Section: Research Paper
ISSN 2063-5346

Synthesis, Characterization and Dielectric Properties of Gd doped $CaCu_3Ti_4O_{12}$ perovskite

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DOI: 10.48047/ecb/2023.12.si4.1664

Abstract

Synthesis, Characterization and Dielectric Properties of pure and Gd doped $CaCu_3Ti_4O_{12}$ (CCTO) were investigated. The X-ray diffraction analysis showed single phase, without any impurity phase. The dielectric property of pure and Gd doped CCTO is exhibit an enormously large low-frequency dielectric permittivity (ε' is of the order of 10^4~10^5). This dielectric feature makes some of them promising for the applications in various microelectronic devices.

1 Introduction

High dielectric constants have been found in oxides of the type $ACu_3Ti_4O_{12}$, the most exceptional behavior is exhibited by $CaCu_3Ti_4O_{12}$ (CCTO), which shows a dielectric constant (about 12,000), and the cubic structure of these materials is related to that of perovskite [1-6], but the octahedral TiO_6 are tilted.

Sinclair *et al.*[7] performed an impedance spectroscopy measurement demonstrating that CCTO ceramics are electrically heterogeneous and consist of semi-conducting grains with insulating grain boundaries, and concluded that the giant-dielectric phenomenon is attributed to a grain boundary internal barrier layer capacitance (IBLC) rather than an intrinsic property associated with the crystal structure.

So far, the IBLC explanation is comparatively widely accepted.[8-13]

Because there are tremendous technical demands for large dielectric constant materials, it is worthwhile to systematically investigate the dielectric properties of the compounds in this system.

2. Experimental Details

Polycrystalline samples of $CaCu_3Ti_4O_{12}$ and Gd doped CCTO were prepared by heating mixed stoichiometric amounts of high purity $CaCO_3$, CuO, Gd_2O_3 and TiO_2, ground in an agate mortar with a pestle. After sufficient grinding, the mixed powder was collected in a crucible, put inside the furnace for heating, the first step is to heat it in air by the ramping rate 5°C/min from room temperature to 850°C, kept the heating temperature for 12 hours, then the cooling rate was 5°C/min was set from 850°C to room temperature.

After the first heating procedure, we ground the powders again, and then heat again under the same procedure, but the precious heating temperature 850°C changed as 950 °C, after the third grinding, the pellets of 10 mm diameter and 1.0 mm thickness each were cold pressed and sintered at 1000 for 12 hours. The disc samples were polished to produce a flat uniform surface and electrode with silver paint and a thin conducting wire so that we can apply an AC voltage source for dielectric measurement.

Crystallographic data for all samples were obtained with powder x-ray diffractometer using Cu K_α radiation at a scanning rate about 1° in 2θ per minute. The scan range is from 15° to 70° for all the samples. The lattice parameters, a, b and c, were obtained by linear regression based on the following equation with given diffraction peaks angle and index.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

In the linear regression program, difference between experimental diffraction angle and the ones generated from the results (a, b, and c) were taken as a simple parameter of error control. The regression results were accepted only when such parameters were below 0.1° for all peaks.

Various scales of SEM (scanning electron microscopy) or FESEM (field

emission scanning electron microscopy) photos were taken for comparing the size and the shape of the grains between different grains. Various scale of the observation was recorded.

Each sintered pellet was coated with silver pasted uniformly and a thin wire was connected to both sides as the electrode, we baked the silver paste gradually by placing the sample under an electric bulb for about 1 h. An alternating voltage was applied, and then the values of capacitance, conductivity were measured. The frequency of the voltage source is applied from 20 Hz to 1 MHz, and the value of real and imaginary dielectric constants, loss tangent were all recorded by HP-4284A LCR meter and the computer software.

3. Results and discussion

X-ray diffraction pattern of the both $CaCu_3Ti_4O_{12}$ and $GdCu_3Ti_4O_{12}$ samples are shown in Fig. 1 with $15 \leqq 2\theta \leqq 70$. The lattice constants of both the samples are deduced from the x-ray pattern are a = 7.389 Å, and 7.383 Å. The lattice constants decreases slightly as the Ca is replaced by Gd.

Selected FESEM photos are shown in Fig. 2, to compare the grains of $CaCu_3Ti_4O_{12}$ and $GdCu_3Ti_4O_{12}$ shows gains of similar size and a shape close to a sphere.

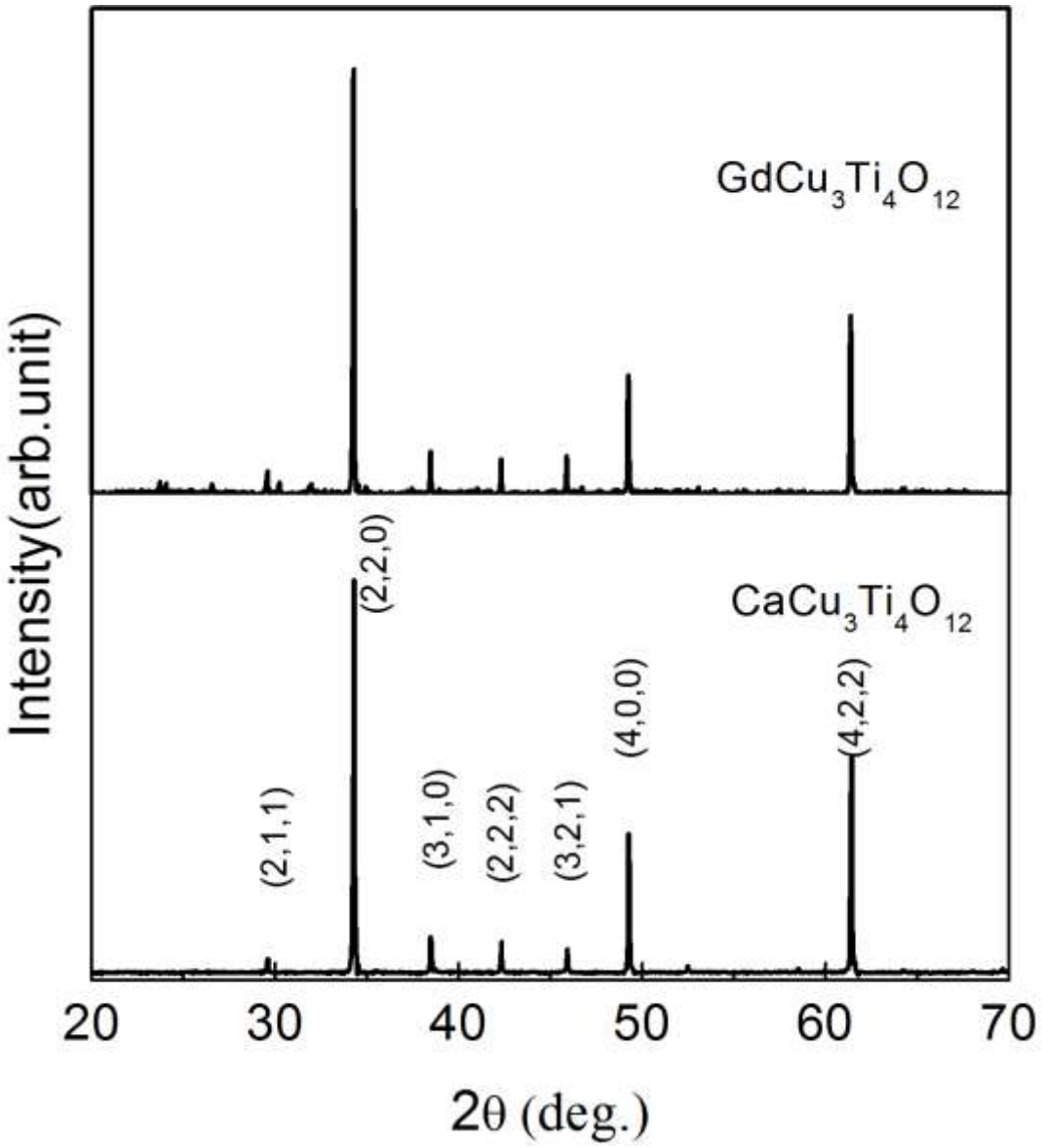

Fig. 1 X-ray diffraction pattern of the $CaCu_3Ti_4O_{12}$ compound with Miller indices of the peaks.

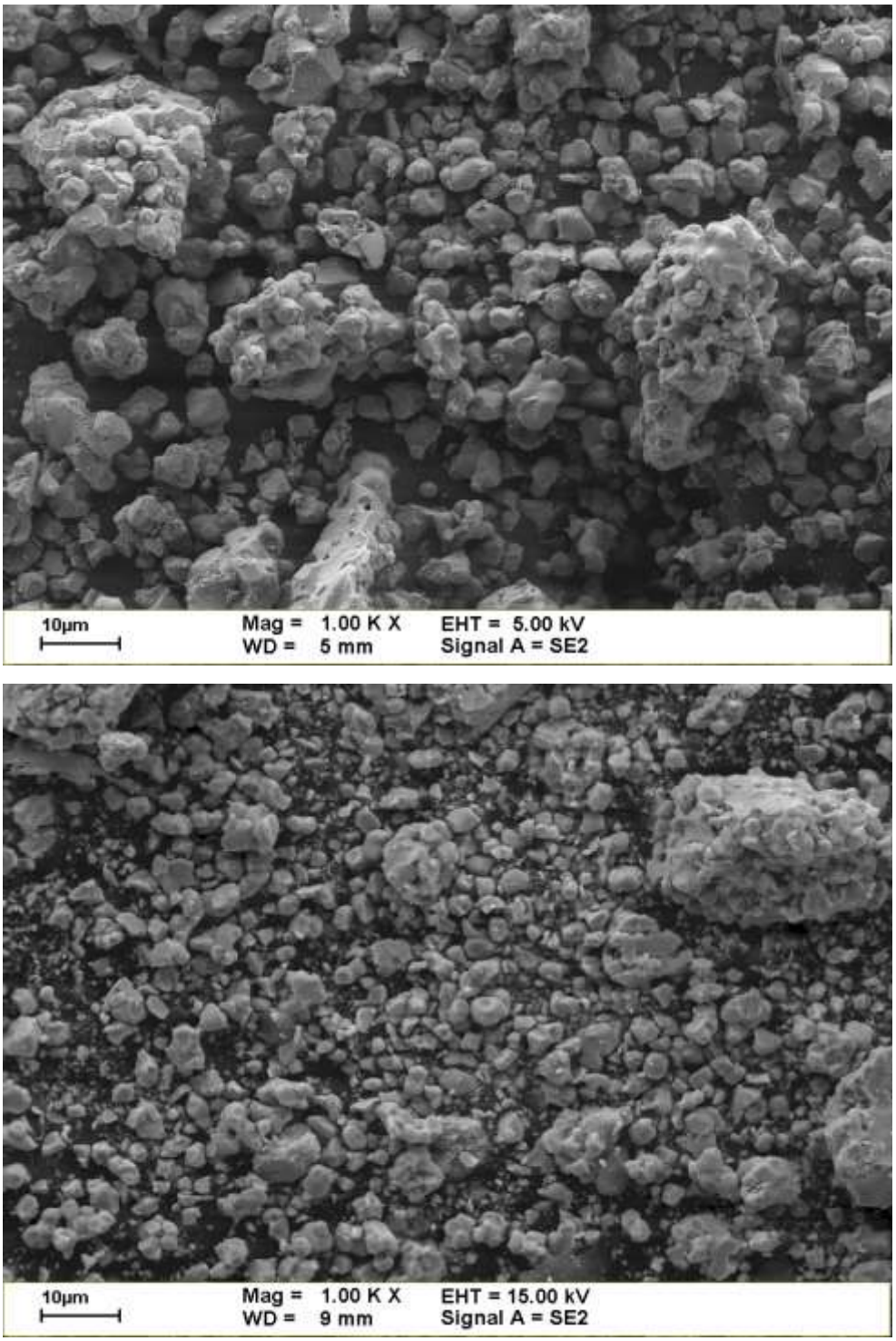

Fig. 2 FESEM photos of the (a) $CaCu_3Ti_4O_{12}$ and (b) $GdCu_3Ti_4O_{12}$ compounds.

The temperature dependence of the relative dielectric permittivity, ε' and dissipation factor, $\tan\delta$ of $CaCu_3Ti_4O_{12}$ sample. The ε' value is only 500 at room temperature under the frequency of 500 Hz.

The ε' values increases as the temperature increases, but decreases as the frequency increases, it experiences a rapid drop when the temperature goes down. Every sample experiences a plateau during some range, shows the most distinguishing characteristic which may be very hopeful to produce a stable electronic device. In fig 3 (a), the dielectric constant shows very little independence on temperature within 150 K ~ 300 K.

The dielectric loss for $CaCu_3Ti_4O_{12}$ are also appears to be a function of temperature, graphs of D-T relations are shown at the bottom of the ε'-T relations ones. Most of the curve goes through two peaks with temperature, indicates that usually two relaxations takes place under 300 K. For a specified frequency, we have both high temperature and low temperature response.

Fig. 3(a) display the temperature-dependence of the real part of the dielectric and loss tangent of $CaCu_3Ti_4O_{12}$, selected values of frequency is shown in the graph. The ε' value is growing by orders.

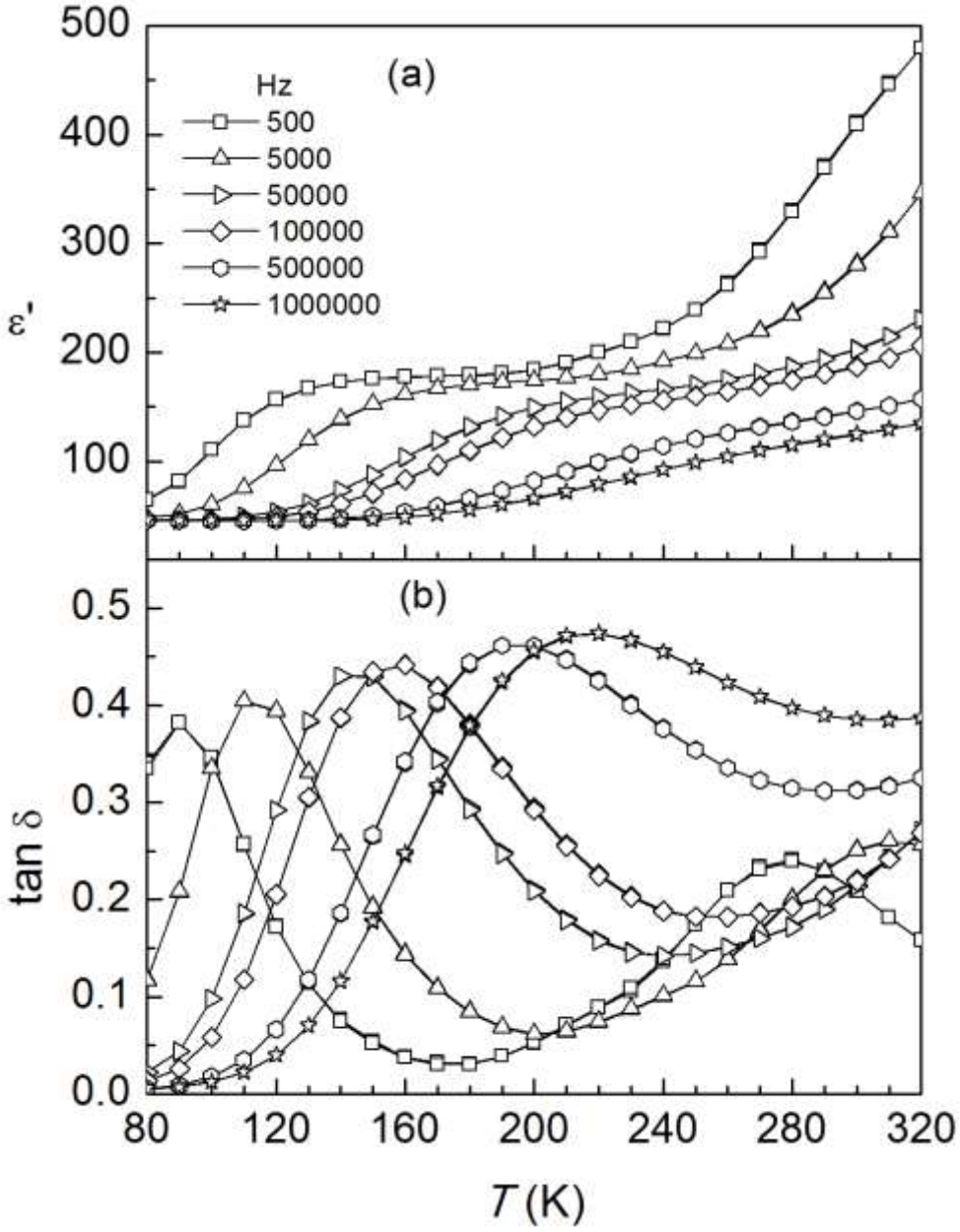

Fig. 3 (a) ε'-T and (b) tan δ-T relation of $CaCu_3Ti_4O_{12}$ compound

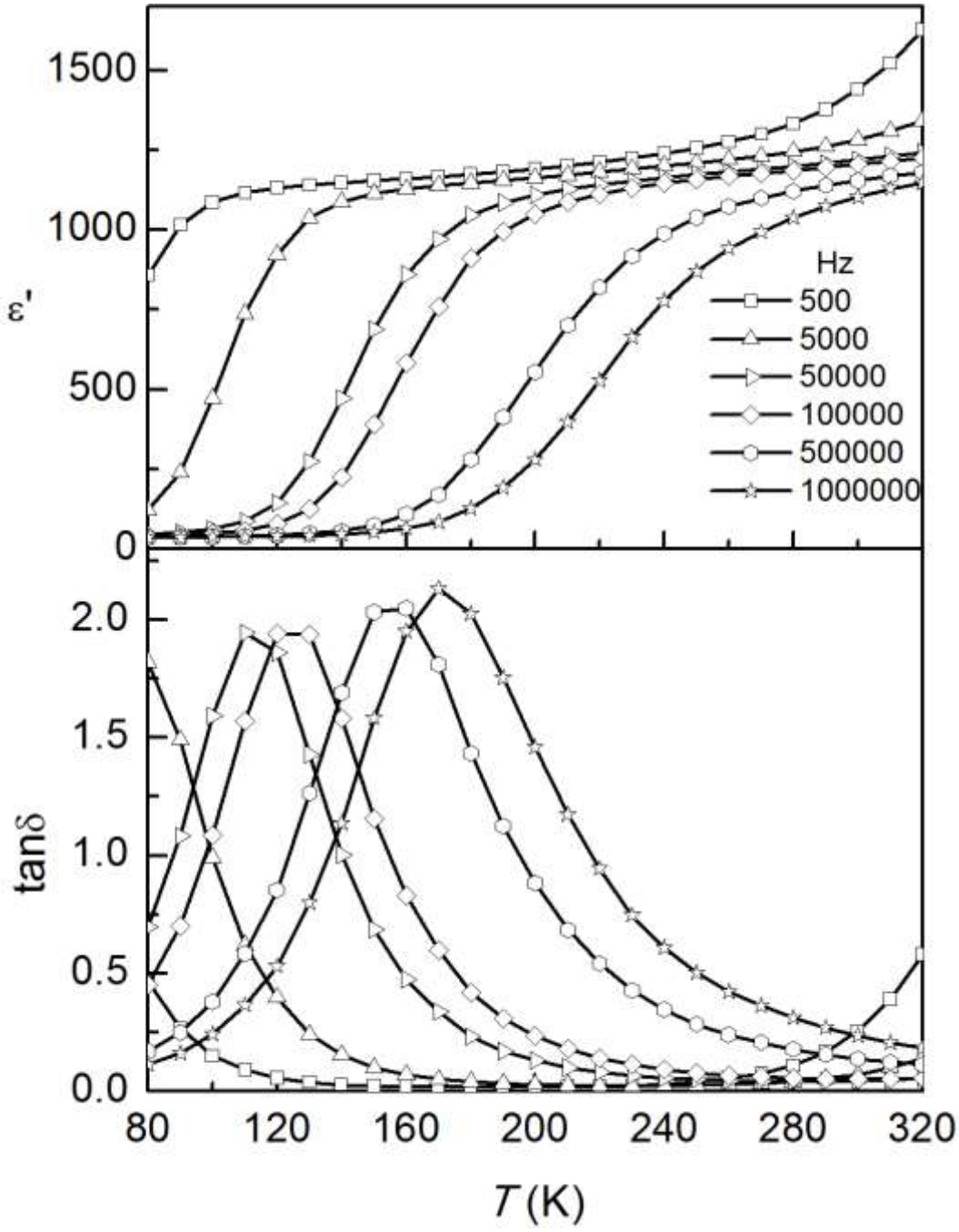

Fig. 4 (a) ε'-T and (b) tanδ-T relation of $GdCu_3Ti_4O_{12}$ compound

In fig.4 (a), to list the frequency dependence of the relative dielectric constant and dissipation factor of $GdCu_3Ti_4O_{12}$ sample, another expression for the same result. The behavior roughly obeys Debye equation. The resonant frequency shifts rightward as the temperature goes up. Some of them show two peaks before the range of frequency reaches 1 MHz. By collecting the values of these peaks, we drew the Arrehenius plot in fig.5 for both samples, (collecting the *T* and f values of every peak, 1/T as the horizontal axis, lnf as the vertical axis) and calculated the activation energy of each sample, as summarized in table 1.

Most of the curves in the D-T graphs exhibit at least one peak, indicates that the relaxation exists. Some of them have two peaks in both low temperature and high temperature range. The first peak (the one in low temperature) is always higher than the other, that is to say, the dielectric loss is little in high temperature.

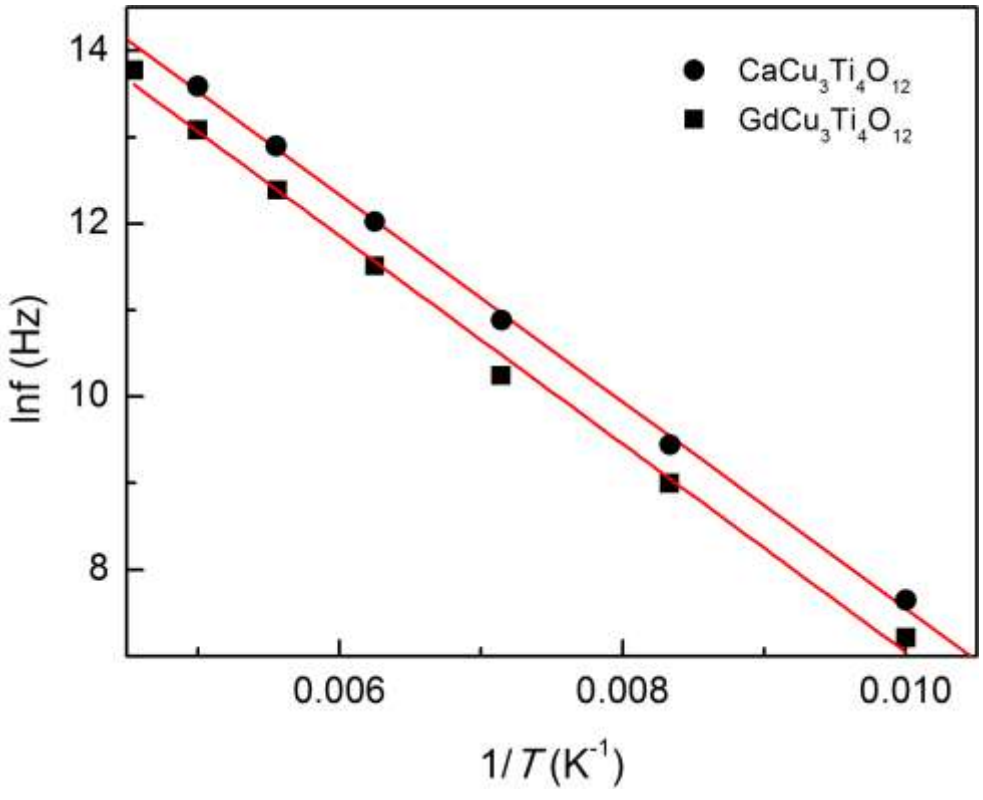

Fig. 5 Activation energy values of $CaCu_3Ti_4O_{12}$ and (b) $GdCu_3Ti_4O_{12}$ compounds from Arrhenius plot

Sample	parameters	
	f_0 (10^8 Hz)	Ea (eV)
$CaCu_3Ti_4O_{12}$	2.66	0.1049
$GdCu_3Ti_4O_{12}$	0.12	0.0532

Table 1 Curve fitting results for $CaCu_3Ti_4O_{12}$ and $GdCu_3Ti_4O_{12}$

4. Conclusions

Synthesis, Characterization and Dielectric Properties of pure and Gd doped $CaCu_3Ti_4O_{12}$ (CCTO) were investigated. The X-ray diffraction analysis showed single phase, without any impurity phase. The dielectric property of pure and Gd doped CCTO is exhibit an enormously large low-frequency dielectric permittivity (ε' is of the order of 10^4~10^5). This dielectric feature makes some of them promising for the applications in various microelectronic devices.

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