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Characteristics of permittivity and permeability spectra in range of 2−18 GHz microwave frequency for $La_{1-x}Sr_xMn_{1-y}B_yO_3$ (B=Fe, Co, Ni)

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Abstract: Doped $LaMnO_3$ has unusual electromagnetic properties, which makes it possible for this material to be used for absorbing microwave. $LaMnO_3$ systems doped by Sr at site A and Fe or Co, Ni at site B were prepared by sol-gel as an microwave absorption material and their permittivity and permeability spectra were measured by microwave vector network analyzer in the frequency range of 2−18 GHz. A novel phenomenon is discovered that the complex permittivity, complex permeability and electromagnetic loss tangent have suddenly a step change at a certain frequency and the step-change frequency is relevant to content of Sr and Fe or Co, Ni. The samples show mainly dielectric loss when microwave frequency is smaller than the step-change frequency, and mainly magnetic loss when larger than that frequency. It is indicated that anti-ferromagnetic clusters in the material can absorb energy quantum of microwave electromagnetic field to change into ferromagnetic clusters because they can overcome higher energy barrier when the frequency of incident microwave reaches a certain value.

Key words: microwave absorption material; complex permittivity; complex permeability; rare-earth Mn oxide; doped $LaMnO_3$

1 Introduction

Rare-earth manganese oxides with perovskite structure have anti-ferromagnetism in general and ferromagnetism if doped at site A of the crystalline cell by alkaline-earth metal element such as Sr, Ca and Ba. The conductivity of rare-earth manganese oxides is enhanced to approach that of metal or semiconductor from insulating state when doped and their colossal magnetoresistance effect(CMR) is remarkable[1−4]. Consequently, they have been a hot spot in research field of magnetic electronic functional materials due to their unusual electromagnetic properties[5−7]. Besides, the electromagnetic properties are important to develop excellent microwave absorption materials. However, there are very few reports at present on the study of microwave absorption properties. In Ref.[8], $La_{1-x}Sr_xMnO_3$ was prepared by a conventional solid state reaction method and its microwave absorbing properties were studied in the frequency range of 8−14 GHz, but its frequency spectra characteristic of complex permittivity and complex permeability was not given. In our work, $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ was prepared by sol-gel method [9−10] and its microwave absorbing properties was studied in range of 2−18 GHz, which is better in the bandwidth and intensity of microwave absorption than $La_{1-x}Sr_xMnO_3$.

In this work, the spectra of permittivity and permeability for $La_{1-x}Sr_xMn_{1-y}B_yO_3$ (B=Fe, Co, Ni) and the change of electromagnetic loss tangent with microwave frequency were studied in detail to discover the absorption mechanism for this kind of material. It is of importance to study the interaction between electromagnetic wave and matter and to develop an excellent microwave absorption material.

2 Experimental

$La_{1-x}Sr_xMn_{1-y}B_yO_3$ (B=Fe, Co, Ni) was synthesized

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by sol-gel method from La_2O_3, $SrCO_3$, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and other chemicals. Based on the nominal composition and the stoichiometry of $La_{1-x}Sr_xMn_{1-y}FeyO_3$, La_2O_3 and $SrCO_3$ were dissolved in HNO_3 to get a transparent colorless solution, and $Fe(NO_3)_3{\cdot}9H_2O$ and $C_4H_6O_4Mn{\cdot}4H_2O$ were dissolved in water to become a colored solution. The above two kind of solutions were joined in the EDTA solution to form a mixture, stirred by the magnetic force and synthesized for 6 h. Then, the mixture was evaporated to be a brown-black loose xero-gel and calcined at 800 ℃ for 2.5 h. $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ crystalline powders were obtained. $La_{1-x}Sr_xMn_{1-y}Co_yO_3$ and $La_{1-x}Sr_xMn_{1-y}Ni_yO_3$ powders were prepared by similar method.

By XRD, SEM analysis and conductivity measurement, it was discovered that the powders were of perovskite structure. Their morphology looked like stick with length of about 100 nm and diameter of about 10−20 nm and the conductivity was within semiconductor range[10].

The above crystalline powders were mixed with paraffin wax by the ratio of 8:3 in mass fraction and pressed to be annular samples. The complex permittivity and permeability of the samples were measured by HP8722ES microwave vector network analyzer in the frequency range of 2−18 GHz.

3 Results and discussion

3.1 Permittivity and permeability spectra of materials

The change of the complex permittivity and permeability with frequency in range of 2−18 GHz is measured to find the microwave absorption mechanism of the materials. It is confirmed by experiments that $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ has best effects in microwave absorption when x is about 0.2 and y is about 0.12[6−7]. The valence electron configurations of the iron family elements, iron, cobalt, nickel respectively, are $3d^64s^2$, $3d^74s^2$, $3d^84s^2$, because they have many similarities in physical properties such as magnetism and have also a lot of common characteristics in the compound. It is discovered that the characteristic of permittivity and permeability spectra for $La_{0.8}Sr_{0.2}Mn_{0.86}B_{0.14}O_3$ (B=Ni, Co) is similar to that of $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ in microwave band.

3.1.1 Permittivity and permeability spectra of $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ in microwave band

Fig.1 shows the microwave permittivity and permeability spectra of $La_{0.8}Sr_{0.2}Mn_{0.90}Fe_{0.10}O_3$. Nearby 10.5 GHz, the complex permittivity and the complex permeability all have a step-change. The real part, ε' of the complex permittivity in range of 2−18 GHz drops with the increase of microwave frequency as a whole, but has a small increase in step type nearby 10.5 GHz (Fig.1(a)). The imaginary part, ε'', has little change below the frequency value of 10.5 GHz and descends to the very low value in step type above 10.5 GHz (Fig.1(a)). The real part and the imaginary of the complex permeability have also a step type change at 10.5 GHz and this change is opposite to the complex permittivity (Fig.1(b)). μ' changes stably below 10.5 GHz, drops suddenly at 10.5 GHz and decreases continuously above 10.5 GHz. μ'' changes slowly below 10.5 GHz, rises at 10.5 GHz in step type and then drops continuously.

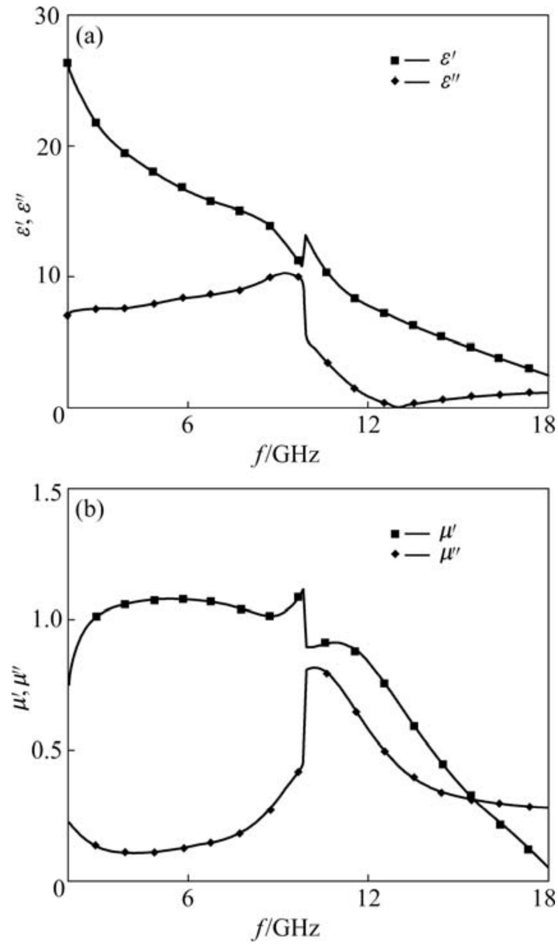

Fig.1 Permittivity (a) and permeability (b) spectra of $La_{0.8}Sr_{0.2}Mn_{0.90}Fe_{0.10}O_3$

Fig.2 shows the permittivity and permeability spectra of $La_{0.8}Sr_{0.2}Mn_{0.88}Fe_{0.12}O_3$ in range of microwave band. Near 12.4 GHz, the complex permittivity and the complex permeability all change suddenly in step type and the tendency of these changes is similar to Fig.1.

The microwave permittivity and permeability spectra of $La_{0.8}Sr_{0.2}Mn_{0.86}Fe_{0.14}O_3$ shown in Fig.3 are very similar to those of $La_{0.8}Sr_{0.2}Mn_{0.88}Fe_{0.12}O_3$ in Fig.2. It is discovered that their positions of the step-change have a small difference that the former occurs nearby 12.5 GHz but the latter nearby 12.4 GHz by making a

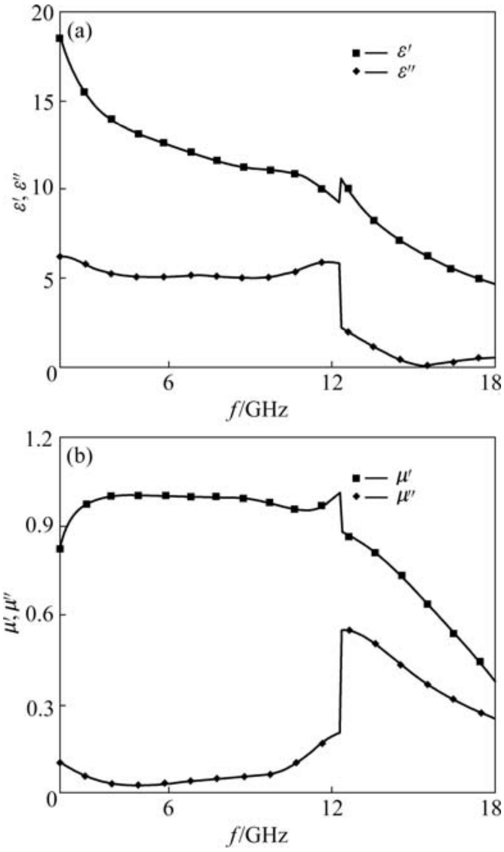

Fig.2 Permittivity (a) and permeability (b) spectra of $La_{0.8}Sr_{0.2}Mn_{0.88}Fe_{0.12}O_3$

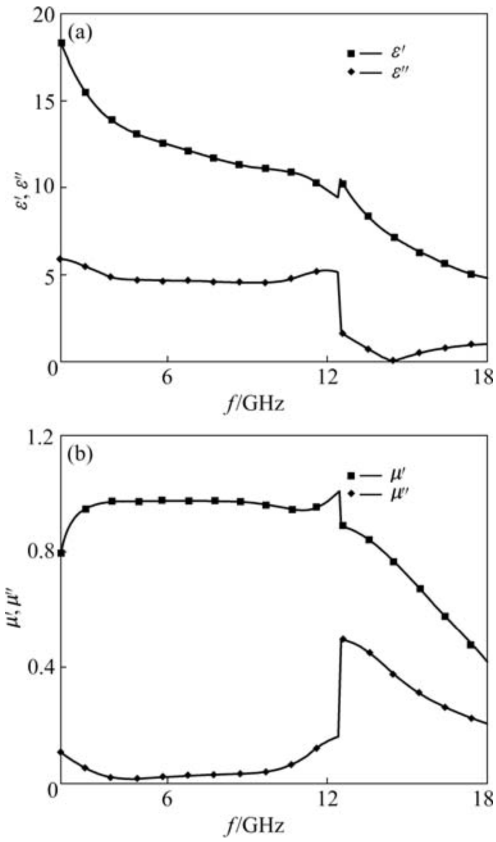

Fig.3 Permittivity (a) and permeability (b) spectra of $La_{0.8}Sr_{0.2}Mn_{0.86}Fe_{0.14}O_3$

comparison between the two primary measurement data.

The microwave permittivity and permeability spectra of $La_{0.85}Sr_{0.15}Mn_{0.86}Fe_{0.14}O_3$ are shown in Fig.4. Nearby 13 GHz, the complex permittivity and complex permeability all have step-changes. The change trend in the rest of the spectra is also similar to that aforementioned.

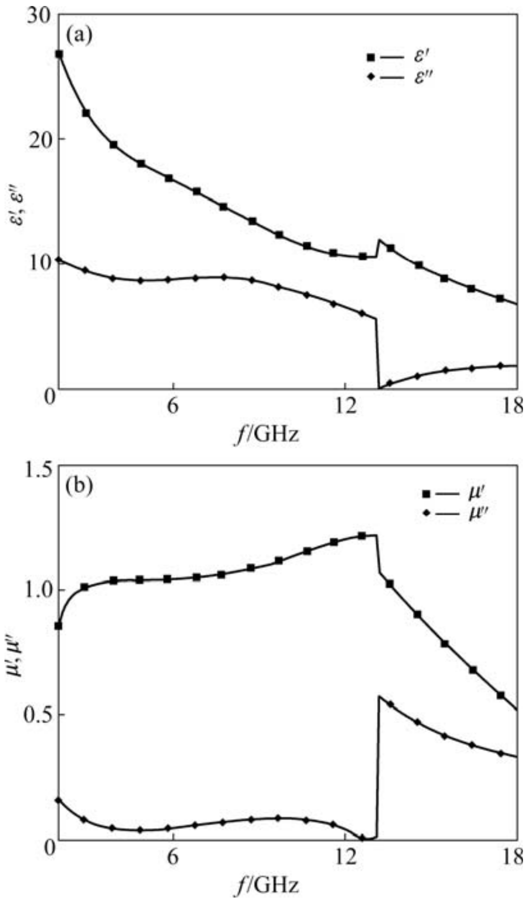

Fig.4 Permittivity (a) and permeability (b) spectra of $La_{0.85}Sr_{0.15}Mn_{0.86}Fe_{0.14}O_3$

The microwave permittivity and permeability spectra of $La_{0.77}Sr_{0.23}$ $Mn_{0.90}Fe_{0.10}O_3$ in Fig.5 are the same basically as Fig.1 and have also a step-change of the complex permittivity or the complex permeability nearby 10.5 GHz.

The common characteristic of the above dielectric and magnetic spectra is that the microwave electromagnetism parameters including the complex permittivity and the complex permeability of $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ system all have the step-change phenomenon in range of 2−18 GHz. This indicates that the microscopic structure of this material has possibly some kind of transformation that should be concerned with the energy of microwave field quantum when microwave interacts with the materials. Sr content at site A and Fe content at site B have certain influence on the

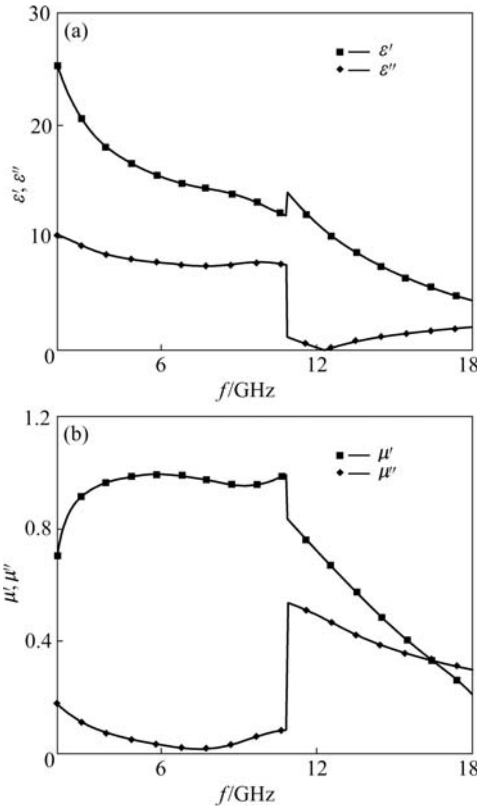

Fig.5 Permittivity (a) and permeability (b) spectra of $La_{0.77}Sr_{0.23}Mn_{0.90}Fe_{0.10}O_3$

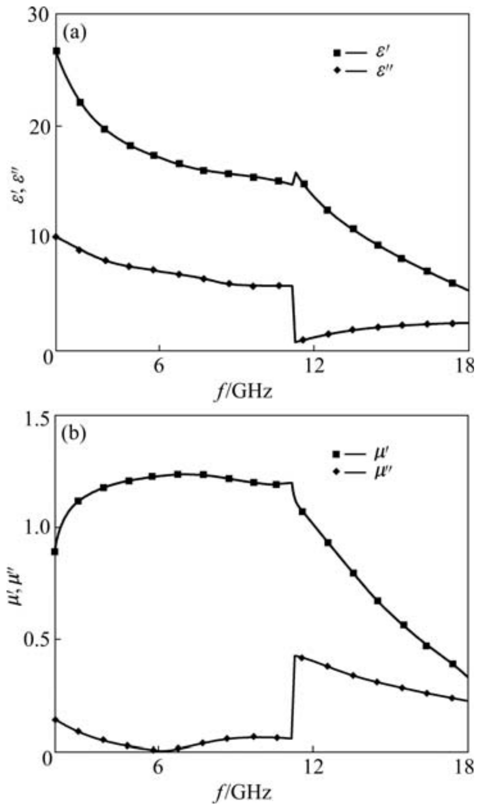

Fig.6 Permittivity (a) and permeability (b) spectra of $La_{0.8}Sr_{0.2}Mn_{0.86}Co_{0.14}O_3$

position of the step-change frequency. When the Sr content is 0.2 and the Fe content is 0.10, 0.12, 0.14, the step-change frequencies respectively are 10.5, 12.4 and 12.5 GHz (Figs.1, 2 and 3). When the Fe content is 0.14 and the Sr content is 0.15 and 0.20, the step-change frequencies respectively are 13 and 12.5 GHz (Figs.3 and 4). When the Fe content is 0.10 and Sr content is 0.2 and 0.23, the step-change frequencies are all 10.5 GHz and the dielectric and magnetic spectra are basically the same (Figs.1 and 5).

3.1.2 Permittivity and permeability spectra of $La_{0.8}Sr_{0.2}$-$Mn_{0.86}B_{0.14}O_3$ (B=Co, Ni) in microwave band

The microwave permittivity and permeability spectra of $La_{0.8}Sr_{0.2}Mn_{0.86}Co_{0.14}O_3$ shown in Fig.6 are similar to $La_{0.8}Sr_{0.2}Mn_{0.86}Fe_{0.14}O_3$ (Fig.3). However, they have different step-change frequencies: ε'' of the Co-doped alloy is greater than that of the Fe-doped and μ'' is smaller. The microwave permittivity and permeability spectra of $La_{0.8}Sr_{0.2}Mn_{0.86}Ni_{0.14}O_3$ shown in Fig.7 are also similar to those of the Fe-doped and the Co-doped at site B aforementioned. This shows that $LaMnO_3$ systems by doping the iron-family elements (Fe, Co, Ni) have the same characteristics of dielectric and magnetic spectra.

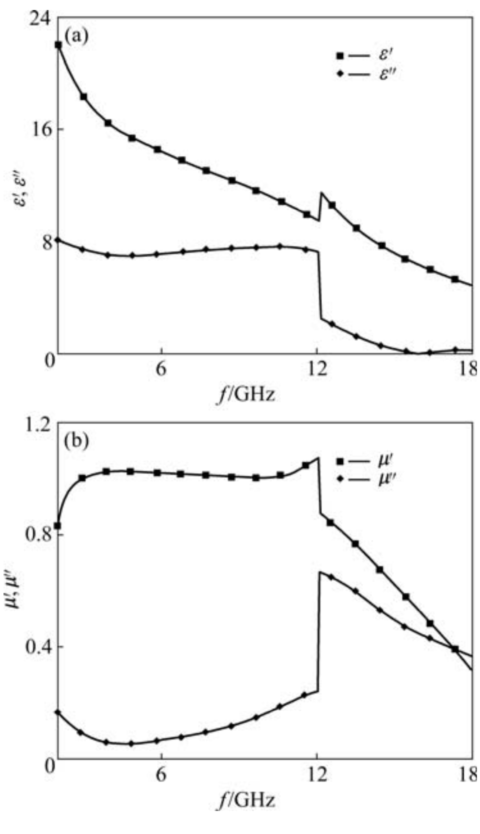

Fig.7 Permittivity (a) and permeability (b) spectra of $La_{0.8}Sr_{0.2}Mn_{0.86}Ni_{0.14}O_3$

3.2 Electromagnetic loss mechanism

The $LaMnO_3$ systems doped by Sr at site A and by Fe, Co, Ni at site B (about x=0.2, y=0.14) have the similar change for the dielectric and the magnetic spectra and their electromagnetism loss mechanism should be the same. Now, the electromagnetism loss mechanism of the materials will be explained by the characteristic change of loss tangent (loss factor) for $La_{0.8}Sr_{0.2}$-$Mn_{1-y}Fe_yO_3$ (y=0.12, y=0.14). According to the data of electromagnetism parameters (complex permittivity and complex permeability), the relations between the dielectric loss tangent($\tan\delta_e$) and magnetic loss tangent($\tan\delta_m$) and microwave frequency for the samples are calculated, as shown Fig.8. In the range of frequency below 12.4 GHz, the value of $\tan\delta_e$ is comparatively greater and the $\tan\delta_m$ is very small. There are the step-changes nearby 12.4 GHz. The $\tan\delta_e$ suddenly falls from an greater value to a smaller one, then to minimum value and rises again. The $\tan\delta_m$ rises suddenly from a smaller value to an greater value, then drops slowly and rises slowly again. It is illustrated that the samples exhibit main dielectric loss below 12.4 GHz and main magnetic loss above 12.4 GHz.

It was thought in general[11−12] that the non-doping $LaMnO_3$ system has anti-ferromagnetic structure. It transforms from the anti-ferromagnetism to

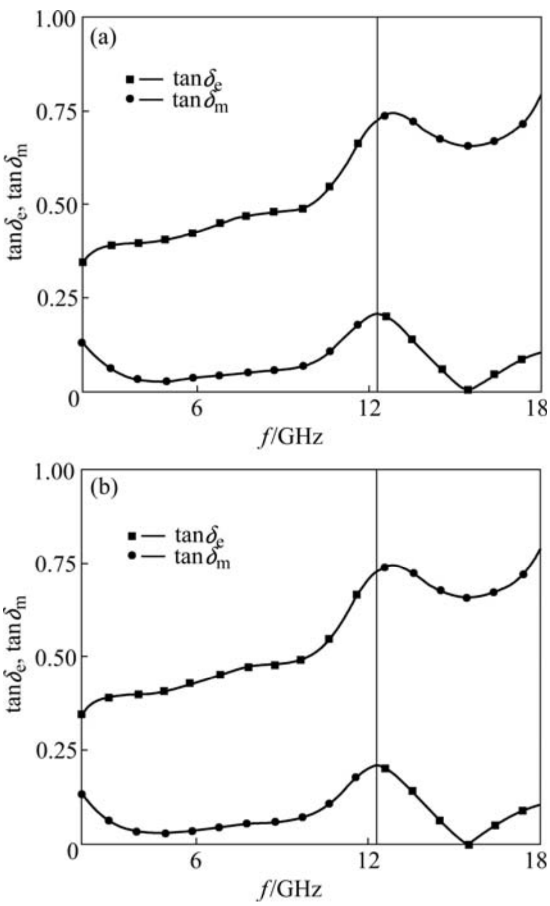

Fig.8 Relationship between loss tangent and microwave frequency for $La_{0.8}Sr_{0.2}Mn_{1-y}Fe_yO_3$: (a) y=0.12; (b) y=0.14

the ferromagnetism and its resistivity reduces greatly to approach that of metal when being doped by Sr at site A and the resistivity in room temperature increases to that of semiconductor again when being doped by Fe at site B[10]. Generally, it is believed that the doping of Fe at B-site affects Mn^{3+}—O—Mn^{4+} to a certain extent and causes a break point on the electronic channel to reduce the quantity of electron jumping positions[13−17], which makes the resistivity increase to be in range of semiconductor. Such suitable conductivity and magnetic transformation will be beneficial to the materials absorbing microwave. The experiments have confirmed that the $LaMnO_3$ system doped by Sr at site A and doped by Fe at site B is an excellent microwave-absorbing material with great intensity and wide band of absorption[6]. The microwave absorption of this material is caused by the common effects of dielectric loss, magnetic loss and ohm loss related to its conductivity.

It can be explained that the permittivity, permeability and two loss tangent all have the step-changes. According to the Refs.[11−12], $LaMnO_3$ is an anti-ferromagnet, but will be transformed into ferromagnet when being doped by Sr at site A because of double exchange mechanism. When doping Fe to replace Mn at site B, an anti-ferromagnetic exchange key may be produced again. Therefore, the samples may contain many atomic clusters (ferromagnet and anti-ferromagnet) with different magnetic properties and the quantity of anti-ferromagnetic clusters may be greater than those of ferromagnetic clusters, so that the samples show a superiority of dielectric loss below the step-change frequency. When the microwave frequency increases to a certain value, many anti-ferromagnetic clusters will absorb microwave energy to cross potential barrier so that they will change into the ferromagnetic clusters [18−19]. As a result, the quantity of ferromagnetic clusters is greater than that of anti-ferromagnetic clusters above the step-change frequency, and the sample exhibits a superiority of magnetic loss. Thus, the step-change frequency can be a critical frequency, at which the anti-ferromagnetic clusters will absorb microwave energy quantum to change into ferromagnetic clusters. Besides, the position of the step-change frequency varies for the different contents of Fe or Sr. The energy state of anti-ferromagnetic clusters could be linked with the content, which affects the potential barrier height between ferromagnetic clusters and anti-ferromagnetic clusters.

4 Conclusions

1) For the $La_{1-x}Sr_xMn_{1-y}B_yO_3$ (B=Fe, Co, Ni) systems prepared by sol-gel, the electromagnetic parameters including the complex permittivity, the

complex permeability and the two loss tangents all have step-changes at a microwave frequency range of 2−18 GHz. Doped contents of Sr and B (B=Fe, Co, Ni) have an influence on the step-change frequency position to a certain extent.

2) With the increase of incident microwave frequency, the superiority of dielectric loss in the material changes suddenly into that of magnetic loss at a microwave frequency. The reason may be that the anti-ferromagnetic clusters at metastable state in the materials absorb microwave quantum energy with a certain value over the energy barrier to change into ferromagnetic clusters at more stable state.

3) The unique properties of doped rare-earth manganese oxides provide an important foundation for developing the materials with strong absorption and wide band for microwave and the materials have wide application prospect.

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