Variable-range-hopping conduction and dielectric relaxation in disordered $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$

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(Received 9 December 1997)

Conduction and dielectric behavior of $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ solid solutions were studied. The temperature dependence of the dc conductivity with $\sigma \propto A\ \exp(-BT^{1/4})$ obtained, indicated a variable-range hopping mechanism. A low-frequency dielectric relaxation was also observed. The activation energy for the variable-range hopping conduction is slightly higher than that for dielectric relaxation, suggesting that the dielectric relaxation is due to the trap-controlled ac conduction. [S0163-1829(98)05819-6]

In numerous ionic oxides with the perovskite structure, low-frequency dielectric relaxation behavior has been observed.[1–5] This low-frequency dielectric relaxation is not related to a phase transition, and probably related to a series of excitations in the solids.[6] Recently, the dielectric relaxation behavior in several materials, $KTaO_3$, $KTaO_3$:Nb, $PbTiO_3$:La, etc., was reported by Bidault *et al.*[1] They found that the values of the activation energies were in the range of 50–80 meV. The authors attributed the dielectric relaxation behavior to the localization of polarons on residual defects, such as oxygen vacancies. Moreover, Iguchi *et al.* reported polaronic conduction in *n*-type $BaTiO_3$ doped with La_2O_3 or Gd_2O_3 accomplished by a low-frequency dielectric loss dispersion with the activation energy of 68 meV, which were explained as being due to the hopping motion of nonadiabatic small polarons.[7] However, due to the complicated characteristics of the real materials including the lattice contribution, different defects, impurities, and coupling effects, a uniform explanation concerning the low-frequency dielectric relaxation behavior is difficult, and needs a firmer experimental basis to be accomplished. Detailed studies are therefore needed to shed light on the physical nature of these phenomena, and more experimental data in different systems are also desirable.

On the other hand, dielectric properties of $SrTiO_3$- and $SrTiO_3$-based materials have been widely studied.[8–11] Fe doped $SrTiO_3$ materials, combining the required stability and interesting transport properties at relatively high temperatures, have been considered for application as electrochemical electrodes and possibly also for resistive oxygen sensors.[12–14] For these applications, special attention has been paid to the electrical transport properties at high temperatures. However, work on both the dielectric and conductive properties, especially at low temperatures, has been rarely done.

The present paper is mainly concerned with the conduction and the low-frequency dielectric relaxation behavior of $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ ceramics at low temperatures. The evidence of a variable-range hopping mechanism for conduction was obtained, and low-frequency dielectric relaxation behavior was also observed.

The ceramic samples with the compositions $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$, where $x=0$, 0.01, 0.02, 0.05, 0.1, 0.2, 0.4, 0.5, and 0.6, respectively, were prepared by solid state reaction. 3% atomic Sr-site deficiency was introduced to enhance the chemical stability.[15] The relative densities of the samples were $\geqslant 97\%$. X-ray powder diffraction (XRD) was carried out to characterize lattice parameters. Dielectric and conductivity measurements were made using a Solartron Impedance Gain-Phase Analyzer and Keithley-617 Programmable Electrometer, with silver and/or ln-Ga electrodes.

The XRD results indicated that all samples were monophasic and exhibited the single cubic perovskite structure. The lattice parameter decreases by increasing the Fe content, as shown in Fig. 1.

The temperature dependence of the dielectric permittivity and loss was measured for all the samples. Typical curves for $x=0.2$ and 0.5 are shown in Figs. 2 and 3. It has been reported[1] that the permittivity for pure $SrTiO_3$ monotonically increased with decreasing temperature, the permittivity reaching the high value of ~ 4000 at 50 K.[8,11] In the temperature range of 0.3–300 K, no permittivity peak occurred.[8,11] Figures 2 and 3 show that the permittivity for the Fe-doped $SrTiO_3$ has greatly decreased; for example, for

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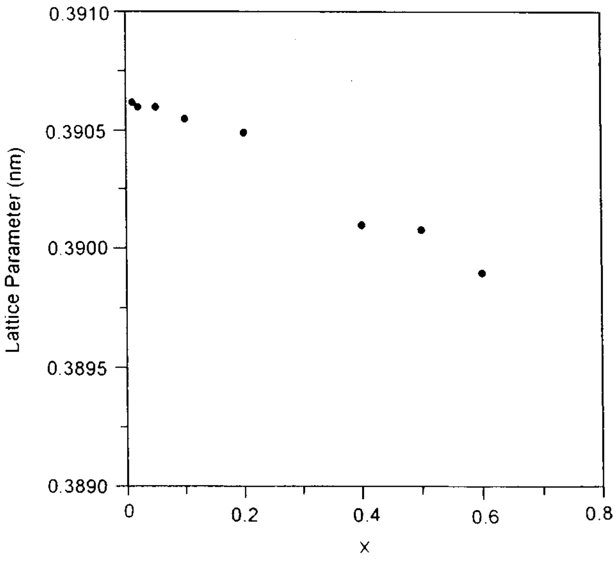

FIG. 1. The lattice parameter versus Fe content.

$x = 0.2$, the permittivity decreases down to 190 at ~50 K. In addition, a permittivity and a dielectric loss peak can be clearly seen.

The sample with $x = 0.2$ was chosen to study the relaxation time distribution. Figure 4 shows the plot of the real part (ε') versus the imaginary part (ε'') of the complex permittivity, i.e., the Cole-Cole plot. The data points fit well into a semicircular arc with the center lying underneath the abscissa. The complex permittivity (ε^*) can be empirically described by the equation[16]

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/[1 + (i\omega\tau)^\beta], \tag{1}$$

where ε_0 is the static permittivity, ε_∞ is the permittivity at very high frequencies, ω is the angular frequency, τ is the mean relaxation time, and β is the angle of the semicircular arc. From Fig. 5, by fitting this arc with the least-squares approach, $\varepsilon_0 = 199$, $\varepsilon_\infty = 177$, and $\beta = 0.73$ at 75 K were obtained. In the temperature range 75–150 K, β takes values between 0.59 and 0.79.

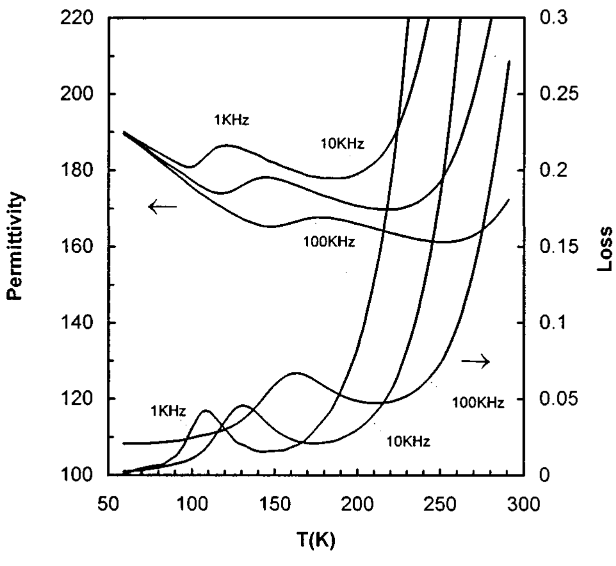

FIG. 2. Temperature dependence of permittivity and loss for the sample with $x = 0.2$.

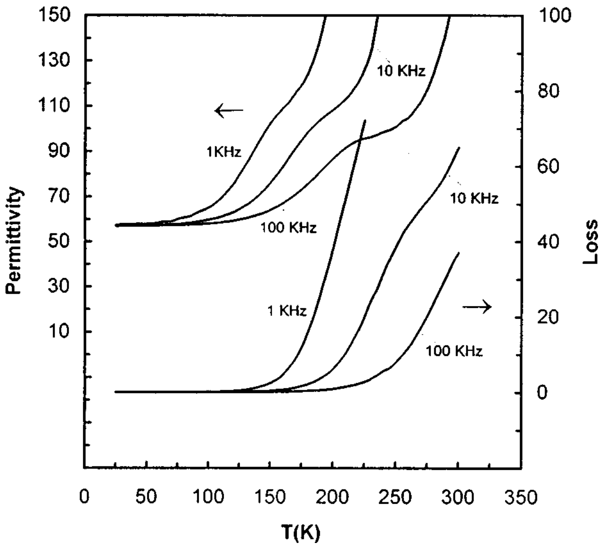

FIG. 3. Temperature dependence of permittivity and loss for the sample with $x = 0.5$.

The real and imaginary parts of the permittivity can be rewritten from Eq. (1) in the following forms:

$$\varepsilon' = \varepsilon_\infty + (\Delta\varepsilon'/2)\{1 - \sinh(\beta z)/[\cosh(\beta z) + \cos(\beta\pi/2)]\}, \tag{2}$$

$$\varepsilon'' = (\Delta\varepsilon'/2)\sin(\beta\pi/2)/[\cosh(\beta z) + \cos(\beta\pi/2)], \tag{3}$$

where $z = \ln(\omega\tau)$ and $\Delta\varepsilon' = \varepsilon_0 - \varepsilon_\infty$. If the dielectric relaxation is related to a thermally activated process, the relaxation time will obey the following relation:

$$\tau = \tau_0 \exp[E_{\mathrm{relax}}/(k_B T)], \tag{4}$$

where τ_0 is the relaxation time at an infinite temperature, E_{relax} the activation energy for relaxation, k_B Boltzmann's constant, and T the absolute temperature.

By using Eqs. (2) and (3), the relaxation time was calculated from 75 to 150 K for $x = 0.2$ at 1 and 10 kHz. The temperature dependence of relaxation time τ is shown in Fig.

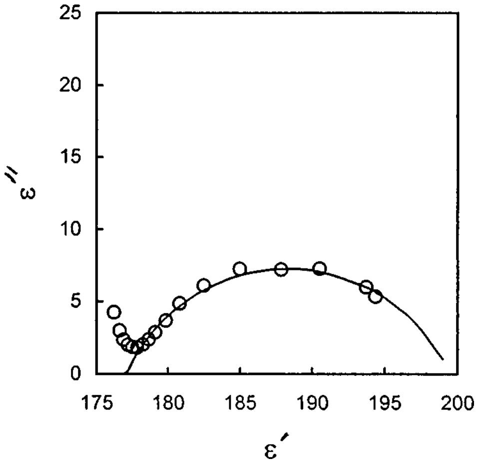

FIG. 4. Cole-Cole plot for the sample with $x = 0.2$ at 75 K.

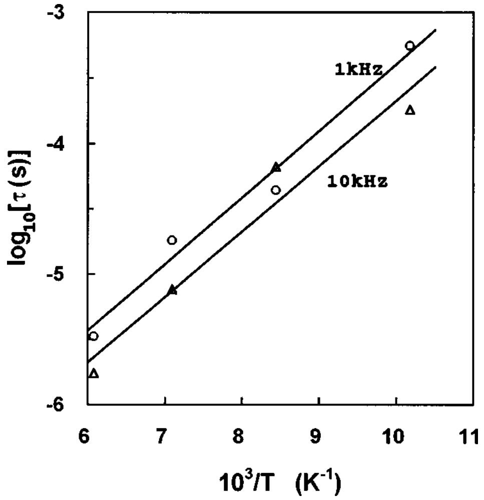

FIG. 5. The relaxation time (τ) versus $1/T$ curve for the sample with $x=0.2$ at 1 and 10 kHz.

5. It revealed a linear relation between $\log_{10}\tau$ and $1/T$ in the temperature range of 75–150 K, from which $\tau_0=\sim3\times10^{-8}$ s and an activation energy of $E_{\mathrm{relax}}=\sim60$ meV were obtained. The value of the activation energy is in good agreement with that reported by Bidault *et al.* and Iguchi *et al.*[1,8]

The results of the temperature dependence of the conductivity (σ) indicate that $\sigma\sim1/T$ cannot be fitted to the general conduction activation mechanism, which is commonly used to characterize the band conduction, $\sigma=\sigma_0\exp[-E_{\mathrm{cond}}/(k_BT)]$, where σ_0 is the preexponential term, and E_{cond} is the activation energy for conduction. However, a satisfactory result was obtained, by fitting the experimental data to a variable-range hopping mechanism described by the following equation:

$$\sigma=\sigma_0\exp[-B/T^{1/4})], \quad (5)$$

where $B=4E/(k_BT^{3/4})$ and E is the activation energy. The plot of σ versus $1/T^{1/4}$ is shown for $x=0.2$ and 0.5 in Fig. 6, other samples showing similar behavior. This is generally indicative of a variable-range-hopping conduction mechanism.[17]

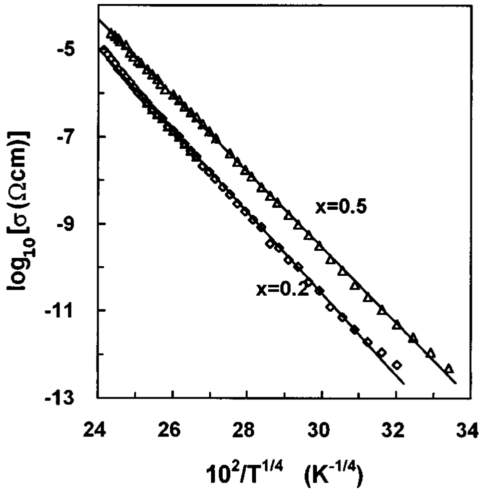

FIG. 6. Temperature dependence of the dc conductivity for the samples with $x=0.2$ and 0.5.

For $x=0.2$, and in the low-temperature regime corresponding to the temperature range of the dielectric peak (50–120 K, at 1 kHz), for example, the conduction activation energy is $E_{\mathrm{cond}}=140$ meV at 100 K. In the high-temperature regime (>180 K), the conduction activation energy (E_{cond}) increased, being $E_{\mathrm{cond}}=330$ meV at 300 K. For $x=0.5$, from 50 to 300 K, a similar behavior was obtained for the dielectric characteristics.

In the $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ solid solutions, several facts have to considered: first, according to the nominal stoichiometry, 3% Sr-site vacancies will be present; second, the cubic crystalline structure suggests that the Fe ions are mainly in the tetravalent Fe^{4+} state,[18] the results of Mösbauer also confirmed that the Fe is mainly Fe^{4+} by the present authors;[19] third, oxygen vacancies are easily formed by loss of oxygen in the high-temperature sintering process, in order to balance the charge mismatch due to the existence of Sr vacancies. On the other hand, for Ti-based ceramics, Ti can easily change valence. Hence, in the $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ solid solutions, electron jumps between $Ti^{4+}\Leftrightarrow Ti^{3+}$ and/or $Fe^{4+}\Leftrightarrow Fe^{3+}$ might possibly occur.

As mentioned earlier, the variable-range-hopping mechanism [Eq. (5)] could fit the experiments. This form of conductivity has been observed in some amorphous materials via "states in the gap," which have been attributed to the divacancies and dangling bonds.[17] In other words, it comes from some type of lattice disorder. The observed variable-range-hopping phenomenon implies, therefore, that the $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ material is highly disordered, with the disorder coming probably from the existence of Sr vacancies, oxygen vacancies, and the random distribution of the Ti and Fe ions. This kind of disorder was also proposed to occur in $SrFeO_3$ ceramics.[18]

Based on the observation of the variable-range-hopping mechanism, the following explanation of the conduction and polarization is proposed. The short-range hopping of weakly bonded defects, such as $Ti^{4+}\Leftrightarrow Ti^{3+}$ and $Fe^{4+}\Leftrightarrow Fe^{3+}$, leads to a net dipole moment, and hence, originates the permittivity relaxation peaks, i.e., the relaxation mechanism is governed by the trap-controlled ac conduction.[20] On the other hand, in the disordered matrix of $SrTiO_3$ with a random distribution of V_{Sr} and Fe ions, the long-range movement of the weakly bonded electrons gives the dc conduction, which can be described by the variable-range-hopping mechanism.

The transient transport of the electrons bonded to Ti^{3+}, Fe^{3+}, and/or Vo from the cathode to the anode, contributing to dc conduction, can have more difficult steps than the small displacement changing dipoles. In this case, the value of E_{relax} is expected to be close to or less than that of the conduction activation energy (E_{cond}) derived from the temperature dependence of the conductivity.[17,20] For the sample with $x=0.2$, the activation energy for dielectric relaxation occurring in the temperature range 50–120 K at 1 kHz ($E_{\mathrm{relax}}=60$ meV) is lower than and also close to the activation energy for the variable-range-hopping conduction at 100 K ($E_{\mathrm{cond}}=140$ meV). This experimental evidence supports the above discussion.

In conclusion, for $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ solid solutions, the XRD results showed that the single cubic structure and stable ceramics were obtained and the lattice parameter decreases with increasing Fe content. The variable-range-hopping mechanism observed for conduction suggests that the $Sr_{0.97}(Ti_{1-x}Fe_x)O_{3-\delta}$ solid solutions are highly disordered. The low-frequency dielectric relaxation with the activation energy ~60 meV was observed. The calculated activation energy for a variable-range-hopping mechanism is higher than the calculated activation energy for dielectric relaxation, which, therefore, suggests that the dielectric relaxation behavior can be due to the trap-controlled ac conduction.

The authors would like to thank JNICT, Portugal, for its financial support. One of the authors (C.A.) also thanks Zhejiang University, People's Republic of China, for permitting his leave and work at the University of Aveiro.

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