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The magnetic and dielectric properties of multiferroic Sr-substituted Zn_2-Y hexagonal ferrites*

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The magnetic and dielectric properties of Sr-substituted Zn_2-Y hexagonal ferrites ($Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$, $1.0 \leq x \leq 1.5$) are studied in this paper. Sr substitution will lead to the variation of cation occupation, which influences both the magnetic and electric properties. As Sr content x rises from 1.0 to 1.5, magnetic hysteresis loop gets wider gradually and the permeability drops rapidly due to the transformation from ferrimagnetic to antiferromagnetic phase. Moreover, permittivity rises with increasing Sr content. Under a certain external magnetic field, the phase transition of helical spin structure of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ at about 295 K seems to open a possibility for the room-temperature ferroelectricity induced by magnetic field. But its low resistivity prevents the observation of ferroelectric and magnetoelectric properties at room-temperature.

Keywords: hexagonal ferrite, Sr substitution, multiferroic, polycrystal
PACC: 7580, 7240

1. Introduction

Hexagonal ferrites have attracted much attention since their discovery by Philips in the 1950s.[1] Among them, Y-type hexagonal ferrite is an important type of high frequency soft magnetic materials due to its strong planar magnetic anisotropy.[2] Owing to its planar magnetocrystalline anisotropy and high permeability, the $Ba_2Zn_2Fe_{12}O_{22}$ (Zn_2Y) hexaferrite was attractive in practical applications, such as microwave devices.[3] Recently, Sr-substituted Zn_2Y ($Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$) hexaferrite was reported as a multiferroic material with electric polarization controlled by magnetic fields, which extends the research of Y-type hexaferrite in a new field.[4−6]

In a multiferroic material with ferromagnetic and ferroelectric ordering simultaneously,[7−11] magnetization is induced by an electric field, and/or electrical polarization is induced by a magnetic field. Single-phase multiferroic materials, such as $BiFeO_3$ and rare-earth manganites have been widely studied.[12−21] However, most of them can only exhibit multiferroic property at low temperatures, so room-temperature (RT) multiferroic material is greatly desired for not only academic research but also practical applications. According to Ref.[4], Sr-substituted Zn_2Y is considered to be a promising candidate for RT multiferroic materials. In this article, we study the RT magnetic and electric properties of the polycrystalline hexaferrite $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ experimentally.

2. Experimental details

Hexaferrites with composition of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ (x = 1.0, 1.1, 1.3, 1.5) were prepared using conventional ceramics method. Mixtures of analytic reagent grade $SrCO_3$, $BaCO_3$, Fe_2O_3, and ZnO were calcined at 1100 °C to prepare powder samples. The dry-pressed pellets were sintered at 1200 °C for 4h. The phase composition of the pellets was investigated by means of powder x-ray diffraction (XRD), and vibrating sample magnetometer (LDJ VSM 9600) was used to measure the magnetic hysteresis loop of the powder sample. The physical property measurement system (PPMS-9) was used to measure the magnetization-temperature curves under different magnetic fields. Measurements of the frequency de-

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pendences of permeability and permittivity were carried out at room temperature using an Agilent 4991A impedance/material analyser in the range of 1 MHz–1 GHz.

3. Results and discussions

It was found that the maximum solubility of Sr in the Y-type hexaferrite is about $x = 1.8$,[22] so Sr substitution for Ba will not affect the Y-type phase formation in the range of $1.0 \leq x \leq 1.5$. Figure 1 shows the XRD patterns of the samples calcined at 1100 °C. All the samples are confirmed to be pure Y-type hexaferrites, after carefully comparing the XRD pattern with standard XRD data.

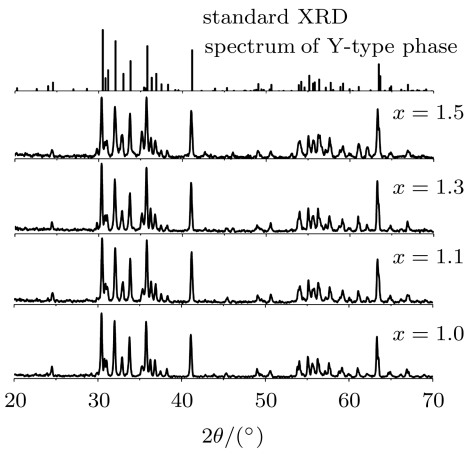


Fig.1. XRD patterns of the powder samples of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$.

Static magnetic characters of the powder samples were measured by vibrating sample magnetometer and physical property measurement system. Figure 2 shows the magnetic hysteresis loops of the samples with different Sr contents. With the rise of Sr concentration, saturation magnetization decreases gradually. For the samples with $x = 1.0$ and 1.1, the loops exhibit typical soft magnetic character. As Sr content rises further, the narrow hysteresis loop expands and gets remarkably wider. This can be attributed to the successive evolution in magnetic structure of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$. In general, the ferrimagnetic order of ferrite originates from the antiparallel and unequal spin moments in neighbouring magnetic sublattices, which is determined by the distribution of transition metal ions. In the Sr-free Zn_2Y hexagonal ferrite, a large amount of magnetic Fe^{3+} ions occupy octahedral sublattice parallel to the total spin moment, while nonmagnetic Zn^{2+} ions prefer to enter antiparallel tetrahedral sublattice. Then, it shows ferrimagnetic order with Néel temperature of 392 K.[4] Sr substitution will influence the cation distribution of transition metal ions; this means that Sr substitution leads to more Fe^{3+} ions entering the tetrahedral sublattice. As a result, the Sr-rich ($x > 1.6$) Zn_2Y samples will show antiferromagnetic character because the spin moments in antiparallel neighbouring sublattices are equal. In the intermediate region of $1.0 < x < 1.6$, the magnetic structure varies gradually.[4] In our experiment, the sample with $x = 1.0$ has soft magnetic hysteresis loop, while the sample with $x = 1.5$ has a wider hysteresis loop due to the antiferromagnetic order.

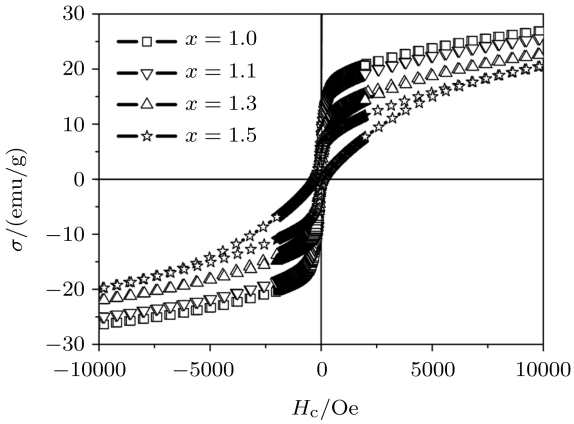


Fig.2. Magnetic hysteresis loops of the powder samples of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$ (1 Oe = 80 A/m).

In the intermediate region between collinear ferrimagnetic order and commensurate antiferromagnetic order ($1.0 < x < 1.6$), Y-type hexaferrite has a noncollinear helical spin structure, which may induce ferroelectricity due to long wavelength magnetic structures.[4] And there are some intermediate phases in the magnetic phase diagram on account of different wave vectors in the helimagnetic structure.[23,24] With the variation of magnetic field or temperature, the magnetic structure evolves gradually. Figure 3 shows the temperature dependence of magnetization of $BaSrZn_2Fe_{12}O_{22}$ and $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ under different external magnetic fields. Under the fields of 800 A/m and 80000 A/m, the peak in $M - T$ curve of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ at about 295 K indicates a phase transition of magnetic structure, probably from slightly modified helix to intermediate I phase.[4] When the field increases from 800 to 80000 A/m, the peak shifts from 293.7 to 295.7 K. If the applied mag-

netic field further rises to 320000 A/m, the peak almost disappears because no phase boundary is crossed under this magnetic field and the magnetic structure keeps in intermediate II.[4] The high phase transition temperature opens a substantial possibility for the RT ferroelectricity induced by a magnetic field, i.e. multiferroic property. In contrast, no phase transition induced by an applied magnetic field can be read out from the $M-T$ curves of $BaSrZn_2Fe_{12}O_{22}$, thus no multiferroic feature is expected.

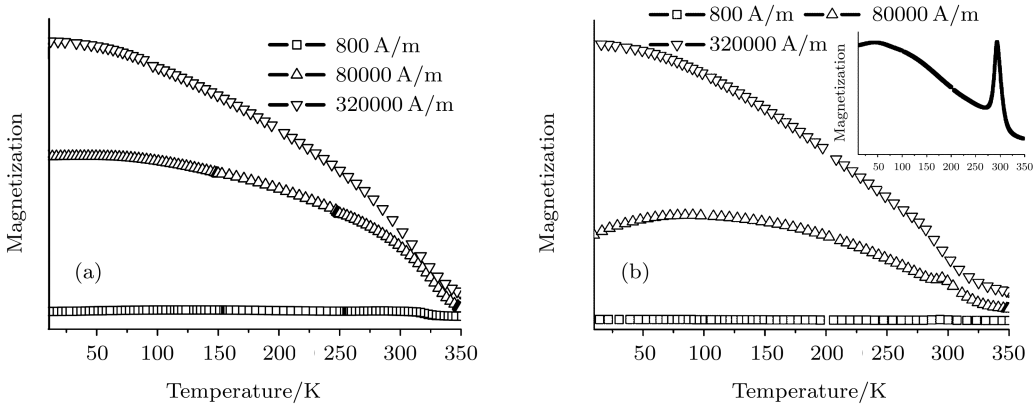


Fig.3. Temperature dependence of magnetization of (a) $BaSrZn_2Fe_{12}O_{22}$ and (b) $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ under different magnetic fields. The inset in (b) shows the $M-T$ curve of $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$under a field of 800 A/m.

Figure 4 shows the frequency dependence of complex permeability (μ) of the samples sintered at 1200 °C. The samples with $x = 1.0 - 1.1$ exhibit high permeability of about 30 due to their ferrimagnetic order. With the rise of Sr amount, the permeability drops rapidly. The permeability of the $x = 1.5$ sample is about 1. This dramatic drop also could be attributed to its antiferromagnetic structure.

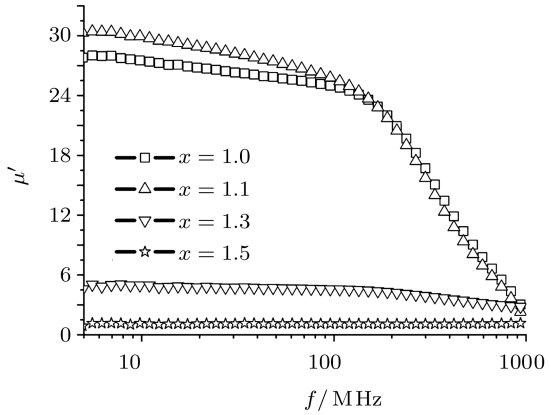


Fig.4. Frequency dependence of the permeability of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$.

Figure 5 shows the frequency dependence of permittivity (ε) of the samples sintered at 1200 °C. As a function of frequency, the permittivity decreases for each sample. As a function of doping concentration, the permittivity increases with the rise of Sr content. For ferrites, the dielectric property is closely related

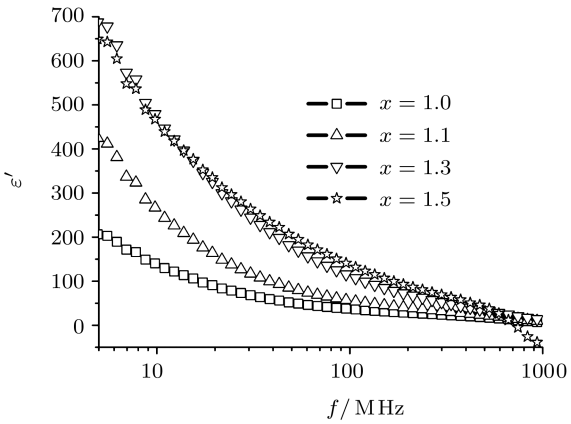


Fig.5. Frequency dependence of the permittivity of $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}$.

to their conductivity mechanism. The measured resistivity of sintered $Ba_{2-x}Sr_xZn_2Fe_{12}O_{22}(1.0\leq x \leq 1.5)$ pellets is about $10^3\,\Omega\cdot$cm, which is at least two times in magnitude lower than that of Sr-free Zn_2Y. The lower resistivity of the sample results in the obvious frequency dispersion character and higher value of permittivity of the samples. In Y-type hexagonal ferrite, the electronic structure and the conductivity are determined by the cation distribution.[5] Zn_2Y is metallic if the tetrahedral sublattice in the spinel block is fully occupied by Fe^{3+} ion, while it is insulating if the tetrahedral sublattice is occupied by zinc or if the fraction of iron equals that of zinc.[5] Sr substitution modifies the relative occupation of Zn^{2+} and Fe^{3+} in

Zn_2Y, so its permittivity increases with the rise of Sr content.

Because the accuracy of measurements of typical multiferroic properties, such as magnetocapacitance, depends on the dielectric character of the samples, the low resistivity prevents the precise measurement of magnetocapacitance at RT. When the capacitance of the pellet sample is measured at 1 kHz under different magnetic fields at RT, stable experimental results cannot be obtained due to the effect of leaky current. Kimura *et al* reported a 4% magnetocapacitance variation in single crystal $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ at 10 K and also predicted RT multiferroic.[4] However, based on *ab initio* electron structure calculation, Knižek and Novák[5,6] pointed out that Sr doping will induce a high conductivity, which prevents RT ferroelectricity. Our results are in good agreement with the above theoretical prediction. Rising of the resistivity is the key to achieve RT multiferroic properties in Sr-substituted Zn_2-Y hexagonal ferrites.

4. Conclusions

In conclusion, polycrystalline Sr-substituted Zn_2Y hexaferrite has been prepared. Sr substitution influences both magnetic and electric properties of Zn_2Y hexaferrite due to the variation of cation occupation. With increasing Sr concentration, the magnetic structure transforms from ferrimagnetism to antiferromagnetism, the magnetic hysteresis goes up, and the permeability drops remarkably while the permittivity increases with the rise of Sr content. The low resistivity of Sr-substituted Zn_2Y, a major obstacle for ferroelectric at RT, can be modified by proper substitution and improvement of sintering process.

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