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Letter

Characterization and dielectric properties of $Sr_4M_2Ti_4Ta_6O_{30}$ (M = Pr and Eu) ceramics

Chunchun Li[a,b], Liang Fang[a,b,*], Xiyang Peng[a,b], Changzheng Hu[a,b], Bolin Wu[b]

[a] State Key Laboratory Breeding Base of Nonferrous Metals and Specific Materials Processing, Guilin University of Technology, Guilin 541004, PR China
[b] Key Laboratory of Nonferrous Materials and New Processing Technology, Ministry of Education, Guilin University of Technology, Guilin 541004, PR China

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ABSTRACT

Polycrystalline samples of $Sr_4Pr_2Ti_4Ta_6O_{30}$ (SPTT) and $Sr_4Eu_2Ti_4Ta_6O_{30}$ (SETT) were prepared by a high temperature solid-state reaction technique. The formation, structure, dielectric and ferroelectric properties of the compounds were studied. $Sr_4Eu_2Ti_4Ta_6O_{30}$ is found to be a ferroelectric phase with filled tetragonal tungsten bronze (TB) structure at room temperature and undergoes a diffuse type ferroelectric–paraelectric phase transition around 90 °C with relaxor properties, while $Sr_4Pr_2Ti_4Ta_6O_{30}$ belongs to paraelectric phase with TB structure at room temperature. At 1 MHz, SPTT exhibits a high dielectric constant of 181 and a low dielectric loss of 3.6×10^{-3} with a negative temperature coefficient of the dielectric constant (τ_ε), and SETT has a high dielectric constant of 192 and low dielectric loss of 7.7×10^{-3} with a positive τ_ε at room temperature, and heterogeneous mixtures of SPTT and SETT or a solid solution between them might be used to manufacture a tungsten bronze-structured temperature-stable dielectrics.

1. Introduction

Materials of tungsten bronze (TB) structure belong to an important family of dielectric materials, which display interesting ferroelectric, pyroelectric, piezoelectric, and nonlinear optical properties for applications in various electric devices, such as transducers, actuators, capacitors, and ferroelectric random access memory [1–3]. Due to the rapid progress in microwave telecommunications, satellite broadcasting and other related devices, the TB structural materials having high performance dielectric properties (i.e. high dielectric constant and low loss) have attracted much attention [4]. The TB structure consists of a complex array of distorted BO_6 octahedron sharing corners in such a way that three different types of interstices (A, B and C) are available for a wide variety of cations occupying in the general formula $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$ [2]. It has been found that different ionic substitutions at the above-mentioned sites have different effects on the dielectric properties [5–8]. So the dielectric properties may be tuned by different ionic substitutions.

In the previous work, a number of Ba-based TB compounds such as $Ba_5DyTi_3V_7O_{30}$, $Ba_4Ln_2Ti_4M_6O_{30}$, $Ba_5LnZnM_9O_{30}$ and $Ba_3Ln_3Ti_5M_5O_{30}$ (Ln = La, Nd, Sm, Eu, Gd; M = Nb, Ta) with high dielectric constant over 100 were reported [4,9,10]. Sebastian et al. proposed some promising compounds with tungsten bronze (TB) structure under the formula $Ba_5MTi_3A_7O_{30}$ [M = Ce, Pr, Nd, Sm, Gd, Dy and Bi; A = Nb, Ta] with dielectric constant (ε_r) varying from 164 to 887 and loss tangent (tan δ) from 10^{-3} to 10^{-2} at 1 MHz [11,12]. The structure and phase transition behavior of ferroelectric phases with the compositions $Ba_2MTi_2X_3O_{15}$ (M = La, Pr, Nd, Sm, Eu, Gd, Dy, Bi; X = Nb, Ta) and $Ba_6MNb_9O_{30}$ (M = Ga, Sc and In) were reported by West et al. and Arnold et al., respectively [13,14]. Recently, some Sr-based TB ceramics such as $Sr_5LnTi_3M_7O_{30}$, $Sr_4Ln_2Ti_4M_6O_{30}$ (Ln = La, Nd, Sm, Gd, Y and M = Nb and Ta) were proposed and investigated [15–20]. Extensive literature on TB compounds reveals that no work has been reported on the titled compounds. Hence, in this paper we report preliminary structural, dielectric and ferroelectric properties of $Sr_4M_2Ti_4Ta_6O_{30}$ (M = Pr and Eu) compounds.

2. Experimental

Stoichiometric amounts of high purity powders of $SrCO_3$ (99.9%), Ln_2O_3 (Ln = Pr and Eu) (99.5%), TiO_2 (99.95%) and Ta_2O_5 (99.9%) were weighed and fully mixed through ball milling for 24 h. The mixtures were dried and calcined at 1400 °C for 4 h. The calcined powders were thoroughly reground and mixed with 3% solution of polyvinyl alcohol (PVA) as a binder. The slurries were then dried, ground and pressed into cylindrical compacts of different thicknesses in the range 2–4 mm and 11 mm in diameter under a pressure of 200 MPa. The compacts were sintered in the range of 1450–1500 °C for 4 h in air and cooled at a rate of 2 °C/min to 1100 °C, then naturally cooled to room temperature.

The densities of the compacts were measured by the Archimedes method. The phase constitutions of the samples were examined using a PANalytical X'Pert PRO X-ray diffractometer (XRD) using CuK_α radiation (λ = 1.54059 Å) in a 2θ range from

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[*] Corresponding author at: State Key Laboratory Breeding Base of Nonferrous Metals and Specific Materials Processing, Guilin University of Technology, 12 Jiangan Road, Guilin 541004, PR China. Fax: +86 773 5896436.
E-mail address: fangliangskl@yahoo.com.cn (L. Fang).

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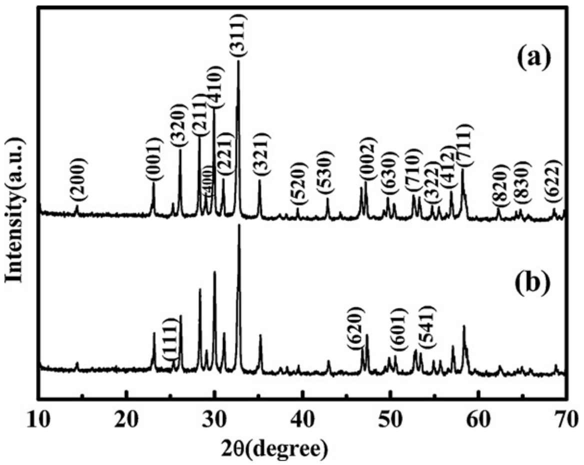

Fig. 1. Room temperature XRD patterns of (a) SPTT and (b) SETT.

10° to 70°. The microstructures were studied using a JSM-6370LV scanning electron microscopy (SEM). Silver paste was applied to the circular faces, then dried at 800 °C for 1 h and cooled naturally to room temperature. Temperature-dependent dielectric measurements were made using an Agilent 4294A precision impedance analyzer equipped with a thermostat from room temperature (20 °C) to 350 °C at the range of 100 Hz to 1 MHz. At room temperature, the hysteresis loop of the samples was measured by an aix ACCT TF Analyzer 2000. The piezoelectric coefficient (d_{33}) was obtained on poled samples (6 kV/cm for 24 h in silicon oil) using a YE2730 piezometer.

3. Results and discussion

The room temperature XRD patterns obtained using CuKa radiation are shown in Fig. 1. Both ceramics were found to exhibit single phase tetragonal TB structure in agreement with JCPDS file No. 40-358 for $Sr_4La_2Ti_4Nb_6O_{30}$. All peaks were indexed, and there was no evidence for the presence of any secondary phase(s). The unit cell parameters of both ceramics refined by the least square method are as follows: $a = b = 1.22879(5)$ nm, $c = 0.38477(2)$ nm for SPTT; and $a = b = 1.22311(3)$ nm, $c = 0.38489(1)$ nm for SETT. It is clear that the unit cell parameters decrease slightly because of the smaller effect of the ionic radius of Eu^{3+} than that of Pr^{3+}.

The compounds were sintered into dense ceramics with relative densities of 95.5% and 96.3% for SPTT and SETT, respectively. Fig. 2 gives the SEM micrographs of the SPTT and SETT ceramics sintered at 1470 °C. The images show typical microstructures containing both equiaxed and acicular grains. Similar microstructures were observed for some TB ceramics such as $Ba_4M_2Ti_4Nb_6O_{30}$ (R = Sm, Nd, and La) ceramics [14,21]. Both ceramics have a close microstructure with low porosity, and the average grain size of SETT is larger than that of SPTT.

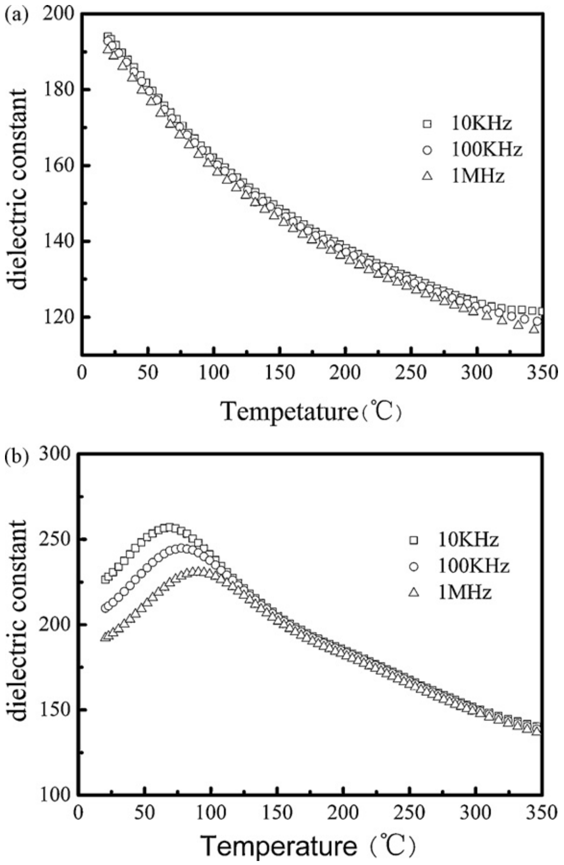

Fig. 3. Temperature dependence of dielectric constant of (a) SETT and (b) SPTT ceramics.

The temperature-dependent dielectric characteristics at 10 kHz, 100 kHz and 1 MHz for both ceramics are shown in Fig. 3. Dielectric constant increases with decreasing frequency due to the presence of all different types of polarization (electronic, ionic, dipole and space charge) at low frequency. At room temperature SPTT and SETT ceramics show dielectric constant of 181 and 192 as well as dielectric loss of 3.6×10^{-3} and 7.7×10^{-3} at 1 MHz, respectively. As temperature increases, there is a broad peak of dielectric constant corresponding to ferroelectric–paraelectric phase transition for SETT, which confirms that SETT belongs to ferroelectric TB phase at room temperature [3,15]. The Curie temperature (T_C) for SETT ceramic at frequency of 10 kHz, 100 kHz and 1 MHz are around 69, 78 and 91 °C, respectively. The T_C is found to shift towards higher temperature side at higher frequencies, and this is the char-

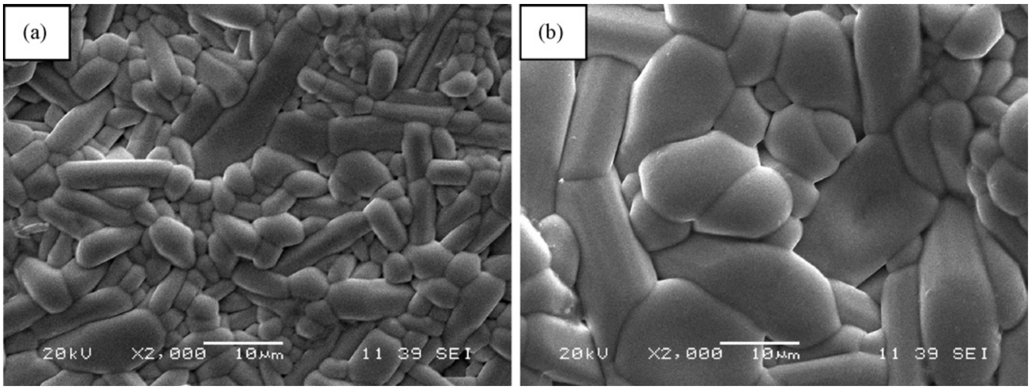

Fig. 2. SEM micrographs of the surfaces of (a) SPTT and (b) SETT ceramics.

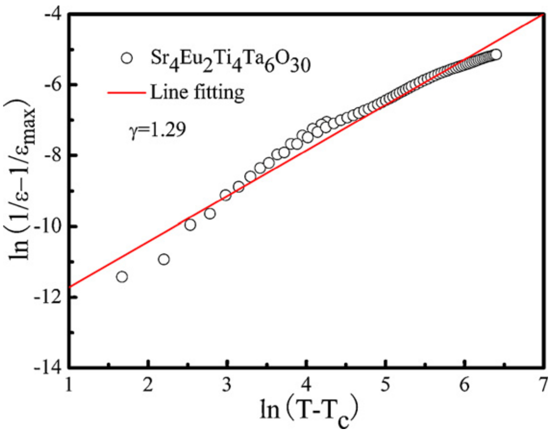

Fig. 4. The value of $\ln((1/\varepsilon) - (1/\varepsilon_{max}))$ as a function of $\ln(T - T_C)$ at 1 MHz for $Sr_4Eu_2Ti_4Ta_6O_{30}$ ceramics [the solid line is the line fitting].

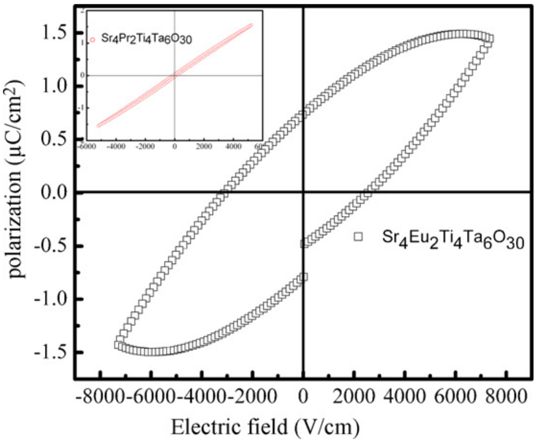

Fig. 5. *P–E* hysteresis loops of SPTT and SETT ceramics at room temperature.

acteristic of relaxor ferroelectrics with TB structure. The degree of disorder or diffusivity (γ) can be calculated using Eq. (1) [22].

$$\ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}}\right) = \gamma \cdot \ln(T - T_C) + \text{constant} \tag{1}$$

The curve of $\ln((1/\varepsilon) - (1/\varepsilon_{max}))$ as a function of $\ln(T - T_C)$ at 1 MHz for $Sr_4Eu_2Ti_4Ta_6O_{30}$ ceramics is shown in Fig. 4. The diffusivity γ calculated at 1 MHz for SETT is 1.29, which confirms the diffused phase transition.

The dielectric constant of SPTT ceramic gradually decreases from 190 to 115 at 1 MHz as temperature increases from 20 to 350 °C, and no dielectric peak for the ferroelectric–paraelectric phase transition is observed, indicating SPTT belongs to a paraelectric phase with TB structure at room temperature. The temperature coefficient of the dielectric constant (τ_ε) at 1 MHz is −2128 ppm/°C. In combination with $Sr_4Sm_2Ti_4Ta_6O_{30}$ with T_C around 30 °C [16], it is found that the T_C of $Sr_4M_2Ti_4Ta_6O_{30}$ (M = Pr, Sm and Eu) decreases with the increase of the ionic radius of the M^{3+} ion, and these results agree with the work of Bhanumathi et al. [23]. Since SPTT has a negative and SETT has a positive temperature coefficient of permittivity at room temperature, heterogeneous mixtures of SPTT and SETT or a solid solution between them might be used to manufacture a tungsten bronze-structured temperature-stable dielectrics suitable for multilayer capacitor applications [21].

The ferroelectric hysteresis loops of both samples were recorded at room temperature, with the application of electric fields of about 5 kV/cm (Fig. 5). There exists a hysteresis loop for $Sr_4Eu_2Ti_4Ta_6O_{30}$ with the remanent polarization ($2P_r$) of 1.464 μC/cm^2, which confirms that the SETT ceramic is ferroelectric in nature. No proper hysteresis loop with saturated polarization was observed. It is difficult to polar the compounds to get saturated polarization because of dielectric breakdown when high electric field was applied. At room temperature, the piezoelectric coefficient (d_{33}) was found to be 11 pC/N. The remanent polarization ($2P_r$) is nearly zero for SPTT, confirming that SPTT is paraelectric at room temperature.

4. Conclusions

$Sr_4M_2Ti_4Ta_6O_{30}$ (M = Pr and Eu) ceramics were prepared and characterized. $Sr_4Pr_2Ti_4Ta_6O_{30}$ is paraelectric phase adopting filled tetragonal TB structure at room temperature, while $Sr_4Eu_2Ti_4Ta_6O_{30}$ belongs to a ferroelectric phase with TB structure at room temperature and undergoes a diffuse type ferroelectric–paraelectric phase transition with relaxor properties around 86 °C. $Sr_4Pr_2Ti_4Ta_6O_{30}$ ceramic exhibits a high dielectric constant of 161, a low dielectric loss of 0.007, and a relatively large negative temperature coefficient of the dielectric constant (τ_ε) of −2128 ppm/°C. The existence of hysteresis loop ($2P_r$ = 1.464 μC/cm^2) confirms the ferroelectric of $Sr_4Eu_2Ti_4Ta_6O_{30}$ at room temperature.

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