Semiconductor/Superconductor Transition of La_2CuO_4 *via* Chemical Oxidation at Ambient Temperature

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The oxocuprate semiconductor La_2CuO_4 can be converted reversibly to a superconductor with $T_c = 44$ K by simple chemical oxidation with hypohalites at room temperature.

High temperature superconductivity was first observed for the La_2CuO_4 system, which has remained of basic interest owing to its compositional and structural simplicity.[1] The oxocuprate has a K_2NiF_4 type anisometric structure and can be converted into a superconductor with Cu^{2+}/Cu^{3+} mixed valence state by (*i*) thermal preparation of phases with partial isomorphous replacement $La^{3+} \rightarrow M^{2+}$ (M = Ca, Sr, Ba) or (*ii*) by treatment with molecular oxygen at high pressures (0.2–23 kbar) above 600 °C.[2–4] (*iii*) A most unusual process that has been reported recently is the anodic electrochemical treat-

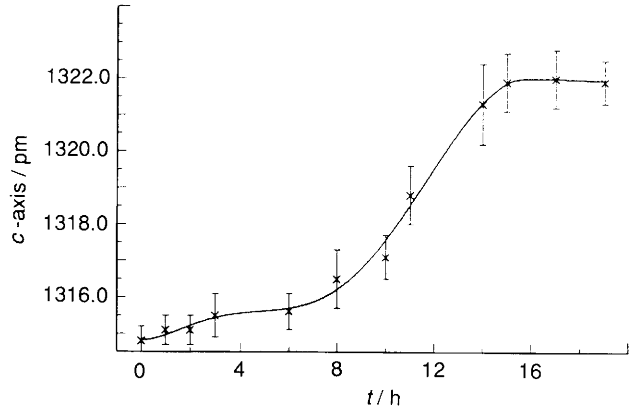

Fig. 1 Kinetics of the oxidation process: change of the lattice parameter *c* with *t* during oxidation of La_2CuO_4 by 1 mol dm^{-3} NaOBr at 300 K

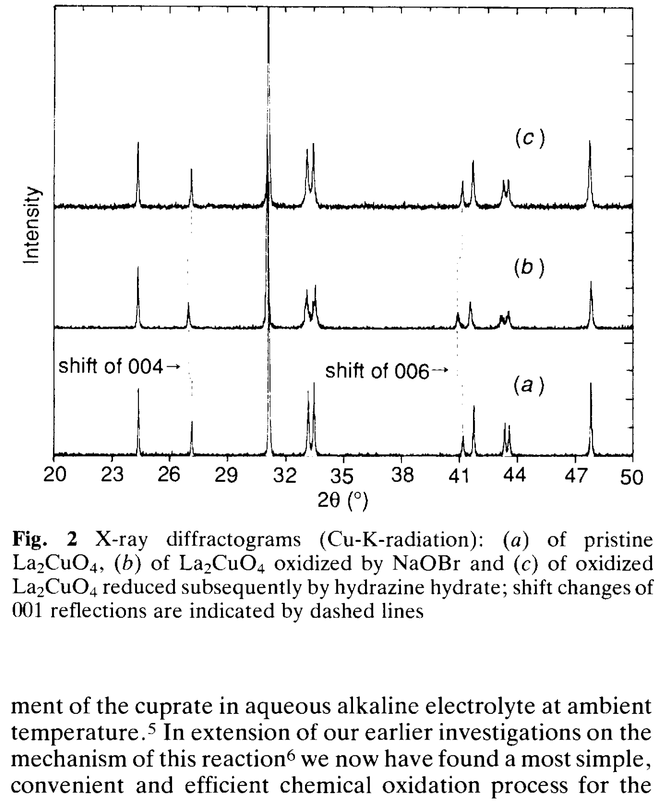

Fig. 2 X-ray diffractograms (Cu-K-radiation): (*a*) of pristine La_2CuO_4, (*b*) of La_2CuO_4 oxidized by NaOBr and (*c*) of oxidized La_2CuO_4 reduced subsequently by hydrazine hydrate; shift changes of 001 reflections are indicated by dashed lines

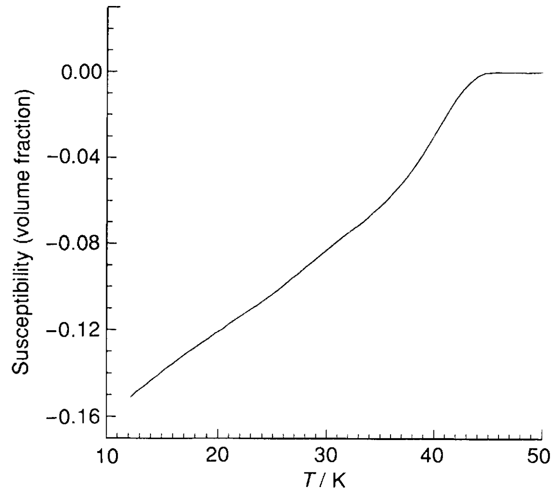

Fig. 3 AC-susceptibility *vs.* *T*/K for La_2CuO_4 oxidized by NaOBr

ment of the cuprate in aqueous alkaline electrolyte at ambient temperature.[5] In extension of our earlier investigations on the mechanism of this reaction[6] we now have found a most simple, convenient and efficient chemical oxidation process for the conversion of La_2CuO_4 at room temperature to a superconductor with $T_c = 44$ K and for the inverse reaction, *i.e.* the chemical reduction of the superconducting phase to the semiconducting state. Systematic screening studies revealed that alkali hypochlorites and hypobromites are able to react with La_2CuO_4 in a topotactic process under retention of the host lattice. A simple and reliable procedure is *e.g.* to treat a suspension of 1 g of La_2CuO_4 in an alkaline sodium hypobromite solution (prepared from 100 ml 5 mol dm^{-3} aqueous NaOH at 0 °C by addition of 2.5 ml Br_2) under strong stirring for 12–16 h. The black solid product is then filtered off, washed with water and acetone and dried in vacuum at 10^{-3} mbar/300 K.

The change in the average oxidation state of copper during the reaction can be determined by iodometric titration; the Cu^{3+} content calculated from these data was 0.000(5) for the starting material and 0.145(5) for the oxidized product. The kinetics of the reaction were also checked *via* the change of the lattice parameters; Fig. 1 demonstrates the S shaped conversion curve which is assumed to originate from surface kinetic hindrance of the electron/ion transfer process in the starting region of the solid state reaction. Under the conditions described the reaction comes to an end after about 15 h, no further change in lattice parameters or average oxidation state is found thereafter.

X-Ray diffractograms show a slight increase of the line width of the product as compared to the starting phase, which is normal for a solid state process at ambient temperature as a consequence of a finite increase in defect concentration (Fig. 2).

The lattice parameters (pm) change from $a = 540.0(2)$, $b = 535.3(2)$, $c = 1314.1(4)$ and $V = 379.86 \times 10^6$ pm^3 for pristine La_2CuO_4 to $a = 540.7(2)$, $b = 533.8(2)$, $c = 1321.3(4)$ and $V = 381.4 \times 10^6$ pm^3 for the reaction product. The total change in unit cell volume of 0.4% is rather small.

The temperature dependence of the magnetic susceptibility (Fig. 3) indicates a sharp T_c(onset) at 44 K with a superconducting volume fraction of 14% at 12 K (powder samples). The volume fraction observed is compatible with that found for polycrystalline phases prepared at high oxygen pressure at 600 °C.[3] The width of the transition is a consequence of the polycrystalline nature of the samples and is comparable to the transition width of samples obtained *via* electrosynthesis.

Heating beyond 400 °C leads to total loss of the superconducting properties. Differential thermal analysis and thermogravimetric studies show that the thermal decomposition process occurs stepwise.

We found that the oxidized superconducting phase can be reduced chemically at 300 K by a wide series of reagents with varying standard reduction potentials from −1.87 to 0.08 V (NH_2OH, N_2H_5OH, $S_2O_4^{2-}$, SO_3^{2-}, H_2O_2, $S_2O_3^{2-}$). Particularly fast kinetics of the reduction process were observed for hydrazine hydrate. The lattice parameters of the products were found to be identical with those of La_2CuO_4 (see also Fig. 2); the samples have lost their superconducting properties and analytical investigations show that all Cu^{3+} has been reduced to Cu^{2+}.

Although the oxidation reaction described is experimentally straightforward and well reproducible, leading to a terminal product that can be clearly characterized in terms of oxidation state, lattice parameters and superconducting properties the mechanism of the reaction is unclear so far.

The process leading to a Cu^{2+}/Cu^{3+} mixed valence state can presently be explained by two different electron/ion transfer models: (*i*) intercalation of oxygen into the La_2CuO_4 lattice and formation of La_2CuO_{4+x}[5] and (*ii*) an oxidative electron/proton transfer process as a consequence of La-defects in the pristine material, compensated by OH-groups.[6] Although we have proposed earlier a model for the high mobility of oxygen in $YBa_2Cu_3O_{7-x}$ type superconductors (beginning at *ca.* 300–400 °C) on grounds of oxygen anion radical transport ($O^{\cdot -}$)[7,8] it remains unclear presently whether such a mechanism may operate with reasonable kinetics at temperatures as low as 300 K.

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References

1 *Superconductivity*, ed. J. G. Bednorz and K. A. Müller, Springer-Verlag, Berlin, New York, Tokyo 1990.

2 G. Demazeau, F. Tresse, Th. Plante, B. Chevalier, J. Etourneau, C. Michel, M. Hervieu, B. Raveau, P. Lejay, A. Sulpice and T. Tournier, *Physica C*, 1988, **153–154**, 824.

3 E. Schirber, B. Morosin, R. M. Merill, P. F. Hlava, E. L. Venturini, J. F. Kubak, P. J. Nigrey, R. J. Baughman and D. S. Ginley, *Physica C*, 1988, **152**, 121.

4 J. Zhou, S. Sinha and J. B. Goodenough, *Phys. Rev. B, Condens. Matter*, 1989, **39**, 12 331.

5 A. Wattiaux, J. C. Park, J. C. Grenier and M. Pouchard, *C. R. Acad. Sci. Ser. 2*, 1990, **310**, 1047.

6 P. Rudolf, W. Paulus and R. Schöllhorn, *Adv. Mater.*, 1991, **3**, 438.

7 H. Eickenbusch, W. Paulus, E. Gocke, J. M. March, H. Koch and R. Schöllhorn, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1188; *Angew. Chem.*, 1987, **99**, 1201.

8 R. Schöllhorn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1392; *Angew. Chem.*, 1988, **100**, 1446.