Journal of King Saud University – Engineering Sciences (2013) **25**, 35–39

King Saud University

Journal of King Saud University – Engineering Sciences

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ORIGINAL ARTICLE

Influence of sintering parameters on melting CuO phase in $CaCu_3Ti_4O_{12}$

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Received 9 June 2011; accepted 10 October 2011
Available online 18 October 2011

KEYWORDS

CuO melt phase;
Microstructure;
CCTO

Abstract Dielectric material $CaCu_3Ti_4O_{12}$ (CCTO) was prepared by solid state technique. $CaCO_3$, TiO_2, and CuO powders were mixed thoroughly in a ball mill for an hour and were calcined at 900 °C for 12 h. This is followed by sintering at a defined standard temperature for this work (1050 °C for 24 h). Other samples were prepared in a similar manner but with different sintering durations. Each of the sample's microstructure was observed by a Scanning Electron Microscope (SEM). Meanwhile, Energy-dispersive X-ray Spectroscopy (EDX) analysis was done on fracture surfaces in order to examine the elements present at grain boundaries. Microstructure observations show the melting and abnormal grain growth with large pores. The solidified liquid at grain boundaries was verified as Cu rich region, as confirmed by EDX analysis. By using the SEM, microstructure of small grains with clear grain boundaries were obtained when sintering was done at temperatures lower than 1050 °C. The microstructure of CCTO was very sensitive to sintering parameters.

1. Introduction

It is known that some perovskite-structured ceramic compounds display interesting dielectric properties. One of the members, which was named as $CaCu_3Ti_4O_{12}$ (CCTO), was recently studied to investigate the origin of the so-called colossal permittivity, and results were published on single crystal, powders and thin film (Chiodelli et al., 2004). This insulating cubic compound CCTO has attracted much interest because of its high dielectric constant (up to 10^5) over a broad temperature range extending from 100 to 600 K. Furthermore, cubic compound CCTOs display a rather wide microwave frequency window (Subramanian et al., 2000; Litvinchuk et al., 2003). This unique property makes CCTO a promising material for microelectronic applications.

However, the nature on how the CCTO exhibits such high dielectric constant at 100 and 600 K is still not well understood (Lin et al., 2002). Many researchers claimed that factors such as grain boundary, presence of twin boundaries or other planar defects and displacement of Ti ions could be the reasons behind those high dielectric constant properties (Litvinchuk et al., 2003; Wu et al., 2005). More extensive research efforts are needed in order to provide a comprehensive explanation to the said phenomena.

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.jksues.2011.10.001

The dielectric properties are very sensitive to processing, such as the mixing, calcination shaping and sintering (Brize et al., 2006). Different parameters in each steps will contribute changes in CCTO properties. In this project, the CCTO was prepared by solid state technique. This involves mixing, calcination, compaction and sintering. Many researchers are concentrating on sintering process, because it is important to find the right sintering parameter such as the duration and temperature. The proper sintering parameter ensures that small grain formation (2–5 μm) with high dielectric constant will be obtained (Brize et al., 2006; Prakash and Varma, 2007). This paper will also be focusing on the sintering parameters. It was stated by some researchers (Valim et al., 2004; Almeida et al., 2002; Kolev et al., 2002) that sintering at 1050 °C for 24 h in the normal atmosphere will produce single phase of CCTO. However, earlier studies on the fabrication of CCTO failed to include microstructure observations. This paper highlights the microstructural observations obtained from this sintering parameter. The results show that there were abnormal grain growth and melting grain with very large pores. Therefore, it is important to investigate the new sintering parameter to ensure the correct microstructure with high dielectric constant property will be obtained. Based on the above facts, a study on the effects of sintering conditions to microstructure is presented in this paper.

2. Method and materials

CCTO samples were prepared by a conventional solid state method. $CaCO_3$ with mean particle size of 15.52 μm (Aldrich, 99%), TiO_2 (0.68 μm) (Merck, 99%) and CuO (6.85 μm) (Aldrich, 99%), respectively, were used as starting materials. Stoichiometric ratios of the reagents (i.e., $CaCO_3$, TiO_2, CuO: 1, 4, 3) were mechanically ball milled for 1 h, with a ball to powder ratio of 10:1. The milling process was done in inert atmosphere. A powder exhibiting free flowing characteristics was then obtained by sieving the dried milled powders. Subsequently, the powder was calcined in air at 900 °C for 12 h. Next, the powders are pressed at 300 MPa, to be made into cylindrical specimens (with dimensions of 5 mm in diameter

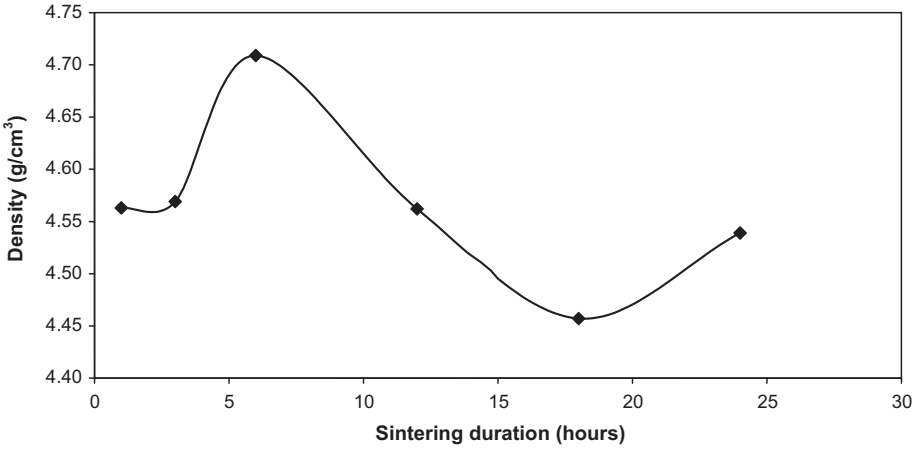

Figure 1 The density results for CCTO sample sintered at different sintering durations.

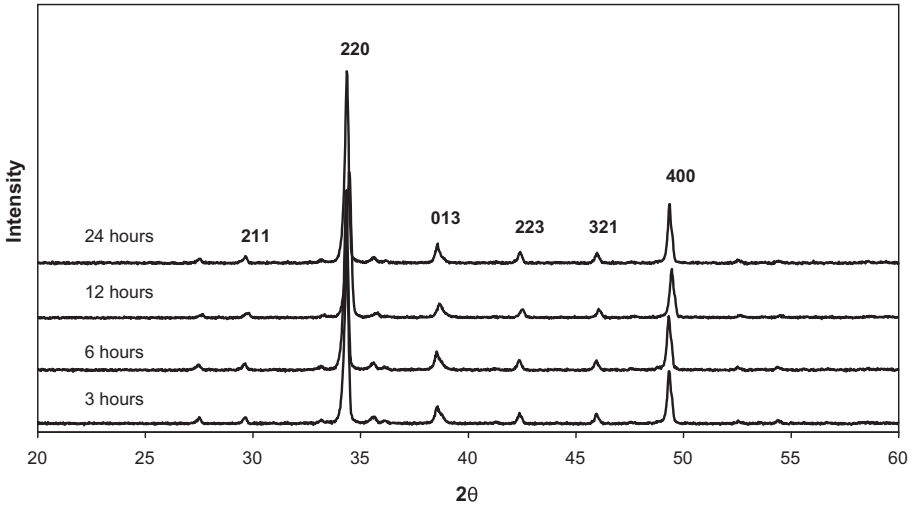

Figure 2 The XRD results for CCTO sample sintered at 1050 °C for different sintering durations.