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# Photoluminescent $CaCu_3Ti_4O_{12}$-Based Thin Films Synthesized by a Sol–Gel Method

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**Results on the characterization of photoluminescent $CaCu_3Ti_4O_{12}$-based films, prepared from a sol–gel precursor and heat treated at 700°C, are reported for the first time. The samples showed two emission bands at 554 and 800 nm when excited with a 488 nm Ar-ion laser. The photoluminescent emission measured at room temperature in thin films was attributed to complex vacancy clusters. The films consisted of $CaCu_3Ti_4O_{12}$ with traces of $TiO_2$, CuO, and $CaTiO_3$ and showed porous structures with an average particle size of 50 nm under atomic force microscopy resolution.**

## I. Introduction

Calcium copper titanate ($CaCu_3Ti_4O_{12}$—CCTO) has gained considerable attention since its huge dielectric constant was first reported in 2000.[1,2] Although it is still the subject of some controversy, the origin of the exceptional dielectric behavior has been attributed to the grain boundary capacitance and extrinsic defects rather than to intrinsic properties associated with the crystalline structure of the material.[2,3] Beyond that debate, CCTO is a promising dielectric material for electroceramic devices such as capacitors,[3–5] gas sensors,[6–8] and varistors.[9,10]

CCTO is mostly synthesized by the mixed oxide route.[2,9,11] However, metal-organic chemical vapor deposition,[4,5] physical methods such as pulsed laser deposition[6] and sputtering,[7] and wet chemical or sol–gel approaches[12–23] have been successfully put into practice. It is important to notice that single-phase CCTO could not yet be synthesized directly by sol–gel or hydrothermal methods; heat treatments are always needed in order to attain single-phase CCTO through solid-state reactions. In fact, the most frequently reported temperatures for phase formation and sintering of this phase are in the 1000°–1100°C range.[2,9–11] In this work, we report for the first time on the photoluminescent response of CCTO-based films synthesized by a sol–gel route. A *sol* of titanium isopropoxide modified with acetic acid was mixed with a solution of a nonionic surfactant in 2-propanol. As proposed by Liu *et al.*,[15] copper and calcium nitrates were dissolved in 2-methoxyethanol and then mixed with the Ti *sol*. Thin films were deposited by spin coating onto oxidized silicon ($Si/SiO_2$) and glass substrates at 3000 rpm for 15 s, left overnight for condensation with atmospheric moisture, and finally annealed at 700° and 600°C, respectively, for 20 min.

Analysis of the surface roughness and grain size distribution was carried out by atomic force microscopy (AFM) (Digital Instruments NanoScope IIIa, Veeco, Barbara, CA) in the tapping mode. Figure 1(a) shows an image of the heat-treated film deposited onto $Si/SiO_2$, where a high degree of porosity is observed as confirmed by scanning electron microscopy. The porous structure is produced due to solvent evaporation during spinning and drying and due to organics burning during heat treatment. AFM data used for roughness measurements revealed quite a smooth surface with an RMS of 5.2 nm in a 2.0 $\mu m^2$ area. The statistical distribution of the grain size was carried out by the watershed technique over AFM images using Gwyddion software (Gwyddion 2.10, GNU General Public License, http://www.gwyddion.net, 2008). The results showed a structure of equiaxial grains with a normal size distribution and a mean grain size of around 50 nm as shown in Fig. 1(a) and in the histogram of Fig. 1(b). Chang *et al.*[12] also reported on the synthesis of nanocrystalline CCTO thin films from a sol–gel precursor with a porous structure and with two types of grains: one below 50 nm and the other above 300 nm. The authors stated that this morphology implies the existence of a second phase or duplex grain structures. In this work, the degree of crystallinity and phases present were assessed by X-ray diffraction (XRD) (Rigaku Rint 2000, Tokyo, Japan). The analysis showed that, in films heat treated at 700°C, as shown in Fig. 2 CCTO is the main phase present, followed by $TiO_2$, CuO, and $CaTiO_3$. Besides, titanium dioxide is present both in the anatase and in the rutile phases. This multiphase system was expected at 700°C because similar or equivalent XRD patterns have been reported after heat treating the gel at 800°[18] and 900°C,[22,23] a fact that clearly indicates that pure, single-crystalline CCTO is obtained by means of solid-state reactions at temperatures above 900°C.

Photoluminescence (PL) spectra were taken using a U1000 Jobin-Yvon (Longjumeau, France) double monochromator coupled to a cooled GaAs photomultiplier with a conventional photon counting system. The 488 nm wavelength of an argon-ion laser, with the laser's maximum output power kept at 25 mW, was used as an excitation source for the PL measurements. A cylindrical lens was used to prevent the sample from overheating. The slit width used was 300 μm, and all measurements were performed at room temperature. Interestingly, as shown in Fig. 3, PL measurements of CCTO-based films deposited onto $Si/SiO_2$ and treated at 700°C showed two main bands with maximum emissions around 554 nm (strong green emission) and 800 nm (weak red emission) when excited with a 488 nm wavelength laser. These peaks can be related to $TiO_5$, $CuO_{11}$, and

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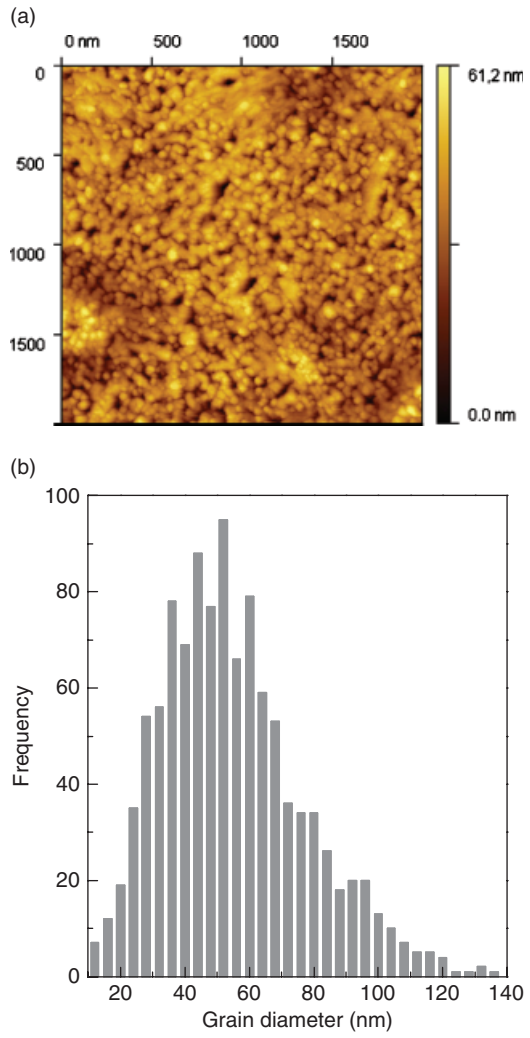


**Fig. 1.** (a) Atomic force microscopy (AFM) image of a 2 μm × 2 μm area of a nanoporous film annealed at 700°C for 20 min and (b) grain size distribution from AFM topographic data.

$CaO_{11}$ vacancy clusters. In fact, $TiO_6$ would be linked to $CaO_{12}$ and/or $CuO_{12}$ clusters. According to the literature, the first PL peak at 554 nm indicates that the $TiO_5$ cluster would be surrounded by four $CaO_{12}$ clusters, whereas the second peak at 800 nm indicates that it would be surrounded by four $CuO_{12}$ clusters.[24–26] The first and second peaks could also be associated with [$CaO_{11}$ $V_O$] and [$TiO_5$ $V_O$] and with [$CuO_{11}$ $V_O$] and [$TiO_5$ $V_O$] clusters, respectively, in which $V_O$ stands for oxygen vacancies.[24–26] These complex defects are deeply inserted in to the band gap, leading to PL emission.

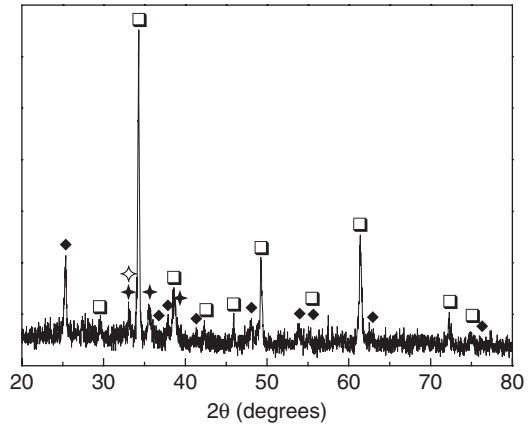


**Fig. 2.** X-ray diffraction (XRD) pattern of the xerogel treated at 700°C for 20 min (❑ $CaCu_3Ti_4O_{12}$ JCPDS 75-2188; ♦ $TiO_2$ JCPDS 78-2485 (rutile); JCPDS 78-2486 (anatase); ✧ $CaTiO_3$ JCPDS 81-0561; ✦ CuO JCPDS 80-1917).

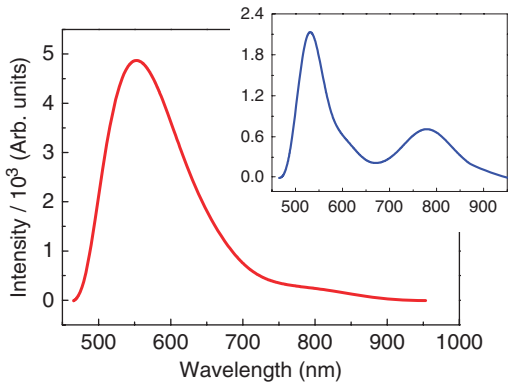


**Fig. 3.** Room-temperature photoluminescence spectra of films deposited onto $Si/SiO_2$ substrates heat treated at 700°C and (inset) of films deposited on glass substrates heat treated at 600°C for 20 min.

The photoluminescent properties of Si nanoparticles, Cu-doped Si, and several silicides have been reported long time ago and were considered in this work.[27,28] Because there exists the possibility of crystallization of Cu–Si nanoparticles, i.e. $Cu_2Si$, in CCTO films deposited onto $Si/SiO_2$, PL measurements were also carried out over samples deposited on glass substrates heat treated at 600°C. The resulting PL spectrum, shown as an inset in Fig. 3, shows peaks of lower intensity located, also, at 540 and 790 nm, approximately. Notice that changes in peak intensity and broadness arise because of compositional changes in the films due to heat-treatment temperature and not due to the nature of the substrate. Films treated at 600°C showed a higher amount of secondary phases ($TiO_2$ and CuO) other than CCTO. This observation confirms the original hypothesis that the photoluminescent response of CCTO-based films deposited on $Si/SiO_2$ substrates is indeed a property of the film itself and is not caused by the possible presence of Cu–Si nanoparticles.

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