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## Near-Debye relaxation processes in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

Z C Xia<sup>1</sup>, C Q Tang<sup>1</sup> and D X Zhou<sup>2</sup>

<sup>1</sup>Department of Physics, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China

<sup>2</sup>Department of Electronics, Huazhong University of Science and Technology, Wuhan, 430074, People's Republic of China

E-mail: xia9020@public.wh.hb.cn

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### Abstract

Lanthanum manganite oxide specimens,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $x = 0.2, 0.3, 0.4$  and  $0.5$ ) have been fabricated and their dielectric spectra have been measured. The experimental results show that the dielectric relaxation processes of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  have near-Debye properties and their dielectric spectra can be fitted with well defined semicircles. In  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , the dielectric relaxation results mainly from the trapped Mn-3d electron hopping via  $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ ; the hopping process can be described as a like-dipole torque. The near-Debye relaxation properties show that the interaction between like-dipole,  $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ , is weak. With increasing Sr-dopant, when  $x < 0.5$ , the dielectric loss peak frequency decreases however, when  $x > 0.5$ , the dielectric loss peak frequency increases.

### 1. Introduction

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  (LSM) is well known to have high electronic conductivity, oxygen ionic conductivity, and high activity as an oxidation catalyst at a high temperature ( $\sim 1273$  K) [1]. It is of potential interest as a cathode material in solid oxide fuel cells (SOFCs). Many studies of the physical and chemical properties of cathode materials have been reported [2–8]. Although some electronic and ionic conducting mechanisms for the perovskite oxides have been proposed, the conduction mechanisms of LSM are not yet fully understood. It is well known that the dielectric spectrum measurement is a useful tool for understanding the origin and nature of the interaction between dipoles. Modern many-body theory of the dielectric relaxation of condensed matter asserts that the ideal Debye relaxation process is physically impossible in an interacting system [9]. Thus, it is very important to ascertain to what extent the response departs from the Debye ideal, since this may give a better insight into the nature of interactions between the dipole species responsible for the relaxation process. In this paper, the varied Sr-dopant LSMs were fabricated and their dielectric relaxation spectra were measured. Meanwhile, the formation and structure of the like-dipole,  $\text{Mn}^{3+}\text{--O--Mn}^{4+}$ , are analysed in this paper. The experimental results and theory analysis may help us to understand the electrical properties of LSM.

## 2. Experimental procedure

The required proportion of starting powders of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and  $\text{MnO}_2$  (all of 99.99% purity) were mixed with ethanol and ball-milled for 24 h, followed by drying at 473 K and calcination at 1423 K in air for 12 h. The calcination process was repeated many times until the reaction products were confirmed by x-ray diffractometry to be of a single phase. The compositions of synthesized powder were  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (referred to in this article as LSM2),  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (LSM3),  $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  (LSM4) and  $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  (LSM5) respectively. Then, these powders were mixed with ethanol, ball-milled for 24 h, and compacted to flat plates by uniaxial pressing (diameter 30 mm and thickness 1.5 mm) respectively. Finally, these plates were sintered at 1473 K in air for 12 h. In order to measure the dielectric properties of these samples, both surfaces of the plates were polished. The dielectric spectra were measured at room temperature in the frequency range 20 Hz–1000 kHz employing an HP4284A and its accessory HP16451B.

## 3. Results and discussion

### 3.1. Experimental results

For each of the samples studied, a well defined semicircle was observed in the dielectric spectrum. Typical spectra are shown in figures 1(a), (b), (c) and (d) for LSM2, LSM3, LSM4 and LSM5 respectively. These dielectric relaxation spectra can be fitted with near-perfect semicircles. For each semicircle, we may obtain the radius,  $R$  (from the intercept on the real axis). The radii of the semicircles of figures 1(a), (b), (c) and (d) are equal to 0.24, 0.5, 0.3 and 1.0 respectively.

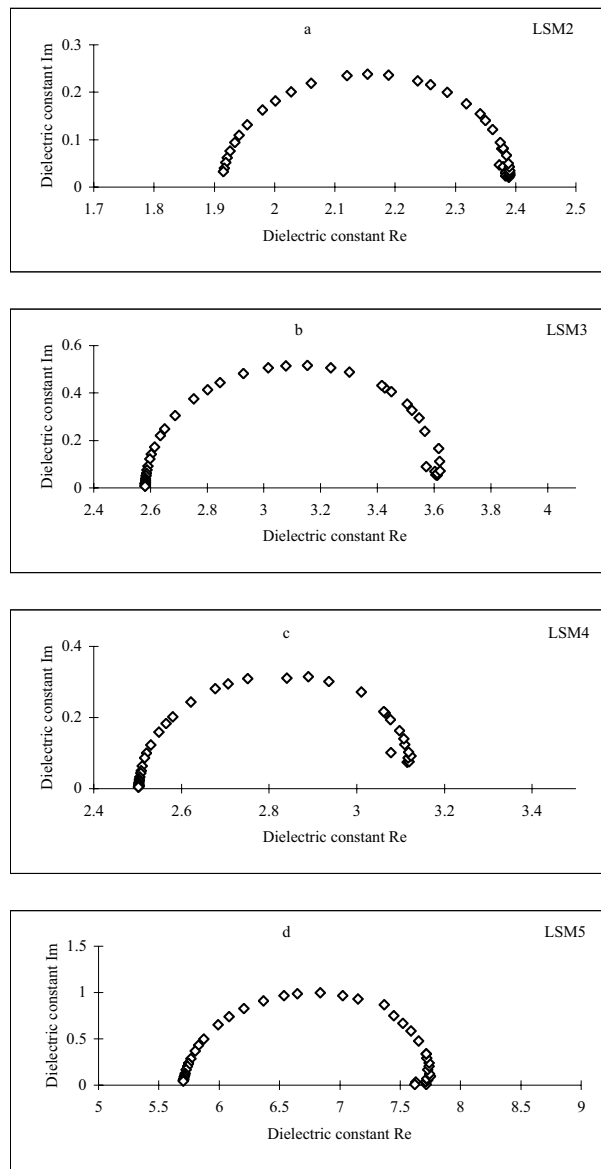
The frequency dependence of the dielectric losses of LSM2, LSM3, LSM4 and LSM5 are shown in figures 2(a), (b), (c) and (d) respectively. For each of the samples, a symmetry dielectric loss peak can be observed at high-frequency range. The dielectric loss peak frequencies are 60, 6, 4 and 10 kHz for LSM2, LSM3, LSM4 and LSM5 respectively.

### 3.2. The dielectric relaxation process

LSM has a slightly distorted pseudocubic perovskite structure, the Mn ions and O ions form  $\text{Mn-O}_6$  octahedrons, in which the Mn ion is situated at the centre of the octahedron and the oxygen ions (or oxygen vacancies) are situated at the six points of the octahedron as shown in figure 3(a).

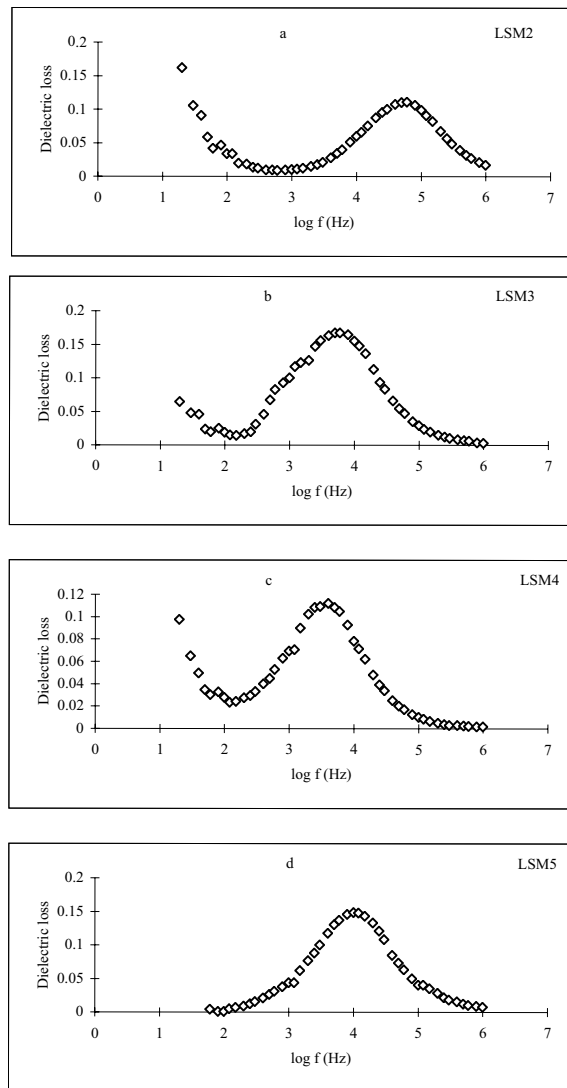
Since the radius of  $\text{Sr}^{2+}$  is similar to that of  $\text{La}^{3+}$ , the  $\text{Sr}^{2+}$  is incorporated in the  $\text{LaMnO}_3$  lattice on the  $\text{La}^{3+}$  site. The difference of the charges between  $\text{La}^{3+}$  and  $\text{Sr}^{2+}$  can be compensated in two ways. The first is  $\text{Mn}^{3+}$  ions give up a d-band electron and form  $\text{Mn}^{4+}$  ions in equal amounts of  $\text{Sr}^{2+}$  ions at high  $P_{\text{O}_2}$  (electric charge compensation), the second is to form oxygen vacancies of half of the amount of  $\text{Sr}^{2+}$  ions at low  $P_{\text{O}_2}$  (ionic charge compensation). Kuo *et al* reported from experimental results and theory calculation that the oxygen vacancy concentration was very low at the  $P_{\text{O}_2} = 0.21$  atm for Sr-doped  $\text{LaMnO}_3$ [10]. In this paper, we considered mainly the first compensation since the samples were sintered in air and the oxygen vacancy concentration was low at room temperature.

In LSM, in order to maintain the maximum entropy of the system, the doped  $\text{Sr}^{2+}$  ions are distributed uniformly at the substituted  $\text{La}^{3+}$  ion sites. Meanwhile, the formed  $\text{Mn}^{4+}$  ions will also be distributed around the  $\text{Sr}^{2+}$  ion sites randomly. Thus, in the LSM system, some of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions form  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds. Under the applied field, the



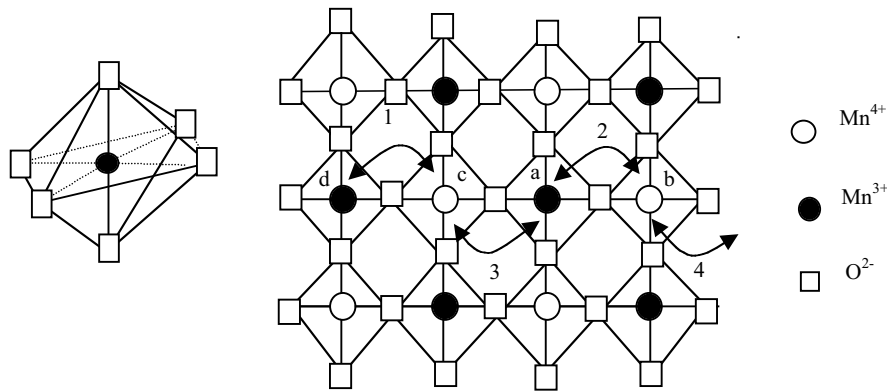
**Figure 1.** The dielectric spectra for samples: (a) LSM2, (b) LSM3, (c) LSM4 and (d) LSM5.

Mn-3d electrons in  $\text{Mn}^{3+}$  ions can hop from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  via the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds [11]. However, the substitution of  $\text{Sr}^{2+}$  in  $\text{La}^{3+}$  and the formation of  $\text{Mn}^{4+}$  ions will make the lattice distort and produce a distortion field. Consequently, the distortion field forms an obstacle to the Mn-3d hopping process. That is, the Mn-3d electrons are trapped or localized by the distortion field. The degree that the lattice is distorted is related to the Sr-dopant,  $x$ . Chen *et al* reported the dielectric relaxation of the perovskite structure  $\text{Sr}(\text{TiFe})\text{O}_{3-\delta}$  could be attributed to the localization of polarons on residual defects, the short-range hopping of weakly bonded defects, such as  $\text{Ti}^{4+} \Leftrightarrow \text{Ti}^{3+}$  and  $\text{Fe}^{4+} \Leftrightarrow \text{Fe}^{3+}$ , leads to a net dipole moment, and hence, originates the dielectric loss peak [12]. The same case was reported for doped  $\text{SrTiO}_3$



**Figure 2.** Frequency dependence of the dielectric loss for samples: (a) LSM2, (b) LSM3, (c) LSM4 and (d) LSM5 at room temperature.

perovskite [13]. In this paper, from the structure analysis, the relaxation processes of LSM are attributed to trapped or localized Mn-3d electron hopping between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  lattice sites via  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds, the hopping process is equivalent to the reorientation of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds. Thus, the dielectric relaxation behaviour of LSM can be ascribed to the trapped Mn-3d electron hopping process, which corresponds to a like-dipole,  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ , torque. Meanwhile, under an applied field, the Mn-3d can transport from a  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  to the other  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  as the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds form a linked path. Thus, the relaxation time of the like-dipole is related to the length of the linked path and the degree of distortion of the lattice. Obviously, the relaxation time of the like-dipole is larger than that of the free electron due to the distortion fields.



**Figure 3.** (a) The structure of  $\text{Mn-O}_6$  and (b) the Mn-3d electron hopping processes on the Mn-O plane.

In figure 1, the dielectric spectra can be fitted with perfect semicircles, the centre of each semicircle locates at the real axis of the dielectric constant. The results show that the relaxation process of LSM can be described as a near-Debye relaxation process. Since less than one  $\text{Mn}^{3+}$  in each  $\text{Mn-O}_6$  octahedron is transformed into  $\text{Mn}^{4+}$  ions as  $x < 0.5$ , the concentration of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond is low, the probability of the formation of an  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  cluster is small. That is, the distribution of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond is isolated and random [14]. According to electrostatics theory, the dipole-dipole interaction decays rapidly with the distance between the dipoles, and so the dipole-dipole interaction is smaller than that between the dipoles and the lattice. Thus, the interaction between dipoles can be neglected and the interaction comes mainly from lattice distortion for LSM; this can be seen from the magnitude of the activation energies of the lattice and dipole respectively. Experimental results show that the activation energy linked with the properties of the lattice is 250 meV, however, the activation energy associated with dipoles is 75 meV for perovskite structure PLTC(20,0) materials [13]. Thus, in the present work, the relaxation process of LSM is mainly attributed to the Mn-3d electron hopping among  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds due to the low activation energy. When the Sr-dopant is low, the concentration of  $\text{Mn}^{4+}$  is low and the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond is separated by other  $\text{Mn}^{3+}$ . Thus, the Mn-3d electron hops to one of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  with low activation energy. The hopping process is shown in figure 3(b), For site  $d$ , the trapped 3d electron may hop between site  $d$  and  $c$  along path 1 with hopping time  $\tau$ .

For LSM, with the increase in Sr-dopant, the concentration of  $\text{Mn}^{4+}$  ions increases due to the electric neutral condition. Thus, the number of  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond increases and the probability of formation of  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  clusters increases. When Sr-dopant  $x = 0.5$ , the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  can form a linked path as shown in figure 3(b). The Mn-3d electrons can hop continuously from  $\text{Mn}^{3+}$  ion to  $\text{Mn}^{4+}$  via more than one  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond. Here, we assume the lattice of LSM is perfect. A Mn-3d electron, located at site  $a$ , hops along path 2, and then continuously hops along path 4 to the next  $\text{Mn}^{4+}$ . Meanwhile, another Mn-3d electron, located at site  $d$ , hops along path 1 to site  $c$ , then, hops along path 3 to site  $a$ , and so on. In the two continuous hopping processes from site  $d$  to  $a$ , the hopping time is equal to  $2\tau$  (here, the difference between paths 1, 2, 3 and 3 is neglected). Therefore, with an increase in the Sr-dopant, the probability of formation of linked  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds increases and the Mn-3d electron hopping time increases. That is, the relaxation time increases, it can be seen

in figure 2(a), (b) and (c) that the dielectric loss peak frequency of LSM2, 60 kHz is larger than that of LSM3, 6 kHz, and larger than that of LSM4, 4 kHz.

When the Sr-dopant  $x \geq 0.5$ , the concentration of  $\text{Mn}^{4+}$  ions increases and is higher than that of  $\text{Mn}^{3+}$  ions. In this case, the  $\text{Mn}^{4+}$  ions may form clusters, namely, more than one  $\text{Mn}^{4+}$  ion becomes a deep well for Mn-3d electrons. When a Mn-3d electron hops to the well, the Mn-3d electron will be trapped, thus, the length and amount of continuous hopping paths decrease, that is, the relaxation time become short and the dielectric loss peak frequency increases. As shown in figure 2(d), the dielectric loss peak frequency of LSM5 is higher than that of LSM4.

From the lattice distortion analysis, with the increasing of Sr-dopant from 0.0 to 0.5, the lattice constant decreases from 5.54 Å to 5.47 Å, and the distance between Mn ions decreases [15]. Thus the interaction between lattice and the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  dipole increases and the localization degree of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  dipole increases, the dipole hopping processes become hard, the hopping time becomes long and the dielectric loss peak frequency decreases. When the Sr-dopant,  $x$ , is larger than 0.5, the distance between Mn ions increases, the same case was reported in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$  [16]. With the increasing of the distance between Mn ions, interaction between the lattice and the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  dipole decreases the localization degree of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  dipole decreases and the hopping processes become easy, the hopping time becomes short and the dielectric loss peak frequency increases. The analysis is the same as the experimental results shown in figure 2.

On the other hand, for the disordered matrix of LSM, in which the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond forms a random distribution and linked path from the cathode to the anode, the long-range movement, from the cathode to the anode, of the bonded Mn-3d electrons gives the DC conduction, which was shown in figure 2 at the low-frequency range. Meanwhile, the oxygen vacancies transported from the anode to the cathode also contributed to DC conduction, a similar phenomenon was reported for  $\text{Sr}(\text{TiFe})\text{O}_{3-\delta}$  [12].

#### 4. Conclusions

The dielectric relaxation process of the LSM system is attributed to the trapped Mn-3d electron hopping from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  via  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds, the hopping can be described as a like-dipole torque.

In the LSM system, the dipole-dipole interactions.  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bonds can be neglected due to the uniform distribution of the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  bond and the weak dipole-dipole interactions. Thus, the relaxation process of the system is similar to Debye relaxation.

With the increase of Sr-dopant,  $x$ , the concentration of the  $\text{Mn}^{4+}$  ions increases, the amount of the like-dipole increases, the length and amount of continuous hopping paths increases and the hopping time increases, thus, the dielectric loss peak frequency decreases.

When the Sr-dopant  $x \geq 0.5$ , the  $\text{Mn}^{4+}$  ions may form a cluster which is a deep well for Mn-3d electrons. When a Mn-3d electron hops to the deep well, it will be trapped, thus, the well will reduce the length of the hopping path and reduce the hopping time. Thus, as  $x > 0.5$ , the dielectric loss peak frequency of LSM5 is higher than that of LSM4.

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