.60, 13.00 and 16.60, respectively, which agreed well with the results of thermogravimetric measurements, i.e. the method is appropriate.

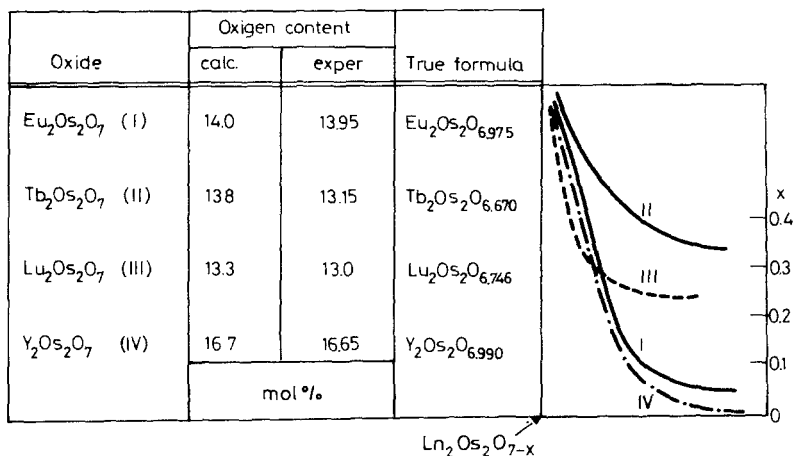


Fig. 1 Oxygen determination in  $\text{Ln}_2\text{Os}_2\text{O}_7$ , with their thermogravimetric curves

OD-102, OD-103 and Q2 (MOM, Hungary) derivatograph were used to carry out systematic oxygen determinations on nonstoichiometric  $\text{BaFeO}_{3-x}$  and rare earth oxocuprates  $\text{Ln}_2\text{CuO}_4$ ,  $\text{Ln}_{2-x}\text{M}_x\text{CuO}_{4-y}$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$  and  $\text{Pb}$ ),  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-y}$  and  $\text{Y}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ . All the oxides have an oxygen deficit either originating from the synthesis or developing after the heating of the stoichiometric oxides. An extreme example is the double oxide  $\text{La}_2\text{CuO}_{4-x}$ , which has  $x$  values between 0.22 and  $-0.25$  (it depending on the synthesis conditions), but the initial structure is the same within this range of  $x$  values.

For the thermal decompositions of the above oxides, the common accuracy of thermogravimetric analyses was within  $\pm 0.2$  at.% oxygen. This limit coincides with that of other analytical methods for oxygen determination. This was confirmed by parallel simultaneous measurements of oxygen contents in oxides by gas-volumetric and neutron-activation methods (for example, see the data for  $\text{Ln}_2\text{Os}_2\text{O}_7$  given above). Using the method for the  $\text{BaFeO}_{3-x}$  family (Fig. 2), we found a dependence of the structural polytype on the deviation from stoichiometry. This result points to the broader possibilities of the method that is to find correlations between stoichiometry and physico-chemical (or structural) features. The study of the thermal stabilities of the complex copper oxides is a good illustration of this.

It is known that the light rare earth element oxocuprates (II) formed in the  $\text{Ln}_2\text{O}_3\text{-CuO}$  systems have the common formula  $\text{Ln}_2\text{CuO}_4$  ( $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Eu}, \text{Sm}$  and  $\text{Gd}$ ), crystallizing in the  $\text{K}_2\text{NiF}_4$  type or a derivative of this [5]. It was later shown [6, 7] that the true  $\text{K}_2\text{NiF}_4$  structure for  $\text{La}_2\text{CuO}_4$  and  $\text{Pr}_2\text{CuO}_4$  ( $\text{La}_2\text{CuO}_4$  below  $248 \pm 3^\circ$  has an orthorhombic structure of distorted  $\text{K}_2\text{NiF}_4$  type) changes

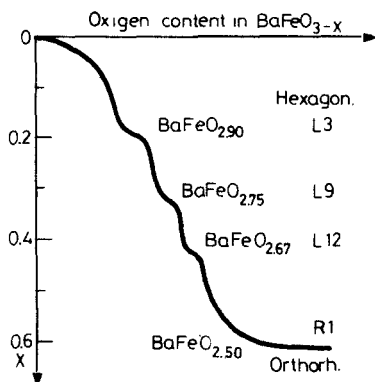
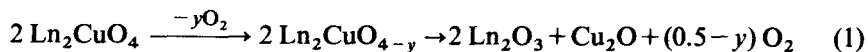


Fig. 2 Oxygen loss and intermediates when  $\text{BaFeO}_{3-x}$  is heated; L3, L9 and L12 phases have hexagonal layer structures with the respective layer number; R1 has orthorhombic symmetry

for the other  $\text{Ln}_2\text{CuO}_4$  ( $\text{Ln} = \text{Nd-Gd}$ ) because of a distortion of the oxygen polyhedra around the Ln atoms, which is manifested as a structure change. During thermal decomposition, it was found that the compounds may be non-stoichiometric, described by the general formula  $\text{Ln}_2\text{CuO}_{4\pm x}$  up to  $x=0.2$ , depending on the conditions of their synthesis and the oxygen partial pressure above the sample. This is well seen for example, in the first member of the series,  $\text{La}_2\text{CuO}_{4-x}$ , in which  $x$  may have both negative and positive values, but nevertheless does not influence the electrical properties of the compound. Similar deviations in stoichiometry lead to the partial disproportionation of copper(II) into Cu(I) or Cu(III), depending on the sign of  $x$ , and also to the formation of  $\text{Cu}^{\text{I}}-\text{O}-\text{Cu}^{\text{II}}-\text{O}-\text{Cu}^{\text{III}}-\text{O}-\text{Cu}^{\text{II}}$  links, etc., with non-equivalent numbers of copper(I) and copper(III) atoms. According to the results and discussion in [5], the electron transport along the Cu-O-Cu links causes the unusual properties of  $\text{La}_2\text{CuO}_4$ , which exhibits metallic conductivity in the rather broad temperature interval 78–750 K.

It has recently been discovered that truly stoichiometric  $\text{La}_2\text{CuO}_4$  is transformed into the superconductive state at  $T_c = 35$  K [8]. The described method was used to study the thermal decompositions of  $\text{Ln}_2\text{CuO}_4$ , including the isostructural solid solution series  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  (I), where  $M$  is Ca, Sr, Ba and Pb. It was found that both the pure compounds  $\text{Ln}_2\text{CuO}_4$  and the solid solutions of type I partially lose oxygen on heating, with preservation of their initial structure up to  $y \approx 0.22$  in the formula  $\text{Ln}_2\text{CuO}_{4-y}$  ( $y$  depends on the nature of the rare earth element, and when the deficit is near or above the tolerance limit for the structure type, the double oxide decomposes. Briefly, the process may follow the equation



From the amount of oxygen evolved, we can use (1) to evaluate the oxygen deficiency of an initial double oxide with an accuracy within  $y=0.02$ . It was found for different  $\text{La}_2\text{CuO}_{4-y}$  samples that an oxide with an oxygen content below 4.0 ( $y$  is positive) does not undergo any transition into a superconductive state before 15 K, while near 50 K metallic  $\text{La}_2\text{CuO}_{4-y}$  becomes a semiconductor. Superstoichiometric oxide  $\text{La}_2\text{CuO}_{4-y}$  (oxygen content above 4.0  $y$  is negative) exhibits a transition into a superconductor between 32 and 40 K. Thus, the data from the two experimental methods (thermogravimetry and electrical conductivity) provide a possibility to explain the superconductivity phenomenon of oxide ceramic substances. In our case, there is a direct influence of the oxygen content on special electrical properties of  $\text{La}_2\text{CuO}_4$ , and this fact confirms the existence of currents along the Cu–O–Cu links [5], and points to a specific role of the Cu(III) in these links as a possible main reason for the appearance of superconductivity.

The same effect has been observed for the solid solutions  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ , where  $M$  is Ca, Sr or Ba (but Pb). They also show a transition into the superconductive state in a broad temperature interval depending on the  $M$  and  $x$  values [9]. The same phenomenon can be seen for solid solutions in the  $\text{Y}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  system, in which for  $x=0.8$  and  $y=-0.12$  the transition into a superconductor occurs at 94 K with a transition width of 2.5 deg. Other compounds of the series  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-y}$  (II) ( $\text{Ln} = \text{Y}$  or RE element) are high-temperature superconductors with  $T_c$  within the range 84–96 K. The  $y$  value influences the  $T_c$  limit, the existence of superconductivity and the crystalline structure and stability of the compounds II.

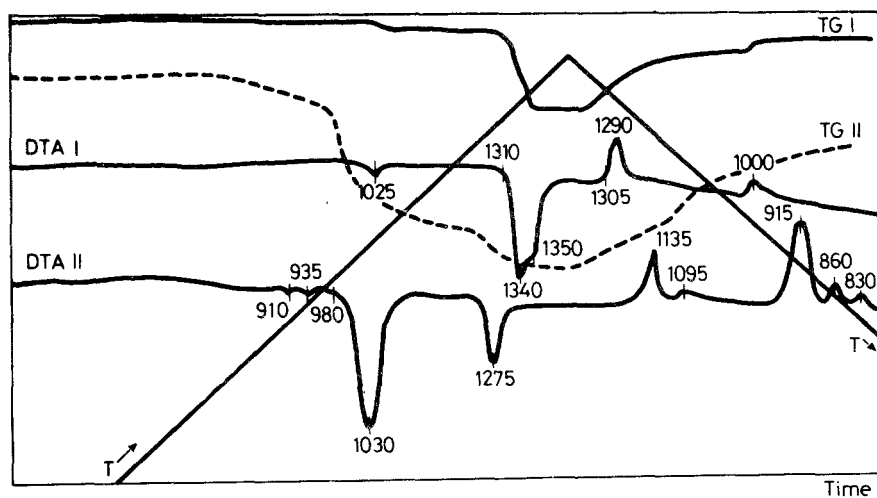


Fig. 3 TG-DTA heating and cooling curves of  $\text{La}_2\text{CuO}_{4-y}$  (I) and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  (II) (heating rate  $7.5 \text{ deg min}^{-1}$ ; sample mass about 0.5 g)

For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ , an orthorhombic structure has been found for  $y < 0.7$ , while oxygen loss leads to a structural transition into the tetragonal type for  $y = 0.7-1.1$ . The new tetragonal modification exhibits no superconductivity. Finally, the compound is transformed into an unstable form at  $y > 1.1$ , and decomposes into a mixture of  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$  and  $\text{Cu}_2\text{O}$  with oxygen evolution. TG-DTA curves of  $\text{La}_2\text{CuO}_{4-y}$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$  are shown in Fig. 3.

For  $\text{Y}_{1-x}\text{M}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$  ( $0.02 \leq x \leq 0.15$ ;  $M$  is an element of group II or III), repetition of the reversible orthorhombic-tetragonal transition several times does not influence the superconductivity of the orthorhombic phase, but the oxygen content decreases during the transition. The copper(III) content is about equal in the former and the latter orthorhombic phase. This would be a subject for speculation in theoretical models according to [10].

The above results point to the important influence of the content of copper ions in different oxidation states on the superconductivity phenomena in complex copper oxides. Thermogravimetric determination of oxygen in the oxides provides an experimental hint concerning the superconductivity phenomenon in these highly interesting modern materials.

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**Zusammenfassung** — Die thermische Zersetzung einer Reihe von komplexen oxidischen Kupferverbindungen sowie weiterer Übergangsmetallverbindungen wurde durch simultane TG-DTA untersucht. Die Sauerstoff-Stöchiometrie dieser Verbindungen wurde durch Thermogravimetrie ermittelt. Bei der Verbindung  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  wurde eine Abhängigkeit der elektrischen Eigenschaften und einiger struktureller Besonderheiten vom Sauerstoffgehalt gefunden.

**Резюме** — Совмещенным методом ТГ и ДТА изучено термическое разложение ряда смешанных окислов меди и некоторых других оксидов переходных металлов. Термогравиметрическим методом определена стехиометрия кислорода. Установлено, что электрические и некоторые структурные особенности соединения  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  зависят от содержания кислорода.