Structural, dielectric, magnetic, and nuclear magnetic resonance studies of multiferroic Y-type hexaferrites

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I. INTRODUCTION

Hexagonal ferrites are largely used in different types of electronic and microwave devices due to their versatile magnetic properties.\(^1\)\(^-\)\(^5\) Hexaferrites are subdivided into six types, according to their chemical formula and structure, namely M-, W-, Y-, Z-, X-, and U-type.\(^6\)\(^,\)\(^7\) Most hexaferrites have M-type structure as one of the basic units. This has the simplest structure among the other six variants and is composed of R and S blocks. The R block has the stoichiometry Ba\(2\)Fe\(8\)O\(14\), with five octahedral sites of two different types, posed of R and S blocks. The R block has the stoichiometry Ba\(2\)Fe\(8\)O\(14\) with 0 ≤ \(x\) ≤ 2, was investigated. Y-type hexaferrite phase formation was not affected by strontium substitution for barium, in the range 0 ≤ \(x\) ≤ 1.5, confirmed by x-ray diffraction and Raman spectroscopy measured at room temperature. Two intermediate magnetic spin phase transitions (at temperatures \(T_1\) and \(T_2\)) and a ferrimagnetic-paramagnetic transition (at Curie temperature \(T_C\)) were identified from the temperature dependence of the magnetic susceptibility. Magnetic transition temperatures (\(T_1\), \(T_2\), and \(T_C\)) increased with increasing strontium content. Magnetic hysteresis measurements indicated that by increasing strontium concentration, the coercivity increases, while the saturation magnetization decreases. The \(^{57}\)Fe NMR spectrum of the Y-type hexaferrite measured at 5 K and in zero magnetic field showed remarkable differences compared to that of other hexaferrites due to their different number of tetrahedral and octahedral iron sites. The temperature and frequency dependence of the dielectric permittivity evidenced broad peaks with frequency dispersion in correspondence of the Curie temperature. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4754532]
made neutral or slightly alkaline (pH = 7–8) by adding ammonia solution. The solution was heated on hot plate with constant stirring until auto-combustion. The resulting powders were heated at 500°C for 3 h to remove the organic impurities. The powders were pressed in disc shape pellets and sintered at 1200°C for 5 h in air.

Powder x-ray diffraction and Raman spectroscopy were used for phase identification. The x-ray diffraction was carried out using a Philips x-ray diffractometer. Raman spectroscopy (Horiba Jobin Yvon Labram HR 800) was performed at room temperature on sintered samples. Vibrating sample magnetometer (VSM, Quantum Design’s 14T–PPMS) was used to measure the magnetic susceptibility and hysteresis loops of the sintered and crushed powder samples. The temperature dependence of magnetization was measured in a broad temperature range (10–850 K). Magnetic hysteresis loops were measured in the range 10–400 K. The solid state NMR (57Fe) spectra were measured using the Fourier transform spin echo technique on Bruker AVANCE II NMR spectrometer. The spectra were recorded at T = 5 K in zero external field, because the signal was noisy and weak at room temperature. The excitation frequency was varied from 69 to 77 MHz in steps of 0.1 MHz to cover the full broad spectral range of lines corresponding to different typical crystallographic iron sites in hexaferrites. For the dielectric measurements, the disk shape pellets were coated with silver electrodes. The temperature dependence of the dielectric permittivity and loss was measured at various frequencies from 1 to 100 kHz using a precision LCR meter (Agilent, 4284A) connected to a high temperature tube furnace.

III. RESULTS AND DISCUSSION

A. Phase identification

Figure 2 shows the XRD patterns of the samples calcined at 1200°C/5h. The x-ray diffractograms reveal that samples Ba2−xSr2Mg2Fe12O32 (with x = 0, 0.5, 1, 1.5) have pure Y-type hexagonal structure, whereas Sr2Mg2Fe12O32 (x = 2) does not exhibit single phase Y-type structure and was therefore not examined in details in the present study. This is consistent with previous structural studies on Zn2Y hexaferrites,19 where the maximum solubility of strontium in the Ba2−xSr2Zn2Fe12O32 ferrite was found to be about 1.8, and complete substitution of Ba2+ by Sr2+ prevented the Y-type phase formation.

Lattice parameters of Ba2−xSr2Mg2Fe12O32 (with x = 0, 0.5, 1, 1.5) calculated and listed in Table I confirmed Y-type hexaferrite phase. The value of lattice parameter “a” decreased with the rise of Sr content, since the ionic radius of Sr2+ (1.32 Å) is smaller compared to Ba2+ (1.49 Å). The c/a ratio increased with increasing strontium content.

The Raman spectra measured at room temperature in Fig. 3 also confirm that Ba2−xSr2Mg2Fe12O32 samples exhibit a hexaferrite structure.22–25 In our knowledge, there are not many Raman studies on Y-type hexaferrites, except a recent publication on Zn2Y hexaferrite.26 Raman peaks become broader with the increase of the value of x from 0 to 1.5 (Fig. 3). Changes in chemical composition, atomic radii, valence, bond length, cell size, and magnetic order might lead to the broadening of Raman peaks.27 In our samples,
peak broadening may be related to changes in magnetic structure on strontium substitution.

B. Magnetic studies

The magnetic phase transition temperatures in Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ for different strontium content ($x = 0, 0.5, 1, 1.5$) were determined from the temperature dependence of magnetic susceptibility measured in an applied magnetic field of 0.1 T (Fig. 4). The ferrimagnetic-paramagnetic transition (Curie temperature, $T_C$) was identified as the temperature where the magnetic susceptibility significantly dropped. The two visible susceptibility peaks in correspondence of temperatures $T_I$ and $T_{II}$ (Fig. 4) are associated with the consecutive magnetic spin transitions. Decreasing the temperature, the magnetic order changes from collinear ferrimagnetic to a proper-screw spin phase at transition temperature $II$, and from screw spin phase to a longitudinal conical spin phase around transition temperature $I$ (see also Fig. 1), as recently suggested for Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ ($x = 0$) based on neutron diffraction.$^{28,30}$

The magnetic transition temperatures of different samples of Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ are given in Table II. It can be seen that all the magnetic transition temperatures increase with increasing Sr content.

Figure 5 shows the magnetic hysteresis loops of Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ measured at 300 K for different strontium content ($x = 0, 0.5, 1, 1.5$). Coercivity was found to be increased with strontium concentration (for $x = 1.5$, the coercivity is two times larger than in case of $x = 0$). Similar behaviour in coercivity was also found by other research groups on Sr substitution in Y-type hexaferrites.$^{19,29}$ The ground state magnetic structure of these hexaferrites {$(BaSr)_2Mg_2Fe_{12}O_{22}, (BaSr)_2Zn_2Fe_{12}O_{22}$} is composed of alternating stacking of the L and S blocks along the c axis.$^{31}$ The magnetic moments of Fe sites lying in the ab plane are in collinear ferrimagnetic structures, within these blocks. The Sr-free sample shows the collinear ferrimagnetic order at room temperature, whereas the antiferromagnetic order increased with the increase in Sr content. The enhancement in antiferromagnetic order for higher concentration ($x = 1.5$) results in increased coercivity, whereas the composition $x = 1$ shows slight decrease in coercivity, possibly due to an

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**TABLE I.** Lattice parameters for different Sr concentration in the Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ samples (with estimated errors).

<table>
<thead>
<tr>
<th>Value of $x$ in Ba$_{2-x}$Sr$<em>x$Mg$<em>2$Fe$</em>{12}$O$</em>{22}$</th>
<th>$a$ (Å) (1%)</th>
<th>$c$ (Å) (0.5%)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.866</td>
<td>43.2683</td>
<td>7.376</td>
</tr>
<tr>
<td>0.5</td>
<td>5.8548</td>
<td>43.3514</td>
<td>7.404</td>
</tr>
<tr>
<td>1</td>
<td>5.8436</td>
<td>43.2799</td>
<td>7.406</td>
</tr>
<tr>
<td>1.5</td>
<td>5.8436</td>
<td>43.2799</td>
<td>7.406</td>
</tr>
</tbody>
</table>

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**FIG. 3.** Raman spectra of Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ bulk samples.

**FIG. 4.** Temperature dependence of susceptibility for Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ samples.
intermediate phase (between proper-screw and conical spin phase) and magnetic frustrations existing at this composition. Enhancement in coercivity in antiferromagnetic phase is understandable, because it needs higher demagnetizing fields as compared to ferrimagnetic material. At room temperature, Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ samples with compositions $x = 0$ and $x = 0.5$ are still in collinear ferrimagnetic phase (show single ferrimagnetic loop), while samples with $x = 1$ and $x = 1.5$ have entered already in the screw spin phase (showed triple loops). The abnormal triple loops are related to the changes in the magnetic phases and intermediate phases produced by strontium substitution in Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ samples. Kimura et al. had also observed the phase change from collinear ferrimagnetic to antiferromagnetic state, with other intermediate phases, depending on Sr substitution for barium ions in Zn$_2$Y hexaferrites. Our Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ samples with higher strontium concentration ($x = 1$ and 1.5) exhibit an intermediate magnetic phase in between proper screw spin phase and conical spin phase at room temperature. This intermediate phase could be responsible for multi-stage abnormal hysteresis loop. This kind of loops has been observed in Ba$_3$Mg$_2$Fe$_{12}$O$_{22}$ samples (at 10 K) by Sagayama et al., and they attributed it to the phase transition of the magnetic structure, which was supported by neutron diffraction studies at low temperatures.

In order to study the magnetic behaviour of the different magnetic phases, magnetic hysteresis loops of Ba$_{0.5}$Sr$_{1.5}$Mg$_2$Fe$_{12}$O$_{22}$ were measured at selected representative temperatures in the range 10–400 K (Fig. 6). Figs. 6(a) and 6(b) show the magnetic hysteresis at 10 and 30 K, respectively, where the conical spin phase is exhibited. In the range 200–350 K, the sample has a screw spin phase and it shows triple M-H loops (Figs. 6(c)–6(e)). At 400 K, Ba$_{0.5}$Sr$_{1.5}$Mg$_2$Fe$_{12}$O$_{22}$ sample has collinear ferrimagnetic order and the magnetic hysteresis curve shows the typical ferrimagnetic behaviour (Fig. 6(f)).

### TABLE II. Coercivities and magnetic transition temperatures (with average estimated errors) of the powder samples of Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$.

<table>
<thead>
<tr>
<th>Value of x in Ba$_{2-x}$Sr$<em>x$Mg$<em>2$Fe$</em>{12}$O$</em>{22}$</th>
<th>Coercivity $H_C$ (Oe)</th>
<th>Transition temperatures (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$T_I$ ($\pm 5$ K)</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>0.5</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>35</td>
</tr>
<tr>
<td>1.5</td>
<td>200</td>
<td>40</td>
</tr>
</tbody>
</table>

C. NMR measurements on Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$

The $^{57}$Fe NMR spectrum of Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ measured at 5 K in zero applied magnetic field is shown in Fig. 7. The NMR spectrum is noisy and broad, consistent with previous NMR measurements on Y-type hexaferrites. Y-type hexaferrites have six sublattice sites (6c$_{IV}$, 3a$_{VI}$, 18h$_{VI}$, 6c$_{VI}$, 6c$_{IV}$*, and 3b$_{VI}$), which could not be distinguished in our NMR spectrum. In case of M-type and U-type barium hexaferrites, the NMR...
spectra consist of five peaks relative to the different lattice iron sites (12k, 4fIV, 2a, 4fVI, and 2b in M-type and 12k, 8fIV, 4a, 4fVI, and 2b in U-type hexaferrites). This unresolved spectrum is probably due to a number of different crystallographic (tetrahedral and octahedral) iron sites in the Y-type structure (see Fig. 1). The other reason of broadening may be related to its different magnetic order, because our Y-type hexaferrite samples are in conical spin order at this temperature (5 K), whereas M- and U-type hexaferrites are usually in collinear ferrimagnetic states at that temperature resulting in well resolved NMR spectra.

D. Dielectric studies

Figure 8 shows the temperature and frequency dependence of the dielectric permittivity $\varepsilon_r$ and loss ($\tan \delta$) of Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$. High dielectric loss is consistent with previous dielectric characterization on Y-type hexaferrites. The dielectric permittivity exhibits very broad peaks in the range 430–680 K (Figs. 8(a)-8(d)). The broadness and position of the peaks changed with strontium content, but no clear trend could be assigned. It is likely that these peaks are associated with the Curie (ferrimagnetic-paramagnetic) transition in the range 550–670 K as previously identified from our magnetic susceptibility data (see Table II). In addition, these peaks showed pronounced frequency dispersion, with the maximum shifting to higher temperature with increasing frequency. Frequency dependent peaks in the dielectric permittivity around the magnetic transition temperatures were also observed in other magnetic systems, such as bilayer manganite (Pr(Sr$_{0.1}$Ca$_{0.9}$)$_2$Mn$_2$O$_7$) and hexagonal ABX$_3$-type antiferromagnets. In the bilayer manganite, it was observed that the broad anomaly around the Curie temperature had an intrinsic capacitive nature, which was also responsible for the frequency dispersion in the dielectric permittivity. For the hexagonal ABX$_3$-type antiferromagnets, the dielectric anomalies and the strong frequency dispersion observed in CsCoBr$_3$ and the weaker dispersion in RbCoBr$_3$ were attributed to spin-lattice interaction. Our results suggest that in Y-type hexaferrite too, the perturbation of the magnetic order during heating produces frequency dependent broad peaks in the dielectric constant. This indicates that the dielectric properties are influenced by the magnetic state. The dielectric loss peaks shown in Figs. 8(a)-8(d), also attributed to the transformation of the magnetic order.

An additional anomaly in the dielectric permittivity was observed at higher temperatures in the range 820–890 K, represented by broad or narrower peaks (see out-set of Figs. 8(a)-8(d)). The broadness and position of the peaks did not show any clear trend with strontium content. The position of the permittivity peaks at high temperatures (above 820 K) did not change with varying the frequency. This normally
occurs in correspondence of structural modifications, suggesting that the dielectric constant peaks observed probably indicate a phase transition.

IV. SUMMARY AND CONCLUSION

Ba$_{2-x}$Sr$_x$Mg$_2$Fe$_{12}$O$_{22}$ samples synthesized by chemical citrate method have single phase Y-type hexaferrite structure in the compositional range 0 ≤ x ≤ 1.5. Strontium substitution alters the magnetic phase transition temperatures and magnetic hysteresis behaviour. Intermediate spin phase transition temperatures and the Curie temperature (ferrimagnetic-paramagnetic phase transition) shifted to higher temperatures with increasing strontium content. Saturation magnetization decreases and coercivity increases with increasing Sr substitution for Ba ions. $^{57}$Fe NMR spectrum measured at 5 K and in zero magnetic field was found to be broad for the Ba$_2$Mg$_2$Fe$_{12}$O$_{22}$ hexaferrite due to a more complex structure when compared to the well resolved NMR spectra for M-type hexaferrites. Broad and frequency dependent peaks were observed in the dielectric permittivity around the Curie temperature, evidencing that a change in the magnetic order affects the dielectric properties.

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