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Soft chemistry synthesis of the perovskite CaCu₃Ti₄O₁₂[☆]

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Abstract

The perovskite CaCu₃Ti₄O₁₂ (CCT) has been obtained after calcination of oxalate precursors at 900–1000 °C in air. Those precursors are prepared using a soft chemistry method, the coprecipitation. The oxalate powders consist of disk-like particles of 2–3 μm diameter and 300–400 nm thickness. By varying the ratio of the initial amounts of metal chlorides, additional phases (CaTiO₃, TiO₂ and CuO) could be obtained besides CCT. The corresponding multiphased ceramics present improved dielectric properties.

Keywords: Oxalates; Oxides; Coprecipitation; Chemical synthesis; CaCu₃Ti₄O₁₂; Capacitor

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1. Introduction

The unusual high dielectric constant ($\sim 10,000$) at 1 kHz of the perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (commonly called CCT) has been reported first by Subramanian et al. [1]. Moreover, between -170 and 100 °C, a quasi-independent behaviour of the permittivity with temperature is observed. These properties are of great importance for the world of electronic devices. Indeed, there is an increasing demand on dielectrics to surpass their properties to be used as capacitors, in particular in the field of microelectronics and power electronics. Especially, the decrease of the size of capacitors is a crucial key point.

Most of the papers reported in the literature mentioned that the CCT materials studied were single phased. Only Subramanian et al. [2] indicated the presence of a minute impurity of CuO. Kobayashi and Terasaki [3] showed a drop of ϵ for a factor 10^2 when introducing manganese and explained it by a dipole moment causing fluctuating ferroelectric domains in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.

The aim of this paper is to report about a successful soft chemistry method, the coprecipitation, to elaborate the single phase $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, or a mixture of CCT and different oxides (CaTiO_3 , TiO_2 and CuO). The synthesis and the powder characteristics (structure, morphology and size) are described.

2. Experimental part

The synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ oxide first requires the elaboration of the oxalate precursors. Oxalate precursors are obtained by the coprecipitation of calcium, copper and titanium chlorides with oxalic acid. The starting materials are CaCl_2 (Prolabo, %min = 96), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Prolabo, %min = 99) and TiCl_3 (Prolabo, %min = 15, $d = 1.20$). TiCl_3 is preferred to TiCl_4 because it is less sensitive to moisture. Indeed in the presence of moist air, liquid TiCl_4 , a well-known smoke material (m.p. = -25 °C), releases thick white smokes due to the formation of finely divided titanium oxichloride. On the contrary, solid TiCl_3 can be easily dissolved in water and the hydrolysis is prevented by acidification. The full oxidation of Ti^{3+} into Ti^{4+} in the solution is ensured by air bubbling during the reaction. The coprecipitation method consists of three stages. (i) The dissolution of the metallic salts in water (800 mL) and at the same time, the dissolution of oxalic acid in ethanol (5 L). When the dissolution is complete, the two solutions are mixed. (ii) The solutions are homogenized with magnetic stirring. The solution is aged for a couple of hours. The precipitate obtained is centrifuged. (iii) Then the precipitate is dried at 100 °C. The overall process is carried out at room temperature. In order to decrease the dielectric constant of the precipitation media, the volume of water is taken much lower than that of ethanol. Since the nucleation of the particles is favoured compared to the growth, smaller particles, homogeneous in size and composition, are likely to be obtained [4].

After drying, the precursor powders are pyrolyzed in air at 900 – 1000 °C for 10 h to obtain the oxides.

The reactants are weighted in various proportions in order to reach different Ca/Cu/Ti ratios in the precursor powders, and consequently in the oxides. The obtained oxide powders are characterized by powder X-ray diffraction using a Bruker D4 diffractometer (Cu $K\alpha$ radiation). The diffraction peaks of the different crystalline phases are compared to the ones given by the JCPDS files (CCT JCPDS 75-2188, CaTiO_3 JCPDS 82-228, CuO JCPDS 80-1917, TiO_2 JCPDS 84-1284). The size and the morphology of the powders are analyzed by SEM (JEOL JSM-35CF) and by SEM-FEG (JEOL JSM 6700).

3. Results

Some modification of the conventional synthesis procedure has to be carried out. For stage (i), preliminary experiments have shown the formation of a precipitate and a gel in the metallic salt solution. The formation of a solid phase can be explained by the electrochemical potential between copper and titanium and by the equilibrium constant of titanium. Indeed, the Ti^{3+} ion can be transformed into titanium hydroxide (gel) while the Cu^{2+} ion is reduced into metallic copper (precipitate). To avoid this problem, a two-step dissolution is necessary. The aim of this additional step is to separate the oxidizing agent from the reducing one. So the chlorides are divided into two different solutions. The first one contains $CaCl_2$ and $CuCl_2 \cdot 2H_2O$ and the second one $TiCl_3$. This procedure allows to obtain two limpid solutions without the apparition of precipitate or gel. The two solutions are mixed at the same time in the solution of oxalic acid. The so-obtained precipitate is centrifuged and dried at $100\text{ }^\circ\text{C}$.

The SEM micrographs of the precursor powders reveal a disc-like morphology with an average diameter of $2\text{--}3\text{ }\mu\text{m}$ and a thickness of $300\text{--}400\text{ nm}$ (Fig. 1). After the decomposition, the oxide powders (Fig. 2) are constituted of homogeneous grains (shape and size). The size approximately ranges from 0.2 to $1\text{ }\mu\text{m}$.

The different phases detected by X-ray diffraction analysis are reported in Table 1. As expected, the pure CCT phase is obtained only when the ratio of calcium, copper and titanium are very close to the stoichiometric ones. An excess of Ca leads to the formation of $CaTiO_3$ phase. In the case of a Cu excess, the copper oxide CuO is detected besides the CCT phase. Finally both TiO_2 and $CaTiO_3$ are observed if more than four Ti per 12 oxygens are analyzed in the powder. The X-ray diffraction patterns of a mixture of the four phases are shown in Fig. 3.

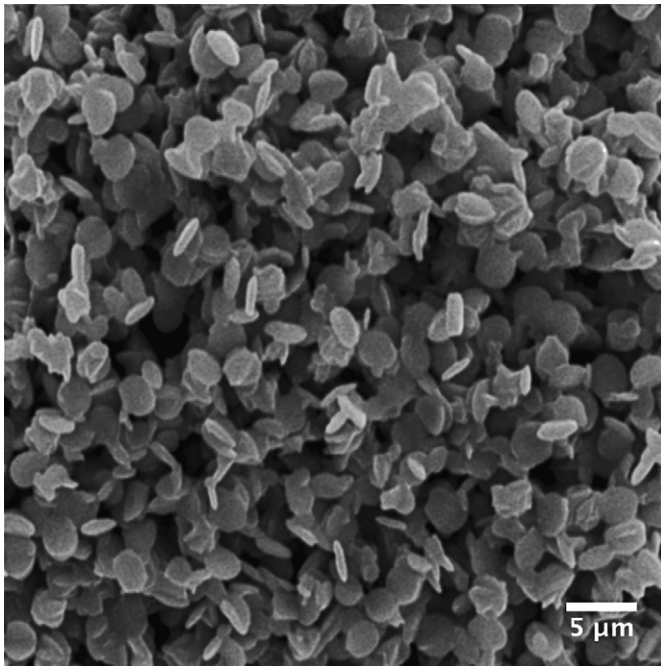


Fig. 1. SEM micrograph of oxalate precursor powders.

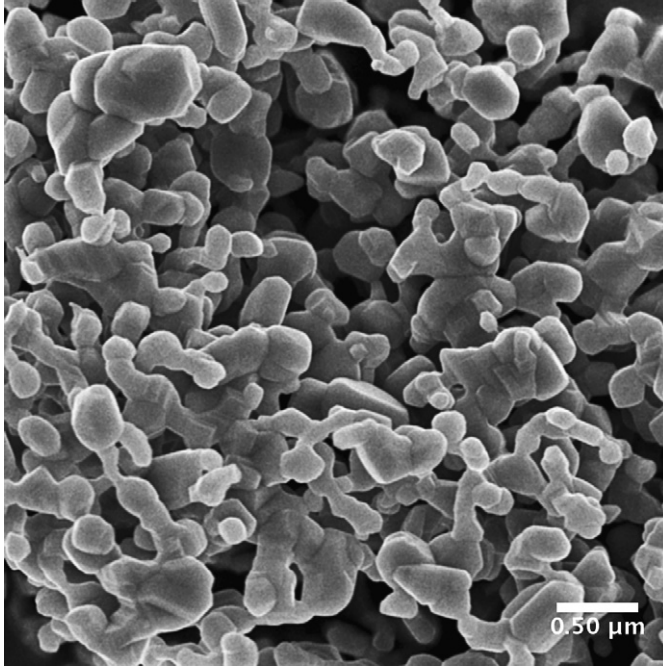


Fig. 2. SEM-FEG micrograph of CCT-based powders calcined at 900 °C for 10 h.

The coprecipitation method is interesting in the sense that the various cation ratios can be easily controlled. The presence of these additional phases gives to this multiphased material an interesting dielectric behaviour, different from the one observed in pure CCT materials. Huge relative permittivity values and relatively low losses are measured in the corresponding sintered ceramics [5].

4. Conclusion

The perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was successfully elaborated after calcination of the oxalate precursors. The coprecipitation method allowed to obtain and to control the apparition of several phases in addition to CCT. The amount of these phases is simply controlled by varying the

Table 1
Chemical analysis and structure of the oxide powders calcined at 1000 °C for 10 h

Reference	Chemical analysis				Observed phases	$\frac{I_{\text{CaTiO}_3}}{I_{\text{CCT}}}$ (%)	$\frac{I_{\text{CuO}}}{I_{\text{CCT}}}$ (%)	$\frac{I_{\text{TiO}_2}}{I_{\text{CCT}}}$ (%)
	Ca	Cu	Ti	O				
CCT	1	3	4	12	Theoretical stoichiometry CCT			
CCT-A1	Excess	—————→			CCT + CaTiO_3	3	—	—
CCT-A2		—————→			CCT + CuO	2	—	—
CCT-B1		Excess	—————→		CCT + CuO	—	5	—
CCT-B2			—————→		CCT + CuO	—	1	—
CCT-C1			Excess	—————→	CCT + TiO_2 + CaTiO_3	5	—	3

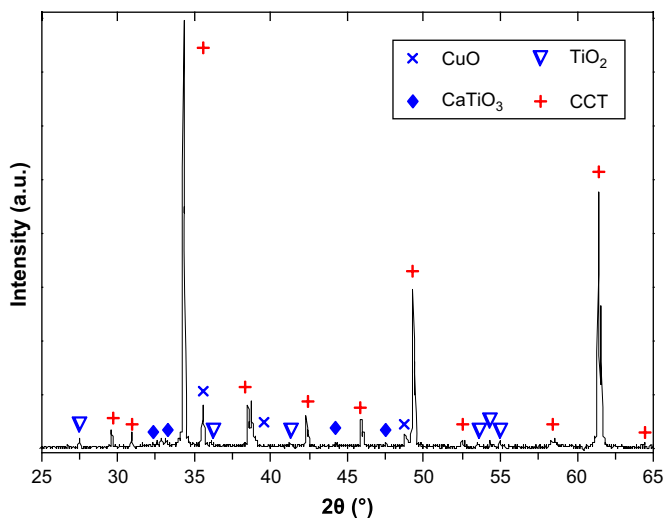


Fig. 3. XRD pattern of the multiphased oxide: $\text{CaCu}_3\text{Ti}_4\text{O}_{12} + \text{CaTiO}_3 + \text{TiO}_2 + \text{CuO}$, calcined at 900°C for 10 h.

ratio of the reactants introduced during the synthesis. Furthermore, it is interesting to note that this multiphased material can be obtained from a single-step processing route, in air, at relatively low temperature.

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