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High dielectric permittivity and hole-doping effect in $La_{1-x}Sr_xFeO_3$

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We have measured the complex dielectric permittivity for ceramic samples of $La_{1-x}Sr_xFeO_3$ ($0.2 \leqslant x \leqslant 0.8$), which, unlike $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xCoO_3$, do not exhibit a metal-insulator transition with a small amount of ($x \sim 0.2$) hole doping. This measurement is carried out as a function of Sr doping ($0.2 \leqslant x \leqslant 0.8$), frequency ($20-10^6$ Hz) and temperature (80–300 K). These results show strong temperature and frequency dependence and high real dielectric constant, $>10^5$, on all compounds at room temperature. This high dielectric polarization is due to a thermally activated process. The associated dipolar thermal activation energy linearly decreases from 260 to 60 meV when Sr doping increases from $x = 0.2$ to 0.6 and it nearly vanishes at $x = 0.8$. The static dielectric constant reaches $\sim 10^7$ in high Sr-doping samples due to an extra low-frequency polarization enhancement where a relatively high ac conductivity is also observed. These results are consistent with the persistence of the insulating phase until high ($x \sim 1$) Sr doping and illustrate the doping effect on the dielectric polarization in $La_{1-x}Sr_xFeO_3$. [S0163-1829(98)02027-X]

I. INTRODUCTION

The study of the perovskite series of $La_{1-x}Sr_xFeO_3$ ($0 \leqslant x \leqslant 1$) can be traced back to the late 1950s.[1] Briefly, both structural and magnetic transitions were observed by Sr hole doping. The parent material $LaFeO_3$ is an antiferromagnetic insulator and the Néel temperature is about 750 K. The magnetic order is weakened by substitution of trivalent La by divalent Sr, which forces the Fe from the stable trivalent to the rare tetravalent state. Structurally, $LaFeO_3$ has orthorhombic symmetry. It becomes rhombohedral for the composition $La_{0.5}Sr_{0.5}FeO_3$. With further Sr substitution of La, the structure approaches cubic.

Recently the interest in these compounds was revived after the discovery of high-temperature superconductivity in cuparates and giant magnetoresistance in manganese oxides. In the perovskite series $LaMO_3$ ($M =$ transition metal) substantial changes on the electronic properties have been found.[2,3] A metal-insulator transition is observed while La is replaced by a divalent element such as Sr^{2+}. The transition mechanism is, however, varied from a Mott-Hubbard type for the early transition metal to a charge-transfer or covalent-insulator class for the late transition metal.[4–14] When M is the middle elements of Mn, Fe, and Co, it is expected to show a crossover behavior on the metal-insulator transition. It is rather surprising that, while $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xCoO_3$ become metallic for $x > 0.2$, $La_{1-x}Sr_xFeO_3$ does not exhibit a metallic phase until $x \sim 1$. The origin of this unexpected behavior may give useful clues for the fundamental mechanism of the metal-insulator transition in these perovskite structures. Furthermore, many perovskite materials have shown high dielectric or ferroelectric properties and the dipolar unit in these systems play an important role in the electronic transport phenomena. It is suspected that the high dielectric polarization, if it exists, may be carried over into the metallic phase but the free electrons prevents from measuring this property.[15] Now with the lack of metallic phase in $La_{1-x}Sr_xFeO_3$ ($x < 1$), it provides an opportunity to examine this hypothesis in detail. In this study, we have measured the complex dielectric constant of $La_{1-x}Sr_xFeO_3$ as a function of Sr-doping concentration ($0.2 \leqslant x \leqslant 0.8$), frequency ($20-10^6$ Hz), and temperature (80–300 K). We have also measured dc conductivity and found that it increases from a good insulator to a semiconductor (or poor metal) by Sr hole doping as expected. The energy gap gradually vanishes when the Sr doping closes to $x = 0.8$. The dielectric measurement shows strong temperature and hole-doping dependence. An extremely high dielectric permittivity, $>10^5$, which is comparable to a ferroelectric value, at low frequency and room temperature for all compounds is observed. At the insulating end ($x = 0.2$), this high dielectric polarizability results mainly from a thermally activated process. The temperature and frequency dependence of the dielectric constants in this region can be described by a Debye relaxation mechanism. An extra enhancement on the dielectric constant is also observed at lower frequency regions. This low frequency dielectric constant becomes more pronounced and quickly reaches $\sim 10^7$ at the conducting end ($x = 0.8$). A relative high ac conductivity, which is accompanied with this low-frequency polarization enhancement, develops simultaneously. It is likely that this high dielectric behavior at low frequency is thus due to free carriers rather than bound structural units.[16] An interesting and potentially important question arises: How does the high dielectric property change from the insulating phase to the more conducting phase? This sets a major goal for the present paper: to examine how this high polarization behavior in $La_{1-x}Sr_xFeO_3$ ($0.2 \leqslant x \leqslant 0.8$) samples is affected by the Sr-doping concentration.

Briefly, the dielectric measurements show that the dipolar strength, which is due to a thermally activated process, substantially reduces with higher Sr doping. The associated activation energies also quickly decrease from 260 to 60 meV while the doping of Sr ratio increases from $x = 0.2$ to 0.6. It becomes ~ 0 when the doping is $x = 0.8$. On the other hand, the low-frequency dielectric enhancement grows as Sr doping increases. It also shows strong frequency and temperature dependence but quite different from the Debye process. The associated ac conductivity exhibits, however, a rather

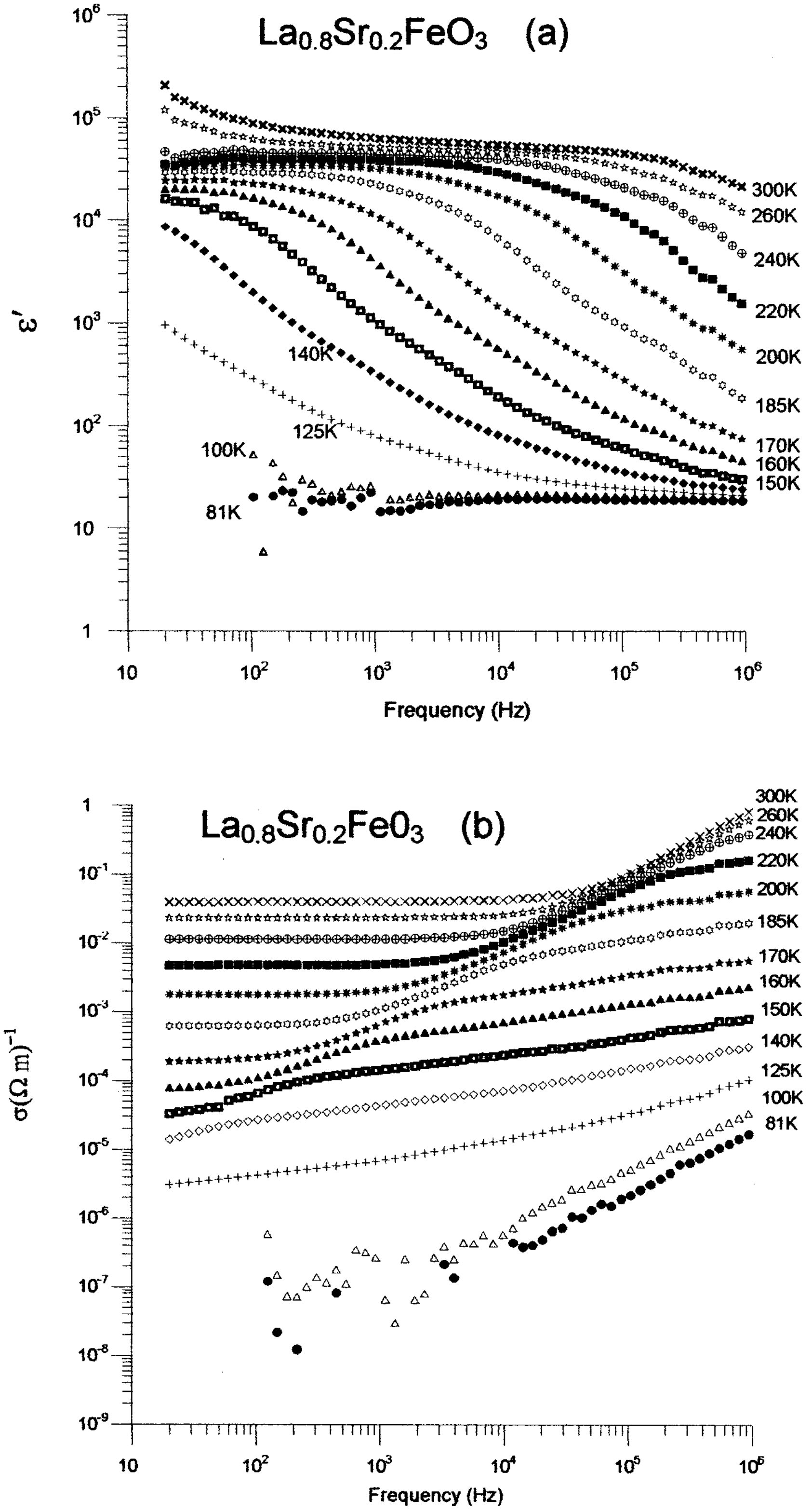

FIG. 1. (a) Real part of the dielectric constant and (b) electrical conductivity vs frequency for $La_{0.8}Sr_{0.2}FeO_3$.

simple exponential temperature dependence (and weak frequency dependence). The energy gaps deduced from the low-frequency ac conductivity and independent dc conductivity measurements are very similar and both decrease whilethe Sr doping increases. Interestingly, these gap energies are very close to the activation energy of the dipolar rotation at various temperatures. This result seems to indicate that both free carriers and bound units are related to each other and this duality of bound and unbound carriers represents a unique feature in these perovskite oxides.

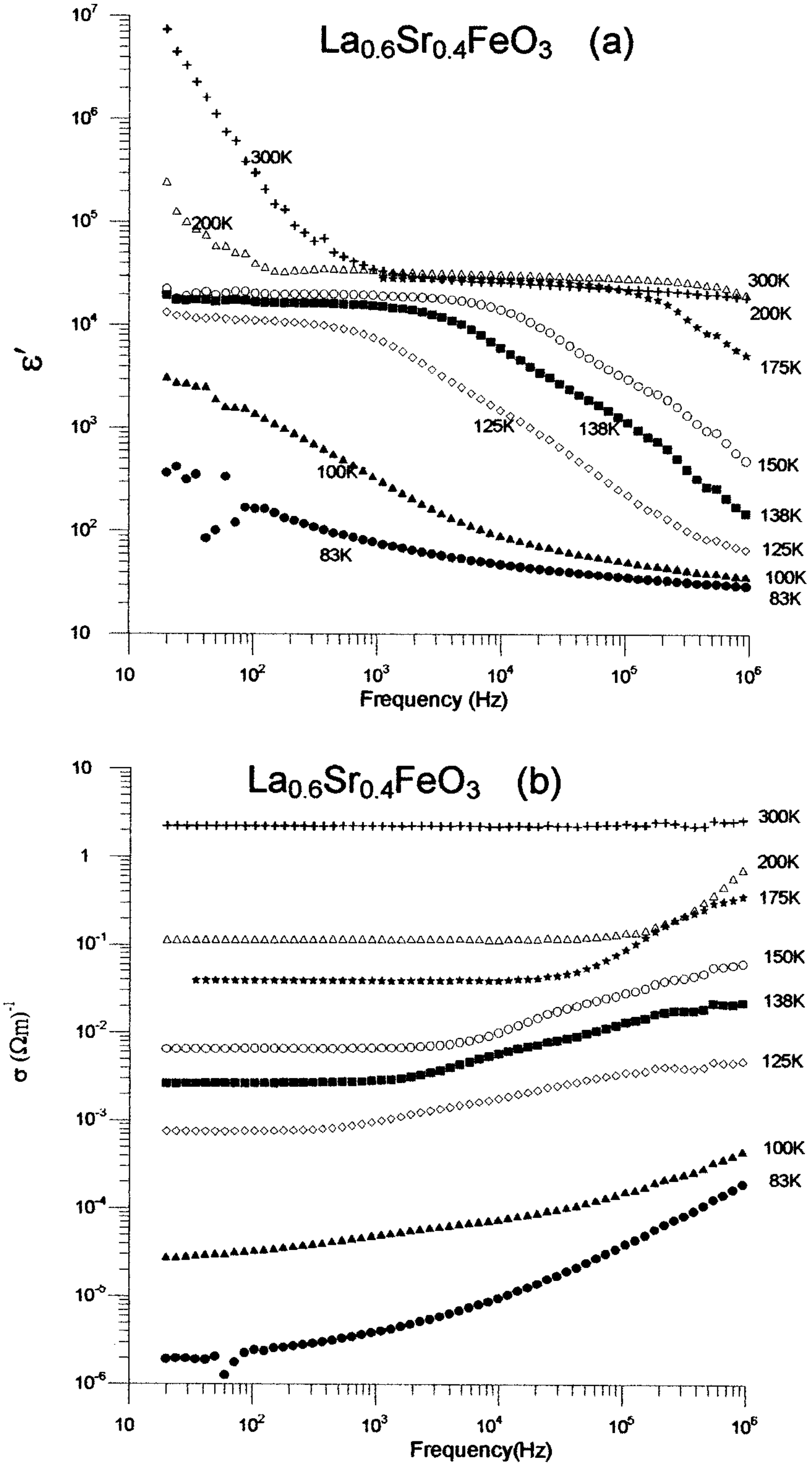

FIG. 2. (a) Real part of the dielectric constant and (b) electrical conductivity vs frequency for $La_{0.6}Sr_{0.4}FeO_3$.

II. EXPERIMENT

A. Sample preparation and x-ray diffraction results

The samples of $La_{1-x}Sr_xFeO_3$ ($0.2 \leqslant x \leqslant 0.8$) were prepared by the solid-state reaction method starting with high purity La_2O_3 (99.99%), $SrCO_3$ (99.999%), and Fe_2O_3 (99.5%) powder in the required proportions. The mixtures were ground and calcined at 950 °C for 24 h. The samples (~0.8 g) were pressed into ~12 mm diameter disks under a compression pressure ~200 kg/cm^2 and then sintered at 1300 °C for 24 h under flowing O_2. The temperature was gradually cooled to room temperature at rate 200 °C/h. The x-ray diffraction measurement showed that the oxide compounds were single phase orthorhombic perovskites for $x < 0.2$ and rhombohedral for $0.4 < x < 0.8$. The lattice parameters all match well with the earlier reported data.[17]

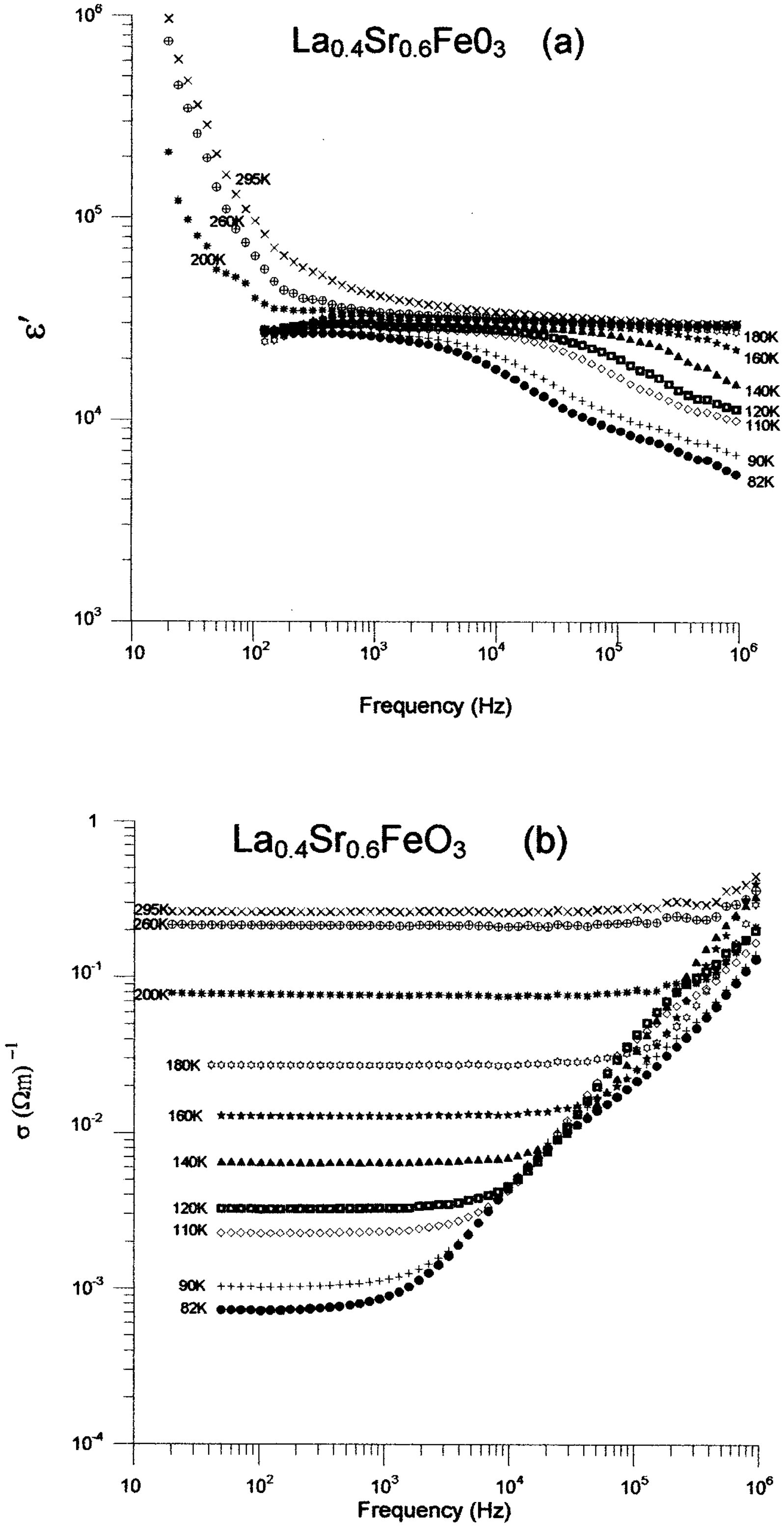

FIG. 3. (a) Real part of the dielectric constant and (b) electrical conductivity vs frequency for $La_{0.4}Sr_{0.6}FeO_3$.

B. Measurements

The complex dielectric constants are obtained from impedance measurements in the frequency and temperature ranges of 20–10^6 Hz and 80–300 K. The data are taken with an HP 4284A Precision LCR meter. The complex quantity-data have been converted to a dielectric constant and electric conductivity using an equivalent circuit of a parallel capacitor and a resistor. The electrical contacts were used with silver paint. A low field strength (1 V/m) is applied through the whole measurement to avoid possible non-Ohmic behavior.[16]

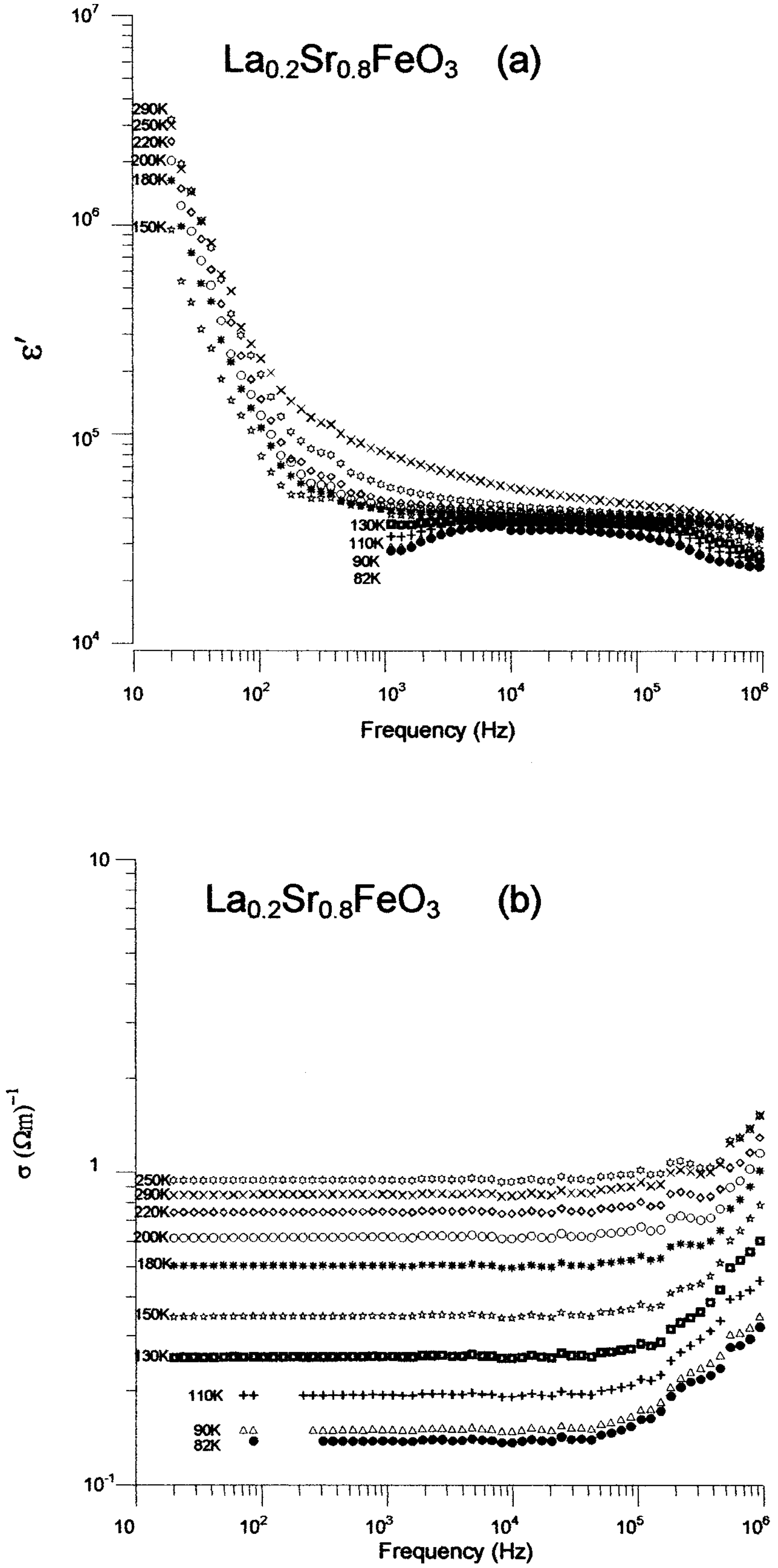

FIG. 4. (a) Real part of the dielectric constant and (b) electrical conductivity vs frequency for $La_{0.2}Sr_{0.8}FeO_3$.

III. RESULTS AND DISCUSSION

A. Frequency- and temperature-dependent dielectric permittivity

Complex dielectric constant of $La_{1-x}Sr_xFeO_3$ ($0.2\leq x \leq 0.8$) series is measured. A representative real dielectric constant and the conductivity ($\sigma = \omega\varepsilon\varepsilon''$, where ε is the permittivity of free space and ε'' is the imaginary dielectric constant) of $La_{0.8}Sr_{0.2}FeO_3$ as a function of frequency at various temperatures is shown in Fig. 1. The real dielectric constant ε' is strongly temperature and frequency dependent. A thermally activated process, shown as a drop of the real dielectric constant in Fig. 1(a), gradually shifts to lower frequency as the temperature decreases. An additional polariza-

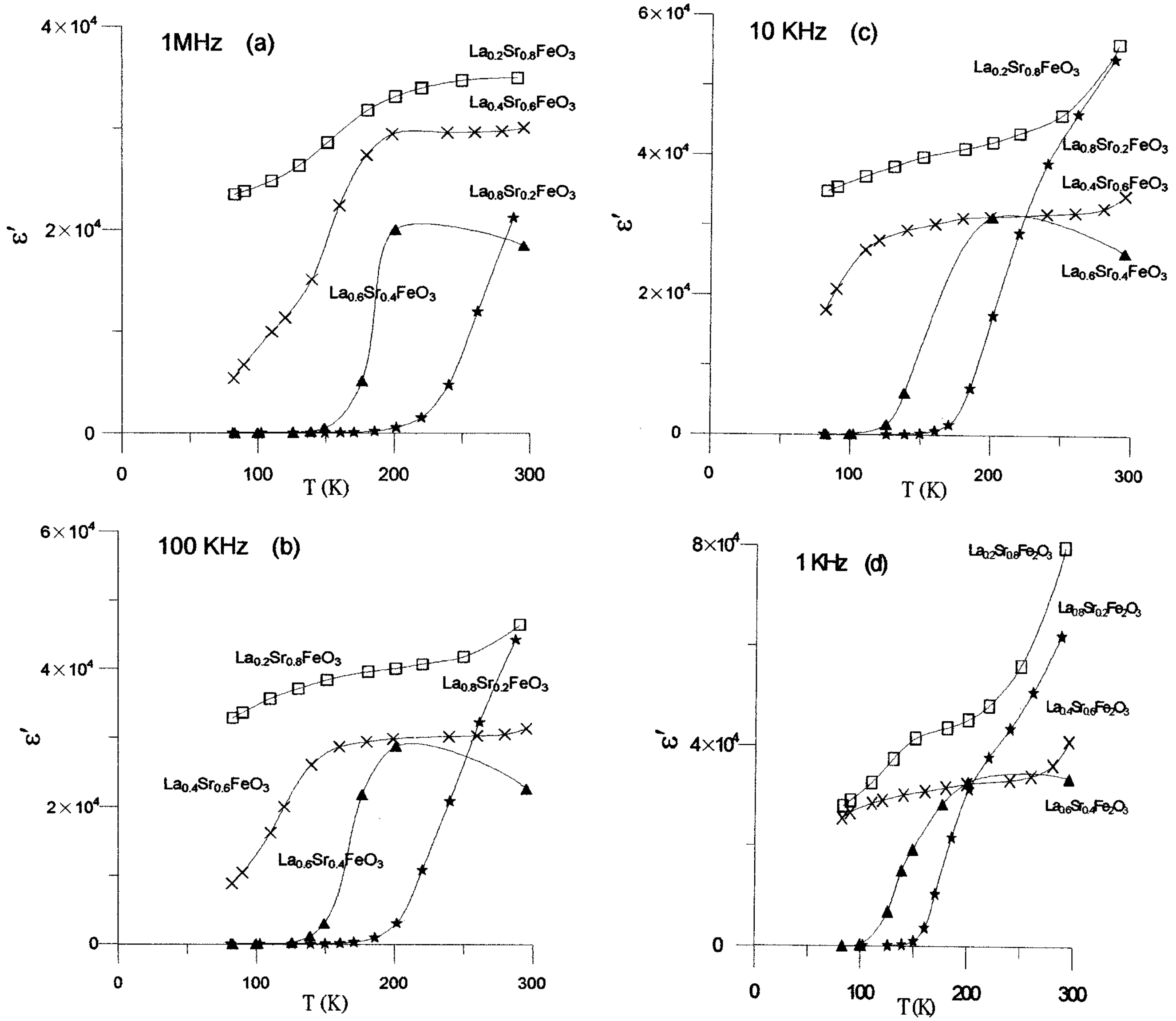

FIG. 5. Real part of the dielectric constant as a function of temperature at (a) 1 MHz, (b) 100 kHz, (c) 10 kHz, and (d) 1 kHz.

tion, which develops while the temperature increases, can be identified especially in the low-frequency region. Note that ε' reaches an absolute maximum value of $\sim 10^5$ at 300 K due to both the thermally activated process and this additional polarization. At lower temperature, however, it drops to ~ 20 with weak frequency dependence.

The conductivity plot, Fig. 1(b), also shows various frequency and temperature dependence. Qualitatively, the frequency-dependent feature at different temperature is very similar. The major effect on the conductivity is shown as a gradual jump from the lower frequency to the higher frequency and it shifts to higher frequency when the temperature increases. This feature reflects the same thermally activated process observed in the real dielectric constant measurements. The conductivity becomes nearly constant in the lower frequency portion. Beyond the local jump the conductivity, which is at the higher frequency end, becomes weakly dispersive and increases as the frequency increases.

The frequency dependence of the dielectric response can be represented by the Cole-Cole relaxation model whose complex permittivity is given by

$$\varepsilon^* = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/[1 + (jw\tau)]^{1-\alpha}, \tag{1}$$

where ε_s and ε_∞ are the static and high frequency limit of dielectric constants, respectively, τ is the most probable relaxation time, α is an empirical constant with values between 0 and 1, and is measured of an assumed symmetrical logarithmic distribution of the relaxation times.[18] It corresponds to the Debye model in the case of $\alpha = 0$, which has a single relaxation time. After the analysis from Eq. (1) we found that the limited region of the polarization of $La_{1-x}Sr_xFeO_3$ satisfies the Cole-Cole mechanism. The relaxation time obtained at different temperature gives the Arrhenious relation and the corresponding activation energy is 260 meV (see below).

B. Sr-doping-dependent dielectric permittivity

The complex dielectric constants of samples with higher Sr doping (0.4–0.8) are also studied with similar temperature and frequency dependence. The results show that all the $La_{1-x}Sr_xFeO_3$ $(0.4 \leqslant x \leqslant 0.8)$ compounds have comparable or even higher dielectric constants. In Figs. 2–4, the real dielectric constant and conductivity of $La_{1-x}Sr_xFeO_3$ ($x = 0.4$, 0.6, and 0.8) are presented. Both real dielectric constant and conductivity in $La_{0.6}Sr_{0.4}FeO_3$ (Fig. 2) show similar results as in $La_{0.8}Sr_{0.2}FeO_3$. Extra enhancement on the real dielectric constant in the low-frequency region becomes even stronger that the ε' increases for another 2 orders of magnitude higher at 300 K. In addition, the thermally activated process, shown as a drop on the dielectric constant, shifts to the low-frequency limit with a slower rate when temperature varies (corresponding to smaller activation energy, see below). Similar behavior is also seen on σ, where the conductivity jump shifts to the relatively higher frequency in the similar temperature region. The enhancement of the real dielectric constant at the low frequency region and the decreases in the activated strength becomes more pronounced when the Sr doping increases (Figs. 3 and 4). The rate of the shift of these activated process is also systematically decreased (in these cases, even at ~ 80 K, the dielectric constant is still strongly frequency dependent). At the highest Sr doping, in $La_{0.2}Sr_{0.8}FeO_3$, the real dielectric constant becomes exponentially varied as a function of the frequency. The thermally activated process can be barely seen at the high-frequency limit. Note that the real dielectric constant still reaches $\sim 10^7$ at low frequency but it remains $\sim 10^4$ at high frequency limit even at 82 K.

C. The dipolar polarization and Sr-doping dependence

In principle, Figs. 1–4 represent all the information of the complex dielectric permittivity of $La_{1-x}Sr_xFeO_3$ ($0.2 \leq x \leq 0.8$) compounds. The physical interests can be better seen, however, from different plots. Basically, part of the dielectric strength is due to a thermally activated process, which is related to the dipolar unit. In addition, the low-frequency dielectric enhancement may be due to more loosely bound carriers. These two dielectric contributions are both seen on these permittivity results. We first concentrate on the thermally activated process, which is related to a dipolar unit in these compounds. It is interesting to know how the hole-doping process affects this dipolar polarizability. In that sense, the high-frequency limit results (less free carrier effect) give better observation on this thermally activated process. In Figs. 5(a)–5(d), the temperature-dependent real dielectric constant for different concentration compounds at fixed frequency of 1 kHz–1 MHz are given. At 1 MHz [Fig. 5(a)], the real dielectric constant increasing from low temperature to higher temperature can be seen on all compounds. The strength ($\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$), however, substantially reduced from $\sim 2 \times 10^4$ to less than 10^4 when the Sr doping increases. Notice that the low-frequency (exponentially varied) background complicates this results especially in the high Sr doping sample. This trend still remains similar in 100 kHz but $\Delta\varepsilon$ in $La_{0.2}Sr_{0.8}FeO_3$ further decreases. At even lower frequency [Fig. 5(c) and 5(d)], the $\Delta\varepsilon$ from the thermally activated process almost disappears and the dielectric constant is replaced by the exponentially varied background.

D. Relaxation time and activation energy

At lower temperature the relaxation time of the thermally activated process becomes extremely long and the dielectric

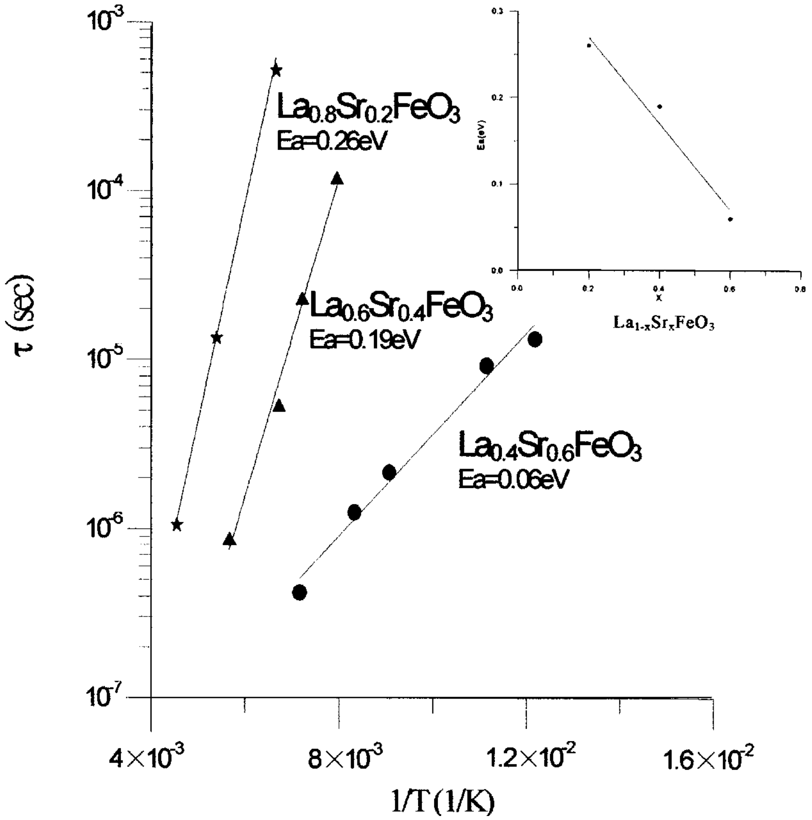

FIG. 6. The relaxation time vs inverse temperature for $La_{1-x}Sr_xFeO_3$ ($x = 0.2$, 0.4, and 0.6). The points are obtained by using the Cole-Cole fit for the experimental data. The slops give the activation energies, Ea, which are plotted as a function of Sr concentration in the insert.

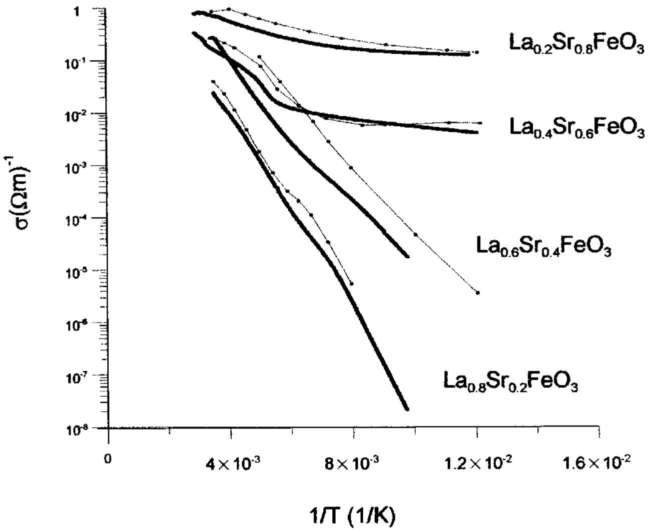

FIG. 7. The dc and ac conductivities vs inverse temperature for $La_{1-x}Sr_xFeO_3$ ($0.2\leq X\leq 0.8$).

results may only show the high-frequency limit. How the changes on the relaxation time τ and the associated activation energy depend on the Sr doping may provide useful information on the metal-insulator transition. Figure 6 shows the relaxation time as a function of $1/T$. The activation energy Ea, which can be obtained from the slops of these plot, is shown as a function of the Sr concentration in the inset of Fig. 6. The extrapolation from the linear plot indicates that the activation energy vanishes around $x=0.8$, which is qualitatively consistent with our experimental result. Notice that a linear behavior of the associated gap energy as a function of the hole-doping concentration has been seen on $La_{1-x}Sr_xVO_3$ compounds before the onset of the metal-insulator transition ($x<0.275$).[19]

E. Low-frequency dielectric constant and conductivity

The other origin of the high dielectric constant in the low frequency is suspected to relate to more freely charge carriers. It is different from the thermally activated process that we discussed in previous sections. The real dielectric constant shows an exponential frequency dependence plus a weak temperature effect. This behavior becomes extremely strong when the Sr doping reaches $x\sim0.8$ [Fig. 4(a)]. In that case, the real dielectric constant is dominated by this low-frequency polarization. Notice that the dipolar polarization strength, $\Delta\varepsilon$, still exists but it is negligibly small compared to the low-frequency polarization. This loosely bound charge effect can be better recognized from the ac conductivity result. The ac conductivity, in the low-frequency region, is all weakly frequency dependent and thus the temperature dependence becomes more important. In Fig. 7, we plot the ac conductivity, at arbitrary fixed low frequency, as a function of the $1/T$ for each compound (as dotted lines). The dc conductivity (as solid lines) is also shown for comparison. The ac and dc conductivity basically agree to each other quite well except a small shift to higher conductivity in ac at some regions. They all decrease as the temperature decreasing, which is consistent with a typical semiconductor (or insulator) behavior. The absolute conductivity is $\sim10^{-8}$ $(\Omega\ \mathrm{cm})^{-1}$ for $La_{0.8}Sr_{0.2}FeO_3$ at 80 K. It quickly increases in the compounds with more Sr doping and becomes 0.1 $(\Omega\ \mathrm{cm})^{-1}$ for $La_{0.2}Sr_{0.8}FeO_3$ at low temperature. Many orders of magnitude changes on the conductivity by Sr doping at low temperature is clearly identified. At higher temperature they all merge to ~0.1 $(\Omega\ \mathrm{cm})^{-1}$ at 300 K for all compounds. Notice that in $La_{0.4}Sr_{0.6}FeO_3$ there is a weak transition on the dc (and ac) conductivity at ~200 K. The slop of the plot clearly increases at this transition temperature suggesting that a insulating phase may have been switched to a semiconductor (or poor metal) at this temperature by cooling. For $La_{0.2}Sr_{0.8}FeO_3$ the conductivity becomes relatively flat but no obvious transition can be seen. A wiggle on the conductivity in $La_{0.8}Sr_{0.2}FeO_3$ (the insulating end) is seen at ~160 K. From the original dielectric constant results (Fig. 1) we know that this weak slop changing on the conductivity is associated with the dipolar activated process. Interestingly, this property extents to the dc conductivity measurement.

IV. CONCLUSIONS

Many $La_{1-x}Sr_xMO_3$ (M is a transition metal) perovskite oxides present the metal-insulator transition with hole doping. These materials possess a feature different from the older metallic materials: the phase proximity between the metallic and insulating states. This feature lets us to perform a measurement to observe how the polarizability in the insulating phase changes while they approach the metal-insulator transition. $La_{1-x}Sr_xFeO_3$ compounds are especially suitable for this purpose because it does not have the transition until $x\sim1$. At insulating site, $x\sim0.8$, the dielectric constant is $\sim10^5$ at low frequency and room temperature. It drops to ~20 at low temperature with weak frequency dependence (a high-frequency limit). This temperature and frequency dependence is well interpreted by a Debye thermally activated process. The activation energy associated with this process is ~260 meV. When the Sr-doping increases, we continuously see this activated process but with gradually decreasing strength. More importantly, the activation energy shows a linear decay and it almost vanishes at $x=0.2$ (metallic side). At the metallic side, $x\sim0.2$, the dielectric constant becomes even higher, reaching $\sim10^7$ but with different origin. The dipolar polarizability still exists but is negligible relative to the new low-frequency polarization. We believe that this part of the dielectric constant is due to more loosely bound charge carriers. One evidence is the high conductivity found in the high Sr doping samples. One interesting observation is that the gap energy deduced from the temperature-dependent-conductivity measurement is very close to the dipolar activation energy. This suggests that in the perovskite oxides there is a unique electronic property that has characteristics of both dipolar unit and loosely bound carriers.

ACKNOWLEDGMENTS

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