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Study of the humidity-sensing mechanism of $CaCu_3Ti_4O_{12}$

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ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO[1]) is observed to respond to water vapor by changing its capacitance. To investigate the underlying reason for the humidity-sensitive properties of CCTO, impedance spectroscopy and electric modulus plot measurements were performed at different relative humidities (RH[2]). Additionally, DC bias was applied to the measurement. The results indicate that the adsorption of water molecules affects the potential barrier capacitances at the CCTO/electrode interface and at the grain boundary, which further changes the total capacitance of CCTO. In addition, new low-frequency polarization relaxations were observed at high RH. The new polarization relaxations may be related to the orientation polarization and space charge polarization caused by the physically adsorbed water molecules. The two polarizations may account for the large increase of capacitance at high RH.

1. Introduction

Humidity detection is highly important in our daily life because environmental humidity can greatly affect our lives. Among various materials for humidity sensors, ceramics, in particular metal oxides, have shown advantages in terms of their mechanical strength, their chemical stability and their thermal and physical stability [1–3]. Ceramic humidity sensors are mainly divided into two types based on their sensing mechanisms: resistive-type and capacitive-type [4]. The former responds to moisture by changing its conductivity, while the latter responds to water vapor by varying its capacitance. The capacitive-type sensors have good prospects given that the capacitor structure is so simple, enabling miniaturization and achieving high reliability and low cost. In addition, capacitance is easily amplified by oscillator circuits [5]. Thus, capacitive-type humidity sensors such as Al_2O_3 [6,7], $(Ba,Sr)TiO_3$ [8,9], CeO_2 [10], and $(K,Na)NbO_3$ [11] have attracted increasing attention in recent years.

$CaCu_3Ti_4O_{12}$ (CCTO) has been studied widely for its extraordinarily high dielectric constant, above 10^4, which is temperature-independent in a wide temperature range of 100–400 K [12–15]. We were the first to report the humidity-sensing property of CCTO [16]. The dielectric constant of CCTO was found to increase greatly upon exposure to humid air, making it a candidate for fabricating new humidity sensors. Complete understanding of the sensing mechanism of CCTO is needed for the further development of advanced devices based on it. Generally, microstructure (e.g., porosity, grain size) can greatly affect the sensing properties of sensor materials. However, our previous study showed that the microstructure has a small effect on the humidity response of CCTO. It is known that the potential barriers at the grain boundary and the CCTO/electrode junction form the grain boundary capacitance and the electrode contact capacitance of CCTO, both of which contribute to the total capacitance of CCTO. The adsorption of molecular water may affect the grain boundary capacitance and electrode contact capacitance, which may further vary the total capacitance at different relative humidity (RH). To investigate the underlying reason for the humidity sensitive properties of CCTO, impedance spectroscopy and electric modulus plot measurements were performed at different RH. DC bias was applied to the measurement.

2. Experimental

$CaCu_3Ti_4O_{12}$ powders were synthesized via the conventional solid-state reaction method from high-purity $CaCO_3$, CuO and TiO_2. The mixed powders were calcined in air at 1000 °C for 12 h and at 1100 °C for 24 h, with an intermediate grinding. The calcined samples were milled and then pressed into pellets 5 mm in diameter and approximately 1 mm in thickness. Next, the pellets were sintered in air at 1100 °C.

Capacitance data, impedance spectroscopy, and electric modulus plots were collected using an Agilent-4294A impedance

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[1] CCTO is the abbreviation of $CaCu_3Ti_4O_{12}$.

[2] RH is the abbreviation of relative humidity.

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analyzer with an AC voltage of 500 mV. The measurements were performed at room temperature over the frequency range of 70 Hz–4 MHz and a DC bias range of 0–15 V. To yield different RH levels, saturated solutions of LiCl (11% RH), $MgCl_2$ (33% RH), $Mg(NO_3)_2$ (53% RH), NaCl (75% RH), KCl (85% RH), and K_2SO_4 (97% RH) were used in closed glass vessels at room temperature [17]. The measurements were performed by putting the samples successively into the vessels with different RH levels.

3. Results and discussion

3.1. Results

The RH dependences of CCTO capacitance measured at 100 Hz, 1 kHz, 10 kHz, and 100 kHz are shown in Fig. 1(a). The capacitance of CCTO increases with increasing RH, and the increment of capacitance also increases with RH. Thus, the humidity response at high RH is greater than at low RH. Furthermore, the humidity response decreases with increasing frequency. When the RH level changes from 11% RH to 97% RH, the capacitance changes for 100 Hz, 1 kHz, 10 kHz, and 100 kHz are approximately 930%, 500%, 340%, and 270%, respectively. The hysteresis behavior of CCTO is shown in Fig. 1(b). The hysteresis error was calculated from the formula

$$\gamma_H = \pm\left(\frac{1}{2}\right)\left(\frac{\Delta H_{\max}}{F_{FS}}\right) \quad (1)$$

where $\Delta H_{\max}$ is the maximum differences value of capacitance in forward and backward operations and F_{FS} is the full scale output [18]. The maximum absolute value of humidity hysteresis error γ_H of CCTO is about 7%, corresponding to 53% RH. The effect of temperature on sensor characteristics of CCTO is also investigated. Fig. 2 shows the temperature-dependent capacitance measured at different RHs. The result indicates that the capacitances at different RHs remain nearly constant in the temperature range of 5–25 °C. Furthermore, since the tests were performed over more than 3 months for room temperatures in the 5–25 °C range, the result also indicates CCTO performs a good reproducibility over a long time.

Complex impedance spectroscopy is an appropriate experimental technique to obtain information about the electric characteristics of polycrystalline materials. Considering the electrical behavior of CCTO with respect to RH, the complex impedance spectra at different RH values were measured at room temperature, as shown in Fig. 3(a). At 11% RH, the complex impedance plot of CCTO shows a circular arc with a nonzero intercept at high frequency (see inset of Fig. 3(a)). The nonzero intercept indicates that there must exist a semicircle in the upper frequency region beyond our measuring frequency range, which is assigned to the bulk response. The circular arc at low frequencies is attributed to the grain boundary response [19]. Because the characteristic frequency of the grain boundary response appears lower than 70 Hz, the semicircle arc is not completed in the complex impedance plot. With increasing RH, the curvature of the circular arc increases. Because the diameter of the low-frequency arc corresponds to the grain boundary resistance, the increase in the curvature of the circular arc indicates that the grain boundary resistance decreases with increasing RH. At a high RH level of 97%, a depressed semicircle is observed in the complex impedance plot, as shown in Fig. 3(b). The oblate semicircle might indicate that more than one polarization relaxation responses with very similar characteristic frequencies overlap in the complex plot at high RH. One is attributed to the grain boundary response. The origins of the others are addressed in Section 3.2.

To explore the humidity-sensing mechanism of CCTO, the capacitance as a function of frequency at different RH values are measured under the various DC bias voltages, as shown in Fig. 4. The low-frequency capacitance of CCTO clearly increases with increasing DC bias at low frequency at 33% and 53% RH, indicating that the sample exhibits the electrode contact response at low frequency and low RH (the reason was explained in detail in Ref. [20]). When the RH increases to high levels of 75% and 97%, the low-frequency capacitance remains almost constant with increasing DC bias, indicating that the electrode contact response is largely depressed at high RH. The imaginary components of the complex modulus (M'') versus frequency (f) are also used to explore the observed results of CCTO. The magnitudes of $M''_{\max}$ at the peak maxima are given by

$$M''_{\max} = \frac{C_0}{2C} \quad (2)$$

where C_0 is the vacuum capacitance. Therefore, the peaks of M'' are dominated by the smallest capacitance. Fig. 5 shows the M'' versus f plots of CCTO at different RH. The DC bias is applied to separate the factors (e.g., grain, grain boundary) contributing to capacitance. Two peaks appear: the large high-frequency peak beyond 1 MHz is attributed to the grain interior with a very low capacitance, while the small peak at low frequency (marked with an asterisk (*)), the peak value of which increases with increasing DC bias, represents the large grain boundary capacitance [20]. It is clear that at low RH values of 33% and 53%, the grain boundary response can be observed in the modulus plot. When the RH increases to a high level (75% RH and 97% RH), the peak of the grain boundary response is replaced by a broad peak. Such a broad peak implies that there might be more than one polarization relaxation responses with very close characteristic frequencies overlapping in the plot. This result corresponds to the result from the impedance plot. The small peak value (compare to bulk response) indicates that the capacitances of the new polarization relaxation responses are much larger than the capacitance of the grain interior. As the RH increases from 75% RH to 97% RH, the peak value of the broad peak decreases, indicating the capacitances of the new polarization relaxation responses increase with the increasing RH.

3.2. Discussion

The electrical response of CCTO to humidity originates from the adsorption of water molecules along the CCTO/electrode interface and grain boundary. According to Traversa [3], when oxides are exposed to humid air, water molecules first chemisorb on the available sites of the oxide surface. Then, the succeeding layer of water molecules are physisorbed. The first layer of physisorbed water molecules involves double hydrogen bonding to single water molecules. As the RH increases, the physisorption changes from monolayer to multilayer. The subsequent layers of physisorbed water molecules are singly bonded. Because the chemisorbed layer begins to desorb at approximately 400 °C [21,22] and our experiment was conducted at room temperature, the electrical response of CCTO to RH originates from the physisorbed water molecules.

As is well known, the microstructure greatly affects the sensing properties of gas-sensing materials. Small grains with large specific surface area will provide more sites for water molecules to adsorb than large grains with small specific surface area. However, our previous study shows that the microstructure seems to have only a minor effect on the humidity response of CCTO [16]. As CCTO is an internal barrier layer material, the potential barriers at the grain boundary and at the CCTO/electrode interface contribute to the total capacitance of CCTO. The adsorption of water molecules at the grain boundary and at the CCTO/electrode interface may affect the potential barrier capacitance, further resulting in changes to total capacitance of CCTO. Our experimental results provide some hints about the effect of water adsorption on the potential barrier capacitance of CCTO. At low RH values of 33% and 53%, a clear electrode contact response was observed at low frequency (see Fig. 4). When RH increases to a high level, the electrode contact response is