

EFFECT OF THE SINTERING TEMPERATURES ON THE DIELECTRIC PROPERTIES OF POLYCRYSTALLINE $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$.

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Abstract: $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics has been prepared by the standard solid state reaction technique. The internal structure, surface morphology and dielectric properties of polycrystalline $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ have been studied by X-ray diffraction, Optical microscopy and Impedance Analyzer, respectively. The X-ray diffraction analysis for the sample calcined at 850 °C confirmed that the sample is single-phase and is formed cubic perovskite structure. Lattice parameters are calculated using the Nelson-Riley function. The sample has been sintered at various sintering temperatures, T_s (1000, 1050 and 1100 °C) for six hours in air. The optical micrographs of the sample with different sintering temperatures exhibit a homogeneous microstructure and the average grain sizes increase with T_s which is determined by the linear intercept method. The dielectric properties of these materials have been measured in the frequency range 100Hz-15MHz. It is observed that the dielectric constant increases with T_s , on the other hand loss tangent decreases with T_s .

Keywords: Perovskite, Standard solid state reaction technique, Sintering temperature, Linear intercept method, Loss tangent.

1. INTRODUCTION

Environmental friendly, temperature independent high dielectric constant materials have numerous important applications in electronic devices such as capacitors, static and dynamical random access memories, and so on. Now a days the commonly used high dielectric constant materials are ferroelectrics and relaxor ferroelectrics, such as SrTiO_3 , BaTiO_3 , PZT and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ in which a sharp or a diffused Curie peak is indicated on curve of dielectric constant vs. temperature. However, both kinds of materials show the huge variation of their dielectric constant with temperature, which is undesirable for many applications [1]. For instance, capacitors need to have stably static dielectric constant values to operate properly under a variety of conditions. If the static dielectric constant, ϵ' has strong temperature dependence, then the device will not be robust and may fail. Most recently, the perovskite-like material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted much attention due to its

extraordinary dielectric properties. It exhibits colossal static dielectric constant at room temperature of $\epsilon' \sim 10^5$ over a wide temperature range (100-600 K) [2]. These outstanding electrical properties are quite unusual since CCTO exhibits a body centered cubic perovskite structure with slightly tilted TiO_6 octahedra facing each other [3]. However, the dielectric loss of this almost temperature independent dielectric material is relatively too high. This high dielectric loss has inevitably limited its practical applications [4].

It is noted that, the dielectric properties of ceramic materials are likely to depend on many variables, including ceramics microstructure (average grain size), processing conditions (sintering temperature) and substituting elements (donor or acceptors). For this reason, CCTO is firstly substituted with various Zn content instead of Ca. The best dielectric properties of Zn substituted CCTO is found for Zn=0.4 content [5] and the compound leads to $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$. This paper gives optimum T_s for

$\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ which exhibits colossal dielectric constant with low loss tangent.

2. EXPERIMENTAL

Commercially available powder of CaCO_3 , ZnO , CuO and TiO_2 were used as raw materials. The powders were weighted in the appropriate composition and ball-milled for 12 h using a polyethylene jar with distilled water and zirconia balls. The distilled water was removed by heating with an electric heater and the powders were dried at 100°C for 6 h and pulverized. The dried mixtures were calcined at 850°C for 6 h in air. X-ray diffraction (XRD) was carried out for these calcined powder with an X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.542\text{\AA}$). The calcined powders were then pressed uniaxially into disk-shape (about 10 mm diameter, 2-3 mm thickness) samples. The samples were sintered at various temperatures (1000 , 1050 and 1100°C) in air for 6 h dwell time. The temperature ramp was $10^\circ\text{C}/\text{min}$ for both cooling and heating.

The surface micrograph of different sintered temperatures samples were visualized under a high-resolution optical microscope (model-Olympus DP70) and then photographed. The frequency dependence characteristics of the polycrystalline $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ samples, i.e., the capacitance and the loss tangent spectra were investigated using an Agilent Impedance Analyzer (model no. 6520A). The complex dielectric permittivity, ϵ' measurements on disk-shaped specimens have been carried out at room temperature on all the samples in the frequency range 100 Hz-15 MHz. The values of the measured parameters obtained as a function of frequency and the real part, ϵ' of complex permittivity has been calculated using the following relations: $\epsilon' = C_s/C_0$, where C_s is the capacitance of the sample, $C_0 = \epsilon_0 A/d$ is derived geometrically; A is the area of cross-section, and d is the thickness of the sample. The loss tangent, $\tan\delta$ is directly obtained from Impedance Analyzer.

3. RESULTS AND DISCUSSION

The XRD patterns for the sample polycrystalline $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ calcined at 850°C are shown in Fig. 1. Analyzing the XRD patterns, it was observed that the positions of the peaks comply with the reported value [6]. All XRD patterns were matched with the major peaks of the pseudo-cubic CCTO with lattice constant $a_0 \sim 7.391\text{\AA}$ provided by Feng *et al.* [7] except for one single peak that is clearly seen in this figure. This small peak is near $2\theta = 35.1^\circ$ can be attributed to CuO [7]. Equilibrium thermodynamics would suggest that, during sintering in air, CuO will reduce to Cu_2O at temperature above 1000°C . Upon cooling, a reoxidation reaction occurs by converting Cu_2O to CuO , though at relatively rapid cooling rates, the reformation of the CuO must reside as a secondary phase is mostly limited to the surface [7]. It is likely that reoxidation reactions also occur on a finer scale within grain boundary networks and other high oxygen diffusion paths. This ultimately contributes

to the electrical heterogeneity observed via the space charge polarization.

The lattice parameter for each peak of the sample was calculated by using the formula: $a = d[h^2 + k^2 + l^2]^{1/2}$, where h , k and l are the Miller indices of the crystal planes. To determine the exact lattice parameter for each sample, Nelson Riley method was used. The Nelson Riley function $F(\theta)$ is given as $F(\theta) = 1/2[\cos^2\theta/\sin\theta + \cos^2\theta/\theta]$, where θ is the Bragg's angle. The values of lattice constant ' a ' of all the peaks for a sample are plotted against $F(\theta)$. Then using a least square fit method, exact lattice parameter ' a_0 ' is determined. The point where the least square fit straight line cut the y-axis (i.e. at $F(\theta) = 0$) is the actual lattice parameter of the sample. The measured lattice parameter for $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ calcined at 850°C for 6 hours in air is 7.372\AA .

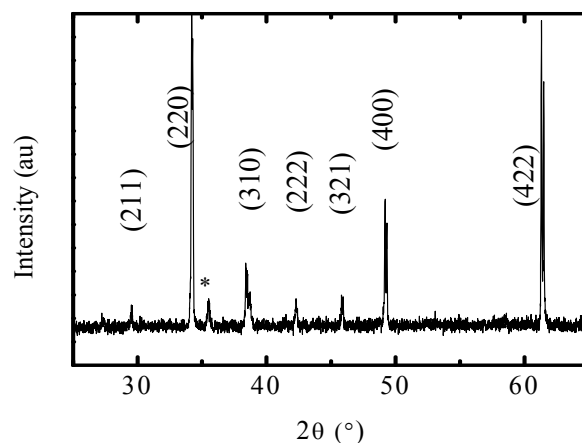


Fig. 1. The X-ray diffraction patterns for the sample calcined at 850°C for 6 hours in air.

3.1 Surface micrographs

The optical micrographs of $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ sintered at 1000 , 1050 and 1100°C are shown in Fig. 2.

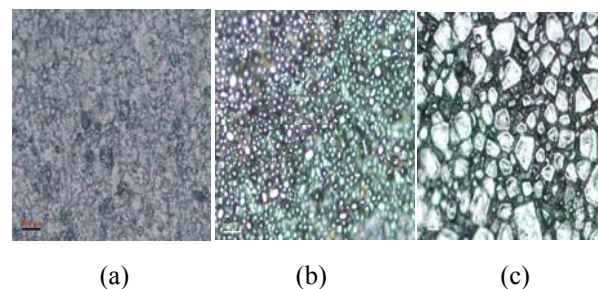


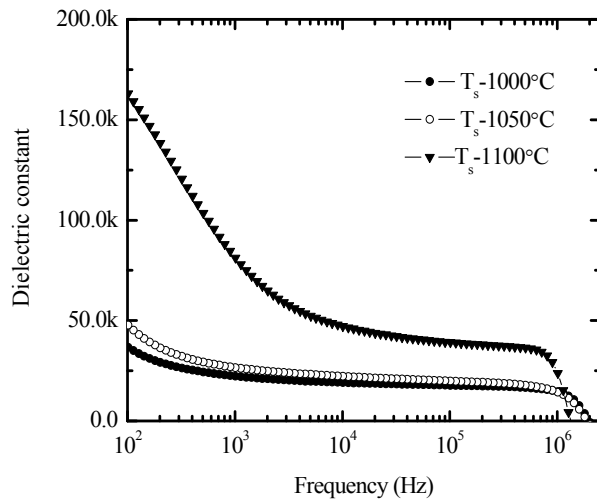
Fig. 2: The optical micrographs of polycrystalline $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ sample sintered at temperatures (a) 1000°C , (b) 1050°C and (c) 1100°C with fixed dwell time 6 hours in air.

From these micrographs, it is observed that the size of the grain increases whereas the porosity decreases with the increase of sintering temperature. It is also observed that the samples sintered at 1000°C with fairly small grains and open porosity devoid of intragranular pores. It indicates that the 1000°C sintering temperature and the 6 hour sintering time

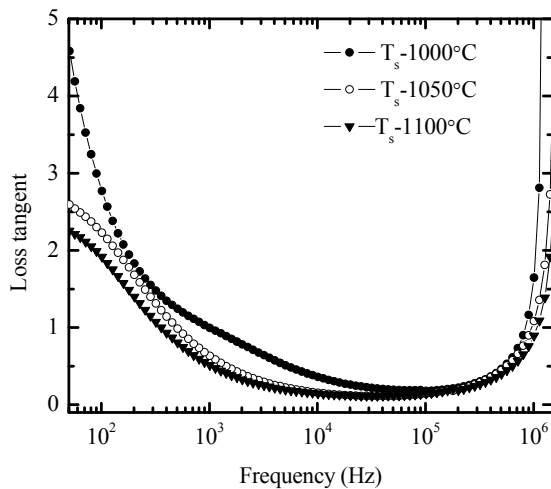
were insufficient for the complete formation of the microstructure. On the other hand, it can be noted that the sintering temperature of 1100°C suffices to produce a homogeneous microstructure with large grain size and a uniform size distribution, Fig. 2(c). This is due to higher thermal energy at the sintering temperature of 1100°C for producing large and uniform grain size.

3.2 Dielectric properties

Figure 3a and b shows ϵ' and $\tan\delta$ for $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ samples sintered at 1000, 1050 and 1100°C as a function of frequencies from 100 Hz to 15 MHz at room temperature.



(a)



(b)

Fig. 3: Frequency dependent (a) dielectric constant and (b) dielectric loss for polycrystalline $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ sintered at various temperatures.

The ϵ' of $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ was increased with the increase of sintering temperature at all the frequencies upto 1 MHz. The similar trend can also be found in the $\tan\delta$ data shown in Fig. 3(b). Here, $\tan\delta$ decreases when the sintering temperature increases from 1000°C to 1100°C. However, an anomalously large ϵ' was found at low frequency range (100 Hz - 10 kHz) for the sample sintered at 1100°C. Same characteristic behavior also found from the very large values of $\tan\delta$ below 100 Hz. These deviations observed in the $\tan\delta$ of 1000°C sintered $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ might be linked to its microstructure where the growth of $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ grains was limited by the lack of sintering temperature, creating more Cu-rich boundary regions [8] contributing to the higher loss. Lastly, it is observed that the best ϵ' of $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ is around 50600 for 1100°C sintered specimens at 10 kHz while its $\tan\delta$ marks as low as 0.12 at the same frequency. This may be due to larger grains formation leads to a higher value of the ϵ' and low $\tan\delta$. The increase of the ϵ' and decrease of $\tan\delta$ values with the grain size supports the argument for an internal boundary layer capacitor model to explain the dielectric behavior of $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$.

4. CONCLUSIONS

In conclusion, it is shown that, grain size of the $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ sample strongly depends on sintering temperatures due to higher thermal energy and larger grains formation leads to enrich the dielectric properties of polycrystalline $\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_3\text{Ti}_4\text{O}_{12}$. A maximum of dielectric constant is found for 1100°C sintered specimens while its $\tan\delta$ is low. This colossal dielectric constant material represents a class of dielectric for barrier layer capacitors applications which may challenge the preeminence of BaTiO_3 and SrTiO_3 -based compositions that have been the keystone of this market for the last forty years.

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7. NOMENCLATURE

Symbol	Meaning	Unit
T_s	Sintering Temperature	$^{\circ}\text{C}$
λ	Wavelength	\AA
a	Lattice constant	\AA
ϵ'	Dielectric constant	Dimensionless
$\tan\delta$	Dielectric loss	Dimensionless