Dielectric and ferroelectric properties of $Sr_4CaSmTi_3Nb_7O_{30}$ with tetragonal tungsten bronze structure*

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(Received 3 January 2014; revised manuscript received 4 March 2014; published online 24 July 2014)

$Sr_4CaSmTi_3Nb_7O_{30}$ ceramics are synthesized and indexed as tetragonal tungsten bronze structure. The dielectric behavior and ferroelectric nature are investigated. Three dielectric anomalies are observed. The phase transition is a displacive phase transition with some diffusive characteristics, which indicates possible compositional variations within the materials on the microscopic scale. The weak distortion disappears in cooling process for differential scanning calorimetry measurement, and the large depression of Curie–Weiss temperature T_0 indicates the difficulty in forming macroferroelectric domain. The ferroelectric nature in these filled tungsten bronze niobates originates from the off-center displacement of B-site cations, but they are primarily dominated by A-site cation occupation. Both the radius and the valence of A1-site cations play an important role on ferroelectric properties of the filled tungsten bronze compounds. Existence of spontaneous polarization with a remanent polarization of 0.16 μC/cm^2 a coercive field of $E_c = 11.74$ kV/cm confirms the room-temperature ferroelectric nature of $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics.

Keywords: dielectric, phase transition, ferroelectric, relaxation

PACS: 77.22.–d, 77.80.B–, 77.80.–e, 77.22.Gm **DOI:** 10.1088/1674-1056/23/9/097701

1. Introduction

Considerable research effort has been addressed to dielectric materials due to fascinating physical property and potential applications.[1] Promising applications of these composites include magnetic field sensors, transducer, filters, oscillators, phase shifters, memory devices, and so on.[2,3] As one kind of important dielectric ceramics, the filled tungsten bronze (TB) ferroelectrics $M_4R_2Ti_4Nb_6O_{30}$ and $M_5RTi_3Nb_7O_{30}$ (M = Ba, Sr; R = rare-earth element) have received much scientific attention.[4–12]

The filled TB structure consists of a complex array of distorted BO_6 octahedron sharing corners in such a way that two different types of interstices (A1, A2) are available for a wide variety of cations occupying the general formula $(A1)_2(A2)_4(B1)_2(B2)_8O_{30}$.[13] For $M_4R_2Ti_4Nb_6O_{30}$, the number of M^{2+} ions is equal to that of A2 (pentagonal) interstices, and M^{2+} and R^{3+} ions occupy the A2 (pentagonal) and A1 (tetragonal) sites, respectively. For $M_5RTi_3Nb_7O_{30}$, the ion occupation is different from that in $M_4R_2Ti_4Nb_6O_{30}$, and it is generally believed that four bigger M^{2+} ions first occupy the larger A2 sites, while two A1 sites are cross occupied by M^{2+} and R^{3+} ions. As the type and size of substituted ions on different sites have significant effects on the dielectric and ferroelectric properties and the amount of disorder in the structure of materials belonging to this family, a large number of filled TB ferroelectrics have been synthesized, such as $Ba_4La_2Ti_4Nb_6O_{30}$,[12] $Ba_5LaTi_3Nb_7O_{30}$,[14] $Sr_5SmTi_3Nb_7O_{30}$,[6] $Sr_5LaTi_3Nb_7O_{30}$,[15] $Ba_4Nd_2Ti_4Nb_6O_{30}$,[7,9,16] $Ba_4Sm_2Ti_4Nb_6O_{30}$,[5] and $Sr_4Sm_2Ti_4Nb_6O_{30}$.[6] In general, $M_5RTi_3Nb_7O_{30}$ tends to be relaxation ferroelectric for their disordered distribution of M^{2+} and R^{3+} ions at A1 site, while $M_4R_2Ti_4Nb_6O_{30}$ tends to be normally ferroelectric due to their ordered structure in which M^{2+} and R^{3+} ions properly occupy the A2 and A1 sites with the exception of $Ba_4La_2Ti_4Nb_6O_{30}$[12] and $Sr_4La_2Ti_4Nb_6O_{30}$,[10] which are confirmed as relaxation ferroelectric.

From the view of ion radius, previous work suggests that different dielectric and ferroelectric natures of filled TB are attributed to the ion radius. Both the ion radius of A1 site and the ion radius of A2 site, and especially the ion radius difference between the A1 and A2 sites (ΔR) are the main parameters governing the dielectric nature. Although having the same formula ($M_5RTi_3Nb_7O_{30}$), $Ba_5SmTi_3Nb_7O_{30}$, and $Ba_4CaSmTi_3Nb_7O_{30}$ display obvious different nature. While $Ba_5SmTi_3Nb_7O_{30}$ is relaxation ferroelectric, $Ba_4CaSmTi_3Nb_7O_{30}$ ceramics change to a normal ferroelectric one.[17] For more information on the ferroelectric transition in these materials, aging effects were also investigated for a series of filled TB compounds.[4] Up to now, investigation on $M_4CaRTi_3Nb_7O_{30}$ compounds is really rare. To further understand the microscopic mechanisms, investigation on $M_4CaRTi_3Nb_7O_{30}$ is of essential importance.

In this paper, compared with other reported $M_4R_2Ti_4Nb_6O_{30}$ and $M_5RTi_3Nb_7O_{30}$ compounds, $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics are synthesized. This com-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11174092 and 51002060).

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pound has formula of $M_5RTi_3Nb_7O_{30}$ and has similar ion radius in A1-site to $Sr_4Sm_2Ti_4Nb_6O_{30}$ ceramics as Sm^{3+} and Ca^{2+} have almost the same ion radius, but it has different B-site ion occupation from $Sr_4Sm_2Ti_4Nb_6O_{30}$. Therefore, investigation on this compound could help us explore the influence of A1-site cation and B-site cation variation on ferroelectric property of TB compounds.

2. Experiment

$Sr_4CaSmTi_3Nb_7O_{30}$ Ceramics were prepared by a standard solid-state reaction method.[18] The weighed raw materials were ground for 8 h and calcinated in high-purity alumina crucible at 1100 °C in air for 3 h, followed by a second grinding to reach a homogeneous granulometric distribution. The reground powder was pressed into cylindrical disks of 12 mm in diameter and 1 mm in thickness under a pressure of 30 MPa. The disks were sintered at 1300 °C for 3 h, and then the ceramics were slowly cooled to 1100 °C at a rate of 2 °C/min and then cooled with the furnace.

The X-ray diffraction (XRD) pattern measured by using Cu Kα radiation (Philips X-ray diffractometer) confirms the tetragonal TB structure. The morphology was characterized with a field emission scanning electron microscopy (SEM). Dielectric characteristics were measured with a broadband dielectric spectrometer (Precision Impedance Analyzer 6500B, Wayne Kerr Electronics). Thermal analysis was performed by using a differential scanning calorimetry (DSC) in N_2 atmosphere (Diamond DSC, PerkinElmer Instruments). Room-temperature ferroelectric hysteresis loop was measured by a standard ferroelectric tester (Precision Premier II, Radiant Technology).

3. Results and discussion

Figure 1 shows the XRD pattern of the fully reacted $Sr_4CaSmTi_3Nb_7O_{30}$. The ceramics are found to exhibit a single phase tetragonal TB structure, in agreement with the previous result reported for $Sr_4R_2Ti_4Nb_6O_{30}$ (R = Sm, Eu) ceramics[19] and JCPDS file No. 00-054-0777. From the SEM image (inset of Fig. 1), dense ceramics are obtained with a few pores on the grain boundaries.

The dielectric characteristics and dielectric loss of $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics are shown in Fig. 2(a). There are three dielectric permittivity peaks. A broad high-temperature dielectric permittivity peak appears at about 283 °C, a middle hump arises between 100 °C and 200 °C (Fig. 2(b)), and a low-temperature dielectric relaxor peak occurs below 100 °C. For the high-temperature dielectric permittivity peak, T_{max} corresponding to the maximum permittivity is obviously not dependent on the frequency. Therefore, the dielectric permittivity peak around 283 °C is likely to be related to a diffused normal ferroelectric transition. This diffusive feature may indicate possible compositional variations within the materials at the microscopic scale.[19] The transition temperature is much higher than the transition temperature of $Sr_5SmTi_3Nb_7O_{30}$ (210 °C), while approaches the transition temperature of $Sr_4Sm_2Ti_4Nb_6O_{30}$ (290 °C) reported by Sun.[6] This indicates that the ion radius of A1 site and the ion radius difference between the A1 and A2 sites (ΔR) have significant influence on the transition temperature of TB compounds. In contrast, the effect of B-site ion occupation is negligible. In addition, compared with $Sr_4Sm_2Ti_4Nb_6O_{30}$, A1 sites are occupied by Ca^{2+} and Sm^{3+} ions with different valence for $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics which may increase the strength of perturbation and shorten the polar correlation length.[17] As a result, the ferroelectric transition temperature T_{max} shifts to lower temperature in $Sr_4CaSmTi_3Nb_7O_{30}$.

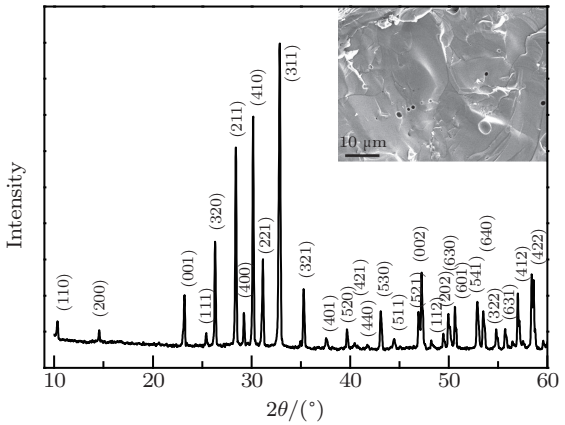


Fig. 1. XRD pattern of $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics. Inset shows the SEM image.

Figure 2(b) shows that the Curie–Weiss fit for the dielectric constant (1 kHz) above 300 °C gives the following parameters: $C = 1.22 \times 10^5$ and $T_0 = 74$ °C, where C is the Curie–Weiss constant. T_{max}–$T_0 = 209$ °C indicates a huge depression of Curie–Weiss temperature T_0. Similar phenomenon has also been observed in $Sr_5EuTi_3Nb_7O_{30}$ and attributed to the complex nature of the tetragonal TB structure.[11] The Curie–Weiss constant with a magnitude of 10^5 could be considered as a signature of a displacive ferroelectric phase transition. Moreover, according to the Curie–Weiss fitting results (see Fig. 2(b)), the permittivity deviates from the Curie–Weiss law at 308 °C, which also indicates the diffuse behavior. Therefore, the phase transition is mainly a displacive transition with some diffusive characteristics.

The middle hump between 100 °C and 200 °C is weak, similar to that in $Ba_5NdCu_{1.5}Nb_{8.5}O_{30}$ ceramics,[20] which may arise from the inhomogeneous structure such as the interfaces between grain boundaries or different phases. The occupation of ions with different valence (Ca^{2+} and Sm^{3+}) at

A1 sites and unequally distributed local electric field cause the local compositional fluctuation.[21]

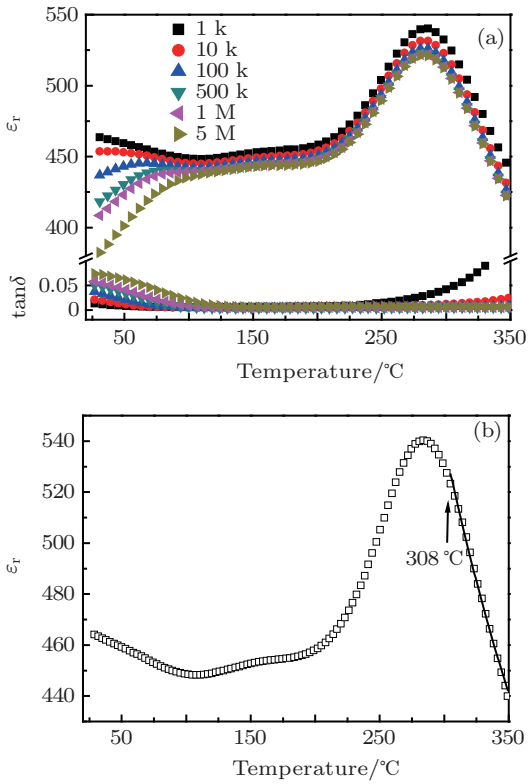


Fig. 2. (color online) (a) Dielectric constant (upper) and dielectric loss (bottom) of $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics. (b) ε_r as a function of temperature measured at 1 kHz fit with Curie–Weiss law.

At temperature below 100 °C, a broad dielectric permittivity peak is observed. The temperature corresponding to the dielectric constant peak of this low-temperature region (T_m) shows a strong frequency dependence, and dielectric loss ($\tan\delta$) shows a similar variation tendency with frequency, indicating a clear low temperature relaxation nature. Low-temperature dielectric relaxation is also seen in many other systems with TB structure, and no matter whether the feature of the ferroelectric transition is normal, diffuse, or relaxor.[7,8,11,15,16,19,22] The Vogel–Fulcher relationship

$$f = f_0 \exp\left[-\frac{E_a}{k_B(T_m - T_f)}\right] \tag{1}$$

is usually used to analyze the frequency dispersion. While in our case, as the low-temperature relaxation peaks are broad and the dielectric constant peaks measured at high frequency even overlapping with the high temperature dielectric constant. The maximal dielectric temperatures are not attainable. Therefore, it is difficult to fit our experimental results with the Vogel–Fulcher formula. To characterize the low-temperature diffusive characteristic, a modified Curie–Weiss relationship[23]

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C'}, \quad 1 \le \gamma \le 2, \tag{2}$$

is applied to measure the dielectric constant at 100 kHz. Here, ε_m is the low-temperature dielectric value at a temperature of T_m, ε_r is the dielectric constant at T, C' is the Curie–Weiss constant of the modified Curie–Weiss formula, and γ is the diffuseness exponent, taking the value between 1 (for normal ferroelectrics) and 2 (for a complete diffuse phase transition), which can also be used to characterize the relaxor behavior. The curve of $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ is shown in Fig. 3. The slope of the fitting curve is used to determine the γ value. The value $\gamma = 1.42$ suggests that the phase transition exhibits an obvious diffuse character, and confirms the low-temperature relaxor feature.

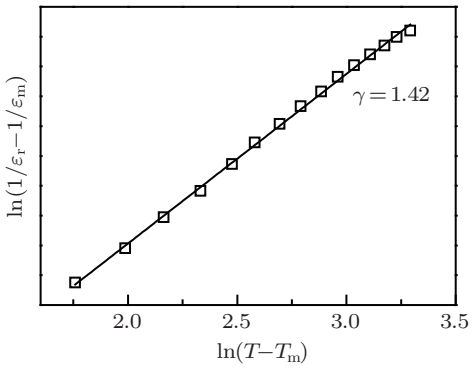


Fig. 3. $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ measured at 100 kHz for $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics.

It was proposed that the freeze-out of the dielectric polarizability in *ab* plane which originates from the Ti/Nb cation displacement is the origin of low-temperature relaxor behavior.[11,19] According to previous reports, $Sr_4Sm_2Ti_4Nb_6O_{30}$ ceramics exhibit an extremely weak low-temperature dielectric relaxation behavior or no low-temperature relaxation behavior in the heating process.[6,19] For present $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics, it is similar to $Sr_5SmT_3Nb_7O_{30}$ ceramics[6] that the low-temperature relaxation feature is obvious. This indicates that the low-temperature relaxation is primarily dominated by the A-site occupation. Compared with $Sr_4Sm_2Ti_4Nb_6O_{30}$ ceramics, $Sr_4CaSmTi_3Nb_7O_{30}$ can be viewed as replacement of a half of Sm^{3+} ions by Ca^{2+} ions in A1 sites. Due to the close ion radius between Sm^{3+} and Ca^{2+} ions ($r^{2+}_{Ca} = 0.099$ nm, $r^{3+}_{Sm} = 0.096$ nm), the effect of ion size is weak. Hence, the enhanced low temperature relaxation should be related to the unequally distributed local electric field caused by that A1 sites are occupied by ions with different valence. The unequally distributed local electric field may affect Ti/Nb cation distribution and their displacement, and hence the low temperature relaxation. Therefore, we can argue that the ferroelectric nature in these filled tungsten bronze niobates originates from the off-center displacement of B-site cations, but the ferroelectric phase transition and the low-temperature dielectric relaxations are primarily dominated by the A1 and A2 site cations and the

site occupation. Both the cation size and the valence of A1-site cations play an important role on the ferroelectric nature of TB compounds.

Figure 4 shows the DSC curves for both heating and cooling processes measured in the temperature range of −50 °C–350 °C. A weak distortion is observed around 255 °C in the heating process (as indicated by the arrow), and it disappears in the cooling process. This phenomenon may be due to the fact that the growth of polar clusters on cooling is much slower. As a result, the macro-ferroelectric domain cannot form during the cooling process. The large depression of T_0 may also reflect the behavior of the polar clusters.[19]

The P–E hysteresis loop of $Sr_4CaSmTi_3Nb_7O_{30}$ measured at room temperature is shown in Fig. 5. The nonlinear hysteresis loop with $P_r = 0.16$ μC/cm^2 and $E_c = 11.74$ kV/cm indicates the existence of spontaneous polarization, which confirms the room temperature ferroelectric nature of $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics.

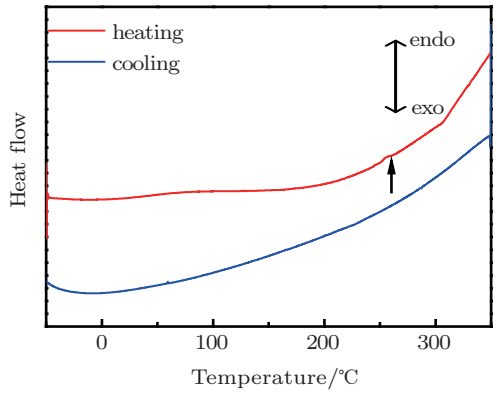


Fig. 4. (color online) DSC results for $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics.

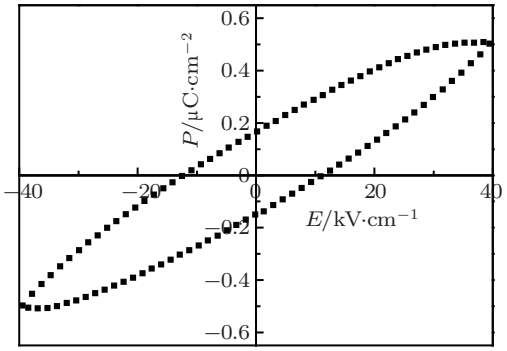


Fig. 5. Polarization (P) as a function of applied electric field (E) measured at room temperature for $Sr_4CaSmTi_3Nb_7O_{30}$.

4. Conclusions

$Sr_4CaSmTi_3Nb_7O_{30}$ ceramics are synthesized and show a pure tetragonal TB crystal structure. Three dielectric anomalies are observed. The phase transition is a displacive phase transition with some diffusive characteristics. The weak distortion disappears in the cooling process for the DSC measurement. The large depression of Curie–Weiss temperature T_0 indicates the difficulty in forming macro-ferroelectric domain. The ferroelectric nature in these filled TB niobates originates from the off-center displacement of B-site cations, but they are primarily dominated by A-site cation occupation. Both the radius and the valence of A1-site cations play an important role on the ferroelectric properties of TB compounds. Existence of P–E hysteresis loop confirms the room-temperature ferroelectric nature of $Sr_4CaSmTi_3Nb_7O_{30}$ ceramics.

Acknowledgments

We appreciate Prof. L. H. Qian for helpful discussion. We would like to thank the staffs of Analysis Center of HUST for their assistance in various measurements.

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