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Oxygen-vacancy-related dielectric relaxation in $SrBi_2Ta_{1.8}V_{0.2}O_9$ ferroelectrics

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The strontium bismuth tantalate vanadate, $SrBi_2Ta_{1.8}V_{0.2}O_9$, (SBTV) layered perovskite ferroelectrics were made by solid state powder sintering. It was found that the SBTV ferroelectrics had the same crystal structure as that of strontium bismuth tantalate, $SrBi_2Ta_2O_9$ (SBT), but an increased paraferroelectric transition temperature at ~360 °C as compared to 305 °C for SBT. In addition, SBTV ferroelectrics showed a frequency dispersion at low frequencies and broadened dielectric peaks at the paraferroelectric transition temperature that shifted to a higher temperature with a reduced frequency. However, after a postsintering annealing at 850 °C in air for 60 h, SBTV ferroelectrics showed reduced dielectric constants and tangent loss, particularly at high temperatures. In addition, no frequency dependence of paraferroelectric transition was found in the annealed SBTV ferroelectrics. Furthermore, there was a significant reduction in dc conductivity with annealing. The prior results implied that the dielectric relaxation in the as-sintered SBTV ferroelectrics was most likely due to the oxygen-vacancy-related dielectric relaxation instead of relaxor ferroelectric behavior. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1366657]

I. INTRODUCTION

Layered perovskite strontium bismuth tantalate, $SrBi_2Ta_2O_9$, (SBT) is one of the most promising fatigue free characteristic ferroelectrics for nonvolatile digital information memory devices.[1–3] The dielectric and ferroelectric properties of the SBT system have been widely studied in the form of bulk materials and thin films, and a sharp dielectric constant peak corresponding to a paraferroelectric transition was reported in the range of 300–320 °C.[4–6] It has been found that small changes in chemical composition, such as strontium deficiency and/or excess bismuth, results in enhanced dielectric and ferroelectric properties including dielectric constant and remanent polarization.[7–9] In a related system, strontium bismuth niobate, $SrBi_2Nb_2O_9$ (SBN), partial substitution of pentavalent niobium ions, Nb^{5+}, with smaller pentavalent vanadium ions, V^{5+}, resulted in enhanced dielectric and ferroelectric properties including both dielectric constants and remanent polarization, which was attributed to an increased ''rattling space'' inside the oxygen octahedra.[10,11] Furthermore, partial substitution of strontium with other cations such as calcium and lanthanium in SBN ferroelectrics was reported to have modified dielectric and electric properties including enhanced paraferroelectric transition temperature and reduced electrical conductivity.[12] Partial substitution in perovskite ferroelectrics may also result in the formation of a heterogeneous microstructure that consists of microdomains that have slightly different chemical compositions. These microdomains with various chemical compositions will have different paraferroelectric transition temperatures, and thus lead to a broadened dielectric peak at the transition temperature.[13] In addition, the paraferroelectric transition of such ferroelectrics varies characteristically with frequency. Such ferroelectrics are known as relaxor ferroelectrics, and typical examples include $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN).[14,15] Although common relaxors have isotropic perovskite structures, dielectric relaxation has also been reported in layered perovskite ferroelectrics. For example, there are reports on the relaxation process below the Curie point in bismuth titanate ceramics and single crystals.[16] Another example is the SBN system with Bi-site substitution by tellurium and strontium by sodium or potassium. A second maximum in the dielectric constant caused by doping is found at higher temperature possibly corresponding to a relaxor ferroelectric.[17]

This article reports the electrical and dielectric properties of the SBTV ferroelectrics. Dielectric constants and tangent loss of SBTV ferroelectrics have been studied as functions of frequency and temperature. Postsintering annealing at 850 °C in air for 60 h was conducted to study the influences of oxygen-vacancy-related dielectric relaxation. In addition, dc conductivity of both as-sintered and annealed SBTV ferroelectrics were analyzed, in order to determine the change of oxygen vacancies with postsintering annealing. The mechanism for the dielectric peak broadening and frequency dispersion in the as-sintered SBTV ferroelectrics has been discussed.

II. EXPERIMENT

Polycrystalline strontium bismuth tantalate vanadate ceramic samples with compositions of $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Ta_{1.8}V_{0.2}O_9$ (SBTV) were prepared by solid state reaction sintering. The process carried out was similar to the procedure applied in the preparation of strontium bismuth niobate vanadate ferroelectrics.[10,11] The starting materials

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used were $SrCO_3$, Bi_2O_3, V_2O_5, and Ta_2O_5 (all with a purity of 99%, Aldrich Chem. Co.). The powders were admixed with the desired molar ratio. Approximately 3.5 wt % excess Bi_2O_3 was added, which was to compensate weight loss of Bi_2O_3 due to its high vapor pressure (750 mm Hg at 1570 °C).[18] Powders were ball milled and then fired in air for 2 h at 850 °C for SBTV and 1000 °C for SBT. The fired powders were ground, admixed with about 1–1.5 wt % polyvinylalcohol (PVA, average M.W.=50 000–85 000, Aldrich Chem. Co.) as a binder and pressed into pellets by uniaxial pressing at ~250 MPa. The pellets were sintered in closed crucibles at 1000 °C for SBTV and 1200 °C for SBT for 2 h in air. The total weight loss was found to be around 7 wt %, including the loss of CO_2 as a result of calcination of $SrCO_3$, the pyrolysis of PVA binder, and the evaporation of the relatively volatile Bi_2O_3. The loss of Bi_2O_3 is estimated to be 2.7 wt %, below the 3.5 wt % excess Bi_2O_3 initially added into the system. Annealing at 850 °C in air for various periods of time was applied to study the oxygen vacancy-related dielectric relaxation.

Phase formation and crystallinity of the sintered samples were characterized by means of x-ray diffraction (XRD) using Cu $K\alpha$ radiation. Microstructures of both samples were analyzed by optical microscopy and scanning electron microscopy (SEM, JSM 5200). For the electrical property measurements, the sintered pellets (~10 mm in diameter) were polished to a thickness of ~1 mm and electroded with silver paste on both sides and cured at 550 °C for 30 min on a hot plate. The dc electrical conductivity was measured at temperatures ranging from 300 to 600 °C using a FLUKE 8842A multimeter (John Fluke Inc.). The dielectric properties and ac conductivity measurements were carried out in the temperature range from 20 to 600 °C at various frequencies using a Hewlett-Packard 4284A Precision LCR meter (Hewlett-Packard Co.) with a signal voltage of 50 mV.

III. RESULTS AND DISCUSSION

Both SBT and SBTV samples had dense microstructures with ~95% theoretical density. XRD analyses indicated both SBT and SBTV ceramics consisted of a single layered perovskite phase with no detectable secondary phase. This indicates that the layered perovskite structure of SBT was preserved with partial substitution of tantalum ions by vanadium ions up to 10 at. %. Although the radius of pentavalent vanadium ions are significantly smaller than that of pentavalent tantalum ions, no appreciable change of lattice constants was found from the XRD spectra. The presence of $Bi_2O_2^{2+}$ layers might impose a restriction to prevent the possible reduction of lattice constants. Similar results were found in the SBNV system with less than 15 at. % vanadium substitution.[19] SEM observation revealed that SBT ceramics showing larger grain size (~2 μm) than that of SBTV ferroelectrics (~1 μm). This is possibly due to the higher sintering temperature used for the SBT system.

Figure 1 shows the dielectric constants of both SBT and SBTV ceramics as a function of temperature measured at 100 kHz. The SBT sample shows a typical paraelectric–ferroelectric transition at 305 °C with a peak dielectric constant of ~400, whereas the SBTV sample has a broad peak around 364 °C with a maximal dielectric constant of 454. In addition, the dielectric constant of the SBTV sample at temperatures above the paraferroelectric transition is significantly higher than that of SBT sample. Higher transition temperature and enhanced maximal dielectric constant at the transition temperature could be attributed to the partial substitution of pentavalent tantalum ions (Ta^{5+}: 69 pm[20]) by smaller pentavalent vanadium ions (V^{5+}: 59 pm[20]) in the B sites in the layered perovskite structure. Similar results were found in the SBN system when partial pentavalent niobium ions were substituted by pentavalent vanadium ions.[10,11] However, the appreciably broadened dielectric peak at the transition temperature and significantly enhanced dielectric constants at temperatures above the transition point of the SBTV sample were not found in the SBNV system. Two possible mechanisms may explain the broadened dielectric constant of the SBTV ferroelectric material at the transition temperature. One is that the partial substitution of tantalum ions by vanadium ions in the B sites in the layered perovskite structure results in the formation of heterogeneous domains, which have various transition temperatures just like isotropic perovskite relaxors such as $Pb(Mg_{1/3}Nb_{2/3})O_3$.[21] Another possible explanation is due to the defect relaxation at elevated temperatures, which has been found in bismuth-doped strontium titanate system.[22] More experiments were carried out in order to get a better understanding of the dielectric properties of the SBTV system.

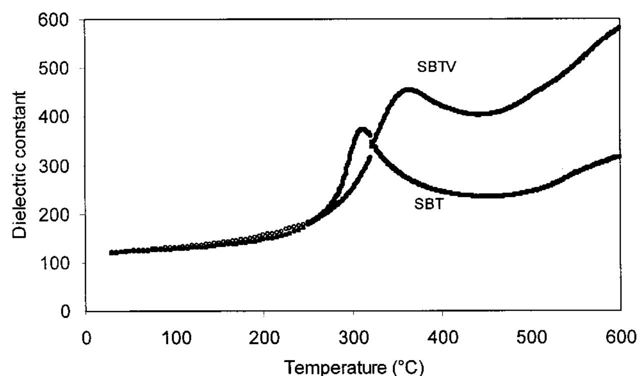

FIG. 1. Dielectric constants vs temperature for SBT and SBTV ceramics at 100 kHz.

Figure 2 shows the dielectric constants of SBTV ferroelectrics as a function of temperature measured at different frequencies ranging from 500 Hz to 500 kHz. At high frequencies, there is a broad peak, whereas at 500 Hz, the broad peak is almost completely shadowed by a gradual increased dielectric constant with an increasing temperature. The paraferroelectric transition temperature is found to increase with a reduced frequency. Another important observation is that the dielectric constants at low temperatures are the same regardless the frequencies used for the measurements, whereas the dielectric constants at high temperatures vary markedly. As the frequency changes from 500 Hz to 500 kHz, the dielectric constants of SBTV at 600 °C reduced from ~4800 to ~400, one order of magnitude reduction. The above results

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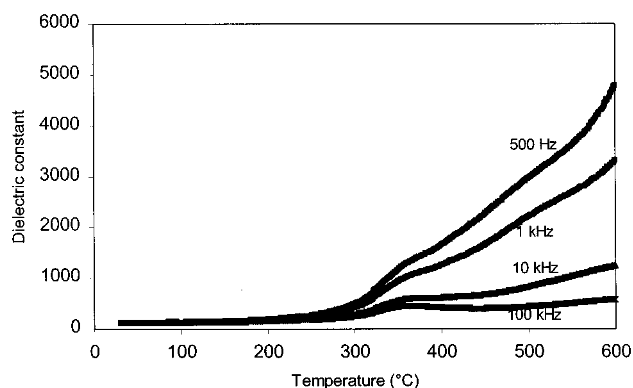

FIG. 2. Dielectric constants vs temperature for SBTV (10 at. % V) ceramics at various frequencies.

imply that there might be an extra mechanism contributing to dielectric polarization at high temperatures, but not at low temperatures. Figure 3 depicts the dielectric constants and tangent loss of SBTV sample as a function of temperature with two frequencies 10 and 100 kHz. The figure shows that the transition temperatures are 378 and 364 °C at 10 and 100 kHz, respectively. The tangent loss increases with temperature; however, the change at 10 kHz is significantly faster than that at 100 kHz. Since the temperature of the dielectric constant maximum shifting to higher temperatures with an increasing frequency has been reported as one characteristic of relaxors,[23–25] this negative shift might not come from the relaxor ferroelectric. Besides, the significantly enhanced dielectric constants with a reduced frequency at high temperatures could not be explained. Defect induced dielectric relaxation would be directly related to the concentration of defect.[26] In the present systems, the defects would be related to the oxygen vacancies. The significantly enhanced dielectric constant at high temperatures may be due to the mobile charge carriers, which may be related to the oxygen vacancies. It is well known that the oxygen vacancies play an important role in the electrical polarization of perovskite materials.[22] Oxygen vacancy induced polarization becomes more predominant at high temperatures due to an increased vacancy concentration, and low frequencies due to the inertia of oxygen ions. This explains the significantly enhanced dielectric constants at high temperatures with a low frequency. The observed ''negative shift'' of apparent paraferroelectric transition temperatures could also be explained as a result of an overlap of the true paraferroelectric transition dielectric constant peak with the increasing defect induced dielectric relaxation at high temperatures. However, the overlap made it difficult to precisely determine the true transition temperature.

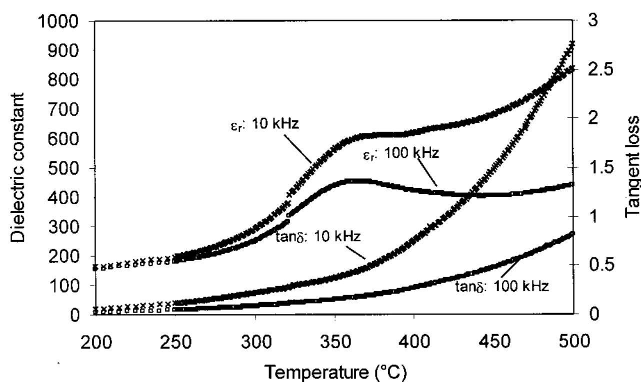

FIG. 3. Dielectric constants and tangent loss of SBTV (10 at. % V) ceramics vs temperature at 10 k and 100 k Hz.

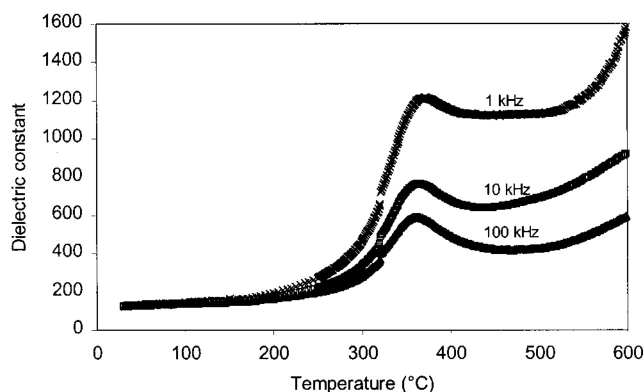

FIG. 4. Dielectric properties of 60 h annealed samples at 1 k, 10 k, 100 kHz (from top to bottom).

Defect induced dielectric relaxation would be directly related to the concentration of defects, which in the present system would be related to the oxygen vacancies. It is known that the oxygen vacancy concentration would change with the postsintering annealing. The change would depend on the annealing temperature, gas atmosphere, and the materials in question. For example, an appreciable change of the oxygen vacancy concentration was found in the SBNV system with postsintering annealing at various atmospheres.[27] In this work, the as-sintered SBTV ceramic sample was annealed at 850 °C for 60 h in air to lower the concentration of oxygen vacancies. Since the annealing temperature is much lower than the sintering temperature, SEM images showed there was no detectable change in the microstructure including grain size and porosity of the SBTV sample before and after annealing. Figure 4 shows the dielectric constants of the SBTV sample annealed in air at 850 °C for 60 h as a function of temperature at frequencies of 1 k, 10 k, and 100 kHz. In comparison with the data in Fig. 2, the dielectric constants of the annealed SBTV sample at high temperatures are lower than that of as-sintered SBTV sample, particularly measured with low frequencies. However, the dielectric constants at temperatures below the paraferroelectric transition remain more or less unchanged. In addition, the transition temperature of the annealed SBTV sample is found to be independent of frequency, whereas the transition temperature shows a negative shift with an increasing frequency for the as sintered SBTV. The above results could be attributed to a reduced concentration of oxygen vacancies by the annealing. Thus the broadening of the dielectric peak and the shift of paraferroelectric transition of as-sintered SBTV ferroelectrics are most likely due to the defect-induced-dielectric relaxation as reported in the Bi-doped $SrTiO_3$ system,[22] not a

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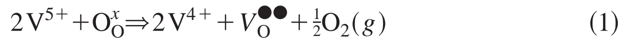
result of diffused phase transition as that in a relaxor ferroelectric.

In the SBTV system, oxygen vacancies could be generated during the sintering and due to the presence of the reduced valence state of vanadium ions. Although it is intended to partially substitute pentavalent tantalum ions, Ta^{5+}, with pentavalent vanadium ions, V^{5+}, in the B sites of the layered perovskite structure, tetravalent vanadium ions, V^{4+}, may form and enter the crystal structure as found in the SBNV system.[19] One oxygen vacancy will form with two tetravalent vanadium ions entering the crystal structure, in order to keep the electroneutrality, and the overall reaction could be described using Kroger–Vink notation:



$$2V^{5+}+O_O^x \Rightarrow 2V^{4+}+V_O^{\bullet\bullet}+\tfrac{1}{2}O_2(g) \quad (1)$$

where $V_O^{\bullet\bullet}$ is the oxygen vacancy with two effective positive charges and O_O^x is the oxygen ion in oxygen site with zero effective charge. It is known from thermodynamics, that annealing at lower temperature would result in further oxidation of low valence-state ions, provided that the atmosphere gas remains unchanged. In the present study, when V^{4+} is further oxidized to V^{5+} during annealing at 850 °C in air, the system will intake oxygen from air to fill the oxygen vacancy. The reaction will be the opposite direction of reaction (1). Decrease of oxygen vacancies as a result of annealing at 850 °C in air for 60 h, would lead to an appreciable decrease in oxygen vacancy related dielectric relaxation.

Contribution to the dielectric constant from the oxygen vacancy induced dielectric relaxation is significantly larger at high temperatures than that at low temperatures, particularly below the paraferroelectric transition. Oxygen vacancy induced dielectric relaxation is a diffusion-related process, which is an activated process and exponentially dependent on temperature. At lower temperatures, there is not enough energy to overcome the diffusion energy barrier and the oxygen vacancy induced dielectric relaxation is negligible. At high temperatures, there is sufficient energy and the contribution of the oxygen vacancy induced dielectric relaxation becomes significant. In addition, the paraferroelectric transition is also a crystal structure transition. At temperatures higher than the transition point, SBTV has a layered tetragonal structure, whereas below the transition, it has an orthorhombic structure.[28] For a given system, tetragonal structure imposes lower activation energy, in comparison with the orthorhombic or other lower symmetric structure.

The annealing at 850 °C in air for 60 h did not result in a distinct shift of the paraferroelectric transition temperature of SBTV ferroelectric as was found in the SBNV system.[27] This difference may be the result of the difference in annealing conditions used in two systems. In the SBNV system, pure oxygen and pure nitrogen gases were used to further oxidize or reduce the vanadium ions, in order to significantly increase or reduce the concentration of oxygen vacancies. In this study, air was used for the annealing. Thus, the change in oxygen vacancy concentration would not be as pronounced as that in the SBNV system annealed in either oxygen or nitrogen. Consequently, the concentration change of penta- and tetravalent vanadium ions would be relatively small. The possible change of paraferroelectric transition

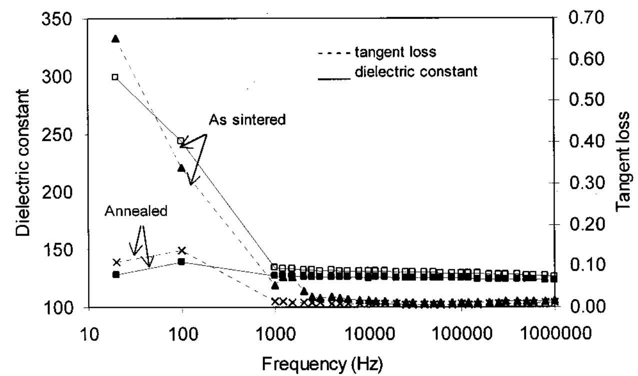


FIG. 5. Room temperature dielectric properties of as sintered and annealed SBVT: (□) dielectric constant of as sintered sample; (▲) tangent loss of as sintered sample; (■) dielectric constant of annealed sample; (×) tangent loss of annealed sample (solid line for dielectric constant and dashed line for tangent loss).

temperature due to the annealing was within the range of experimental error. However, annealing at 850 °C in air for a prolonged period of time, for example 160 h, resulted in an increase of transition temperature at 100 kHz from 364 °C of the as-sintered SBTV sample to 369 °C of 160 h annealed sample.

Figure 5 shows the room temperature dielectric constants and tangent loss of as-sintered and 60 h annealed SBTV ceramics as a function of frequency. Both dielectric constants and tangent loss of the as-sintered SBTV sample have a sharp decrease as the frequency increases from 20 to 100 Hz and become constant at frequencies above 1000 Hz. In contrast, dielectric constants of the annealed SBTV sample remain almost constant throughout the frequency range, though there is a slight decrease of tangent loss at low frequencies from 20 to 1000 Hz. A sharp decrease of both dielectric constants and tangent loss as frequency increases from 20 to 1000 Hz can be explained by the space charge polarization.[29] In the SBTV system, space charge polarization is attributed to the limited motion of oxygen vacancies, since the concentration of multivalent vanadium ions in the SBTV crystal is below the minimum to form a percolated network and no electrical conduction would be possible via the hopping mechanism. The significant reduction of both dielectric constants and tangent loss of annealed SBTV sample at frequencies below 100 Hz indicates that the annealing reduced the concentration of oxygen vacancies as a result of further oxidation of tetravalent vanadium ions to pentavalent ions.

The effect of annealing on the concentration of oxygen vacancies in the SBTV samples could also be verified from the dc conductivity measurements. dc conductivity of both as-sintered and annealed SBTV ferroelectrics as a function of temperature is plotted in Fig. 6. Throughout the temperature range, the dc conductivity of annealed SBTV ferroelectric sample is one order of magnitude lower than that of as-sintered SBTV sample, which could be attributed to the reduced concentration of oxygen vacancies after annealing. The dc conductivity, σ_{dc}, of the SBTV sample can be described as the ordered diffusion of oxygen vacancies under

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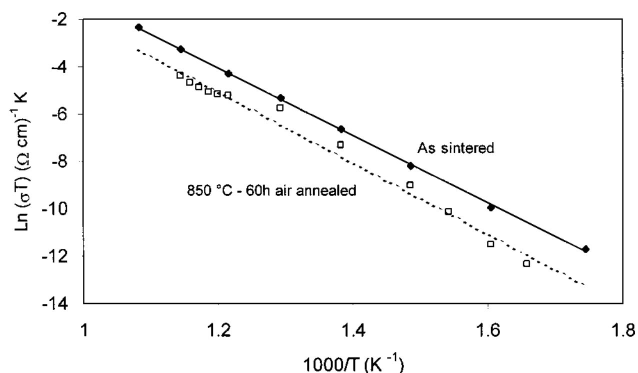

FIG. 6. dc conductivity of the as-sintered SBVT (♦) and air annealed sample (□).

an applied electric field, and is given by the following equation, assuming no appreciable contribution from intrinsic defects:

$$\sigma_{\rm dc}=nq\mu=\frac{4nD_0}{RT}\exp\left(\frac{-E}{RT}\right), \tag{2}$$

where n is the concentration of oxygen vacancies, q is the number of charges of each charge carrier, μ is the mobility of oxygen vacancies, D_0 is the preexponential constant of diffusion, and E is the activation energy of oxygen vacancy diffusion. According to Eq. (2), it is evident that the decrease in dc conductivity of the SBTV samples after 60 h annealing is attributed to the reduction of oxygen vacancies. In addition, the activation energy for the dc conductivity increased from $\sim$1.16$\pm$ eV for the as-sintered SBTV sample to $\sim$1.26$\pm$ eV for the 60 h annealed sample.

Figure 7 plotted both dc and ac conductivity of the as-sintered SBTV ferroelectrics as a function of temperature. ac conductivity, $\sigma_{\rm ac}$, is given by considering a sinusoidal voltage:[29]

$$\sigma_{\rm ac}=2\pi f\epsilon_0\epsilon_r\tan\delta, \tag{3}$$

where f is the frequency, ϵ_0 is the permittivity of vacuum, ϵ_r is the dielectric constant, and the tan δ is the tangent loss. At a given temperature, the ac conductivity would increase with increasing frequency. However, at high temperatures, both the dielectric constant and the tangent loss at low frequencies increase much faster than at high frequencies.

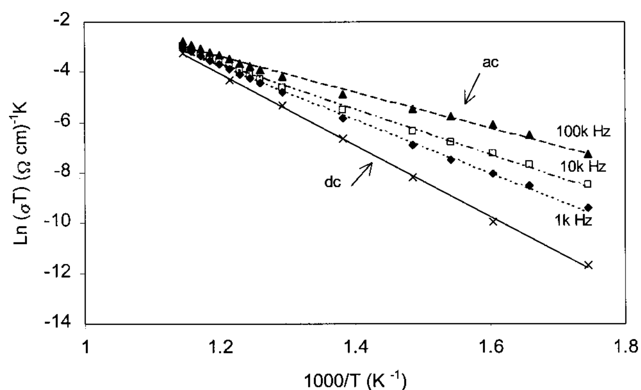

FIG. 7. dc and ac conductivities of as-sintered SBVT sample.

Efforts were made to determine the amount of oxygen vacancies and/or tetravalent vanadium ions presented in the SBTV samples prior to and after annealing. The maximal possible weight change as a result of the formation or elimination of oxygen vacancies is calculated to be $\sim$0.162%, assuming all vanadium ions would have a tetravalence state prior to annealing and change to the pentavalent state when subjected to annealing. In practice, only a very small fraction of tetravalent vanadium ions would be present in the SBTV system, as indicated by the dielectric properties. This would explain that no weight loss was found during the annealing. X-ray photoelectron spectroscopy (XPS) was also applied to determine the valence states of vanadium ions in the SBTV samples. Although there was an indication of the presence of V^{4+} ions prior to annealing, no definite conclusion could be drawn about the change of valence states of vanadium ions from the measurements. In the SBTV samples, only 10 at. % tantalum ions were replaced by vanadium. It is most likely that only a very small fraction of vanadium may have a tetravalence state, and a definite measurement of valence change of vanadium ions could be very difficult using XPS. However, the change of the valence state of vanadium ions has been reported in sol-gel prepared vanadium oxide films that underwent different heat treatment conditions.[30] XPS results from SBTV samples revealed that annealing did not result in any detectable change in other ions. Extended X-ray absorption fine structure (EXAFS) experiments were also conducted to obtain some information of the valence state of vanadium ions; however, no definite conclusion could be derived from these EXAFS analyses at this moment. Furthermore, EXAFS experiments revealed that there were no changes in other constituent elements with annealing.

IV. CONCLUSION

Partial substitution (10 at. %) of pentavalent tatanlum ions by pentavalent vanadium ions with a relatively smaller ionic radius in the SBT layered perovskite ferroelectrics leads to an enhanced dielectric constants, a broadened peak, and a reduced stability of layered tetragonal perovskite structure, as evidenced by an increased paraferroelectric transition temperature. It was found that the frequency dependence of paraferroelectric transition temperature and broadening of dielectric constant peak in the SBTV system resulted from oxygen-vacancy-induced dielectric relaxation, not from diffused phase transition. Postsintering annealing at 850 °C in air appreciably reduced the concentration of oxygen vacancies and thus, led to a reduced dielectric constant and tangent loss, particularly at high temperatures. In addition, dc conductivity of the SBTV sample was reduced with postsintering annealing.

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[1] C. A. P. de Araujo, J. D. Cuchlaro, L. D. McMillan, M. C. Scott, and J. F. Scott, Nature (London) **374**, 627 (1995).
[2] S. B. Desu and D. P. Vijay, Mater. Sci. Eng., B **32**, 75 (1995).
[3] R. E. Jones, Jr., P. D. Maniar, R. Moazzami, P. Zurcher, J. Z. Witowski, Y. T. Lii, P. Chu, and S. J. Gillespie, Thin Solid Films **270**, 584 (1995).
[4] Y. Torii, K. Tato, A. Tsuzuki, H. J. Hwang, and S. K. Dey, J. Mater. Sci. Lett. **17**, 827 (1998).
[5] N. Seong, C. Yang, W. Shin, and S. Yoon, Appl. Phys. Lett. **72**, 1374 (1998).
[6] R. Dat, J. K. Lee, O. Auciello, and A. I. Kingon, Appl. Phys. Lett. **67**, 572 (1995).
[7] H. Watanabe, T. Mihara, H. Yoshimori, and C. A. P. de Araujo, Jpn. J. Appl. Phys., Part 1 **34**, 5240 (1995).
[8] T. Noguchi, T. Hase, and Y. Miyasaka, Jpn. J. Appl. Phys., Part 1 **35**, 4900 (1996).
[9] T. Atsuki, N. Soyama, T. Yonezawa, and K. Ogi, Jpn. J. Appl. Phys., Part 1 **34**, 5096 (1995).
[10] Y. Wu and G. Z. Cao, Appl. Phys. Lett. **75**, 2650 (1999).
[11] Y. Wu and G. Z. Cao, J. Mater. Res. **15**, 1583 (2000).
[12] M. J. Forbess, S. Seraji, Y. Wu, C. P. Nguyen, and G. Z. Cao, Appl. Phys. Lett. **76**, 2934 (2000).
[13] L. E. Cross, Ferroelectrics **76**, 241 (1987).
[14] M. Kahn, D. Burks, I. Burn, and W. Schulze, in *Electronic Ceramics*, edited by L. M. Levinson (Dekker, New York, 1988), pp. 191–274.
[15] H. Fan, L. Kong, L. Zhang, and X. Yao, J. Appl. Phys. **83**, 1625 (1998).
[16] H. S. Shulman, D. Damjanovic, and N. Setter, J. Am. Ceram. Soc. **83**, 528 (2000).
[17] P. Duran-Martin, A. Castro, P. Millan, and B. Jimenez, J. Mater. Res. **13**, 2565 (1998).
[18] *CRC Handbook of Chemistry and Physics*, 61st ed., edited by R. C. Weast and M. J. Astle (CRC, Boca Raton, FL, 1974).
[19] Y. Wu, C. Nguyen, S. Seraji, M. J. Forbess, S. J. Limmer, T. Chou, and G. Z. Cao, J. Am. Ceram. Soc. (in press).
[20] R. D. Shannon and C. T. Prewitt, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **25**, 925 (1969).
[21] D. W. Wan, J. Wang, S. C. Ng, and L. M. Gan, J. Mater. Res. **14**, 537 (1999).
[22] A. Chen, Y. Zhi, and L. E. Cross, Phys. Rev. B **62**, 228 (2000).
[23] H. K. Guo, X. G. Tang, J. X. Zhang, S. W. Shan, M. M. Wu, and Y. J. Luo, J. Mater. Sci. Lett. **17**, 1567 (1998).
[24] J. Ravez and A. Simon, Eur. Phys. J.: Appl. Phys. **11**, 9 (2000).
[25] A. Chen, Y. Zhi, and J. Zhi, Phys. Rev. B **61**, 957 (2000); A. Chen, Y. Zhi, P. Lunkhemer, and A. Loidl, *ibid.* **59**, 6670 (1999).
[26] A. Chen, J. F. Scott, Y. Zhi, H. Ledbetter, and J. L. Baptista, Phys. Rev. B **59**, 6661 (1999); A. Chen, Y. Zhi, J. Hemberger, P. Lunkhemer, and A. Loidl, *ibid.* **59**, 6665 (1999).
[27] Y. Wu, M. Forbess, S. Seraji, S. Limmer, T. Chou, and G. Z. Cao, J. Phys. D (submitted).
[28] M. A. Rodriguez, T. J. Boyle, B. A. Hernaandez, C. D. Buchheit, and M. O. Eatough, J. Mater. Res. **11**, 2282 (1996).
[29] A. J. Moulson and J. M. Herbert, *Electroceramics: Materials, Properties, Applications* (Chapman & Hall, London, 1990).
[30] S. Lu, L. Hou, and F. Gan, J. Mater. Sci. **28**, 2169 (1993).

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