Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

Positron annihilation and defect structure of $La_{1-x}Sr_xFeO_3$ Electronic Ceramic

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$La_{1-x}Sr_xFeO_3$ electronic ceramics with different amount of Sr additions were prepared and sintered in different conditions. Their positron annihilation spectral and conductivity under different temperatures and partial pressure were measured and analysed. The defect structure of $La_{1-x}Sr_xFeO_3$ is proposed to account for its electrical conduction behaviour, and the conduction mechanism was discussed.

1. Introduction

Some perovskite-type oxides with high electronic conductivity, such as $LaCoO_3$-$SrCoO_3$, $LaFeO_3$-$SrFeO_3$, have been investigated as potential electrode materials for electrochemical and thermal processing applications. Mizusaki et al have proposed solid solution perovskite-type oxides based on $LaFeO_3$ as candidate materials for MHD electrode [1]. The conductivity and Seebeck coefficient were measured and relate to the defect chemistry. It was found that the electrical properties of $LaFeO_3$ were determined not only by the concentration of oxygen vacancies, but also by the La/Fe ratio [2].

In $La_{1-x}M_xBO_3$ (M: divalent cation; B: transition metal), it is generally believed that the concentration of p-type carriers depends on $[M'_{La}]=x$ which is much higher than $[V'''_{La}]$. Therefore, the conductivity of $La_{1-x}Sr_xFeO_3$(LSF) is higher than that of $LaFeO_3$. Moreover, because of the valence-control effect of B associated with M'_{La}, the conductivity is expected to be less sensitive to impurities or deviations in the ratio of A-site metal ions to B-site metal ions [3].

In addition, $La_{1-x}Sr_xFeO_3$ was found to possess positive humidity-sensitive characteristics (its conductivity increases with the increasing relative humidity), and its complex impedance spectral were measured and related to its conduction under different r.h. [4,5]. Since it is very important to investigate its defect structure in order to understand its conduction mechanism, the purpose of the present work is to investigate its electrical conduction and defect structure using the positron annihilation and electrical conduction analysis under different conditions.

2. Experiment

$La_{1-x}Sr_xFeO_3$ ($0\leq x\leq 1$) ceramic materials were prepared by conventional ceramic process as described below. La_2O_3, $SrCO_3$ and Fe_2O_3 oxide powders were mixed together in the proper La:Sr:Fe ratios of (1-x):2x:1, and ball milled using acetone. The powders were calcined at 800°C for 24h in air, followed by heat treatment at 1000°C

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**The work was supported by the National Natural Science Foundation of China under grant No. 68901003.

for 24h in oxygen. The oxide powders thus obtained were ball milled again and pressed into pellets of 6-20mm in diameter and 1-2mm in thickness, and then sintered at different temperatures and atmospheres.

Differential thermal analysis (DTA), thermogravimetric analysis (TG) and X-ray diffraction (XRD) analysis were carried out in order to study the synthesis mechanism of the materials. DTA and TG measurement for mixing powders of La_2O_3, $SrCO_3$ and Fe_2O_3 oxides with different molar ratios were conducted using a heating rate of 10°C/min over the temperature range of 20°C and 1200°C. The electrical conduction of the samples was measured at different temperatures and partial pressure Po_2. The oxygen Po_2 were monitored using a ZrO_2 oxygen sensor.

The positron lifetime spectral in all LSF samples were measured with a time resolution of 220ps from ^{60}Co. Each spectrum contained a total of 1×10^6 counts. After substrating background and source contributions, each lifetime spectrum was analysed with three components by the computer program POSITRONFIT-EXTENDED. The mean lifetime τ_m was calculated based on the intensity and lifetime of the first two components.

3. Results and Discussions

For thermal analysis, there exists an endothermic peak in DTA and a slight weight loss in TG at about 800°C, which might relate to the formation of LSF. Based on the phase diagram of $La_2O_3+Fe_2O_3$, a liquid phase will appear when the temperature is above 1490°C. A temperature of 800°C was used for the calcination followed by sintering at temperatures below 1400°C. XRD analysis has confirmed that LSF begins to form at 800°C and only LSF diffraction peaks exist for samples sintered at 1300°C.

La^{2+} was substituted by Sr^{2+} in some A-site positions in the perovskite structure, which might result in an increase in the crystal lattice constant. However XRD experiments indicated that the crystal parameters of the sample increased with the increasing amount of Sr, which might suggest that the partial transformation of Fe^{3+} to Fe^{4+} could account for the decrease in crystal lattice parameters.

Figure 1 shows the resistance of the samples with differing amounts of Sr. As can be seen from the figure, $LaFeO_3$ has a very high resistivity while LSF (x>0) demonstrates a very high conductivity with the maximum value at 0.1 to 0.3.

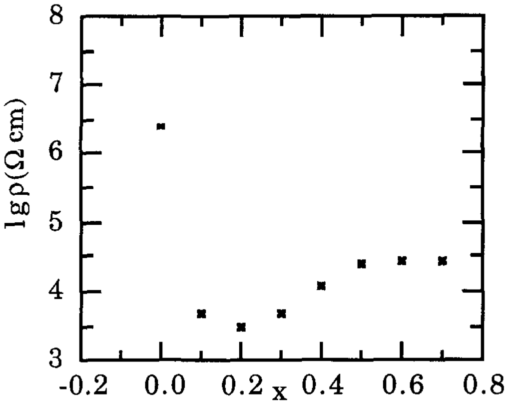

Fig. 1 Resistivity of LSF at 25°C

The results of the resistance-temperature properties measurement indicate that LSF shows very high conductivity, especially when temperature is above 300°C. Figure 2 shows the electrical conduction-Po_2 relationship measured at 700°C. As it can be seen from the diagram, its conduction is also determined by the ambient atmospheres.

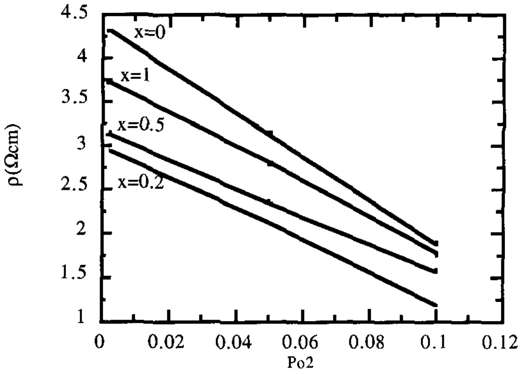

Fig. 2 Po2 dependence of resistivity for $La_{1-x}Sr_xFeO_3$ at 700°C

The composition dependence of the lifetime τ_1 and the mean lifetime τ_m is shown in Fig. 3, and that τ_2 is shown in Fig. 4, respectively.

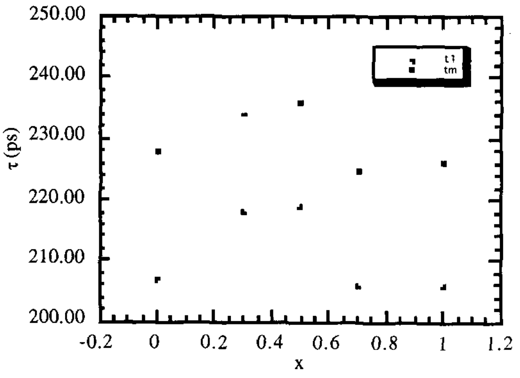

Fig. 3 Positron lifetime τ_1 and τ_m as function of x in $La_{1-x}Sr_xFeO_3$

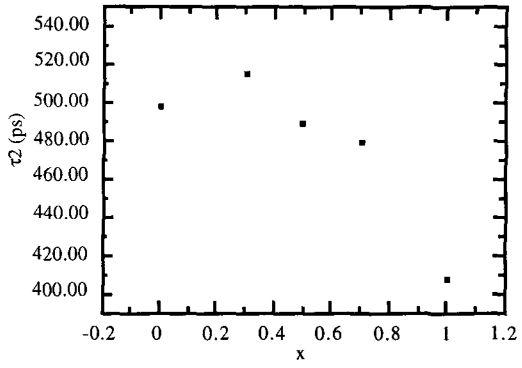

Fig. 4 Positron lifetime τ_2 as a function of x in $La_{1-x}Sr_xFeO_3$

As can been seen in the figures, τ_2 shows a monotone decreasing with x (x>0), while τ_1 experiencing a similar change to τ_m. This indicates that with increasing x, the change of τ_1 associates with the main change in the materials. Since τ_m is inversely proportional to the density of the electron (which is proportional to the conductivity) in the materials, the electrical conduction and positron annihilation has a good agreement with each other if we compare Fig. 3 with Fig. 1.

It is known that in LSF, there exist many kinds of defects such as oxygen vacancies, grain boundaries, voids and dislocations, which all trap positron. Although it is very difficult to relate exactly with which positron states the components τ_1 and τ_2 associate, respectively, we can basically think that the component τ_2 is mainly contributed by positron annihilation in the oxygen vacancies, and τ_1 is a weighted average of the lifetimes of free positrons and positrons in some shallow trap states. As can be seen in Fig. 3, with decreases in τ_m and increases in x (when x>0), the oxygen vacancies concentration increases with higher value of x. Comparison of the resistance-composition curve in Fig. 1 reveals that conductivity of the samples is not simply a matter of determining oxygen vacancies. There are other positron states, such as $[\mathrm{Sr}'_{\mathrm{La}}]$, $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$ and $[\mathrm{Fe}'_{\mathrm{Fe}}]$ in the LSF ceramic (in this paper the Kroger-Vink notation is used). When $0.1 \le x \le 0.3$, there exists a big difference in conductivity between $x=0$ and $0.1 \le x \le 0.3$ while τ_2 remains similar. This might result from the change in the Fe^{4+} concentration.

The conduction of LSF could be changed by the adjustment in the composition of the materials. To make the electroneutrality, some of the Fe^{3+} will change to Fe^{4+} owing to the introduction of Sr^{2+}. The electron exchange between $\mathrm{Fe}^{4+}/\mathrm{Fe}^{3+}$ $\{[\mathrm{Fe}'_{\mathrm{Fe}}]/\mathrm{Fe}^{\times}_{\mathrm{Fe}}]\}$ and $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ $\{[\mathrm{Fe}^{\times}_{\mathrm{Fe}}]/\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]\}$ contributes to the p-type and n-type conduction respectively. The ratio of $\mathrm{Fe}^{4+}/\mathrm{Fe}^{3+}$ changes with the substitution of La^{2+} by Sr, which will lead to the change in the electrical conduction. In addition, electrical conduction can also be altered by the Po_2 due to the change of $\mathrm{Fe}^{4+}/\mathrm{Fe}^{3+}$ as well.

Considering the following two ionisation processes

$$\mathrm{O}^{\times}_{\mathrm{O}} \rightarrow (1/2)\mathrm{O}_2 + \mathrm{V}^{\bullet\bullet}_{\mathrm{O}} \tag{1}$$
$$2\mathrm{Fe}^{\times}_{\mathrm{Fe}} \rightarrow \mathrm{Fe}'_{\mathrm{Fe}} + \mathrm{Fe}^{\bullet}_{\mathrm{Fe}} \tag{2}$$

And the electroneutrality condition

$$x_p + 2[\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}] = x_n + [\mathrm{Sr}'_{\mathrm{La}}] \tag{3}$$

where x_p and x_n are molar fractions of p-type and n-type carriers respectively. So the main defects in LSF are $[\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}]$, $[\mathrm{Sr}'_{\mathrm{La}}]$, $[\mathrm{Fe}'_{\mathrm{Fe}}]$ and $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$.

Based on Eq. (1), as Po_2 increases, $[\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}]$ and x_n are expected to decrease, so at high Po_2, eq. (3) becomes

$$x_p = [\mathrm{Sr}'_{\mathrm{La}}] = [\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$$

So $[\mathrm{Sr}'_{\mathrm{La}}]$ and $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$ are the main defects at high Po_2, and will increase with higher value of Po_2.

When Po_2 decreases, $[\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}]$ will increase and x_p is expected to decrease, we get

$$2[\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}] = [\mathrm{Sr}'_{\mathrm{La}}]$$

So, $[\mathrm{Sr}'_{\mathrm{La}}]$ and $[\mathrm{V}^{\bullet\bullet}_{\mathrm{O}}]$ are the main defects at low Po_2.

5. Conclusions

The composition dependence of the positron lifetime parameters for LSF suggest that besides oxygen vacancies there exist other positron states, such as $[\mathrm{Sr}'_{\mathrm{La}}]$, $[\mathrm{Fe}'_{\mathrm{Fe}}]$ and $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$ in LSF ceramic. The electrical properties of the material can be described by considering the defect structure. It is found that the main defect in $\mathrm{La}_{1\text{-}x}\mathrm{Sr}_x\mathrm{FeO}_3$ are $[\mathrm{Sr}'_{\mathrm{La}}]$ and $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$ under high Po_2, and the carriers' concentration is determined by $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$. Besides, the concentration of $[\mathrm{Fe}^{\bullet}_{\mathrm{Fe}}]$ will increase with increasing Po_2 .

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