



## Chemical versus electrochemical doping of layered complex perovskites $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$ ( $\text{Ln} = \text{La}, \text{Eu}, \text{Tb}$ )

P. Gómez-Romero\*, M.R. Palacín, C.R. Michel, N. Casañ-Pastor

*Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Barcelona, Spain*

### Abstract

Complex perovskites  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Tb}$ ) present the topology typical of high- $T_c$  superconducting cuprates. Doping of this series has been attempted and several cationic substitutions accomplished. Under regular reaction conditions oxygen contents readjust leaving the oxides effectively undoped. This can be overcome in certain cases by using stronger oxidizing conditions like high oxygen pressure annealing. We have also performed electrochemical oxidation of these compounds in a molten salt electrolyte. The oxygenation of  $\text{Ln}_2\text{Ba}_2\text{Cu}_{2+x}\text{Ti}_{2-x}\text{O}_{11-y}$  ( $\text{Ln} = \text{La}, \text{Eu}$ ) and  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$  ( $\text{Ln} = \text{Tb}$ ) by means of these methods is described, and a comparison of high-pressure versus electrochemical results made.

*Keywords:* Layered perovskites; Cuprates; High-pressure; Electrochemistry; Fused-salts; Oxidation; Doping; Superconductors

*Materials:*  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$  ( $\text{Ln} = \text{La}, \text{Eu}, \text{Tb}$ )

### 1. Introduction

The series of oxides  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Eu}, \text{Tb}$ ) contain double layers of corner-sharing  $\text{CuO}_5$  polyhedra with the topology common to many of the p-doped high- $T_c$  cuprate superconductors. [1,2]. These layers are separated by double layers of corner-sharing  $\text{TiO}_6$  polyhedra. Thus, bidimensionality is attained in these phases within the framework of an all-perovskite structure, rather than with NaCl-type intergrowths (see Fig. 1). We have studied in detail the synthesis and extension of this series as well as its crystal structure [1-4]. We have

prepared the La, Nd, Eu and Tb compounds whereas independent work by other laboratories has centered on the corresponding Gd compound [5] as well as on mixed lanthanide systems [6].

Doping of these oxides has been attempted with poor success [7]. First of all, the narrow stability range of the phases makes it difficult to substitute cations as a first step for doping. Indeed, the lanthanide ion (one of the most commonly substituted in other phases) turned out to be the most difficult to substitute for these particular oxides. Several cationic substitutions were possible especially when centered on the transition metal (Ti) [7]. Nevertheless, under normal (ambient pressure) reaction conditions, the oxygen contents of the substituted samples get self-adjusted as to maintain the formal oxidation state of copper (+2).

\*Corresponding author. Fax: +34 3 580 5729; e-mail: pedro.gomez@icmab.es

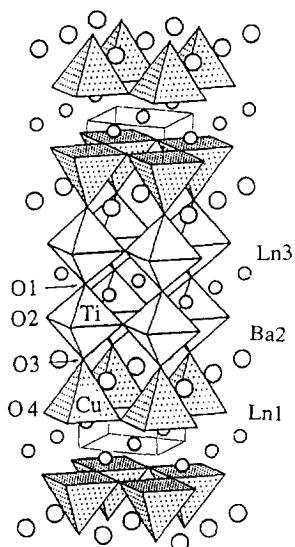


Fig. 1. Structure of the series  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$  ( $\text{Ln} = \text{La-Tb}$ ) showing the ordering of Cu/Ti and Ln/Ba and the bidimensionality.

This difficulty in doping (in chemical terms, the difficulty to oxidize the compound) has been overcome in certain cases by using high oxygen pressure, annealing the samples at 500°C and 5 kbar [7].

We present here the results of applying an alternative driving force for the oxidation of these phases, namely by an electrochemical potential, and present a comparative study of these results with those obtained by high O<sub>2</sub> pressure. Thus, we have carried out electrochemical oxidations of  $\text{Ln}_2\text{Ba}_2\text{Cu}_{2+x}\text{Ti}_{2-x}\text{O}_{11-y}$  ( $\text{Ln} = \text{La, Eu, Tb}$ ) (the La compound was also successfully doped at high pressures). Preliminary experiments showed that the potential needed for these oxidations in an aqueous basic medium is higher than that required for water oxidation. Therefore, a non-aqueous medium successfully used in the oxidation of  $\text{La}_2\text{CuO}_4$  [8] was chosen. Specifically, the electrolyte consisted of an alkali nitrate flux with either a neutral salt ( $\text{NaClO}_4$ ) or a base (KOH) added. The results obtained exemplify the usefulness of this medium for oxygen intercalation in oxides that otherwise can only be oxidized under high pressure conditions.

## 2. Experimental

Samples of  $\text{Ln}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$  ( $\text{Ln} = \text{Tb}$ ) and  $\text{Ln}_2\text{Ba}_2\text{Cu}_{2.15}\text{Ti}_{1.85}\text{O}_{11-\delta}$  ( $\text{Ln} = \text{La, Eu}$ ) were synthesized as reported earlier [2,3,7] and were routinely characterized by X-ray powder diffraction. The oxides  $\text{Ln}_2\text{Ba}_2\text{Cu}_{2.15}\text{Ti}_{1.85}\text{O}_{11-\delta}$  ( $\text{Ln} = \text{La, Eu}$ ) were annealed under oxygen pressure according to the following procedure: about 200 mg of the samples were placed in a small alumina crucible inside an autoclave where liquid oxygen was condensed in the amount corresponding to yield 5 kbar at 500°C. The sample was treated at 500°C and 5 kbar for 24 h, then the temperature was lowered to 300°C (corresponding to a pressure of 3.5 kbar) where it was kept for another 24 h and afterwards it was slowly cooled to room temperature. The overall treatment took 60 h. The oxygen content of samples before and after high pressure treatments was analyzed by TGA in Ar/5 vol.% H<sub>2</sub>.

Cyclic voltammograms (CV) and electrochemical oxidations were carried out using as electrolyte 0.1 M solutions of  $\text{NaClO}_4$  or KOH in a molten eutectic mixture of  $\text{KNO}_3\text{-LiNO}_3\text{-NaNO}_3$ . Single-compartment three-electrode cells were set up in a teflon container (Fig. 2). The working electrode consisted of a pellet (13 mm diameter, 1 mm thick) of each oxide prepared by pressing and sintering at the synthesis temperature. Final pellet densities ap-

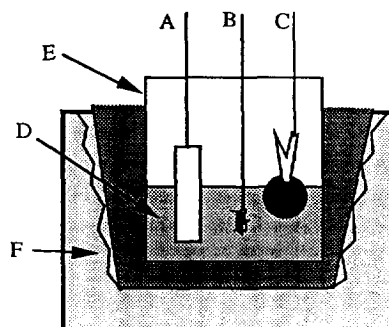


Fig. 2. Electrochemical cell used for oxidation in molten salts. (A) Quasireference electrode (Ag). (B) Counterelectrode (Pt). (C) Working electrode (oxide pellet). (D) Molten salts bath. (E) Teflon container. (F) Heating element.

proached 80% of the theoretical value. Platinum wire (area 1.25 cm<sup>2</sup>) was used as counterelectrode, and silver wire (area 2 cm<sup>2</sup>) as quasireference electrode. The temperature of the bath was kept at 150°C [25°C above the temperature of the eutectic (125°C)] using a temperature controller in order to avoid heterogeneous solidification of the bath. Oxidations were carried out at constant potential for periods of 15 to 70 h. Typical current values were 0.2 to 1.5 mA. In turn the amount of charge passed through the cell was one order of magnitude larger than that required for oxidation if the efficiency had been 100%. After oxidation the pellets were rinsed with alcohol and dried under vacuum. The molten nitrates melt impregnate the pellet during the oxidation process preventing a precise analytical study of the oxygen contents.

Magnetic measurements were carried out by use of a Quantum Design SQUID magnetometer under zero-field cooled and field cooled conditions in order to detect any possible diamagnetic signal arising from superconducting properties. The magnetization data plotted in the figures were obtained at 10 000 gauss in all cases except in the case of the Tb oxidized compound where the field was 5000 gauss. These data have been corrected in all cases for atomic diamagnetism. Magnetic properties are expressed as the effective magnetic moment (Bohr magnetons) related to magnetic susceptibility as follows:  $\mu_{\text{eff}} = (8\chi T)^{1/2}$ , where  $\chi$  is the magnetic susceptibility (emu mole<sup>-1</sup>) and  $T$  the absolute temperature (K).

X-ray diffraction patterns were obtained by a Siemens D-500 diffractometer using Cu K $\alpha$  radiation. Oxygen contents were determined in favourable cases by thermogravimetric analysis at 650°C under Ar/H<sub>2</sub> (5 vol.%) using a TGA7 Perkin Elmer thermobalance.

### 3. Results and discussion

Oxidation under high oxygen pressure increased the oxygen content only for the phase Ln<sub>2</sub>Ba<sub>2</sub>Cu<sub>2.15</sub>Ti<sub>1.85</sub>O<sub>11- $\delta$</sub>  with Ln = La up to the stoichiometric value ( $\delta = 0$ ). The Eu compound did not get oxidized under the same conditions. Cation

substitutions attempted on the Tb compound of the 2222 family were not successful and led in all cases to decomposition products with partially oxidized Tb. For that reason oxidation at high temperatures (and high oxygen pressure) was not attempted for the Tb compound.

Cyclic voltammograms for Ln<sub>2</sub>Ba<sub>2</sub>Cu<sub>2</sub>Ti<sub>2</sub>O<sub>11</sub> (Ln = Tb) and Ln<sub>2</sub>Ba<sub>2</sub>Cu<sub>2.15</sub>Ti<sub>1.85</sub>O<sub>11- $\delta$</sub>  (Ln = La, Eu) in molten nitrates show oxidation potentials substantially higher than the one observed for La<sub>2</sub>CuO<sub>4</sub> in the same media and under the same conditions (+0.7 V vs. Ag) [8] (Fig. 3). There is also a clear change from stoichiometric to cation-doped samples in the oxidation potential. The phases with Ln = La and Eu present oxidation waves around +1.1 V vs. Ag while the stoichiometric phase with Ln = Tb shows an oxidation wave with  $I_{\text{max}}$  at +1.4 V vs. Ag. The stoichiometric (2222 unsubstituted) La phase did not show any oxidation wave.

Correspondingly, the changes observed in magnetic properties upon electrochemical oxidation (expressed in the plots of effective magnetic moment vs. temperature) for Ln = La, Eu are perceptible but much smaller than the change observed for the stoichiometric Tb compound (Figs. 4–6). The reason for this could be of different origins. While oxidation is assumed to affect directly the oxidation state of copper in the cases where the lanthanide is La or Eu, Tb<sup>+3</sup> is known to be oxidized easier than copper in these phases. Therefore, the changes in the effective magnetic moment for Ln = La are expected to be within the range of the copper typical magnetic moment. Thus, oxidation of Cu<sup>+2</sup> to Cu<sup>+3</sup> would decrease the effective magnetic moment per copper ion since Cu<sup>+3</sup> is diamagnetic, but it could also raise the value of the magnetic moment due to the breakdown of the existing antiferromagnetic coupling between Cu<sup>+2</sup> ions. In either case the change will be of the order of 1 or 2  $\mu_{\text{B}}$ .

In the case of Ln = Eu, if the lanthanide is not involved in the magnetic exchange and its oxidation state is not modified by the oxidation, the changes expected would be of the same order of magnitude in terms of magnetic susceptibility. High-pressure oxidation in this case has been very small and  $\delta$  was found near zero within analytical error. Accordingly, the change observed in the effective magnetic mo-

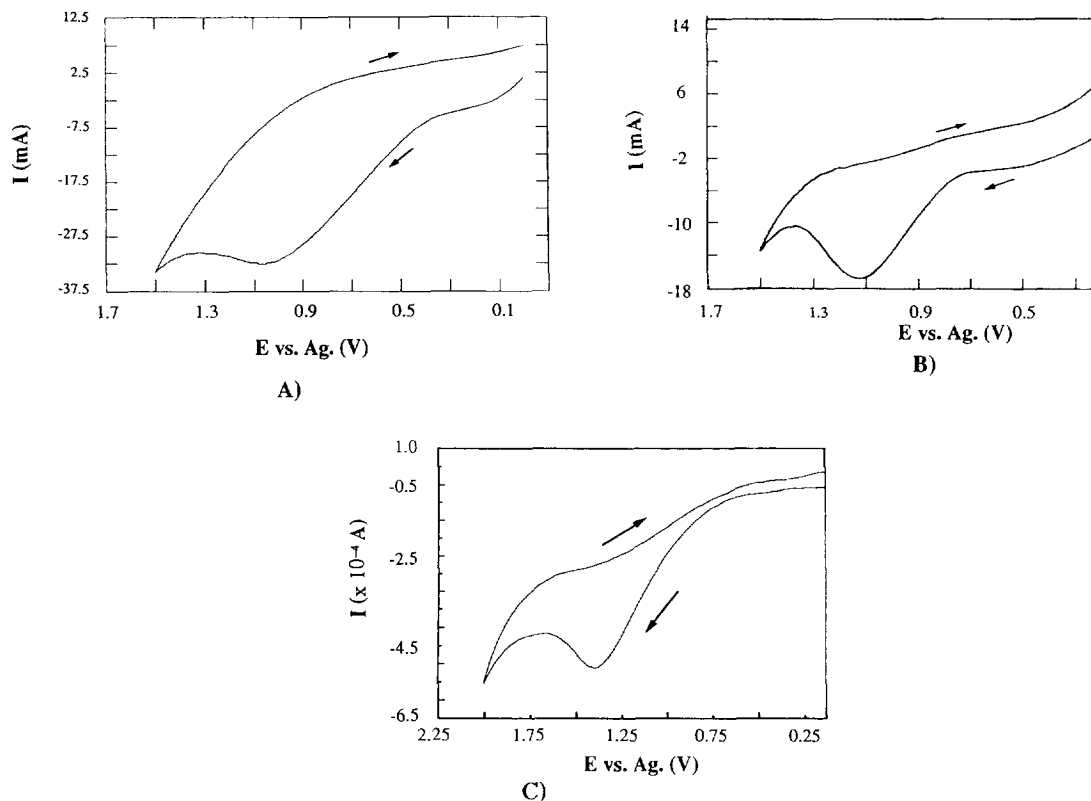


Fig. 3. Cyclic voltammograms in molten nitrates ( $\text{KNO}_3\text{-NaNO}_3\text{-LiNO}_3$ , 53:17:30 wt.% with 0.1 M KOH) at  $150^\circ\text{C}$  for samples: (A)  $\text{La}_2\text{Ba}_2\text{Cu}_{2.15}\text{Ti}_{1.85}\text{O}_{11-\delta}$ , (B)  $\text{Eu}_2\text{Ba}_2\text{Cu}_{2.15}\text{Ti}_{1.85}\text{O}_{11-\delta}$ , (C)  $\text{Tb}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$ .

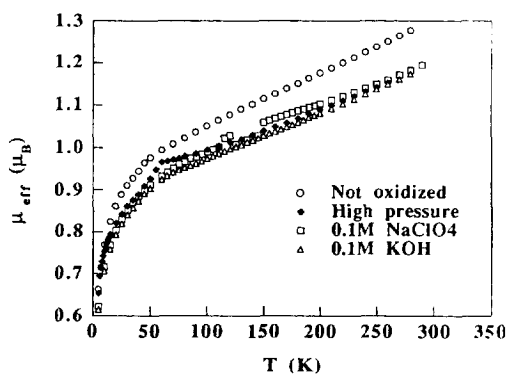


Fig. 4. Magnetic properties of  $\text{La}_2\text{Ba}_2\text{Cu}_{2.15}\text{Ti}_{1.85}\text{O}_{11-\delta}$  before and after oxidation. The effective magnetic moment (Bohr magnetons) is plotted vs. temperature.

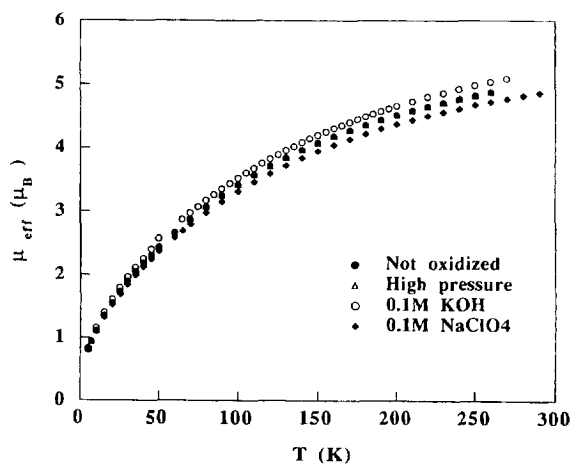


Fig. 5. Magnetic properties before and after oxidation for  $\text{Eu}_2\text{Ba}_2\text{Cu}_{2.15}\text{Ti}_{1.85}\text{O}_{11-\delta}$ . The effective magnetic moment (Bohr magnetons) is plotted vs. temperature.

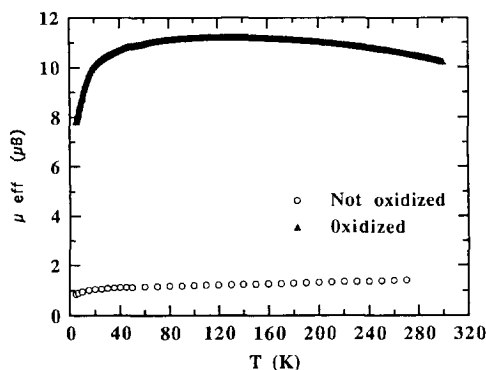


Fig. 6. Magnetic properties before and after electrochemical oxidation for  $\text{Tb}_2\text{Ba}_2\text{Cu}_2\text{Ti}_2\text{O}_{11}$ . The effective magnetic moment (Bohr magnetons) is plotted vs. temperature.

ment is very small. The electrochemically oxidized sample also shows a very small change in magnetic properties although of opposite sign, implying a very small extent of oxidation.

On the other hand, the plots of the effective magnetic moment vs. temperature for the Tb stoichiometric phase change more markedly upon oxidation. Since Tb is one of the lanthanides for which oxides with  $\text{Ln}^{+4}$  are known, and taking into account the possibility of oxidizing  $\text{Tb}^{+3}$  to  $\text{Tb}^{+4}$  instead of  $\text{Cu}^{+2}$  to  $\text{Cu}^{+3}$ , the changes expected are less predictable. In that sense the  $\text{Tb}^{+3}$  ion has typically, in the absence of any magnetic exchange, a room temperature typical magnetic moment near  $9.7 \mu_B$  [9]. The fact that the 2222 phase shows such a small value of magnetic moment previous to oxidation in the whole temperature range implies the existence of a strong antiferromagnetic coupling affecting the rare earths. The considerable increase upon oxidation observed for  $\text{Ln} = \text{Tb}$  needs to come therefore from a breakdown of antiferromagnetic coupling between rare earth ions that could have been caused by a change in Tb oxidation state and therefore in its electronic ground state. With the data available at present, however, it is not possible to evaluate the influence of the ordering of excess oxygen upon the change in magnetic properties. Further experiments are being carried out to elucidate the nature of the magnetic properties observed for the Tb compound.

#### 4. Conclusions

Electrochemical oxidation offers an alternative driving force that may yield materials with the same

properties as those obtained by high pressure oxidation techniques, but at ambient pressure and nearly ambient temperature. However, the oxidation medium must be carefully chosen according to the actual oxidation potentials, directly related to the resistance against oxidation of the material. In this sense molten alkali nitrates offer a unique example of chemically inert media for oxidation of cuprates at potentials as high as +1.5 V vs. Ag. The reported data in this paper show evidence that the materials used are quite similar to the ones obtained by high-pressure annealing methods.

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