Preparation and dielectric properties of co-contained unfilled tungsten bronze ceramics Ba$_4$RCo$_{0.5}$Nb$_{9.5}$O$_{30}$

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ABSTRACT
In this study, Ba$_4$RCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (R = La, Nd, Sm, Eu) (BRCN) ceramics were synthesized using a high-temperature solid-state reaction. The XRD refinement results show that ceramic samples are tetragonal tungsten bronze (TTB). As the radius of rare-earth ions decreases, the unit cell volume of BRCN ceramics decreases, and the radius difference between Ba$^{2+}$ and R ions increase, which results in BO$_6$ octahedral distortion and the Raman peaks shift to high frequency. In addition, as the radius of rare-earth ions decreases, the ionic displacements increase and thus the dielectric constant peak temperature goes up. The high-temperature impedance results show that there exists n-type electronic conduction in the samples. The remanent polarization of the P–E curve at low frequencies increases from 0.470 to 1.038 μC cm$^{-2}$ as the rare-earth ion radius decreases.

1 Introduction

The tetragonal tungsten bronze (TTB) structure exists multiple ion positions and has a flexible crystal structure, which has aroused extensive research interest. It is the most striking ferroelectric material after the perovskite structure [1–3]. Ferroelectrics, as an essential functional material, have attracted increased attention and research due to their excellent dielectric, pyroelectric, piezoelectric, and photovoltaic properties [4]. The common structure of a TTB can be written as (A1)$_2$(A2)$_4$(C)$_4$(B1)$_2$(B2)$_8$O$_{30}$. TTB cell is composed of corner-connected BO$_6$
octahedra. Where the A-site is usually filled with large-radius ions, B-site generally has a highly coordinated ion filling, and C-site is generally a vacant filling [5, 6]. The complex structure of tungsten bronze compounds allows manual manipulation. The lattice structure can be changed by altering the respective proportions of A-site and B-site ions to further change the electrochemical characteristics.

Hong et al. found that the dielectric constant of the Ba$_x$Sm$_{2}$Fe$_{4-2x}$Ti$_4_x$Nb$_{6+x}$O$_{30}$ ($0 < x < 2$) ceramics reduce with the increase of the element Fe and Nb. In addition, when $x$ is less than 0.5, the sample exhibits relaxor ferroelectric; when the amount of substitution reaches the maximum, normal ferroelectric behavior can be observed [7]. Although iron has an irreplaceable regulating effect, the dielectric loss of iron-containing tungsten bronze structural compounds is relatively high. As a transition element same to Fe, can Co replace iron in the structure of tungsten bronze, thereby reducing dielectric loss and increasing dielectric constant? As the B-site Co$_{3+}$ replaces Fe$_{3+}$ in Ba$_4$Nd$_2$Fe$_2$Nb$_8$O$_{30}$, the dielectric loss decreases obviously [8]. In the Ba$_{4-x}$Sm$_2$Fe$_{2-x}$Nb$_{8+x}$O$_{30}$ series ceramics, with the decrease of Fe and the increase of Nb, the Curie temperature moves to higher temperature [9]. But this is closely related to the decrease of Ba$^{2+}$ doping amount, perhaps more closely related to the ionic radius of the A-site. Introducing Na$^+$ in (Sr$_{0.53}$Ba$_{0.47}$)$_{2.5-0.5x}$Na$_x$Nb$_5$O$_{15}$ ceramics ($0.0 < x < 2.5$) can lead to the stronger crystal structural distortion and restrict vibration space for the ions inside the BO$_6$ octahedra, which will increase the ionic displacements and thus improve the Curie temperature [10]. Zuo et al. found that the distortion caused by the introduction of Ca$^{2+}$ into the A-site of Ba$_4$Nd$_2$Fe$_{1.5}$Co$_{0.5}$Nb$_9$O$_{30}$ ceramic can adjust the dielectric and ferroelectric properties [11]. The incorporation of Ca$^{2+}$ improves the structural distortion and reduces the low-temperature dielectric loss. Under the same electric field conditions, the more Ca$^{2+}$, the greater the remnant polarization. It has been proposed that replacing the A-site atoms in Ba$_3$RZr$_3$Nb$_7$O$_{33}$ (R = La, Nd, Sm) ceramics with rare-earth ions can improve the remnant polarization. As the average ion radius of A1 decreases, the maximum dielectric constant temperature increases. This may be due to the different occupancy of the ions at the A1 position, which will stretch or compress the octahedron, thereby affecting the tilt mode and distortion degree of the octahedron, resulting in different dielectric behaviors [12]. Chen et al. used rare-earth elements (Ln = La, Nd, Sm) to replace the A1-site ions in filled tungsten bronze Ba$_3$SrLn$_2$Fe$_2$Nb$_6$O$_{30}$ ceramics and studied dielectric characteristics. It was found that Ba$_3$SrLn$_2$Fe$_2$Nb$_6$O$_{30}$ demonstrates the characteristics of a relaxing ferroelectric. When the ionic radius decreases, the maximum temperature of the dielectric constant ($T_{\text{max}}$) increases. This is because of the occupancy of different valence and ionic radii in the same position, resulting in the Fe/Nb dipole deviating from the center, and the long-range order at low temperature is disrupted by the distribution field, thus facilitating the formation of relaxor ferroelectrics [13, 14].

In TTB structural ceramics, the A-site ion radius plays a decisive role in its dielectric properties. The dielectric properties of the material can be adjusted by changing the ion radius of the A-site, as well as the position of the dielectric relaxation peak. Most studies on Co-containing TTB structural ceramics have focused on the magnetic properties. There are few studies on the dielectric properties of ceramics after Co-doping with Nb and replacing A-site ions. In this paper, Ba$_4$RCO$_{0.5}$Nb$_{9.5}$O$_{30}$ (R = La, Nd, Sm, Eu) (BRCN) ceramics were synthesized by the high-temperature solid-state method. A systematic study was conducted on the influence of rare-earth ions on the phase structure, microstructure, and dielectric properties of ceramics.

### 2 Experimental procedures

In this experiment, high-purity oxide powders BaCO$_3$ (Aladdin, > 99.99% purity), La$_2$O$_3$ (Ansheng, > 99.99% purity), Nd$_2$O$_3$ (Ansheng > 99.99% purity), Sm$_2$O$_3$ (Ansheng > 99.99% purity), Eu$_2$O$_3$ (Ansheng > 99.99% purity), Co$_2$O$_3$ (Sinopharm > 99.95% purity), and Nb$_2$O$_5$ (Conghua > 99.99% purity) were used as experimental material. Ba$_4$RCO$_{0.5}$Nb$_{9.5}$O$_{30}$ (R = La, Nd, Sm, Eu) ceramics were successfully synthesized by the high-temperature solid-phase reaction. The unmixed powders were ball-milled in nylon jars with zirconia balls for 8 h, dried and pressed into a column, and then calcined for 6 h at 1423 K. After secondary ball milling, 5 wt% polyvinyl alcohol was added as a binder to the prefired powder. After sieving, they were placed in a 5-mm-radius pillar and pressed into sheets of 1 mm thickness at 100 MPa. The sample was heated at...
823 K for 4 h, enabling PVA discharge from the sample. Then, in order to obtain dense ceramics, the ceramics were sintered for 6 h at 1553–1573 K. The two sides of the sintered ceramics were polished and coated with silver paste and then heated at 923 K for 30 min.

The actual density of the ceramic obtained was calculated using the Archimedes method. The ceramics were characterized by PANalytical X’Pert PRO powder diffractometer (XRD) ($\lambda_{CuK\alpha}$ = 0.15406 nm). The Hitachi S-4800 field emission scanning electron microscope (SEM) was used to observe the micro-morphology of the ceramic surface. The Raman spectrum of the ceramics was obtained using the DXR laser confocal microscope (Raman spectrometer, Thermo Fisher Scientific). The laser source was a 532 nm incident light source generated by an Ar ion laser. The Agilent 4294A precision impedance analyzer with TZDM-200-300 temperature control system was used to obtain the dielectric constant and dielectric loss of Ba$_4$RCo$_{0.5}$Nb$_{9.5}$O$_{30}$ ceramics at different frequencies (100 Hz to 1 MHz) and at varying temperatures (98 K to 523 K). The alternating current (AC) impedance spectra at different frequencies are shown in Fig. 3. With the increase of temperature, the dielectric constant at a low frequency is relatively unstable, and the frequency dispersion phenomenon occurs at high temperature. The temperature of the maximum dielectric constant ($T_m$) of BLCN and BECN ceramics differs by more than 100 K. Table 3 lists the $T_m$ and $\varepsilon_r$ of the dielectric constant peaks of BRCN ceramics measured at specific frequencies and the value by calculating $T_m$ of 1 MHz minus $T_m$ of 10 kHz. The dielectric behavior of ceramics is affected by the ionic radius of the A1 position. As the radius of rare-earth ions decreases, the $T_m$ difference between high frequency and low frequency becomes smaller, and the dielectric constant peak presents a wider relaxation peak. The decrease of the ionic radius will not only cause the change of the lattice structure but also increase the ion oscillation space inside the BO$_6$ octahedra [16], as $T_m$ of all samples gradually move toward higher temperature. In addition, when the temperature rises, the dipoles in the ceramics gradually unify under the action of external electric field, which will aggravate the collision between the dipoles and lead to an increase in conductance loss. Some studies have shown that the appearance of dielectric loss is also related to the thermal activation energy of carriers [17, 18].

In order to make the abnormal dielectric peak more significant, we focus on the dielectric constant of the BRCN ceramics measured at the test frequency of 1 MHz minus $T_m$.

3 Results and discussion

We used Fullprof software to refine the XRD patterns of BRCN ceramics, and the results are shown in Fig. 1a–d. It can be seen that rare-earth ions and Ba$^{2+}$ ions occupy A1-sites and A2-sites, respectively, while Co$^{3+}$ and Nb$^{5+}$ ions occupy B1-sites and B2-site positions randomly. All ceramic samples crystallize in the TTB structure with space group $P4_{2}m$ and no secondary phase is observed. We calculated the cell parameters and R factor values as shown in Table 1. Then the crystallographic information file (cif) of the structure was used to draw the cell structure, as shown in Fig. 1e. Table 2 lists the tolerance factor and electronegativity of the ceramics as calculated. With the A2-site tolerance factor ($t_{A2}$) invariant, a decrease in the radius of the rare-earth ion leads to a gradual decrease in the A1-site tolerance factor ($t_{A1}$), the overall tolerance factor ($t$), and the electronegativity difference ($\delta$) of the BRCN ceramics. The closer the tolerance factor is to 1 and the smaller the electronegativity, the more stable the structure [15]. Therefore, the decrease in radius of rare-earth ions results in reduced stability of Co-substituted tungsten bronze structural ceramics.

Figure 2a–d are SEM images of BRCN ceramics as-sintered surface. As the ionic radius decreases, their apparent size decreases slightly. The figure shows that the surface grains of all samples are closely packed columnar grains, indicating that all samples have good compactness. The tested densities of all the samples are 5.44, 5.60, 5.50, and 5.54 g cm$^{-3}$. Moreover, the relative densities of the Ba$_4$LaCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BLCN), Ba$_4$NdCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BNCN), Ba$_4$SmCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BSCN), and Ba$_4$EuCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BECN) ceramics are 97.7%, 99.6%, 97.7%, and 98.1%, respectively.

The dielectric constant and loss of BRCN ceramics related to different frequencies are shown in Fig. 3. Figure 2a–d are SEM images of BRCN ceramics as-sintered surface. As the ionic radius decreases, their apparent size decreases slightly. The figure shows that the surface grains of all samples are closely packed columnar grains, indicating that all samples have good compactness. The tested densities of all the samples are 5.44, 5.60, 5.50, and 5.54 g cm$^{-3}$. Moreover, the relative densities of the Ba$_4$LaCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BLCN), Ba$_4$NdCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BNCN), Ba$_4$SmCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BSCN), and Ba$_4$EuCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (BECN) ceramics are 97.7%, 99.6%, 97.7%, and 98.1%, respectively.
1 MHz and the temperature range of 101–523 K, using the Curie–Weiss law (Eq. 1) [12] to fit in Fig. 4:

$$\varepsilon_r = C/(T - T_0),$$

(1)

where $C$ is the Curie–Weiss constant and $T_0$ is the Curie–Weiss temperature. The Curie–Weiss constants $C'$ and $C$ reflect the slope of the reciprocal of the dielectric constant below and above $T_m$ as temperature change. As shown in Fig. 4, the $C$ values of BLCN, BNCN, BSCN, and BECN ceramic samples are $0.862 \times 10^5$, $0.532 \times 10^5$, $0.437 \times 10^5$, and $0.467 \times 10^5$, respectively. Their order of magnitude is
close to $10^5$, indicating that all samples are displacement type ferroelectrics [19]. Under normal circumstances, the ratio of $C/C'$ greater than 4 is the first-order ferroelectric phase transition, while less than 4 is usually the second-order ferroelectric phase transition. The $C/C'$ values of BRCN ceramics were 2.19, 2.60, 2.36, and 1.81, respectively, indicating that all specimens present second-order ferroelectric phase transition characteristics. Additionally, BLCN, BNCN, BSCN, and BECN ceramic samples' dielectric constant fitting reciprocals deviate from the Curie-Weiss law at 251.54 K, 269.01 K, 303.45 K, and 335.92 K, respectively. These four temperatures that deviate from $T_m$ are defined as the Burns temperature.

### Table 1

| Sample  | $a$ (Å)   | $c$ (Å)   | $V_{\text{unit}}$ (Å$^3$) | $c/a$ | $R_p$ (%) | $R_{wp}$ (%) | $\chi^2$ |
|---------|-----------|-----------|---------------------------|-------|-----------|--------------|-----------|
| BLCN    | 12.5128(5)| 3.9559(2) | 619.39(4)                | 0.3162| 3.38      | 4.37         | 6.48      |
| BNCN    | 12.4921(6)| 3.9477(2) | 616.06(5)                | 0.3160| 3.83      | 5.57         | 7.14      |
| BSCN    | 12.4814(5)| 3.9447(2) | 614.53(4)                | 0.3160| 3.20      | 4.61         | 6.94      |
| BECN    | 12.4811(4)| 3.9464(1) | 614.76(3)                | 0.3162| 3.26      | 4.78         | 7.94      |

### Table 2

| Sample  | $t_{A1}$ | $t_{A2}$ | $t$ | Electronegativity difference ($e$) |
|---------|----------|----------|-----|-----------------------------------|
| BLCN    | 0.957    | 0.998    | 0.984 | 2.073                             |
| BNCN    | 0.926    | 0.998    | 0.974 | 2.063                             |
| BSCN    | 0.916    | 0.998    | 0.971 | 2.055                             |
| BECN    | 0.905    | 0.998    | 0.967 | 2.048                             |

Fig. 2 SEM images of the a Ba$_4$LaCo$_{0.5}$Nb$_{9.5}$O$_{30}$, b Ba$_4$NdCo$_{0.5}$Nb$_{9.5}$O$_{30}$, c Ba$_4$SmCo$_{0.5}$Nb$_{9.5}$O$_{30}$, d Ba$_4$EuCo$_{0.5}$Nb$_{9.5}$O$_{30}$ ceramics.
Fig. 3 Temperature dependence of dielectric constant ($\varepsilon_r$) and dielectric loss ($\tan\delta$) of the a Ba$_4$LaCo$_{0.5}$Nb$_{9.5}$O$_{30}$, b Ba$_4$NdCo$_{0.5}$Nb$_{9.5}$O$_{30}$, c Ba$_4$SmCo$_{0.5}$Nb$_{9.5}$O$_{30}$, and d Ba$_4$EuCo$_{0.5}$Nb$_{9.5}$O$_{30}$ ceramics.

Table 3 Temperature and value of dielectric constant peak for Ba$_4$RCo$_{0.5}$Nb$_{9.5}$O$_{30}$ (R = La, Nd, Sm, and Eu) ceramics at various test frequencies

| Sample | $T_m$ (K)/$\varepsilon_r$ (10kHz) | $T_m$ (K)/$\varepsilon_r$ (100kHz) | $T_m$ K)/$\varepsilon_r$ (1MHz) | $T_m$ (1 MHz) $- T_m$ (10 kHz) |
|--------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| BLCN   | 198/402.70                      | 219/391.07                      | 248/392.52                      | 50                              |
| BNCN   | 228/432.30                      | 240/423.23                      | 265/430.10                      | 37                              |
| BSCN   | 268/532.10                      | 283/518.68                      | 302/527.85                      | 34                              |
| BECN   | 316/530.84                      | 327/516.24                      | 340/520.45                      | 24                              |
A deviation from temperature is generally considered to occur in a range below the $T_B$, which is likely due to the structural fluctuations caused by the ionic vibrations of polarization in tungsten bronze ceramics. This disrupts the long-range order of the dipoles, resulting in strong fluctuations in the nanometer zone, and hence the dielectric constant curve deviates from Curie's law.

Based on the results of the above analysis, we infer that when the temperature rises to the vicinity of the Burns temperature, the dielectric constant curve begins to deviate from the Curie–Weiss law. The deviation signifies that there is a dispersion phenomenon in the dielectric constant peak of BRCN ceramics. To further investigate this dispersion phenomenon, we can obtain the dispersion index ($\gamma$) through the revised Curie–Weiss law [21], and the formula is

$$\ln \left( \frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} \right) = \gamma \ln(T - T_m) + C,$$

where $\varepsilon$ is the dielectric constant, $\varepsilon_m$ is the maximum value of the dielectric constant, and $C$ is the Curie constant. Figure 5a–d shows the functional relationship between $\ln(1/\varepsilon - 1/\varepsilon_m)$ and $\ln(T - T_m)$ of BRCN ceramics at 1 MHz frequency. As shown in the figure, the $\gamma$ values were obtained from Eq. 2, which are 1.38, 1.46, 1.69, and 1.71, respectively. $\gamma$ value is between 1 and 2. When $\gamma = 1$, the ceramics belong to normal ferroelectrics, and when $\gamma = 2$, the ceramics are ideal relaxor ferroelectric. When the radius of rare-earth ions increases in the A-sites' substitution, BRCN ceramics’ $\gamma$ value increases gradually, exhibiting an increase in the dispersion degree of the sample.

To further investigate the effect of the rare-earth ions on the conductivity of the BRCN ceramics, impedance was employed, as shown in Fig. 6a–d. It is
an excellent method to test the electrical properties of tungsten bronze structure, and it can simulate the equivalent circuit by using grain and grain boundary and electrode contact surface. The response of a single volume element can be described using a semi-circular arc [22, 23]. We use AC impedance plots to measure and analyze the contribution of charge transport at different rare-earth ions of BRCN ceramics. All impedance spectrum curves are incomplete semi-circular arcs, and the center of all semicircles is not on the real axis, but below the real axis, indicating that the relaxation of the ceramic sample are non-Debye relaxation in the frequency range of our study [24, 25].

Figure 7a–d shows the normalized imaginary part of impedance ($Z''$) curve of BRCN ceramics at different temperatures with the change frequency. As shown in Fig. 7a–d, the curves of the normalized imaginary parts of the impedance at different temperatures vary with the frequency, exhibiting the symmetric peak, and the corresponding frequency of the symmetric peak is the relaxation frequency. When the temperature increases, the normalized peak shifts to the high-frequency direction, indicating that the relaxation experienced by all samples is the relaxation behavior of thermal activation. This may be due to the free transport of carriers and the space charge in grain boundaries causing the carrier transition between adjacent lattice points. Researchers usually use the Arrhenius equation (Eq. 3) to describe the relationship between relaxation frequency and temperature [26, 27]:

$$f_{\text{max}} = f_0 \exp \left( - \frac{E_{\text{rel}}}{k_B T} \right),$$  \hspace{1cm} (3)
where \( f_0 \) is the pre-factor, \( E_{\text{rel}} \) is the relaxation activation energy, and \( k_B \) refers to the Boltzmann constant. As shown in Fig. 7e, the relaxation activation energies of BRCN ceramics are 0.87 eV, 0.83 eV, 0.81 eV, and 0.91 eV, respectively, through the linear fitting of the Arrhenius equation.

Figure 8a–d shows the relationship among the AC conductance of BRCN ceramics that change with frequency at four specific temperatures. From the graph, we can determine that the AC conductance of all samples demonstrate dispersion phenomena moving toward higher frequency with the increase of test temperature. Furthermore, we can see that the AC conductance of all ceramic samples decrease with the decrease of frequency and eventually tend to be stable at a specific frequency, almost unchanged. These indicate that direct current (DC) conductance are dominant at this time. In the specific temperature change and frequency range, the relationship between conductance and frequency follows the "dielectric universal response" (UDR) rule [28]. The formula is as follows:

\[
\sigma_{\text{dc}} = \sigma_{0} + A \omega^{n} \quad (0 < n < 1),
\]

where \( \sigma_{\text{dc}} \) is the DC conductance, \( A \) is the temperature-dependent constant, \( \omega \) is the frequency, and \( n \) is the exponent dependent on frequency and temperature. This formula describes the processes and phenomena of the interaction between dipoles and charges. Therefore, the relationship between DC conductance and temperature also follows the equation (Eq. 5) [29]:

\[
\sigma_{\text{dc}} = \sigma_{0} \exp\left(-E_{\text{dc}}/k_B T\right),
\]

where \( \sigma_{0} \) is the pre-factor, \( E_{\text{dc}} \) is the activation energy of DC conductivity, and \( k_B \) is the Boltzmann constant. As shown in Fig. 8e, we have obtained the DC conductance activation energy of BRCN ceramics by 0.82 eV, 0.76 eV, 0.74 eV, and 0.83 eV by the Arrhenius equation. The change trend of the DC conductance activation energy of all ceramics keeps up with the relaxation activation energy: as the radius of rare-earth ions decreases, the DC conductance activation energy increases first and then decreases. The DC conductance activation energy is caused by the
generation of charge carriers and the long-range migration or hopping of charge carriers.

In order to further prove the conduction mechanism, we measured the impedance at low frequency. Fig. S1 shows the impedance diagrams of sample BLCN recorded under different oxygen partial pressure ($p_{O_2}$) conditions at 873 K and 923 K. Fig. S1(a) shows that the impedance under $H_2$ is significantly lower than the sample in other atmospheres. When tested at 923 K in the $H_2$ atmosphere, we found that the sample was reduced (Impedance diagram appears in the fourth quadrant, inductance arc appears at low frequencies [30]). In Fig. S1(b), the impedance arc is still semicircular. The result shows...
that the volume resistance corresponding to the high-frequency arc is almost the same in the pure oxygen atmosphere and a low $pO_2$ of $10^{-4}$ atm. Electron conduction is considered to be the main conduction mechanism of electrode resistance, oxide-ion transport number ($t_{\text{ion}}$) as small as almost 0 [31]. In addition, the response tail of the Warburg-type electrode should be able to be observed if it is oxide ion conduction. But it does not appear in this figure, so the possibility of oxide ion conduction is ruled out at low frequencies. In Fig S1(c), the conductivity of the sample is almost unchanged under $N_2$ and $O_2$. But when the sample is reduced under $H_2$, the conductivity drops dramatically; this is associated with Co$^{3+}$ reduction, and conductors are extra free electrons. XPS results showed in Fig. S1(d) confirm the conjecture. These results indicate that the sample is n-type electrically conductive [32, 33].

Fig. 8 AC conductivity ($\sigma_{ac}$) at different temperatures of the a $\text{Ba}_4\text{LaCo}_{0.5}\text{Nb}_{9.5}\text{O}_{30}$, b $\text{Ba}_4\text{NdCo}_{0.5}\text{Nb}_{9.5}\text{O}_{30}$, c $\text{Ba}_4\text{SmCo}_{0.5}\text{Nb}_{9.5}\text{O}_{30}$, and d $\text{Ba}_4\text{EuCo}_{0.5}\text{Nb}_{9.5}\text{O}_{30}$ ceramics; the frequency dependence of the e DC conductivity ($\sigma_{dc}$) obtained from fitting universal Arrhenius to the AC conductivity.
The ceramics’ room-temperature Raman spectra with wavenumber in the range of 50–1200 cm\(^{-1}\) are shown in Fig. 9. All samples’ Raman spectra are similar, with three characteristic peaks near 250, 630, and 840 cm\(^{-1}\). According to the relevant literature, typical TTB compounds have two vibration modes near the Raman peaks: the O–B–O bending vibration mode (\(v_5\)) exists at 250 cm\(^{-1}\) and the B–O stretching vibration mode (\(v_2\) and \(v_1\)) exists at 630 and 840 cm\(^{-1}\). When the wave number is less than 200 cm\(^{-1}\), the Raman displacement is related to the movement of Ba\(^{2+}\) ions, which is the BO\(_6\) octahedra external vibration mode. When the wave number is greater than 200 cm\(^{-1}\), the Raman displacement is related to the internal vibration mode of the octahedra [17].

4 Conclusion

Ba\(_4\)RCo\(_{0.5}\)Nb\(_{9.5}\)O\(_{30}\) (R = La, Nd, Sm, Eu) unfilled tungsten bronze structural ceramics were prepared by high-temperature solid-state synthesis. The effects of different rare-earth ions on the phase structure, microstructure, and dielectric properties of ceramics were studied. Room-temperature XRD analysis showed that the tetragonal unfilled TB structure in space group \(P4bm\) is obtained for BRCN ceramics, rare-earth ions occupying A1-sites. As the radius of the substituted ion at the A-site decreases, the \(T_m\) moves to higher temperature, and the dielectric dispersion phenomenon becomes more obvious. Typical relaxation ferroelectric phase transition characteristics are observed in BRCN ceramics. Through high-temperature impedance analysis, it is determined that all the ceramics are n-type electronic conduction. All samples have undergone thermal activation relaxation behavior, among which BSCN has the highest relaxation activation energy, which is also proved by the DC conductance activation energy fitted by the Arrhenius equation. Raman spectroscopy shows that the Raman peaks shift to high wave numbers as the radius of rare-earth ions decreases, indicating that the distortion of BO\(_6\) octahedra is slightly increased. The remanent polarization of the P–E curve at low frequencies increases.
from 0.470 to 1.038 μC cm−2 as the rare-earth ion radius decreases.

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