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Poly (Vinylidene Fluoride)/Mg Doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Composites with Improved Dielectric Properties

Hanghang Wang, Huiwu Cai, Wenying Zhou and Shengnan Liu

(College of Chemistry & Chemical Engineering, Xi'an University of Science and Technology, Xi'an, 710054 China)

Abstract. The $\text{CaCu}_{3-x}\text{Mg}_x\text{Ti}_4\text{O}_{12}$ (CCMTO) particles were prepared by sol-gel method, ceramic/polymer composites made of CCTO and CCMTO particles as filler and polyvinylidene fluoride (PVDF) as matrix were prepared by powder mixing method. The microstructure and dielectric properties of the PVDF, CCTO, CCMTO particles and CCMTO/PVDF composites were investigated. The results indicate that the dielectric permittivity and the dielectric loss increased with increasing ceramics particles loading. The dielectric permittivity could reach 93 and dielectric loss was 0.2 when mass fraction of CCMTO is 60wt% at 100 Hz. SEM results show that CCTO and CCMTO particles dispersed well in the PVDF matrix. Doping Mg can improve dielectric permittivity of the CCTO/PVDF composites and slightly reduce the dielectric loss, compared raw CCTO/PVD composites.

1. Introduction

Microelectronic devices were inclined to miniaturization, lightness and high performance with the rapid development of the information technology. Dielectric materials with high dielectric constant, low dielectric loss and good temperature stability are highly desirable [1, 2]. Nowadays, polymer-based materials were widely used in electronic components especially in embedded circuits for their good thermal stability and process easily [3, 4]. However, polymer-based materials have low dielectric constant in range of 3-10, which limited their applications in electronic components [5]. Recently, ceramic-polymer composites were first introduced as a potential material for the application of electronic components because they combined the process ability of the polymer and the dielectric properties of the ceramics. Generally, polymer materials such as poly (polyvinylidene-trifluoroethylene) [6], polyethersulfone [7], polyvinylidene fluoride (PVDF) and polyimide [8] had been used as the matrix. PVDF would be selected as polymer matrix due to its high permittivity ($\epsilon_r=8-13$), and could be easily processed by injection melting process and better thermal stability [9]. Meanwhile, some high dielectric constant ceramics, such as Pb (Ti, Zr) [10], BaTiO_3 [11] and $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ [12], were selected as fillers. The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has attracted considerable attention in the past decade, due to its high and nearly temperature independent dielectric constant (Up to 10000 1kHz at room temperature) over a wide temperature rang (100-600K) [13]. Therefore, CCTO should be good filler.

To further improve dielectric constant of CCTO, CCMTO particles were prepared by sol-gel method. And then the PVDF composites were prepared by powder mixing and hot-pressing. Dielectric properties of CCTO-PVDF and CCMTO-PVDF were investigated, respectively.



2. Experimental

2.1. Preparation of CCMTO Powers

The sol-gel method was used to prepare CCTO and $\text{CaCu}_{3-x}\text{Mg}_x\text{Ti}_4\text{O}_{12}$ ($x=0.05$; $x=0.1$; $x=0.2$) powers as follow, the $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99.5% from Tianjin-Fuchen in Tianjin, China), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.0% from Tianjin-Fuchen in Tianjin, China) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0% from Tianjin-Fuchen in Tianjin, China) in the stoichiometric ratio were dissolved in ethanol, and formed A solution, $\text{C}_{16}\text{H}_3\text{O}_4\text{Ti}$ (99.0% from Kermel in Tianjin, China) was dissolved in ethanol to form B solution. A solution, B solution and water were mixed with constant stirring, changed pH (PH=1-2) through adjusting the dosage of the glacial acetic acid and citric acid. The formed gels were dried at 180 °C for 10h, and then were calcined at 700 °C for 10h to form CCTO and CCMTO particles.

2.2. Preparation of CCMTO/PVDF Composite

The prepared CCTO and CCMTO powders were thoroughly mixed with PVDF (From 3F in Shanghai, China) particles by melt mixing the mixtures, respectively. The mixtures were dissolved into N, N-dimethylformamide (from Sic-Tech Co, Ltd in Guangzhou, China) at room temperature to obtain a suspension, the obtained suspensions were stirred by magnetic stirring for 7 h. Then the suspensions was heated and stirred on an electric furnace until it became gelatinous, dried at 80 °C in an oven for 8 h and then molded by hot pressing at 220 °C and 20MPa, the final disk shape sample has a thickness of about 2 mm and a diameter of 15 mm.

2.3. Characterization Techniques

The phase structure of CCTO, CCMTO and CCMTO/PVDF composites were identified by X-ray diffraction technique (XRD D8 Advance). The surface morphology was measured by a scanning electron microscope (SEM JSM-7000F). The dielectric properties of CCTO/PVDF and CCMTO/PVDF composite were measured by an impedance analyzer (Agilent 4294A).

3. Results and Discussions

3.1. Structural Analysis

X-ray diffraction patterns of CCTO, CCMTO PVDF and the composites with 40wt%, 50wt% and 60wt% $\text{CaCu}_{2.98}\text{Mg}_{0.02}\text{Ti}_4\text{O}_{12}$ in PVDF have been shown in Fig. 1(a-b). In the case of pure CCTO and CCMTO, the diffraction peaks corresponding to the planes (220), (310), (222), (321), (400), (422) and (440) confirm the formation of single phase compound [14]. There is no secondary phase in CCMTO. Pure PVDF crystallizes in a phase with characteristic peaks at 17.7°, 18.7° and 19.9° corresponding to (110), (020) and (111) reflections respectively [14]. Diffraction peaks corresponding to (220), (400) and (422) planes of CCTO and CCMTO are also present in the diffraction patterns of the composites. The intensities of the peaks pertaining to the PVDF are not significant. And with the higher content of ceramic powder, the weaker the characteristic peak of PVDF.

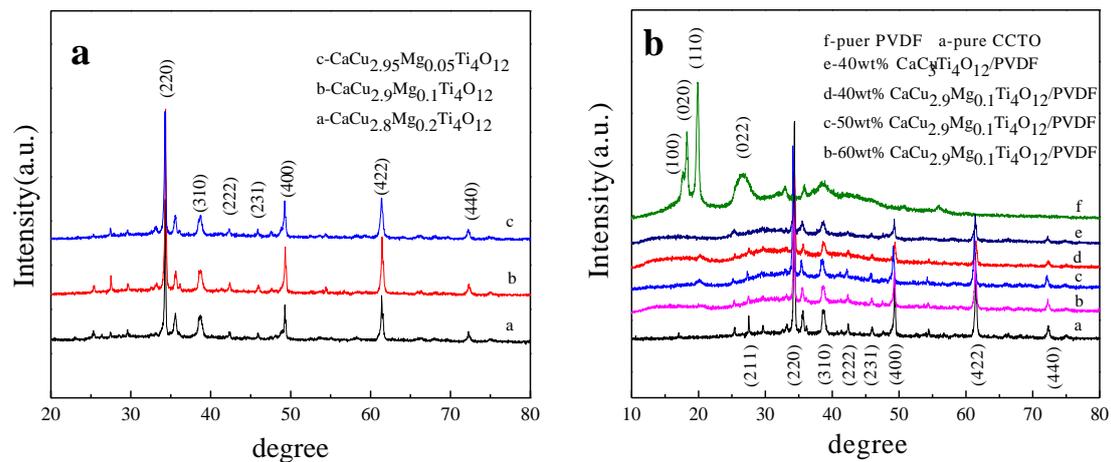


Figure 1. XRD diffraction patterns for CCTO, pure PVDF, CCMTO and the composites with 40wt%, 50wt% and 60wt% $\text{CaCu}_{2.98}\text{Mg}_{0.02}\text{Ti}_4\text{O}_{12}$ in PVDF

3.2. Morphology

The SEM micrographs of composites containing various mass fractions of CCTO filler are shown in Fig. 2(a-c). It is seen that the CCTO fillers were homogeneously dispersed in the PVDF matrix without aggregation when the mass fraction of CCTO is 40wt%, and when the CCTO is 50wt% and 60wt%, the sample appears aggregation.

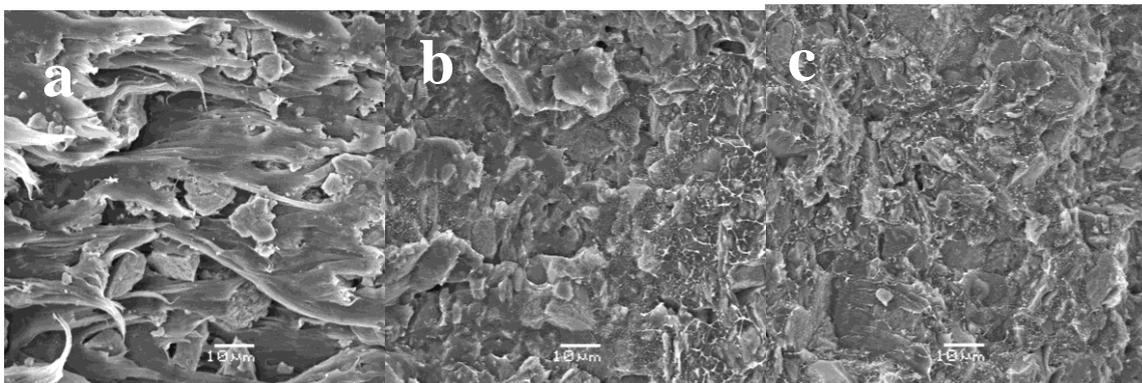


Figure 2. SEM images of fractured cross surfaces of CCTO/PVDF composites with various mass fraction of CCTO (a) 40wt% CCTO/PVDF, (b) 50wt% CCTO/PVDF, and (c) 60wt% CCTO/PVDF.

3.3. Dielectric Properties

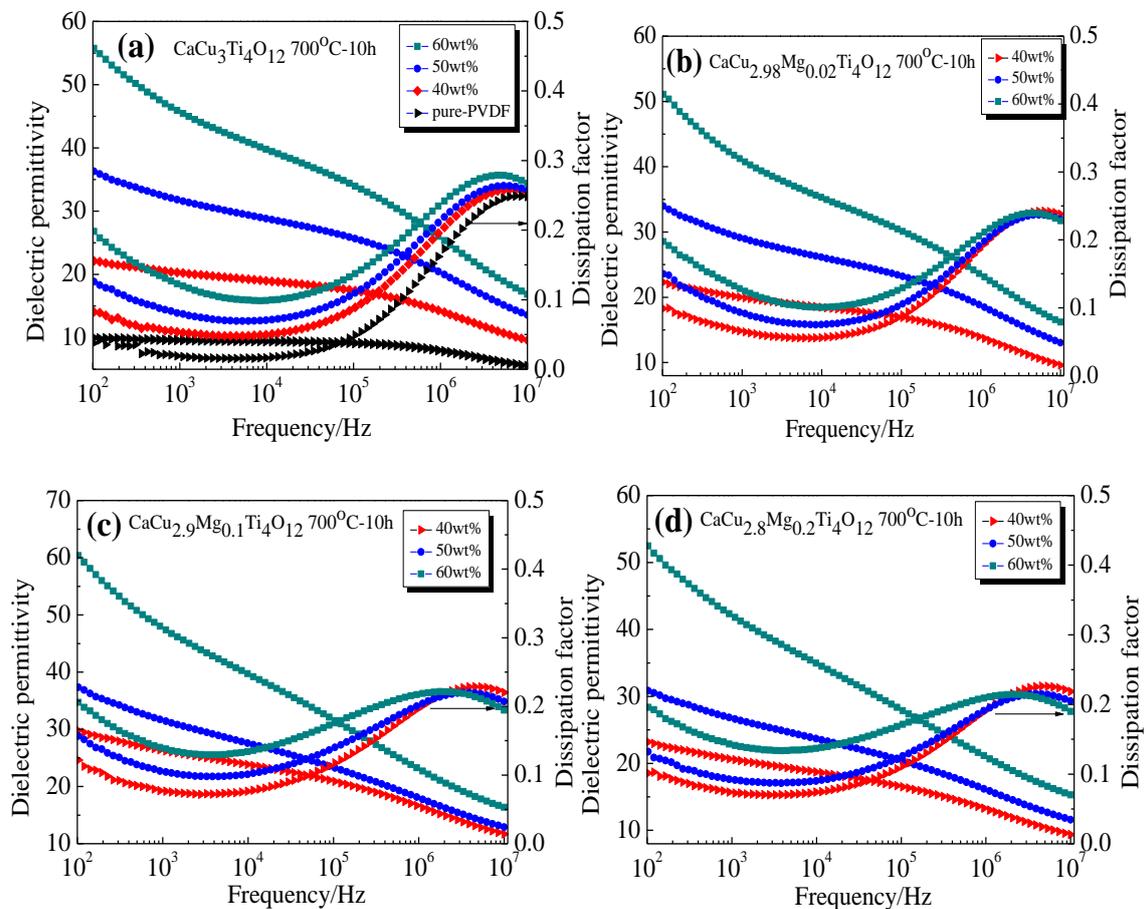
The frequency dependence of dielectric permittivity, dissipation factor and electric conductivity for PVDF, CCTO/PVDF and CCMTO/PVDF with various filler loading is shown in Fig. 3(a-h). As shown in Fig. 3(a-d) the permittivity of CCTO/PVDF and CCMTO/PVDF composites were significantly enhanced with increasing the CCTO or CCMTO content. For the CCTO/PVDF composites, when the mass fraction of particles were 40wt%, 50wt% and 60wt%, the dielectric constant of the CCTO/PVDF composites were 32, 40 and 57 in the frequency range of 100Hz at room temperature, respectively. The CCMTO/PVDF ($x=0.1$) exhibits larger dielectric permittivity than that of CCTO/PVDF. The dielectric response in CCTO is due to formation of barrier layers at the interface between the grains and the grain boundaries because of difference in their conductivity. This gives rise to interfacial polarization. The giant permittivity depends on the microstructure [15]. Doping Mg significantly modifies the formation of IBLC by increasing the difference between the conductivity of the grains and grain boundaries, which increases the relative permittivity.

Doping Mg reduces the dielectric loss, for the CCTO/PVDF composites, when the mass fraction of particles were 40wt%, 50wt% and 60wt%, the dissipation factor of the CCTO/PVDF composites were

0.082, 0.126 and 0.198, respectively, in the frequency range of 100Hz at room temperature. The CCMTO/PVDF ($x=0.1$; $x=0.2$) exhibits low dissipation factor than that of CCTO/PVDF. The CCMTO/PVDF ($x=0.1$) exhibits low dielectric loss than that of CCTO/PVDF. The loss undergoes two relaxations; one in the low frequency region and the other at high frequencies. The relaxation beyond 1 MHz is related to the glass transition relaxation of PVDF and is denoted as α_a relaxation.

Similarly, the relaxation peak that appears below 10^2 Hz could be attributed to α_a relaxation associated with molecular motion in the crystalline regions of PVDF [16]. It is observed that (Fig. 3a-d) the dielectric loss decreases in the 10^2 Hz to 10^4 Hz frequency range and then subsequently increases in the 10^4 to 10^7 frequency range.

The frequency dependence of electric conductivity for PVDF, CCTO/PVDF and CCMTO/PVDF are shown in Fig. 3e-f. We can see that they all samples show typical insulator characteristics.



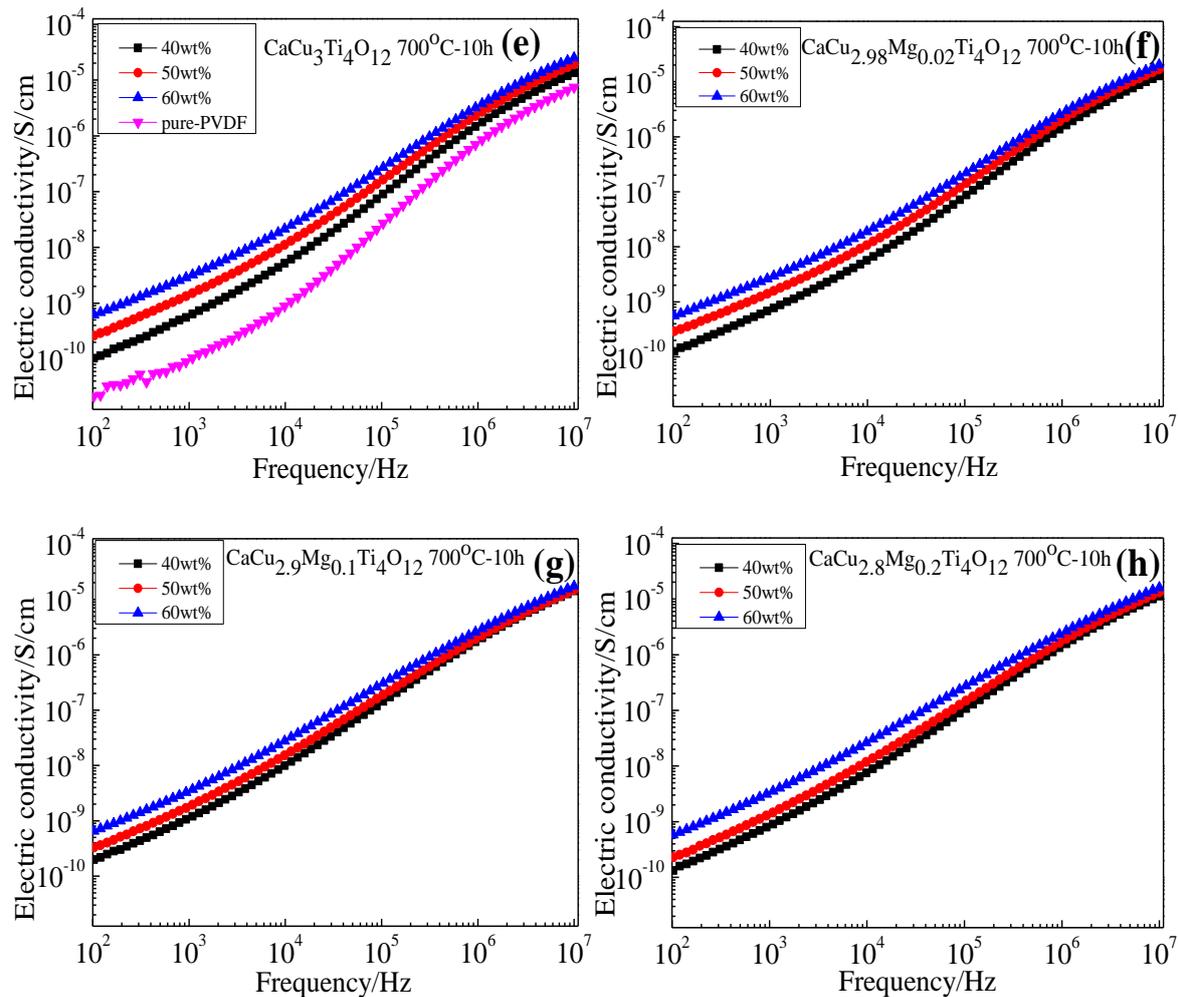


Figure 3. The frequency dependence of dielectric permittivity, dissipation factor ((a) CCTO composites and (b) CCMTO ($X=0.05$) composites and (c) CCMTO ($X=0.1$) composites and (d) CCMTO ($X=0.2$) composites)) and electric conductivity ((e) CCTO composites and (f) CCMTO ($X=0.05$) composites and (g) CCMTO ($X=0.1$) composites and (h) CCMTO ($X=0.2$)) for pure PVDF, CCTO/PVDF and CCMTO/PVDF with various filler loading

4. Conclusion

In this study, CCMTO ceramics were successfully synthesized by the sol-method, and CCMTO/PVDF composites were prepared and their dielectric properties were investigated. The dielectric permittivity increases with the increasing of the addition of CCMTO as well as the dielectric loss increased. The dielectric permittivity of the composite is 93 when the mass fraction of CCMTO ($x=0.1$) is 60wt% which is higher than CCTO/PVDF (-55). The dielectric loss of the composite is 0.2 at the mass fraction of CCMTO ($x=0.1$) is 60wt% which has been below CCTO/PVDF (0.23). Doping Mg can improve dielectric properties of the CCTO/PVDF composites.

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