

Dielectric Properties of Melt and Heat Treated $K_2O-Al_2O_3-SiO_2-CaO-CuO-TiO_2$ Samples

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Abstract—The $K_2O-Al_2O_3-SiO_2$ samples containing different amounts of CaO, CuO and TiO_2 were successfully prepared by conventional melting technique followed by heat treatment method. The X-ray diffraction (XRD) results show the existence of crystalline $CaCu_3Ti_4O_{12}$ phase in both the as-synthesized and heat treated samples. In addition, dielectric measurements were carried out in the frequency range of 40 Hz-1 MHz. The highest dielectric constant ($\epsilon_r \sim 53$) of the $CaCu_3Ti_4O_{12}$ -containing sample is about 9 times that of pure $K_2O-Al_2O_3-SiO_2$ glass.

Keywords- $CaCu_3Ti_4O_{12}$; Glass; Dielectric constant; Dielectric loss

I. INTRODUCTION

Dielectric materials have been playing an increasingly important role in electric power systems. Among the dielectrics, ceramics have low dielectric breakdown strengths (BDS) owing to the existence of pores, while polymers have low dielectric constants and poor thermal stability which limits their practical application [1]. Glass-ceramics, which are prepared via quenching followed by crystallization upon heat-treatment, have high dielectric constants and large breakdown strengths [2-5]. As a result, glass-ceramics can be used as energy storage capacitor [6-8]. Therefore, dielectric glass-ceramics are greatly concerned.

In recent years, $CaCu_3Ti_4O_{12}$ (CCTO) has been attracted much attention due to its giant dielectric constant, ϵ_r , up to $\sim 10^4$ at room temperature [9-11]. In this work, different amount of CaO, CuO and TiO_2 were added to $K_2O-Al_2O_3-SiO_2$ glass system so as to improve the dielectric constant of sample.

Stoichiometric amounts of CaO, CuO and TiO_2 corresponding to $CaCu_3Ti_4O_{12}$ were introduced into a $K_2O-Al_2O_3-SiO_2$ glass system. Although the melts of $K_2O-Al_2O_3-SiO_2-CaO-CuO-TiO_2$ devitrified during the process of quenching and forming, the products showed larger dielectric constants than that of $K_2O-Al_2O_3-SiO_2$ glass. The dielectric constants of the as-synthesized samples increased after the thermal treatment.

II. EXPERIMENTAL SECTION

Raw materials including analytical grade reagents of K_2CO_3 , SiO_2 , Al_2O_3 , TiO_2 , CuO and $CaCO_3$ were weighed in proportion and mixed to prepare batches. The batch compositions have $K_2O: Al_2O_3: SiO_2$ molar ratios of 1: 1: 4 and $CaO: CuO: TiO_2$ molar ratios of 1: 3: 4. The total amount of CaO, CuO and TiO_2 (abbreviated as CCT) accounted for

70 or 80 wt% of the batch, respectively, with the balance of K_2O , Al_2O_3 , SiO_2 being 30wt% or 20wt%. Accordingly, the synthesized samples were designated as 70CCT or 80CCT corresponding to the weight percentage of CCT in the batch. And the heat treated samples were designated as 70CCT-HT or 80CCT-HT.

The batches were put into silica crucibles and heated in an electric furnace at 1450 °C for 2 h. Then the melt was poured on a preheated steel plate. The cast samples were immediately annealed at 500 °C for 4 h. The annealed samples were cut into slices sized 10×10×2 mm before thermal treatment. Finally, the samples were heat treated at 980 °C for 2 h.

X-ray diffraction (XRD) measurements were performed on a D8-advanced diffractometer (Bruke, Germany) to identify the crystalline phases in both the as-synthesized and the thermally treated samples. For the dielectric measurements, Ag electrodes were painted with Ag pastes on both sides of the samples and sintered at 600 °C in air for 20 min. Then the dielectric properties in the frequency range of 40 Hz to 1 MHz were measured using an impedance analyzer (4294A, Agilent, USA).

III. RESULTS AND DISCUSSION

A. The Density and XRD Analysis

TABLE I. THE DENSITY OF THE SAMPLES

Density	Sample			
	70CCT	70CCT-HT	80CCT	80CCT-HT
(g/cm ³)	3.2321	3.2664	3.3469	3.3701

The density data of both the as-synthesized and the thermal treated samples are listed in TABLE. It shows that after the thermal-treatment the densities of samples 70CCT, 80CCT increase from 3.2321 to 3.2664 g/cm³, and from 3.3469 to 3.3701 g/cm³, respectively. The densities of thermal-treated samples are larger than that of as-synthesized, indicating the increasing devitrification. It is also seen that the density of 80CCT is larger than that of 70CCT suggesting the increase of devitrification with increasing CCT from 70% to 80%.

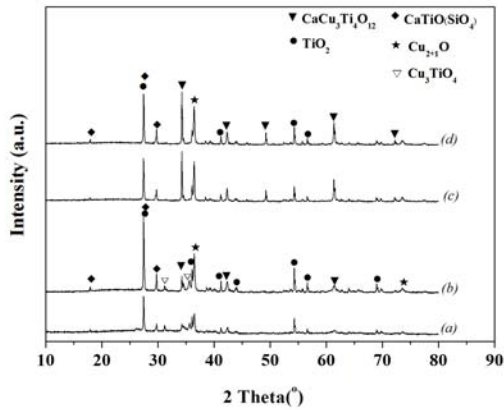


Figure 1 XRD patterns of the as-synthesized (a, b) and heat-treated (c, d) samples: (a)70CCT (b)80CCT (c) 70CCT-HT (d) 80CCT-HT

The XRD patterns of the as-synthesized and thermally treated samples are shown in Fig. 1. The patterns of the as-synthesized samples have sharp diffraction peaks (Fig. 1a, b). The crystalline phases are identified as Cu_3TiO_4 (JCPDF card No.83-1285), TiO_2 (JCPDF card No. 21-1276), $\text{CaTiO}(\text{SiO}_4)$ (JCPDF card No. 25-0177) and Cu_{2+1}O (JCPDF card No. 05-0667). The results indicate that as-synthesized samples were devitrified. As can be seen from Fig. (a) and (b), the diffraction peak intensity of 80CCT is higher than that of 70CCT indicating the devitrification increase with increasing CCT from 70% to 80%. In addition, both patterns have indication of the existence of glass phase.

After the heat treatment, the thermally treated samples show the decrease of the glass phase. Compared with the patterns of the as-synthesized samples, some peaks become stronger, while others become weaker or disappear (Fig. 1c, d). The crystalline phases include CCTO (JCPDF card No.75-2188) devitrified phase, Cu_{2+1}O (JCPDF card No. 05-0667), TiO_2 (JCPDF card No. 21-1276) and $\text{CaTiO}(\text{SiO}_4)$ (JCPDF card No. 25-0177). The results show that TiO_2 and CCTO are two major crystalline phases. Moreover, the peaks of the CCTO phase become stronger with the content of CCT. However, the $\text{CaTiO}(\text{SiO}_4)$, Cu_{2+1}O crystalline phases also increase at the same time.

The data in TABLE II shows different amounts of crystalline phases in the thermal-treated samples. It is shown that the contents of $\text{CaTiO}(\text{SiO}_4)$ and TiO_2 phases decrease with the increase of CCT. However, as can be seen from the results, the percentages of CCTO and Cu_{2+1}O phases increase with the increase of CCT, indicating the increase of CCT from 70% to 80% favors the crystallization of these two phases. The result also indicates that the peak intensity of the TiO_2 crystalline phase turn to be the strongest peak, with the proportion of 44.53%. Moreover, the $\text{CaTiO}(\text{SiO}_4)$ phase decreases from 19.41% to 18.37%, suggesting a possible chemical reaction between glass phase and TiO_2 . However, with increasing CCT from 70 to 80%, the proportion of CCTO and Cu_{2+1}O phases increase from 27.45% to 29.47%, and from 8.58% to 10.04%, respectively, which suggests a possible dynamic change between glass phase and crystalline

phases. It seems that the evolution of the crystalline phases is sensitive to the content of CCT.

TABLE II. AMOUNT OF CRYSTALLIZATION PHASES IN THE SAMPLES

Sample	Amount of crystallization phases			
	CCTO (%)	CaTiO(SiO ₄) (%)	TiO ₂ (%)	Cu ₂₊₁ O (%)
70CCT-HT	27.45	19.41	44.53	8.58
80CCT-HT	29.47	18.37	42.12	10.04

B. Dielectric Properties and Frequency Dependence

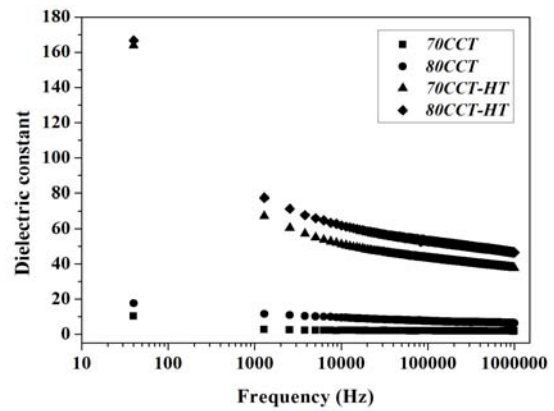


Figure 2 Dielectric constants of the samples at room temperature

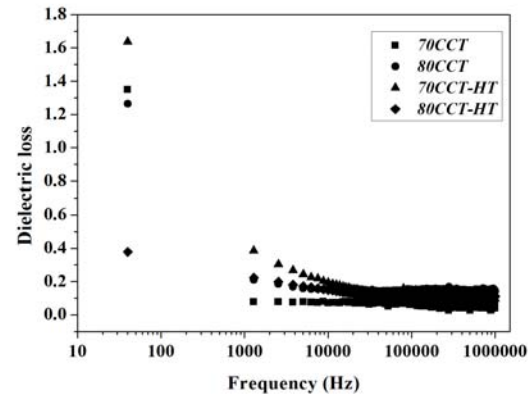


Figure 3 Dielectric loss of the samples at room temperature

Fig. 2 and 3 show the variations of dielectric constant and dielectric loss of the studied samples in the frequency range of 40 KHz to 1 MHz at room temperature. It is shown that the dielectric constants of both the as synthesized and the thermal treated samples decrease with increasing frequency. With the application of electric field, charge carriers can hop easily out of the sites at low frequencies, which contributes

to large dielectric constant of sample. On the contrary, the charge carriers can not be able to rotate with enough speed at higher frequency, leading to the lagged oscillation of the charge carriers. As a result, the decrease in the dielectric constant is observed at high frequencies [12]. In addition, the dielectric constants increase with increasing the amount of CCT. The dielectric constant of as-synthesized sample is from 2 to 8 at 100 kHz. After thermal-treated, the dielectric constant of sample presents from 43 to 53 at 100 kHz. These values are 7~9 times that of the CCT-free $K_2O-Al_2O_3-SiO_2$ glass ($\epsilon_r \sim 5.8$). This increase in dielectric constants is due to the addition of Ca, Cu and Ti ions with large polarization behavior.

Dielectric constant reflects the polarization ability of the material while dielectric loss is related to the energy loss due to the polarization and ionic conduction. Fig. 3 shows dielectric loss of the samples at room temperature. It is shown that the dielectric loss of both the as-synthesized and the thermal treated samples decrease with the increase of frequency. With the application of electric field, charge carriers can hop easily out of the sites at low frequencies, which contributes to large dielectric loss of sample. However, the charge carriers can not be able to rotate with enough speed at higher frequency. As a result, the decrease in the dielectric loss is observed at high frequencies. Taking 70CCT as an example, it exhibits higher dielectric loss than that of others due to the higher energy loss at low frequencies. The results show that the dielectric loss of as-synthesized sample is from ~ 0.04 to ~ 0.14 and the dielectric loss of heat treated samples displays from ~ 0.09 to ~ 0.11 at 100 kHz.

The results demonstrate that heat treated samples containing the CCTO phase have high large dielectric constants.

IV. CONCLUSIONS

The $CaCu_3Ti_4O_{12}$ crystalline phase containing samples were successfully prepared by introducing CaO, CuO and TiO_2 into $K_2O-Al_2O_3-SiO_2$ system. The heat treated sample prepared with the addition of CaO, CuO and TiO_2 has dielectric constant of 53 (about 9 times as $K_2O-Al_2O_3-SiO_2$ glass). However, the dielectric loss is about 0.09 at 100 kHz.

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