

Grain sizes and dielectric properties of CC(3.1)TO ceramics with various sintering temperature prepared by molten salt method

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ABSTRACT

In this research, $\text{CaCu}_{3.1}\text{Ti}_4\text{O}_{12.1}$ ceramics were prepared by molten salt method. The optimum calcinations temperature for obtaining the pure phase was 700 °C for 4h. The calcined powders were ground and pressed and then sintered at 1000, 1025, 1050, 1075 and 1100 °C for 4h. The phase of the sintered samples at various sintering temperatures was investigated by X-ray diffraction technique (XRD). The microstructural evolution of the sintered samples was examined by scanning electron microscopy (SEM). The average grain size of samples was calculated by linear interception method. Density of the sintered samples was measured by Archimedes method with distilled water as the fluid medium. Dielectric constant was measured using a LCR meter at room temperature and 1 kHz frequency. It was found that, all of XRD patterns showed pure phase and could be matched with a JCPDS file number 75-2188. The microstructure indicates a monophasic constitution with uniformly packed parallelogram shape in grain. The average grain sizes and density of CC(3.1)TO ceramics were increase with increasing sintering temperature. The dielectric constant of CC(3.1)TO ceramics increase with increasing grain sizes.

Keywords: CC(3.1)TO ceramics, Molten salt, Dielectric constant

INTRODUCTION

The typical high dielectric materials used today are normal ferroelectric oxides such as BaTiO_3 or relaxor ferroelectrics like $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. However, these dielectric oxides lack either temperature and/or high voltage or do not possess giant dielectric permittivity. Recently, synthesized giant dielectric constant material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted much attention because of its potential technological applications. It shows extremely high dielectric constant ($> 10^4$) at room temperature (Subramanian *et al*, 2000; Ramirez *et al*, 2000; Homes *et al*,

2001). However, it appears that the dielectric properties of CCTO are very sensitive to processing. Dielectric constants from 478 to 300,000 have been measured for this material processed in different manners (Choudhary and Bhunia, 2002; Adams *et al*, 2002). The original work done by Subramanian *et al.* (2000) and Ramirez *et al.* (2000) using conventional mixed-oxide processing via mortar and pestle showed room temperature dielectric constants from 10,000 to 20,000. Other researchers using the same technique have reported dielectric constants of 478, 2400, and 18,700 (Choudhary and Bhunia, 2002; Jha *et al*, 2003; Sinclair *et al*, 2002). Cann *et al.* (2003) used a vibratory mill to mix their oxides together and reported a room temperature dielectric constant of 7600.

In this work, the effect of sintering temperatures on grain sizes and dielectric constant of $\text{CaCu}_{3.1}\text{Ti}_4\text{O}_{12.1}$ (or CC(3.1)TO) ceramics prepared by molten salt method is investigated. We selected the calcinations temperature of CC(3.1)TO powders from calculation perovskite phase and lattice parameters of this powder agree well with the value from the report of C. Puchmark (2009) and these patterns could be matched with a JCPDS file number 75-2188 (Powder Diffraction File, 2000). The effect of sintering temperature on microstructure, physical properties and dielectric properties were also studied.

EXPERIMENTAL PROCEDURE

In this research, $\text{CaCu}_{3.1}\text{Ti}_4\text{O}_{12.1}$ (CC(3.1)TO) ceramic powders were prepared by the molten salt method. The starting materials including CaCO_3 , CuO and TiO_2 were mixed in ethanol medium for 24h. The slurry was dried and ground to powder for mixing with salt mixtures (an equal molar ratio of inorganic salt mixtures, NaCl and KCl mixed by hand-grinding for 20 min). The mixture powders and mixture salts were mixed by hand-grinding at a 1 : 1 weight ratio and calcined at 500-900 °C for 2h with heating rate 5 °C/min. The remaining salt was washed with hot de-ionized water until no free chloride-ions were detected by silver nitrate solution. Formation of pure phase compound was confirmed via X-ray diffraction (XRD) using $\text{Cu}_{K\alpha}$ radiation. Perovskite phase and lattice parameters of all powders were calculated using equation (1) (Swart and Shrout, 1982).

$$\% \text{ perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{CaCO}_3} + I_{\text{CuO}} + I_{\text{TiO}_2}} \right) \times 100 \quad (1)$$

The selected calcinations temperature of CC(3.1)TO powders was various dwell time for 2-24h with heating rate 5 °C/min. The results of perovskite

determined the optimum calcinations temperature in this work. The calcinations of the CC(3.1)TO powder was ball milled with 1% PVA in ethanol for 12h using the same method as mentioned earlier. The slurry was dried, ground and pressed into a disc shape and then sintered at 1000, 1025, 1050, 1075 and 1100 °C for 4h. The phase of the sintered samples at various sintering temperatures was investigated by X-ray diffraction technique (XRD). The microstructural evolution of the sintered samples was examined by scanning electron microscopy (SEM). The average grain size of samples was calculated by linear interception method from SEM micrograph. Density of the sintered samples was measured by Archimedes method with distilled water as the fluid medium. For the dielectric properties measurement, silver paste was applied to the both sides of circular faces of the ceramics, then dried at 600 °C for 15 min and cooled naturally to room temperature. Dielectric constant and loss of dielectric were measured using a LCZ meter at 1 kHz frequency.

RESULTS AND DISCUSSION

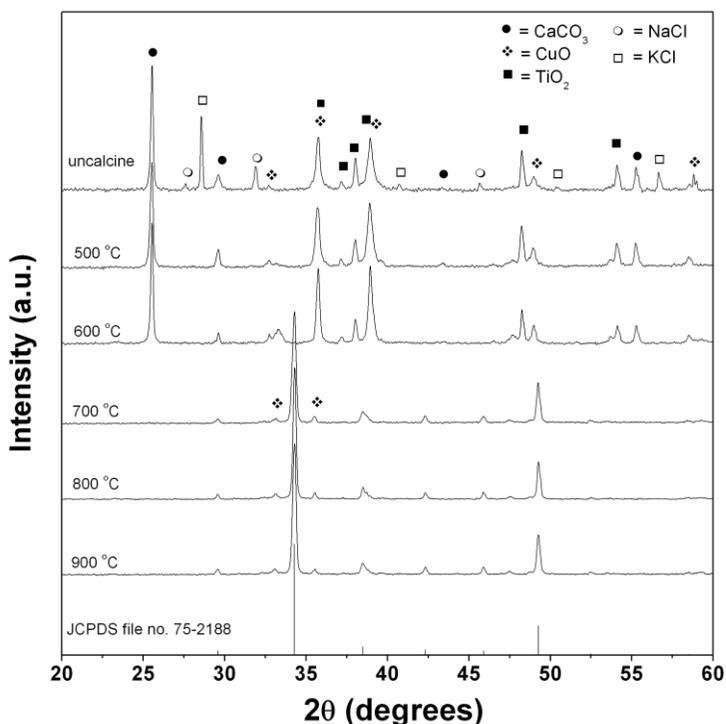


Figure 1. XRD patterns of CC(3.1)TO powders uncalcined and calcined at 500-900 °C for 2h.

X-ray diffraction patterns CC(3.1)TO powders uncalcined and calcined at 500-900 °C for 2h as shown in Fig. 1. CC(3.1)TO powders with calcinations

temperature from 500-600 °C for 2h were found remain as precursor phases and small amount of the other phases compared with the patterns of uncalcined CC(3.1)TO powders. Phase perovskite with 97% yielding was found when temperature at 700 °C as shown in Fig. 2.

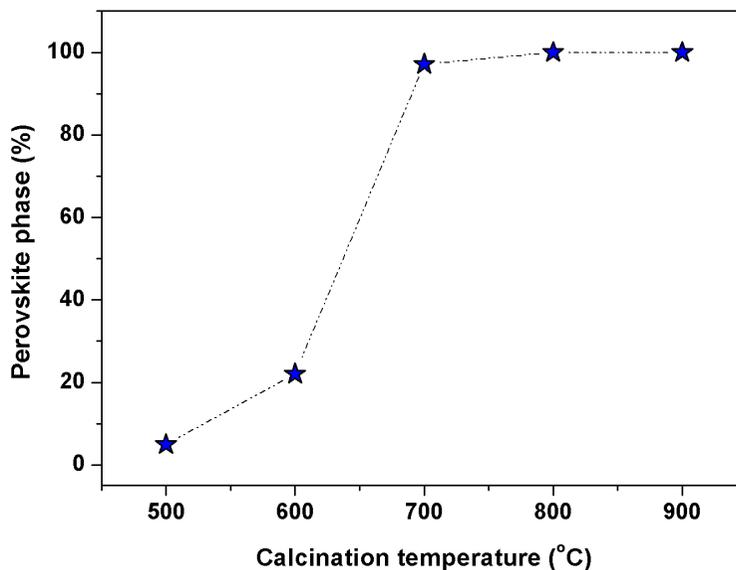


Figure 2. Perovskite phase of CC(3.1)TO powders calcined at 600-900 °C for 2h.

After that, calcinations temperature of CC(3.1)TO powders at 700 °C was various dwell time for 2-24h with heating rate 5 °C/min. X-ray diffraction patterns of CC(3.1)TO powders and calculated phase perovskite are shown in Fig. 3 and Fig.4, respectively. These patterns could be matched with a JCPDS file number 75-2188 (Powder Diffraction File, 2000). We have found that powder sample that calcined at 700 °C for 4-24h presents as pure phase.

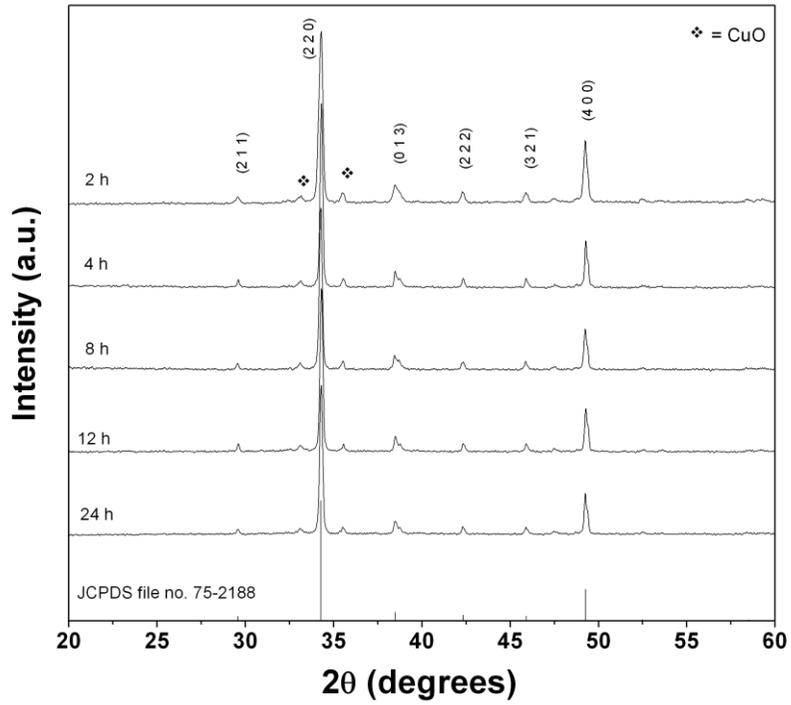


Figure 3. XRD patterns of CC(3.1)TO powders calcined at 700 °C for 2-24h.

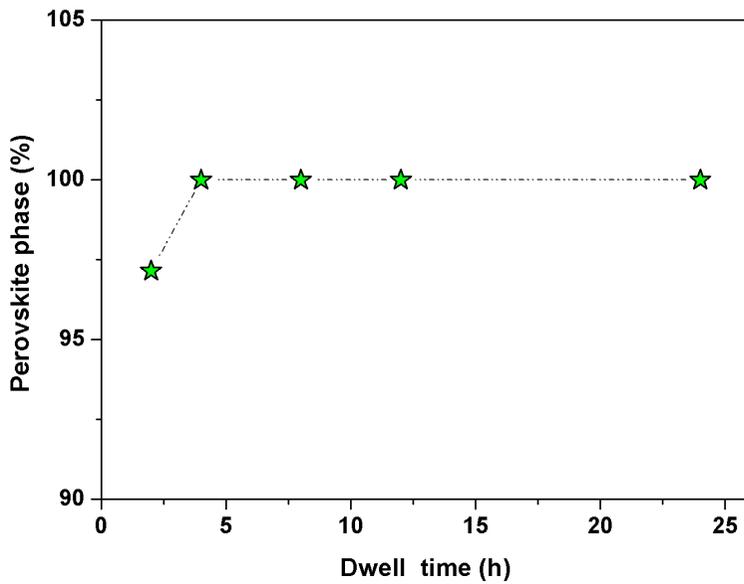


Figure 4. Perovskite phase of CC(3.1)TO powders calcined at 700 °C for 2-24h.

The optimum calcinations temperature for this research was selected at 700 °C for 4h. Figure 5 shows XRD patterns of CC(3.1)TO ceramics sintered at 1000, 1025, 1050, 1075 and 1100 °C for 4h. All XRD patterns could be matched with a JCPDS file number 75-2188 (Powder Diffraction File, 2000).

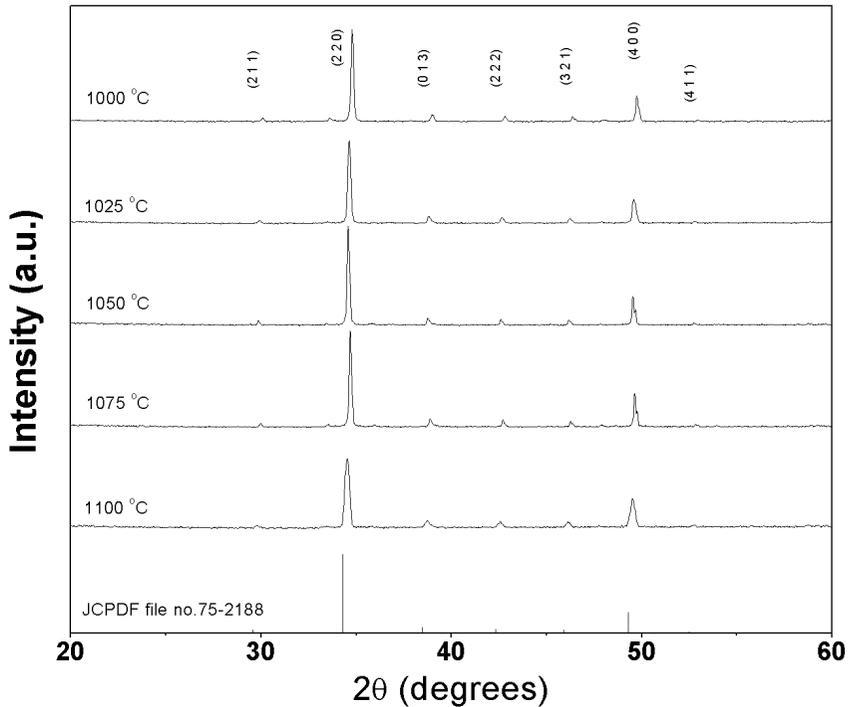


Figure 5. XRD patterns of CC(3.1)TO ceramics sintered at 1000-1100 °C for 4h.

For CC(3.1)TO ceramics sintered at 1000, 1025, 1050, 1075 and 1100 °C for 4h, their microstructure reveal a monophasic constitution with uniformly packed parallelogram shape in grain as shown in Fig. 6. CC(3.1)TO ceramic sintered at 1000 °C for 4h showed the smaller grains with the average size of 0.62 μm . While at higher sintering temperature (1025, 1050, 1075 and 1100 °C for 4h) the CC(3.1)TO ceramics showed larger grains with the mean grain size of 1.46, 1.51, 2.26 and 2.48 μm , respectively as shown in Fig. 7. The average large grain size of CC(3.1)TO ceramics were increased with increasing sintering temperature.

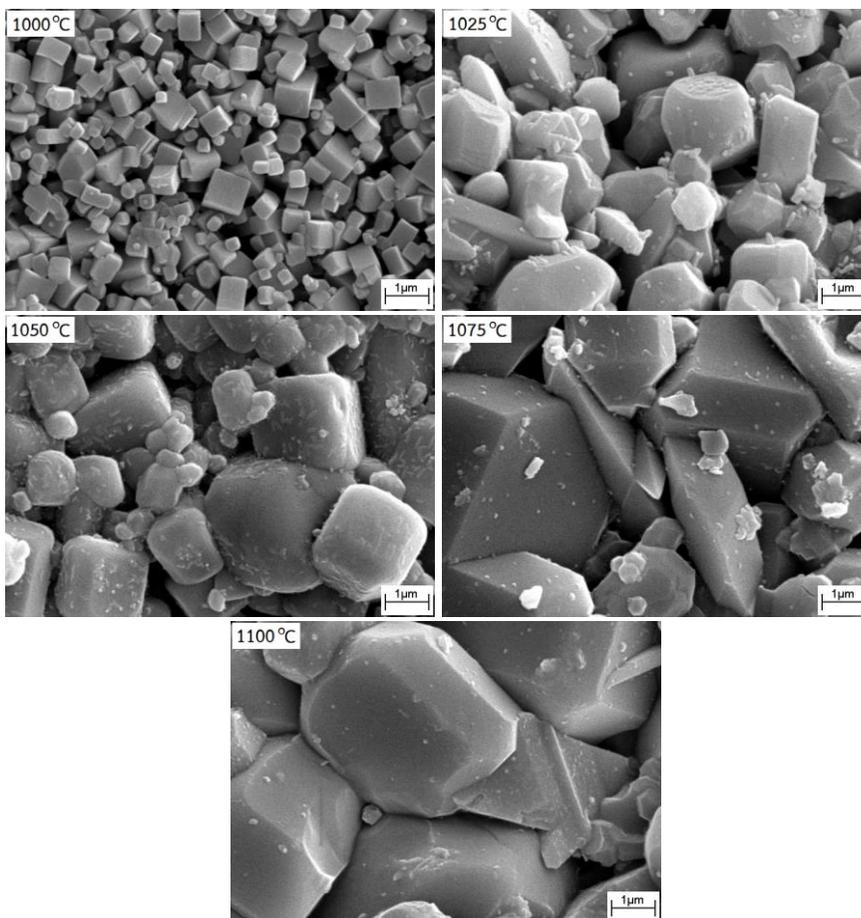


Figure 6. SEM photographs of top and fracture surface of CC(3.1)TO ceramics sintered at: 1000, 1025, 1050, 1075 and 1100 °C.

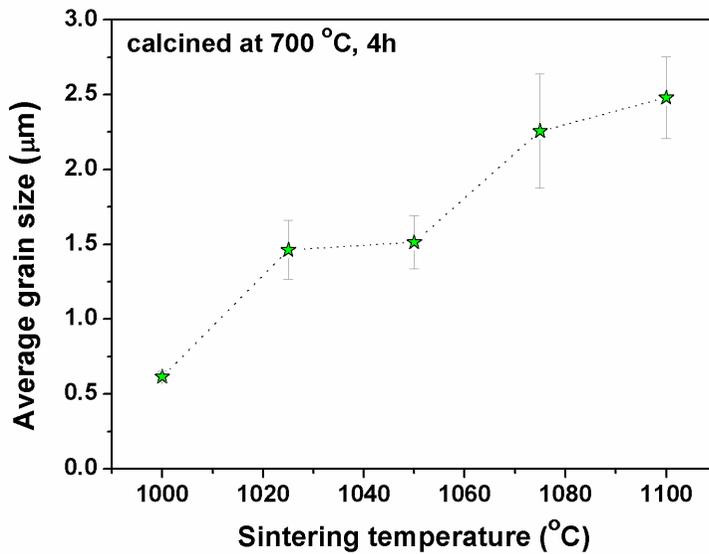


Figure 7. Average density of CC(3.1)TO ceramics sintered at 1000-1100 $^{\circ}\text{C}$.

The value of density is in the range of 2.94-4.73 g/cm^3 . The densification of CC(3.1)TO ceramics was improved significantly by increasing the sintering temperature correspond with SEM micrograph in Fig. 6 (the porosity was decrease with higher sintering temperature). Plots of density of CC(3.1)TO ceramics versus sintering temperature are shown in Fig. 8.

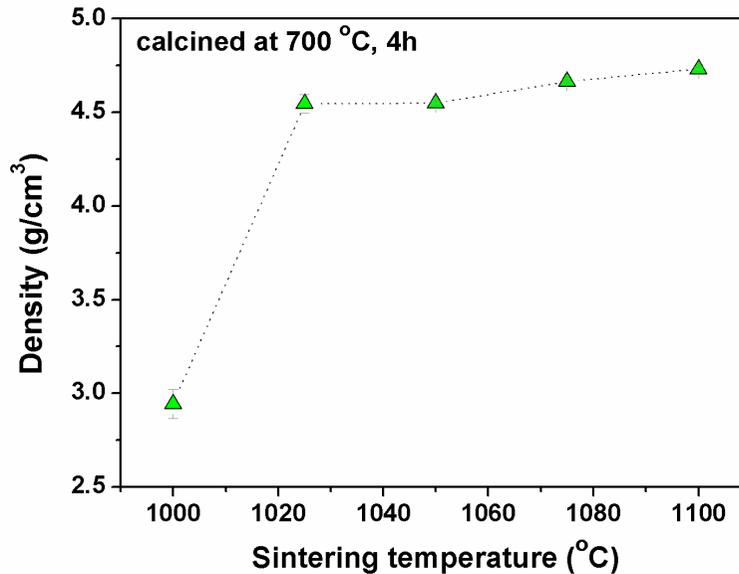


Figure 8. Average density of CC(3.1)TO ceramics sintered at 1000-1100 $^{\circ}\text{C}$.

The dielectric constant and dielectric loss with 1 kHz frequency at room temperature for CC(3.1)TO ceramics sintered at 1000, 1025, 1050, 1075 and 1100 °C for 4h as shown in Fig. 9. The dielectric constant for all samples increases with increasing sintering temperature. The dielectric losses for all sintered samples are lower than 0.45. The CC(3.1)TO ceramic sintered at 1100 °C showed the highest and giant dielectric constant of 10236 but dielectric loss of this frequency was 0.45. The lowest dielectric loss of 0.10 was found in CC(3.1)TO ceramic sintered at 1050 °C. The optimum dielectric properties condition for CC(3.1)TO ceramics was found at 1050°C (dielectric constant = 5287, dielectric loss = 0.10).

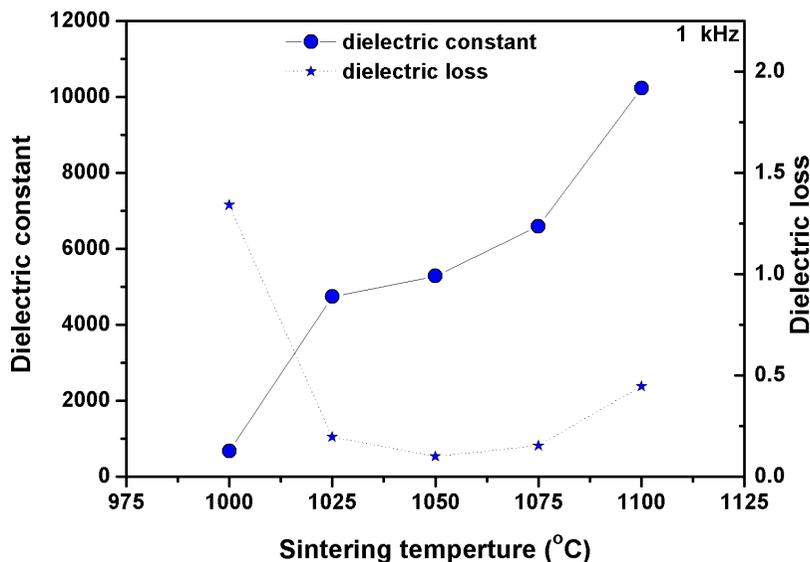


Figure 9. Plot of dielectric constant and dielectric loss with 1 kHz frequency at room temperature for the CC(3.1)TO ceramics sintered at 1000-1100 °C.

CONCLUSION

The CC(3.1)TO powders and ceramics were prepared by molten salt method. The pure phase of CC(3.1)TO powder were found at temperature higher than 700 °C with dwell time 2h. The optimum condition for calcinations temperature was found at 700 °C for 4h. The microstructure of CC(3.1)TO ceramics indicates a monophasic constitution with uniformly packed parallelogram shape. The density, average grain size and dielectric constant were increased with increasing the sintering temperature. The optimum dielectric properties condition for CC(3.1)TO ceramics was found in the sample sintered at 1050 °C measurement at 1 kHz frequency at room temperature.

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