AC Impedance Characterization for Microwave Dielectric Material BaEu₂Ti₄O₁₂

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Abstract The electrical properties of BaEu₂Ti₄O₁₂ were characterized by means of AC impedance spectroscopy in the frequency range of 10⁻¹ ~ 10⁷ Hz. The experiment results indicate: (i) the permittivity value measured in this low frequency range is compatible with the published value measured in microwave range. The permittivity value obtained in high frequency range is net effect of bulk and grain boundary permittivities; better-sintered ceramic has thinner grain boundary and may have larger permittivity value; (ii) when the sample was cooled down slowly from elevated temperature or annealed in O₂-rich atmosphere, the conductivity was reduced, which may be explained by the reduction of oxygen vacancies in crystal. These treatments may lower the dielectric loss in microwave range.

Keywords: AC impedance, BaEu₂Ti₄O₁₂, Microwave dielectric

It is well known that phases BaR₂Ti₄O₁₂ (R = rare earth elements) are used as microwave dielectrics. A lot of research has been reported on the composition, structure, solid solution as well as electrical properties of these phases [1-9]. BaR₂Ti₄O₁₂ phases only exist for larger rare earth elements, such as La, Pr, Nd, Sm, Eu and Gd. These phases form solid solutions with mechanism: 3Ba²⁺ ↔ 2R³⁺ and the more suitable formulae may be represented as Ba_{6-3x}R_{8+2x}Ti₁₈O₅₄. Among the six analogues, Nd and Sm perform better microwave properties. Recent research [10-11] showed that for Nd phase, $\epsilon = 87$, $Qf = 8\,710$ GHz, and for Sm phase, $\epsilon = 82$, $Qf = 5\,180$ GHz, $\tau_f \approx -19.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. In published research, most measurements of the electrical properties were conducted at fixed MHz or GHz frequency. The variations of the electrical properties with frequency are seldom reported. AC impedance spectroscopy (IS) is a popular technique for investigating the electrical properties of electroceramics. In this work, measurements for all BaR₂Ti₄O₁₂ phases in the frequency range from 10⁻¹ to 10⁷ Hz were carried

out. All samples showed similar IS behaviours, however the resolution of IS plots for Eu phase was better than others. Therefore, the details only on Eu phase are represented and discussed. Since only the sample with composition of $x = 0.5$ was considered, for convenience, the formulae BaEu₂Ti₄O₁₂ was applied.

1 Experimental

Samples were prepared through solid state reactions at high temperatures. Reagent grade BaCO₃, TiO₂ and Eu₂O₃ as well as other rare earth oxides were used as starting materials. These materials were dried at 700 ~ 900 °C overnight except that BaCO₃ was dried at 300 °C overnight in order to minimise its decomposition. The starting materials were weighed out accurately in the required amounts and were mixed together using an agate mortar and pestle. A small amount of acetone was also added in order to mix the materials homogeneously. The samples were initially fired on Au foil at 900 °C for a few hours to expel CO₂. These were then pressed into pellets and refired at 1 250 °C

for 3 ~ 6 days with regrinding every one to two days.

AC impedance measurements were carried out by using a Schlumberger Solartron 1250 Frequency Response Analyser in conjunction with a 1286 Electrochemical Interface and a Hewlett-Packard 4192A LF Impedance Analyser. A Pellet for AC impedance measurements was prepared by cold pressing powder at $2 \times 10^3 \text{ kg} \cdot \text{cm}^{-2}$ prior to sintering at 1350°C for 3 days. The relative density of the pellet was about 90%. Electrodes were made by adhering two pieces of gold strips to the opposite faces of the pellet with Engelhard gold paste (code T-10112); the pellet faces were Au coated. Then the sample was heated gradually to 600°C over a period of around 2 h to decompose the organometallic paste and harden the electrodes. The pellet, with electrodes attached, was placed on a conductivity jig in a silica-glass tube and inserted in a vertical tube furnace controlled to $\pm 2^\circ\text{C}$ by an Eurotherm PDI temperature controller. The actual temperature of the sample was monitored using an Eurotherm 810 thermometer connected to a chromel-alumel thermocouple that was incorporated into the jig. The sample was measured every 50°C over the range from 300 to 750°C . For each temperature, the sample was kept about 30 min for thermal equilibration. Some measurements were undertaken in various atmospheres, such as air, O_2 or N_2 (all dried with CaCl_2). The jig capacitance was calibrated for data analysis.

2 Results and discussions

2.1 Equivalent circuit

For analyzing AC impedance data of ceramic samples, approximately the brickwork model^[12] and related equivalent circuit is used to represent the electrical properties. The circuit (Fig. 1) is a series combination of bulk and grain boundary components, both of which are parallel RC elements, where R_b and C_b are bulk re-

Fig. 1 The equivalent circuit used to analyze the IS data of $\text{BaEu}_2\text{Ti}_4\text{O}_{12}$

sistance and capacitance respectively; R_{gb} and C_{gb} are grain boundary resistance and capacitance respectively. The electrical properties of ceramic samples can be illustrated by various IS plots, depending on the questions discussed. In present research, the dielectric property was represented by $\lg \varepsilon / \lg f$ plot, where ε is permittivity and f is frequency; the resistant property and conductive property were represented by Z''/Z' plot and $Y'/\lg f$ plots, where Z'' and Z' are imaginary and real parts of impedance as well as Y' is real part of admittance.

2.2 $\lg \varepsilon / \lg f$ plot

The dielectric property was analysed by permittivity spectra, which is also named as $\lg \varepsilon / \lg f$ plot in short. Fig. 2 gives the experimental permittivity spectra of Eu phase in various temperatures. Approximately the plots may be considered as two plateaux. At 400°C , the permittivity of low frequency plateau ($< 10^5 \text{ Hz}$) varies around 10^3 , which may be assigned to the grain boundary permittivity, ε_{gb} . Here ε_{gb} is actually not a constant; it decreases gradually with frequency. Since $\varepsilon_{gb} = C_{gb}d/(\varepsilon_0 S)$, C_{gb} also decreases with frequency, where ε_0 is the free space permittivity, $8.854 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$, whereas d and S are thickness and area of pellet sample respectively. All of these means that the equivalent circuit in Fig. 1 only approximately represented the situation of the sample. For high frequency plateaux ($> 10^6 \text{ Hz}$), the permittivity value tends to 70. The microwave value of permittivity for Eu phase is not available. However, Sreemoolanadhan's work^[13] indicated that the permittivity values of $\text{BaR}_2\text{Ti}_4\text{O}_{12}$ phases decrease from 88 to 72, when R varies from La to Sm. Thus we believe our IS result is compatible with the microwave data. This implies that the permittivity

Fig. 2 Permittivity spectra of Eu phase at various temperatures

data measured at MHz frequencies can be extended to GHz frequency range. Thus, in the search for high permittivity materials, AC impedance measurements are useful. When temperature increases, ε_{gb} increases and grain boundary plateaux extend to higher frequencies. At 700 °C, ε_{gb} varies in the range of $10^3 \sim 10^4$, while the grain boundary plateau extends to $\sim 10^6$ Hz. Owing to the measurement limitation, at higher temperatures, the bulk plateaux can not be measured.

The equivalent circuit illustrated in Fig. 1 is widely used for analysing conducting ceramics [12]; it is rarely used for microwave ceramics. According to this equivalent circuit, it can be simply deduced that the permittivity value obtained from the high frequency plateau should be assigned to ε_{net} , instead of ε_b , the bulk permittivity. In fact, ε_{net} is the applied parameter for dielectric materials, which is related to both ε_b and ε_{gb} :

$$\begin{aligned} \varepsilon_{net}^{-1} &= \varepsilon_b^{-1} + \varepsilon_{gb}^{-1} \\ \text{i. e.} \quad \varepsilon_{net} &= \varepsilon_b \varepsilon_{gb} / (\varepsilon_b + \varepsilon_{gb}) \end{aligned} \quad (1)$$

In ceramic dielectrics, grain boundary effect is normally difficult to be omitted, thus according to equation (1), the bulk permittivity, ε_b , can not be measured directly; instead ε_{net} is measured. In other words, the permittivity value of ceramic dielectrics at high frequencies is ε_{net} , instead of ε_b . ε_{net} is approximately equal to ε_b , but it is affected by the grain boundary permittivity. The equation clearly shows that ε_{net} is always less than ε_b . But larger ε_{gb} value gives larger ε_{net} value. The maximum possible value of ε_{net} is ε_b , when $\varepsilon_{gb} \rightarrow \infty$. Generally speaking, well-sintered ceramics have thin grain boundaries, thus they have large ε_{gb} . As a result, ε_{net} increases. By this point of view, high quality sintering benefits the ceramic per-

mittivity.

2.3 Z''/Z' plot and $Y'/\lg f$ plot

The AC impedance complex plane plot and admittance spectrum are also called Z''/Z' plot and $Y'/\lg f$ plot in short, respectively. The conductive properties of the sample were analyzed by using these two plots. The typical Z''/Z' plot and $Y'/\lg f$ plot (at 600 °C) for Eu phase are illustrated in Fig. 3(a) and (b). In Fig. 3(a), Z''/Z' plot, the semicircle with capacitance $2.4 \times 10^{-10} \text{ F} \cdot \text{cm}^{-1}$ at the maximum of the impedance semicircle is attributed to the grain boundary response. At this temperature, the bulk semicircle cannot be seen, although bulk resistance, R_b may be obtained from the high frequency intercept on the Z' axis of the grain boundary arc. No electrode responses were observed at lower frequencies, hence, it is believed that conduction in this material does not involve ionic motion. $Y'/\lg f$ plot, Fig. 3(b), consists of two plateaux. The value of the low frequency plateau equals $(R_{gb} + R_b)^{-1}$. Due to $R_{gb} \gg R_b$ here, the value of the low frequency plateau is approximately equal to the grain boundary conductivity, σ_{gb} . Commonly, the expression for the value of the high frequency plateau is complex. Here, due to $R_{gb} \gg R_b$ and $C_{gb} \gg C_b$, it can be deduced that the value of the high frequency plateau is approximately equal to the bulk conductivity, σ_b . The impedance data in various temperatures from 300 ~ 750 °C were measured in heating and cooling cycle. The conductivity values of σ_{gb} and σ_b were taken from $Y'/\lg f$ plots because they give clearer values than Z''/Z' plot.

Both Z''/Z' plot and $Y'/\lg f$ plots consist of bulk and grain boundary responses. For this low conductive material, the conductivity varies with temperature fol-

Fig. 3 AC impedance complex plane plot (a) and admittance spectrum (b) of Eu phase at 600 °C in air

lowing Arrhenius equation:

$$\sigma = A \exp(-E_a/RT) \quad (2)$$

where A is a constant, E_a is activation energy, R is the gas constant and T is absolute temperature. Fig. 4 illustrates this relation for both σ_b and σ_{gb} . Below 550 °C, the conductivity values in heating cycle for both σ_b and σ_{gb} are much higher than the values in cooling cycle. Above 550 °C, the heating cycle and cooling cycle give identical values. From 450 to 550 °C, on heating, the bulk conductivity was in a transition range; when the temperature was held constant, the conductivity decreased; the low limitation was the cooling value. The conductive behaviours shown in Fig. 4 can be understood as below [14-15].

It may be considered that electron trapped oxygen vacancies, $V_O^\times$ exist in the material annealed at elevated temperature. The conduction involves electron hopping between the oxygen vacancies. This hopping mechanism is common for low conductivity oxides. Above 550 °C, $V_O^\times$ are generated in both bulk and grain boundary:

Where $O_O^\times$ represents oxygen atoms on oxygen positions in lattice. It was known that $V_O^\times$ can supply two hopping electrons, therefore, high concentration of $V_O^\times$ enhances the conductivity. Below 450 °C, equilibrium (3) no longer pertains. $V_O^\times$ generated at high temperature can be 'frozen' in the material. When the pellet was quenched from high temperature, more $V_O^\times$ was

Fig. 4 Arrhenius plots of the bulk and grain boundary conductivity for Eu phase

Fig. 5 Admittance spectra of Eu phase at 400 °C after different heat treatments

'frozen', whereas when the pellet is slowly cooled, less $V_O^\times$ remains. Since the pellet was air-quenched from high temperature before the heating cycle measurements, the conductivity values for both bulk and grain boundary in the heating cycle were higher than those in the cooling cycle. This result was confirmed by another experiment shown in Fig. 5. A quenched pellet (from above 600 °C) gave higher conductivity values for both bulk and grain boundary, while a slowly cooled pellet presented lower conductivity. On the other hand, equilibrium (3) shows that reducing O_2 partial pressure benefits the concentration of $V_O^\times$ and conductivity. Thus if the atmosphere were changed from O_2 or air to N_2 , O_2 partial pressure decreased and the conductivity values for both the bulk and grain boundary should increase. If the atmosphere was changed back to O_2 , the conductivity should decrease again. The experiment results (at 600 °C) shown in Fig. 6 proved these. The charge carriers in this material are the hopping electrons contributed by $V_O^\times$, thus this material has n -type conduction. On the heating cycle, over the range 450 to 550 °C, the equilibrium (3) goes

Fig. 6 Admittance spectra of Eu phase at 600 °C in various atmospheres

in the direction from right to left. Possibly because the reaction rate is slow in the bulk and the equilibrium could not be set up immediately, the concentration of $V_O^\times$ is kinetically controlled and decreased with time. As a result, the conductivity deviates from the Arrhenius equation. Above 550 °C, the activation energy consists of two items: generating energy of $V_O^\times$ (E_1) and potential energy for electrons jumping over (E_2). Below 450 °C, the temperature is too low to generate $V_O^\times$ and $V_O^\times$ comes from high temperature quenching and the activation energy only contains E_2 item. Therefore Fig. 4 shows the higher activation energy at high temperatures than that at low temperatures.

2.4 Some comments

The dielectric loss is a very important deleterious property for dielectrics, which is proportional to conductivity [16]:

$$\tan\delta = \frac{\sigma}{\omega\epsilon\epsilon_0} \quad (4)$$

Where ω is angular frequency of electrical field. However, $\tan\delta$ calculated from the conductivity values obtained in this research is only the current leakage at low frequencies, rather than the dielectric loss at microwave frequencies. The dielectric loss at microwave can also be represented by equation (4), but the meaning of conductivity σ is different.

At microwave frequencies, the dielectric loss is associated with anharmonic lattice vibration [17-18]. The anharmonic parameters can be represented by using conductivity, although it does not mean the real charge transport in the lattice,

$$\sigma = \epsilon\epsilon_0(\gamma/\omega_T)\omega^2 \quad (5)$$

where γ is the damping factor and ω_T is the resonant angular frequency of the lattice vibration. γ mainly depends on the structure and bonding features of the materials and it is also affected by lattice imperfections, such as impurity atoms and oxygen vacancies. These imperfections result in the increase of the damping factor and the dielectric loss. Although the dielectric loss at microwave can not be obtained by IS measurements, but the IS data in the present research indicated that slow cooling pellets from high temperature and annealing sample in oxygen-rich atmosphere decrease

the conductivity. That also means the decrease of the concentration of oxygen vacancies. Therefore it may be deduced that these treatments reduce the imperfections of the materials, furthermore, they reduce the dielectric loss. However this is only a deduction, further research is necessary for conducting the measurements at microwave, which will be our work in next stage.

3 Conclusions

The AC impedance measurements were conducted for all BaR₂Ti₄O₁₂ analogues, all of which show similar electrical behaviours. Details only for Eu phase were presented and discussed, since it gave better resolution for IS plots. The results indicate that: i) the permittivity values obtained by IS measurements are compatible to the published data measured at microwave range; ii) all analogues have *n*-type conduction and electrons arising from electron trapped oxygen vacancies are the charge carriers; iii) quenching sample leads to increase of the conductivity and slow cooling causes decrease of it; iv) increasing O₂ partial pressure in annealing reduces the conductivity. As results, it can be believed that slow cooling and annealing in O₂ benefit the reduction of the dielectric loss for BaR₂Ti₄O₁₂ analogues. Research on microwave measurements is worth doing in next stage for further understanding the dielectric properties of materials at this frequency range.

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微波介质材料 $\text{BaEu}_2\text{Ti}_4\text{O}_{12}$ 的交流阻抗谱表征

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摘要 采用交流阻抗谱技术对微波介质材料 $\text{BaEu}_2\text{Ti}_4\text{O}_{12}$ 进行了表征。分析了 $\lg \varepsilon' / \lg f$, Z'' / Z' 和 $Y' / \lg f$ 等图谱的特征与材料性能的关系。研究结果表明: 1) 阻抗谱测试得到的介电常数与所发表的微波测试结果有很好的一致性, 高频下得到的介电常数实际上是晶粒和晶界的净结果, 高质量烧结的材料应具有薄的晶界, 因而应表现出较大的介电常数; 2) 如果将材料从高温下缓慢降温或在 O_2 气氛中退火, 材料的导电性都会下降, 其原因可以理解为这样处理的材料氧空位浓度降低, 进而可以推测这有利于降低材料的介电损失。

关键词: 交流阻抗谱, $\text{BaEu}_2\text{Ti}_4\text{O}_{12}$, 微波介质材料

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