Structural, electronic, and magnetic properties of $\text{Sr}_2-x\text{Ba}_x\text{FeMoO}_6(0 \leq x \leq 2)$

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I. INTRODUCTION

During recent years, interest has grown in the research of B-site ordered double perovskite compounds, $A\text{B}'\text{BO}_6$ (A being alkaline earth or rare-earth ion, while $A'$ and $B'$ are hetrovalent transition-metal ions) which exhibit colossal magnetoresistance (CMR) phenomenon.\(^1\) The ideal structure of these compounds can be visualized as a regular arrangement of corner sharing $\text{BO}_6$ and $\text{B}'\text{O}_6$ octahedra, alternating along cubic axes in all three directions, with the $A$-site cations occupying the voids in between the octahedra. A remarkable negative magnetoresistance (MR) at low fields has been observed in $\text{Sr}_2\text{FeMoO}_6$ (Ref. 1) and $\text{Ba}_2\text{FeMoO}_6$ (Ref. 2) even at room temperature due to the spin-dependent scattering of the charge carriers at the grain boundaries. The origin of low-field MR (LFMR) in polycrystalline samples of these materials has been attributed to the spin-dependent scattering of electrons at grain boundary.

Substitution at the $A$ site with cations of different sizes leads to the change in the bond lengths and bond angles, which influences the extent of orbital overlap between the $B$-site cations. In the present study, we attempted to explore the effect of varying the average $A$-site ionic radii on the structural, electrical, and magnetic properties. For this purpose, we have synthesized a series of double perovskite compounds $\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6$ $(0 \leq x \leq 2)$. The substitution of larger $\text{Ba}^{2+}$ in place of $\text{Sr}^{2+}$ results in an expected increase of lattice parameters and also a structural transition from tetragonal to cubic along the series. We report here the magnetic and magnetotransport studies on this system.

II. EXPERIMENT

A series of compounds $\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6$ $(x=0, 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, \text{ and } 2)$ were synthesized via the solid-state route under reducing atmosphere. Synthesis of all the samples was carried out simultaneously in order to ensure homogeneity in preparation conditions for all the compounds.

X-ray powder diffraction patterns were recorded on a PANalytical x-ray diffractometer using Cu $K\alpha$ radiation. Magnetization measurements were carried out on either a LakeShore vibrating-sample magnetometer (VSM) or a homemade Faraday balance setup. The electrical resistivity of the samples was measured using the standard dc four-probe technique in a continuous flow cryostat. Electron-spin resonance (ESR) spectroscopy studies were carried out on Varian X-band ESR spectrometer.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of the samples confirm the formation of single phase for all the compositions synthesized. Rietveld analysis of the XRD data reveals a structural transition from tetragonal ($I4/m$) for Sr-rich compositions $(x \leq 0.6)$ to cubic ($Fm\overline{3}m$) for Ba-rich compositions $(x \geq 1.6)$. For intermediate compositions $(0.8 \leq x \leq 1.4)$ the best fit is obtained with orthorhombic $Fmmm$ space group. A linear increase in the cell parameters is observed with in-
creasing Ba substitution. This increase in the lattice parameters is quite expected as the average A-site radii increase due to the larger size of Ba\(^{2+}\) (1.61 Å) in comparison to Sr\(^{2+}\) (1.44 Å). The variation of unit-cell parameters along the series is depicted in Fig. 1. In order to study the effect of substitution on the MR properties, the electrical transport measurements were performed in zero applied field and under a field of 0.8 T (maximum field obtainable with our electromagnet) from 80 to 300 K. Resistivity behavior for sample with \(x=0.6\) is presented in Fig. 2 as a typical example. Its variation of % MR with temperature is given in the lower right inset of Fig. 2, which clearly shows a regular increase in MR with decreasing temperature. All other samples show a similar metallic resistivity and MR behavior over the entire temperature range. The upper left inset in Fig. 2 gives the MR observed at 80 and 300 K for all the compositions. It is apparent that MR increases as \(x\) increases, goes through a maximum for intermediate compositions and then decreases with further substitution.

Magnetization measurements were carried out at 80 K for fields up to 2 T. The representative \(M-H\) plots for composition with \(x=0, 1,\) and 2 are reproduced in Fig. 3. Inset in the figure shows the saturation magnetization (\(M_s\)) recorded for all the compositions at 80 K. The \(M_s\) value increases almost linearly from around 2 \(\mu_B/\text{f.u.}\) to 3 \(\mu_B/\text{f.u.}\) in the range of 0 \(\leq x \leq 1.6\), beyond which it essentially remains as a constant. However, these values are significantly lower than the theoretically expected value of 4 \(\mu_B/\text{f.u.}\) for these compounds. Such a drop in \(M_s\) has been earlier explained on the basis of antisite defects present in the system.\(^3\) Hence the increase in \(M_s\) along the series may indicate a reduction in antisite defects with increasing average A-site ionic radii. The magnetization as a function of temperature under an applied field of 0.3 T is presented in Fig. 4 for samples with \(x=0, 1,\) and 2. The inset reproduces the Curie temperature (\(T_C\)) for the samples from these measurements, which shows a systematic decrease with increasing Ba concentration. This is in contrast with the results reported by Feng et al.\(^4\) where an initial increase in \(T_C\) is observed which is explained on

\[\text{FIG. 1.} \quad \text{Dependence of lattice parameters on Ba concentration} \ x \ \text{in} \ \text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6. \ \text{The lines shown in the figure are just a guide to the eye.}\]

\[\text{FIG. 2.} \quad \rho \ vs \ T \ \text{plot for} \ \text{Sr}_{1.4}\text{Ba}_{0.6}\text{FeMoO}_6 \ \text{in a magnetic field of 0 and 0.8 T. The lower right inset gives its temperature dependence of} \ % \ \text{MR of 0.8 T. In the upper left inset the} \ % \ \text{MR values at 80 and 300 K for all the compositions} \ \text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6(0 \leq x \leq 2) \ \text{are plotted.}\]

\[\text{FIG. 3.} \quad M \ vs \ H \ \text{plots for} \ \text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6 \ (x=0, 1, \text{and} 2) \ \text{at} \ 80 \text{K for fields up to} \ 2 \text{T. Inset shows the values of saturation magnetization obtained at} \ 80 \text{K across the series} \ \text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6(0 \leq x \leq 2).\]

\[\text{FIG. 4.} \quad M \ vs \ T \ \text{plots for} \ \text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6 \ (x=0, 1, \text{and} 2) \ \text{under an applied magnetic field of} \ 0.3 \text{T. The} \ T_C \ \text{of the samples as determined from the inflection point of the} \ M-T \ \text{curve (□) as and estimated from the ESR measurements (●) is given in the inset.}\]
the basis of decreased antisite defects. However, the antisite defects observed in our samples are much higher (as inferred from the saturation magnetization) than that observed by Feng et al. and may be the reason for the regular decrease of $T_C$. The drop in $T_C$ despite of the increase in $M_s$ as average A-site radii increases implies that the strength of ferromagnetic interactions is reduced.

An interesting observation in the magnetotransport behavior in this system is the increase in MR noticed for the intermediate compositions. Although the parent composition shows a poor MR as compared to the earlier reported results, the increase seen in MR for the compositions near to the structural transition at $x=0.8$ is quite significant. The low value of MR obtained in the parent compound may be assigned to the metallic nature of the samples prepared. It has been shown that in these systems poor MR properties are realized for metallic samples in comparison to samples showing insulating or semiconducting behavior. Resistivity of the samples is very sensitive to the synthesis conditions and largely dependent upon the nature of grain boundaries, as the grains themselves are metallic. Since all the samples were processed simultaneously, so the preparation condition for the samples is exactly alike. Hence the appreciable increase in MR for intermediate compositions may be attributed to the change in the magnetic properties along the series. It is evident from the magnetization studies that $M_s$ is increasing across the series, which means there is a decrease in antisite defects. This in turn implies higher spin polarization of the charge carriers which is central to the realization of better LFMR. Hence the increase in MR is to be expected in conjunction to improvement in saturation magnetization. However, it is to be noted that despite an increase in $M_s$, there is also a decrease in $T_C$ with increasing $x$. This suggests the weakening of ferromagnetic coupling between the adjacent Fe sites due to the increase in Fe–O–Mo–O–Fe distances which is reflected in larger lattice parameters for samples with higher $x$. As a consequence of which there is a reduction in the spin polarization of electrons in the system. Hence we see a drop in MR for composition with higher Ba concentration, in spite of their better $M_s$ values.

The ESR spectra recorded at various temperatures show that, for $T<T_C$, the resonance magnetic field shifts towards higher fields upon increasing the temperature. Further, the narrowing of the linewidth occurs with increasing temperature, whereas for spectra at $T>T_C$, a constant value of the resonance magnetic field is observed. It is also seen that for temperatures greater than magnetic transition temperature, the linewidth increases slightly and the intensity drops quickly with increasing temperatures. The Curie temperatures estimated from ESR spectra are in good agreement with the results obtained from the magnetization measurements and are given in the inset of Fig. 4.

IV. CONCLUSIONS

In conclusion, the effect of variation of average A-site ionic radii in double perovskite compounds on the structural, magnetoelectrical transport, and magnetic properties was ascertained for a series of compounds $\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6(0 \leq x \leq 2)$. A structural transition from tetragonal for the initial compositions to cubic for the final ones was observed. The compounds with intermediate composition show a significantly higher MR in comparison to those at the ends. Although the magnetization at 80 K shows an increasing trend along the series, the Curie temperatures show a regular decline with increasing $x$. Hence, it may be concluded that increasing the average A-site ionic radii results in an improvement of B-site cationic ordering but the strength of ferromagnetic coupling of the Fe - sites is reduced.

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