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Zener relaxation in manganites?

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Abstract

We conducted internal friction (IF) and elastic modulus measurements on several manganites in the temperature range 100–500 K. The $La_{1-x}Ca_xMnO_3$ series, with $x = 0$, 0.1, 0.2, 0.33 and 1, was studied showing the magnetic phase transitions and two additional IF peaks around 320 and 400 K, respectively. Both, peaks associated to relaxations, present activation enthalpies of 2–3 and 3–6 eV, whose intensity depends on x. In this work we associate the 400 K IF peak to a Zener relaxation of the cations that occupied the same crystallographic site. We believe that the 320 K IF peak is due to different crystalline states of the samples.

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Keywords: Manganites; Zener relaxation; Internal friction

1. Introduction

Perovkites of manganese have been studied since 1950. Jonker et al. [1] began a systematic study of these perovskites, whose general formulae is ABO_3, where O is oxygen, A is La^{3+} or Ca^{2+}, Sr^{2+}, Ba^{2+}. B is manganese in this case and the partial substitution of A^{3+} ions by other A^{2+} ions gives rise to a mix of Mn^{3+} and Mn^{4+}. They found, in these mixed- valence manganites, an anomalous fact that shows, at the same time, ferromagnetic (FM) and metal–insulator transitions. These facts were explained by Zener in 1951 [2], introducing a new mechanism called "double exchange", where the localized electrons of Mn^{4+} cores are FM coupled and the extra electron in Mn^{3+} ions can jump between the manganese ions with the same FM spin polarization. Consequently, the material became ferromagnetic and also metallic. The later addition of extra effects as Jahn–Teller distortions, magnetic polarons, etc. explained the overall magnetic and electric behavior of these manganites.

Our group began to study the anelastic properties of these manganites in 1999. We found that there was a huge internal friction peak near 400 K in $La_{2/3}Sr_{1/3}MnO_3$ with 5.4 eV of relaxation activation enthalpy [3].Later, we found the same relaxation in other manganites like $La_{2/3}Ca_{1/3}MnO_3$, $La_{2/3}Ba_{1/3}MnO_3$, $Pr_{0.65}Ca_{0.35}MnO_3$ and $Pr_{0.5}Ca_{0.5}MnO_3$. All of them had activation enthalpies between 3 and 6 eV [4,5].

This anelastic relaxation is very interesting because it is larger than that obtained in the ferromagnetic transition and does not appears in other physical properties measured (resistivity and magnetization).

In the search for the microscopic origin of this anelastic relaxation, we have measured the anelastic spectrum of $CaMnO_3$ and $LaMnO_3$. In both cases we found no evidence of this relaxation at 400 K. Hence we prepared $La_{0.9}Ca_{0.1}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$. In this paper we resume our results of those measurements. The conclusion was that this anelastic relaxation at 400 K might be a Zener relaxation or links reorientation. This effect was studied in detail in the compound ZnAg [6] and it claims, in our case, an interchange of La and Ca site ions.

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2. Experimental

All measurements were performed in an inverted forced torsion pendulum able to change the sample temperature between 4 and 500 K and the measuring frequency between 0.01 and 10 Hz. The deformations used were less than 10^{-4}, depending upon the sample. The temperature rates were 0.5–1 K/min.

Samples have different synthesized routes. $CaMnO_3$, $La_{0.9}Ca_{0.1}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$ were prepared starting with the corresponding quantities of dried La_2O_3 (4 N), CO_3Ca (2 N) and MnO_2 (2 N), pressing a pellet, heating at 1200°C and grinding several times.

$LaMnO_3$ samples have two origins. One was made at Universite of Geneve (SS) and the other at Centro Atómico Constituyentes (BsAs) (GL).

The $LaMnO_3$ (GL) sample was obtained by a denitration process under microwave irradiation and a thermal treatment at 1000°C in air atmosphere. The powder was pelletized and sintered at 1000°C in air atmosphere.

The other $LaMnO_3$ (SS) sample was prepared following the solid solution reaction. Adequate quantities of dried La_2O_3 (4 N) mixed with MnO (2 N) were heated for 24 h in an argon flux atmosphere at 1375°C. This process was repeated three times. Finally they were pelletized and pressed at 1.5 ton and again heated for 8 h in an argon atmosphere at 1375°C.

3. Results

Measurements on $CaMnO_3$ and $LaMnO_3$ are shown in Figs. 1 and 2. There is one IF peak at 300–350 K in each sample. These peaks are of anelastic relaxation with an activation enthalpy of $H = 2.8 \pm 0.2$ eV in $CaMnO_3$ and $H = 2.2 \pm 0.2$ eV in $LaMnO_3$ (SS).

Fig. 3 shows the results for $La_{0.9}Ca_{0.1}MnO_3$ ($Ca_{0.1}$), $La_{0.8}Ca_{0.2}MnO_3$ ($Ca_{0.2}$), $La_{2/3}Ca_{1/3}MnO_3$ ($Ca_{0.3}$) and $LaMnO_3$ ($Ca_{0.0}$) for comparision. This figure shows that the IF peaks measured in $LaMnO_3$ and $CaMnO_3$ are due to another origin and are in a temperature position 300–350 K, lower than the studied relaxation at 400 K. In this figure we can see both peaks and how the 400 K peak increases with Ca concentration. Also shown is the baseline of the background of IF at 400 K for $LaMnO_3$ (SS), showing that there is no IF peak around 400 K.

The intensity of the internal friction peak is related to the concentration of the substitutional ion [7]. We have plotted in Fig. 4 the intensity of the IF peaks vs. Ca concentration.

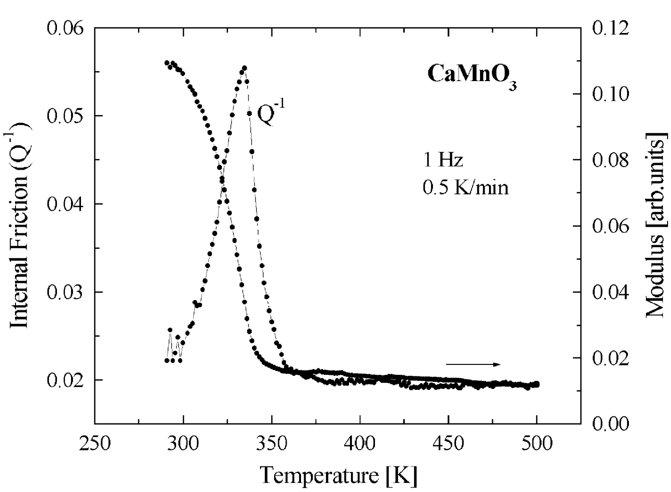

Fig. 1. $CaMnO_3$ mechanical spectrum.

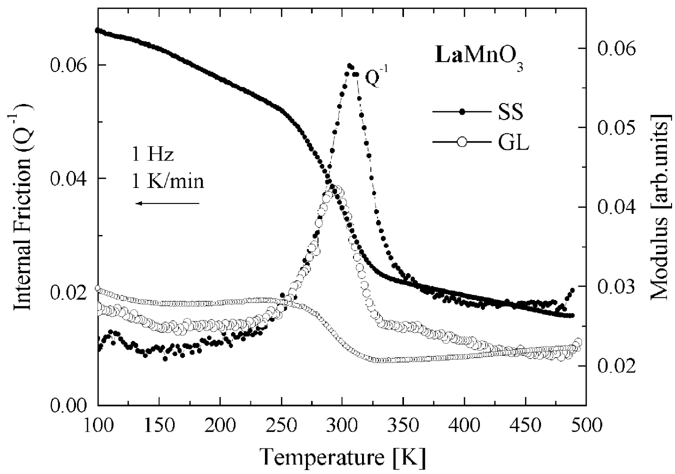

Fig. 2. $LaMnO_3$ mechanical spectrum.

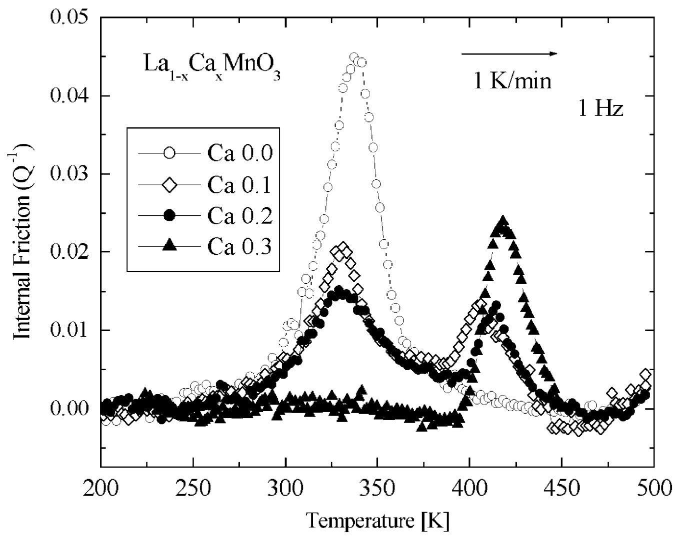

Fig. 3. Mechanical spectrum of several manganites.

4. Conclusions

These measurements show us two anelastic relaxations, the first at 300–350 K and the second around 400–450 K. The first one, present in almost all the samples except $La_{2/3}Ca_{1/3}MnO_3$, has an activation enthalpy of 2–3 eV. The second has an activation enthalpy of 3.7 eV in $La_{2/3}Ca_{1/3}MnO_3$ and was not measured in the other two samples ($La_{0.9}Ca_{0.1}MnO_3$ and $La_{0.8}Ca_{0.2}MnO_3$). We have not enough evidence to elucidate if the microscopic origin

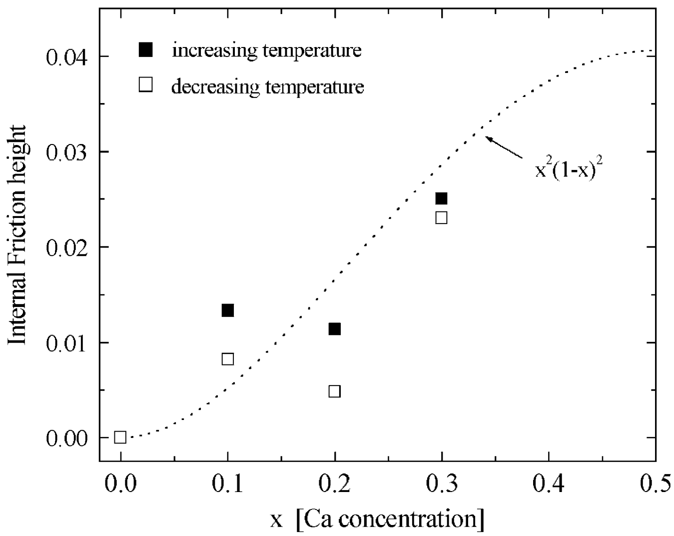

Fig. 4. Intensity of IF peak vs. Ca concentration.

of the 300–350 K anelastic relaxation is a problem of sample synthesis (grain size after sintering) or anything else. In Fig. 3 we can see that there is no IF peak for $LaMnO_3$ in the 400–450 K range. Including Ca as a substitution of La makes an IF peak appear and increases with Ca concentration up to $x = 0.3$. The theory of anelastic Zener relaxation predicts [2,7] that there is a relation between the intensity of the IF peak and the concentration x of the substitutional ion proportional to x^2 $(1-x^2)$. Zener relaxation involves Ca reorientation links. These are jumps of substitutional ions (Ca) that occupy the same crystallographic site of La and are induced by alternative deformation during mechanical analysis. All these facts made us conclude that there might be Zener relaxation in manganites when we replace A site ions. Further measures, with samples prepared under the same chemical conditions, are in progress to increase the experimental basis of the explanation of the 400–450 K IF peak in manganites.

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