

Room Temperature Chemical Oxidation of Delafossite-Type Oxides

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IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

Examination of the delafossite-type structure of CuLaO_2 and CuYO_2 suggests that there is room enough to accommodate intercalated oxide ions and the charge compensation resulting simply from the oxidation of an equivalent amount of Cu^+ into Cu^{2+} . Reaction with hypohalites in an aqueous solution leads to color change. Evidence of the formation of Cu^{2+} is given by TGA, iodometric titration, and magnetic (static and EPR) measurements. The obtained La and Y compounds seem to behave in a different way: whereas CuLaO_{2+x} appears as a single phase, CuYO_{2+x} corresponds to a two-phase mixture, with respectively low and high x values, the latter being isostructural with the thermally oxidized compound recently reported by Cava *et al.* Comparison is stressed between the oxides obtained by oxidation at room and those obtained at higher temperatures. © 1994 Academic Press, Inc.

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the Cu-Cu distances are of 3.5 Å for CuYO_2 and of 3.8 Å for CuLaO_2 (Fig. 1). The last value represents nearly twice the Cu^{2+} -O distance in a copper oxide such as Sr_2CuO_3 (1.956 Å). In CuLaO_2 the copper(I) atoms usually occupy linear sites able to give rise to square planar positions quite suitable for Cu^{2+} ions thanks to intercalation of two equatorial oxygen atoms. Due to the high electrical resistivity of CuYO_2 and CuLaO_2 the chemical oxidation seemed more appropriate than the electrochemical one, at least in a first step.

However, Cava *et al.* have recently shown in a very attractive paper that the thermal oxidation at higher temperatures, i.e., around 300°C, is also an efficient way for oxidizing delafossite-type materials (6). We have confirmed their results in order to compare the two oxidizing processes.

INTRODUCTION

Recently a Bordeaux group has shown that it was possible to oxidize various transition element oxides using an electrochemical process (1-3). The process has then been extended to chemical oxidation by oxidizing agents such as alkali hypohalites in aqueous solution (4, 5). From the point of view of the structural evolution the reaction involves intercalation of oxide anions into the crystal lattice.

One may easily assume that at least two major conditions are required to achieve such a reaction: on one hand the involved transition element must exhibit several oxidation states (at least one higher than that already present in the precursor), and on the other hand the precursor structure must be able to accommodate the intercalated oxygen atoms.

Clearly both conditions are fulfilled in the CuLaO_2 and CuYO_2 oxides: copper (I) can be easily oxidized into copper (II). But the structure also seems appropriate for the following reason: The delafossite-type structure exhibits a threefold symmetry sublattice of copper atoms in which

PREPARATION

CuLaO_2 has been prepared from stoichiometric amounts of Cu, CuO, and La_2O_3 . The homogenized starting mixtures were heated in evacuated sealed silica tubes at 950°C for 2 days and then quenched.

CuYO_2 has been obtained from the thermal decomposition of $\text{Cu}_2\text{Y}_2\text{O}_5$ in an argon flow at 1050°C for 24 hr. $\text{Cu}_2\text{Y}_2\text{O}_5$ was synthesized from a mixture of Y_2O_3 and CuO dissolved in 14 N nitric acid; after evaporation of the solution the nitrates were decomposed at 800°C and the reaction was completed by annealing in air at 1000°C for 24 hr.

Approximately 1 g of the starting material was immersed into a solution of hypohalite and strongly stirred for various periods given in Table 1 together with other experimental conditions. For CuLaO_2 a 2 N aqueous solution of hypochlorite and for CuYO_2 a solution of hypobromite prepared by dissolving 5 ml bromine in a 5 N sodium hydroxide solution were used. Reaction products were separated by filtration, washed with distilled water, and dried in air at 130°C.

All samples exhibit a strong color change from clear yellow to black for CuLaO_2 and from clear grey to black for CuYO_2 .

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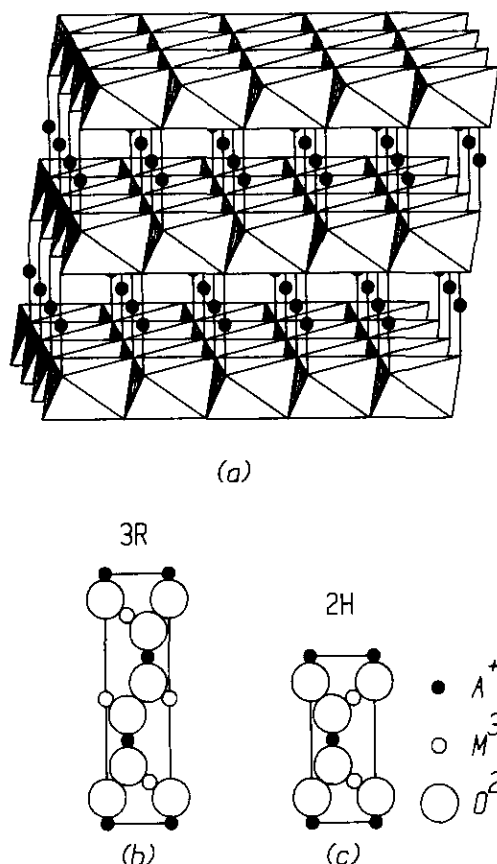


FIG. 1. Delafossite structure showing the (a, b) 3R- and (c) 2H-type close packing of $(\text{O}-\text{Cu}-\text{O})^{3-}$ linear groups and the octahedral sites occupied by the rare earth atoms.

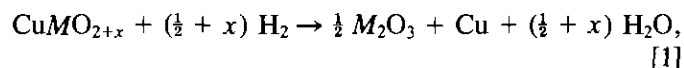
Thermal oxidation has been carried out using a procedure similar to that of Cava *et al.* (6). Our TGA results are in good agreement with those of the AT&T Bell Laboratories group. Our best conditions for achieving a maximum oxygen uptake without decomposition corresponded to a 24-hr treatment at 380°C in an oxygen flow.

RESULTS

Chemical Analysis

The average oxidation state of copper has been determined by iodometric titration: the sample is dissolved in hydrochloric acid (2 *N*) in presence of a large excess of potassium iodide. Iodine formed during the reaction is titrated with a solution of sodium thiosulfate (0.1 *N*).

As a preliminary IR spectroscopy experiment did not reveal an absorption band in the frequency range corresponding to O-H bonds we have assumed that neither water molecules nor hydroxide ions were present in our samples, at least in significant amounts. The total oxygen content of the sample has been estimated using TGA in a reducing gas flow (10% of H_2 in N_2) according to the reaction



where $M = \text{Y}, \text{La}$. Typical TGA curves are given in Figs. 2 and 3, which show two differences between chemically and thermally modified samples: the onset of the mass

TABLE 1
Preparation Conditions and Results of Chemical Analysis for CuMO_{2+x} Oxides ($M = \text{La}, \text{Y}$)

Sample	Precursor	Experimental conditions	Reaction		x values from:			
			Temperature (°C)	Time (hr)	TGA		Iodometric titration	Curie constants ^c
					Eq. [2] ^a	Eq. [1] ^b		
La-0	CuLaO ₂	NaClO, 2 <i>N</i>	20	0	0.02	0.02	0.013	0.005
La-1				16	0.19	0.16	0.13	0.076
La-2				48	0.20	0.21	0.17	0.093
La-5				120	0.44	0.50	0.18	
La-10				240	0.39	0.43	0.22	0.17
La-T ^d	CuYO ₂	O ₂ , flow NaBrO, 2 <i>N</i>	380	24	—	0.63	0.61	
Y-0				0	—	0.02	0.01	0.003
Y-1				16	0.04	0.03	0.04	
Y-2				48	0.09	0.11	0.09	
Y-5				120	0.22	0.25	0.20	
Y-10				240	0.35	0.36	0.25	
Y-T				24	—	0.51	0.47	

^a From the mass loss at the plateau and Eq. [2].

^b From the total mass loss and Eq. [1].

^c Assuming a theoretical spin only value of 0.38 (see text).

^d Sample La-T does not follow the Curie-Weiss law (Fig. 7).

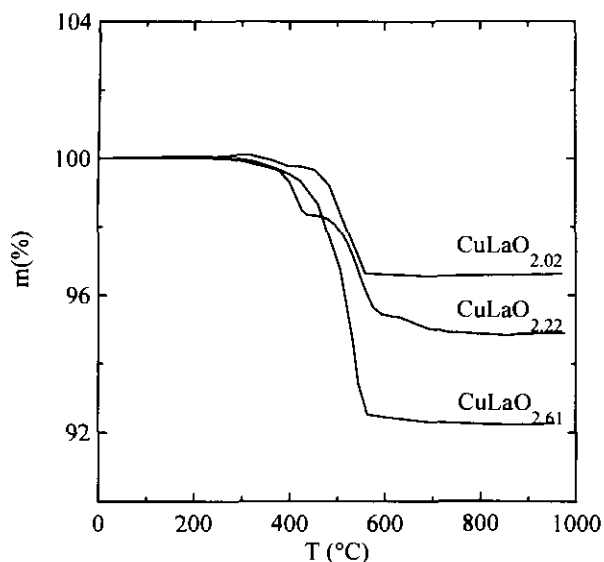


FIG. 2. TGA curves under reducing conditions (H_2/N_2 , 1/9) of CuLaO_2 (sample La-0), chemically oxidized $\text{CuLaO}_{2.22}$ (sample La-10), and thermally oxidized $\text{CuLaO}_{2.61}$ (sample La-T).

loss occurs at lower temperatures for the Y oxides obtained at room temperature and the curves exhibit a large plateau-like shoulder for both systems.

Results of both iodometric titration and reducing TGA are gathered in Table 1. The recorded x values are those calculated on the basis of Eq. [1] as well as (for the samples prepared at room temperature) those determined from the mass loss at the intermediate plateau assuming that at that decomposition stage a stoichiometric CuMO_2

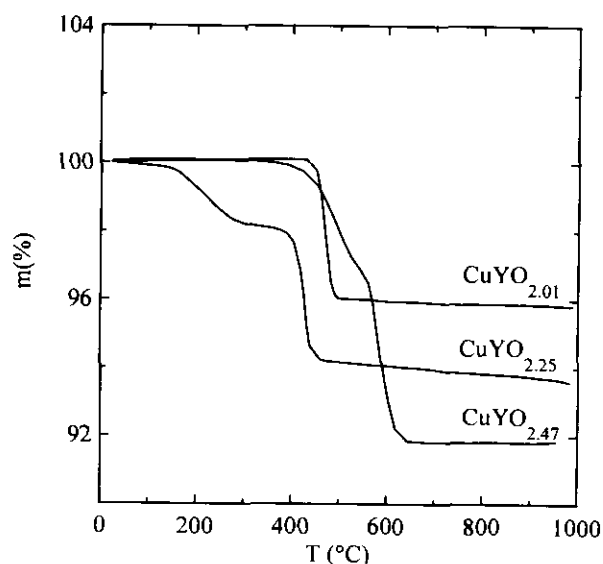


FIG. 3. TGA curves under reducing conditions (H_2/N_2 , 1/9) of CuYO_2 , chemically oxidized $\text{CuYO}_{2.25}$ (sample Y-10), and thermally oxidized $\text{CuYO}_{2.47}$ (sample Y-T).

composition is reached according to reaction



X-Ray Diffraction

CuLaO_2 crystallizes with a 3R polytype structure. In contrast CuYO_2 shows either a 2H (7) or a 3R stacking (8). Our material is of the 2H type containing only a very small amount of the 3R form.

X-ray diffractograms of the starting material, a chemically and a thermally intercalated sample, are compared in Figs. 4 and 5 for La-based and Y-based compounds, respectively. Whereas sample La-10 (see Table 1) is a single-phase material (Fig. 4), obviously sample Y-10 represents a mixture of a phase isostructural with 2H CuYO_2 and of a $\text{CuYO}_{2.5}$ oxide obtained by thermal oxidation (sample Y-T) and previously identified by Cava *et al.* (6) (Fig. 5).

The variation of the lattice constants with x is given in Fig. 6 for both systems.

Magnetic Properties of CuLaO_2 and CuYO_2

The molar magnetic susceptibility of untreated CuLaO_2 can be fitted with the equation

$$\chi_M = C_M/T + \chi_0, \quad [3]$$

which corresponds to a summation of a Curie law and of a temperature-independent term χ_0 including, at least, the diamagnetic contribution of ion close shells χ_{dia} , which can be calculated using tabulated values (9). We have experimentally found $\chi_0 = -50 \times 10^{-6}$ emu, which is very close to the calculated χ_{dia} value (-56×10^{-6}). The temperature-dependent term can be attributed to a small amount of divalent copper although the value found for the Curie constant (0.003 emu K) is smaller than that expected from the results of the iodometric titration (0.010).

The behavior of CuYO_2 is similar to that of the La compound with following parameters: $\chi_0 = -46 \times 10^{-6}$ and $C_M = 0.002$.

Using the χ_0 values for correcting the measured susceptibility values of the CuLaO_{2+x} samples we obtain the χ_M^{-1} vs T curves of Fig. 7 revealing a Curie-type behavior for the lanthanum series except for the thermally prepared sample (La-T), which can be ascribed to strong Cu^{2+} - Cu^{2+} interactions. The x values deduced from the experimental Curie constants on the basis of a theoretical spin only value ($C_{\text{th}} = 0.38$) are given in Table 1.

As X-ray diffraction revealed a two-phase mixture for the reaction products of the chemical oxidation of CuYO_2 , results of magnetic measurements will not be reported here.

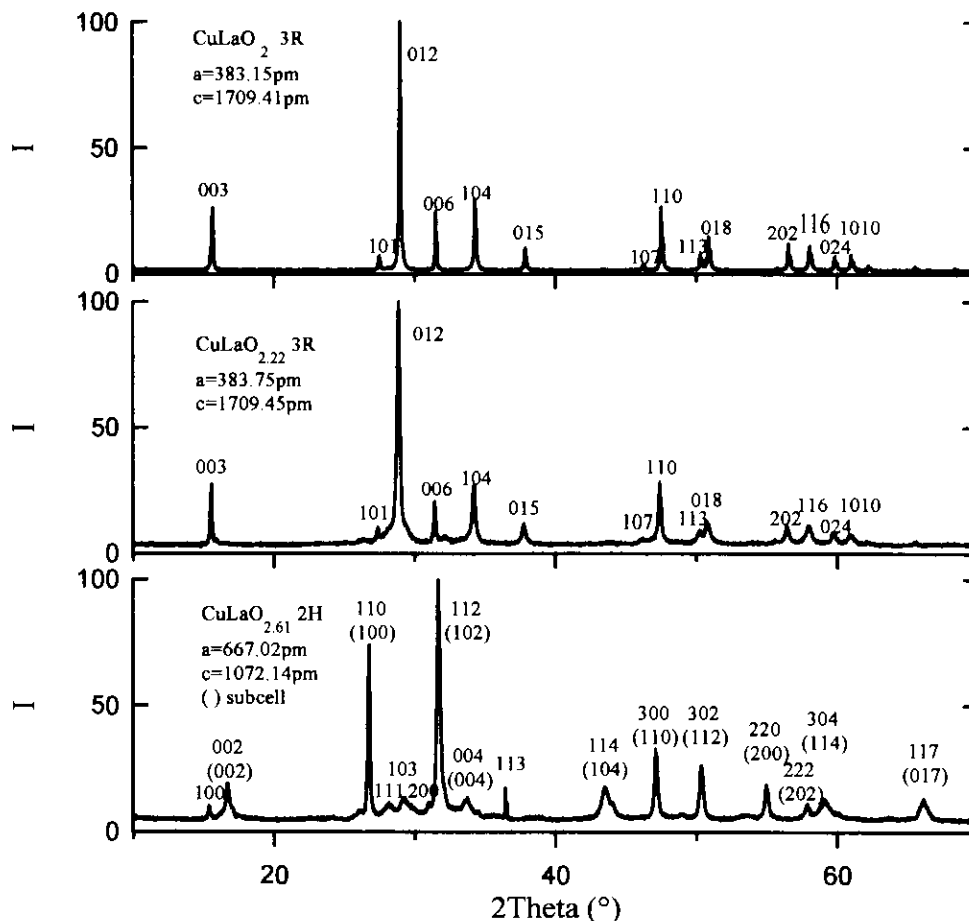


FIG. 4. Comparison of the X-ray diffractograms of pure CuLaO_2 , chemically oxidized $\text{CuLaO}_{2.22}$ (sample La-10), and thermally oxidized $\text{CuLaO}_{2.61}$ (sample La-T). For the latter sample both superstructure and $2H$ -subcell indices are given.

DISCUSSION

Table 1 shows a discrepancy between the results of TGA and those of iodometric titration for the largest oxidation rates ($x \geq 0.2$). We have also found that the values of the experimental Curie constants are much smaller than those expected from the divalent copper concentration deduced from chemical analysis. Whether this result is due to oxidizing species differing from Cu^{2+} and diamagnetic or to a partial disproportionation of Cu^{2+} into Cu^+ and LS Cu^{3+} or even to pairing of some Cu^{2+} ions is still an open question. Solving these two problems will require further investigation.

The kinetics of the oxidation process are illustrated in Fig. 8 where the x values are deduced from the iodometric titration. The behavior of the La and Y materials appears different, which can be ascribed to their nature—either single phase or two phases—as discussed below.

X-ray diffractograms have shown that, in the usual limit of accuracy, and neglecting the formation of an amorphous phase, the lanthanum materials constitute single phases. For CuLaO_2 the $3R$ polytype structure re-

mains unchanged during the room temperature oxidation process (Fig. 4); only a small and progressive increase of the a parameter is observed while c remains constant (Fig. 6). On the other hand thermal oxidation leads to the formation of a compound (sample La-T) with a superstructure derived from a $2H$ polytype—as indicated by weak additional reflections—and similar to the phase previously reported by Cava *et al.* (6).

As mentioned above, the product of the chemical (room temperature) oxidation of CuYO_2 contains two phases. They are either isostructural with or closely related to the $2H$ polytype. The majority phase has lattice parameters very close to those of the CuYO_2 precursor. It is interesting to emphasize that the a parameter first increases slightly for small x values ($x \leq 0.05$) and then remains constant, suggesting that there is no further oxygen intercalation into the precursor, but formation of a second phase. It seems actually to be identical with the product obtained by thermal oxidation and first identified by Cava *et al.* It is characterized by a $2H$ subcell with an orthorhombic superstructure.

Such a result is supported by a preliminary EPR inves-

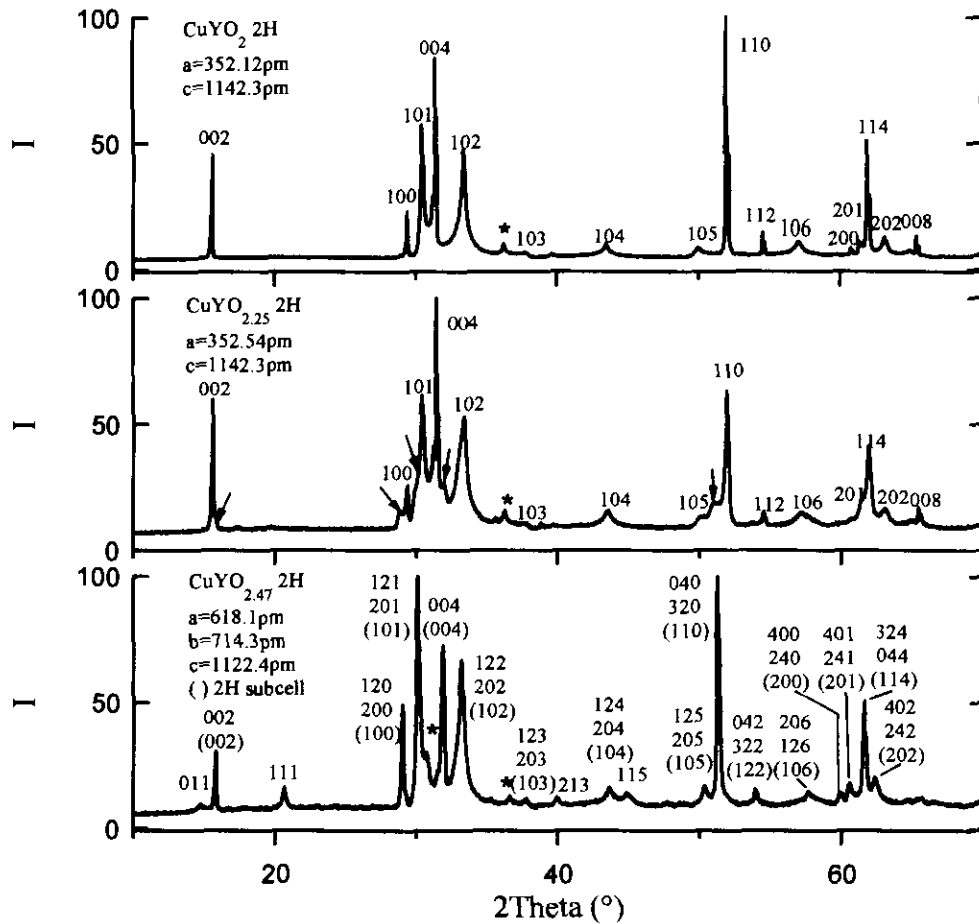


FIG. 5. Comparison of the X-ray diffractograms of pure CuYO_2 , chemically oxidized Y-10 sample, and thermally oxidized CuYO_2 (sample Y-T). Peaks marked by an asterisk belong to the 3R polytype (see text). For the Y-10 sample the peaks corresponding to the Y-T specimen are marked by arrows.

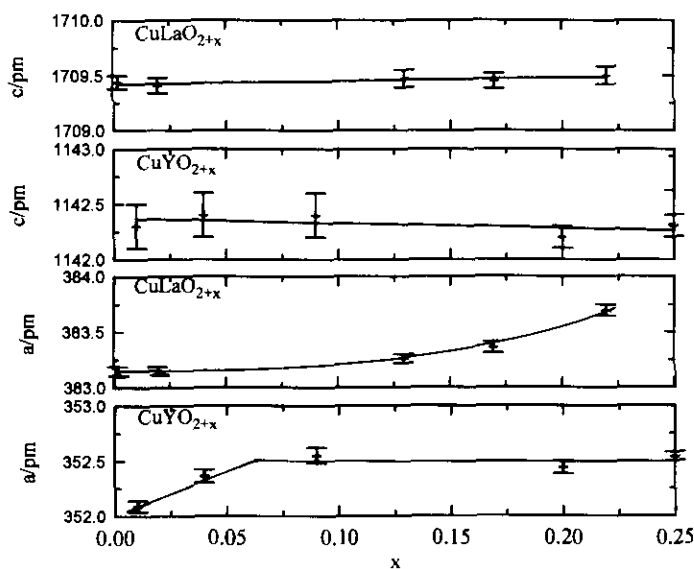


FIG. 6. x -dependence of the unit cell parameters of the CuMO_{2+x} oxides prepared at room temperature (x values obtained from iodometric titration).

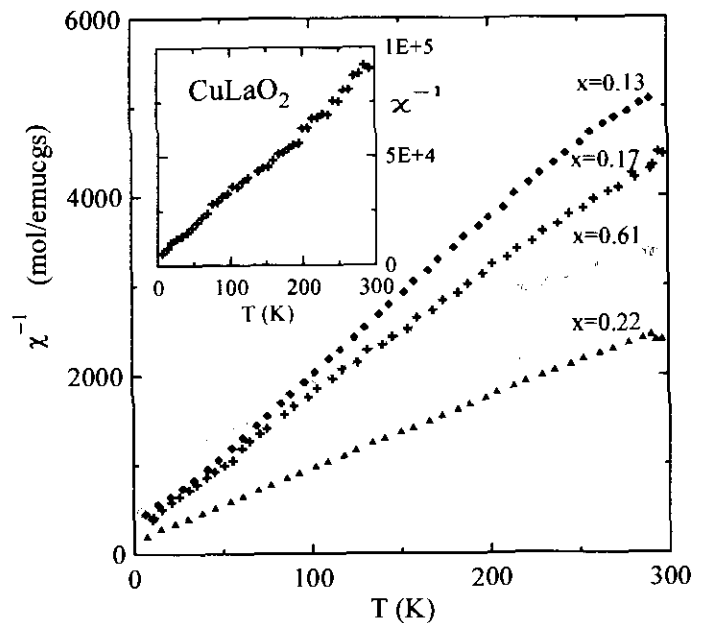


FIG. 7. Thermal variation of the reciprocal molar magnetic susceptibility of CuLaO_{2+x} (x values obtained from iodometric titration).

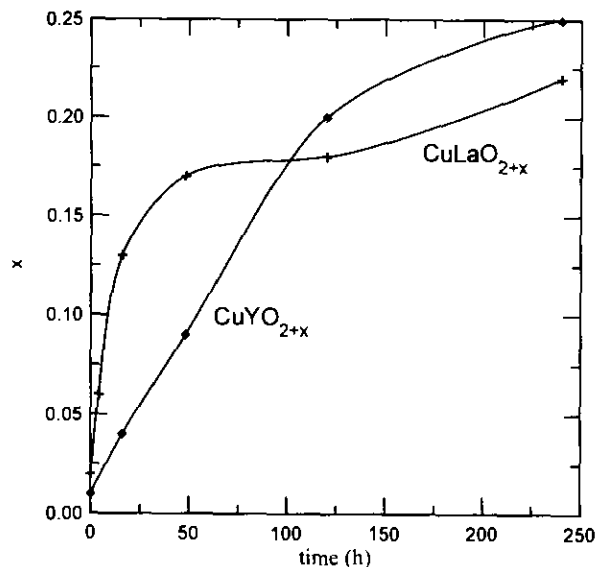


FIG. 8. Kinetics of the oxidation of CuLaO_2 and CuYO_2 by hypohalites in aqueous solutions (x values obtained from iodometric titration).

tigation performed on samples La-10 and Y-10. Figure 9 shows that for both compounds two absorption lines are observed: a broad one due to interacting Cu^{2+} ions and a much narrower asymmetric one, typical of more diluted Cu^{2+} ions, located in an elongated octahedral or square planar site. However, the relative intensities of the lines differ strongly in both systems. For the La system the line resulting from dilute Cu^{2+} is very weak and can be ascribed to a small amount of only slightly doped material while the majority phase exhibits a x value not far from the average value found by chemical analysis. In con-

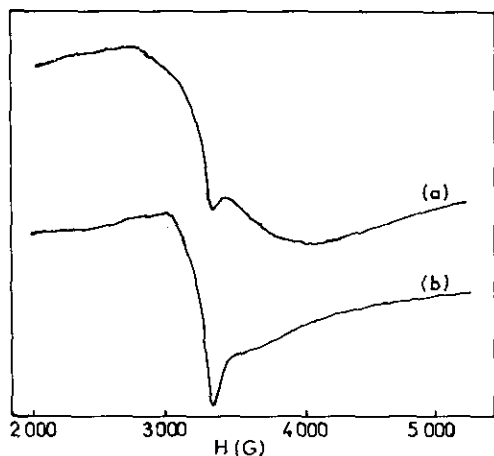


FIG. 9. x -band EPR spectra of (a) CuLaO_{2+x} (sample La-10) and (b) sample Y-10.

trast, for the Y system the corresponding line is much stronger, revealing a large amount of a slightly doped material and, therefore, an equivalent amount of a phase exhibiting a x value much larger than the average value found by chemical analysis.

TGA curves in reducing conditions for starting materials, products prepared at room temperature, and thermally oxidized ones are compared in Figs. 2 and 3 for La and Y oxides, respectively. Two very important differences clearly appear:

(i) for both La and Y series in the case of room temperature samples a plateau begins at a temperature for which the mass loss is equal to the oxygen excess, whereas for the thermally oxidized samples such a feature is no longer observed in the whole temperature range;

(ii) for CuYO_2 -based materials the mass loss starts at a much lower temperature for RT samples than for HT samples.

Obviously the explanation of the point (i) must differ for both material types: In the case of La compounds, the intercalated oxide ions are first removed from the 3R-type samples prepared at room temperature and then further reduction occurs; in contrast, in thermally prepared samples a higher temperature favors a structural reorganization and the reduction mechanism is different.

For the Y oxides, we may describe the material as made of grains, the surface of which is saturated in oxygen, giving rise to a phase similar to that obtained at higher temperature. However, a different texture can be invoked to explain the shift of the reaction temperature to lower values (ii). Therefore, for Y compounds, the mass loss between room temperature and the plateau corresponds to the reduction of the oxygen-saturated layer, and then the mass loss between the plateau and reaction completion concerns the reduction of remaining pure—or only slightly doped— CuYO_2 .

CONCLUSION

We have shown that the intercalation of oxide species into the delafossite lattice of CuLaO_2 and CuYO_2 and the oxidation of copper ions are possible at room temperature. The La and Y compounds seem to behave in very different ways: whereas CuLaO_{2+x} appears as a single phase, CuYO_{2+x} clearly represents a mixture of two phases, one of low x value and one of high x value, isostructural with the thermally oxidized compound. Some discrepancies between TGA, iodometric titration, and magnetic measurements require further investigations. Use of oxidizing agents other than hypohalites, electrochemical oxidation of samples which became conductors by weak doping, electron diffraction and microscopy, and electrical measurements are now in progress.

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