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Synthesis and investigation of magneto-dielectric effect in $A_2FeMn_{0.5}W_{0.5}O_6$ (A = Ca, Sr, Ba) double perovskites

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ABSTRACT

New perovskite oxides of the formula $A_2FeMn_{0.5}W_{0.5}O_6$ (A = Ca, Sr and Ba) have been prepared and their structure, magnetic, dielectric properties have been investigated. $Ca_2FeMn_{0.5}W_{0.5}O_6$ and $Sr_2FeMn_{0.5}W_{0.5}O_6$ compounds crystallize in cubic double perovskite structure (space group *Fm*-3*m*) whereas $Ba_2FeMn_{0.5}W_{0.5}O_6$ adopts the hexagonal 6H-type perovskite structure (space group $P6_3/mmc$). Magnetic measurements indicate that compositions are weakly ferromagnetic with dominating antiferromagnetic interactions at low temperatures. The dielectric behavior of $A_2FeMn_{0.5}W_{0.5}O_6$ (A = Ca, Sr and Ba) compounds is similar to that of relaxor ferroelectrics exhibiting the frequency dependence with a broad maxima around 350 K. Under 1 T applied magnetic field, the Ca and Sr members show a change in dielectric behavior indicating coupling between their magnetic and dielectric properties, while the Ba member did not show such effect. Further, on introducing oxygen vacancies ($\delta \sim 0.28$), the Ba compound undergoes a structural transformation from hexagonal to cubic and this transformation is reversible. The oxygen deficient member $Ba_2FeMn_{0.5}W_{0.5}O_{5.72}$ exhibits a significant enhancement in its magnetic behavior compared to that of the oxygen stoichiometric parent composition, $Ba_2FeMn_{0.5}W_{0.5}O_6$.

1. Introduction

Double perovskite (DP) oxides, $A_2B'B''O_6$ have been widely investigated due to their interesting electrical and magnetic properties. DP oxides contain two different transition metal atoms (B′ and B″) that occupy alternate B-sites forming a rock salt type arrangement, and such ordering is favored when the two cations largely differ in their ionic radius or in their formal charge [1–4]. The B′–O–B″ interactions in DP structure can often lead to remarkable electronic structure, for example half-metallic ferromagnetism [5] where the Fermi level intersects only one type of spin channel. Because of this special electronic state, DP oxides such as Sr_2FeMoO_6 and Sr_2FeReO_6 display a large carrier spin polarization and exhibit tunneling magnetoresistance under a small applied magnetic field [6–8]. Consequently, for the past one decade DP oxides have been intensely investigated for possible spintronic applications. Besides, Rogado et al. [9] have shown that La_2NiMnO_6, a DP oxide, exhibits remarkable multiferroic [10–14] behavior near room temperature. This demonstrates the possibility of coupling between magnetic and electric dipoles in a DP structure leading to the manifestation of multiferroic behavior. Thus, DP oxides are special class of compounds exhibiting multiple functions such as magnetoresistance, magnetocapacitance through the complex interplay between charge, spin and dipoles. Another advantage is that they exhibit fairly high ferromagnetic T_c often near room temperature. Also for magnetoelectric applications it is more favorable to have ferroelectric T_c near room temperature so that spontaneous electric polarization could be easily switched.

In a quest for finding new 'multiferroic materials' we have been interested in investigating the magnetic and dielectric properties of double perovskites containing Fe and Mn. The A_2FeWO_6 (A = Sr, Ba) compounds first reported by Fresia et al. [2] are antiferromagnetic insulators with low $T_N \sim 35$ K [15,16]. A large MR about—24% has been observed at 300 K for Sr_2FeWO_6 under 1 T magnetic field [17]. So we contemplated that by the partial substitution of Mn for W, it would be possible to induce a ferro/ferri magnetic interaction between Fe^{3+} and Mn^{4+} in the structure. According to Goodenough–Kanamori rule [18,19], the 180° superexchange interaction between two cations with d^3–d^5 electron configuration which are bridged via oxygen is ferromagnetic. Also, we believe that $A_2FeMn_{0.5}W_{0.5}O_6$ compounds would be good dielectrics as well due to the following reasons: firstly, compounds containing Fe^{3+} cations have been extensively studied for possible ferroelectricity [20]. Secondly, W^{6+} with a d^0 electron configuration undergo second-order Jahn–Teller distortion stabilizing distorted WO_6 octahedra [21], such a distortion of metal–oxygen network would induce a net dipole moment to the structure analogous to ferro-

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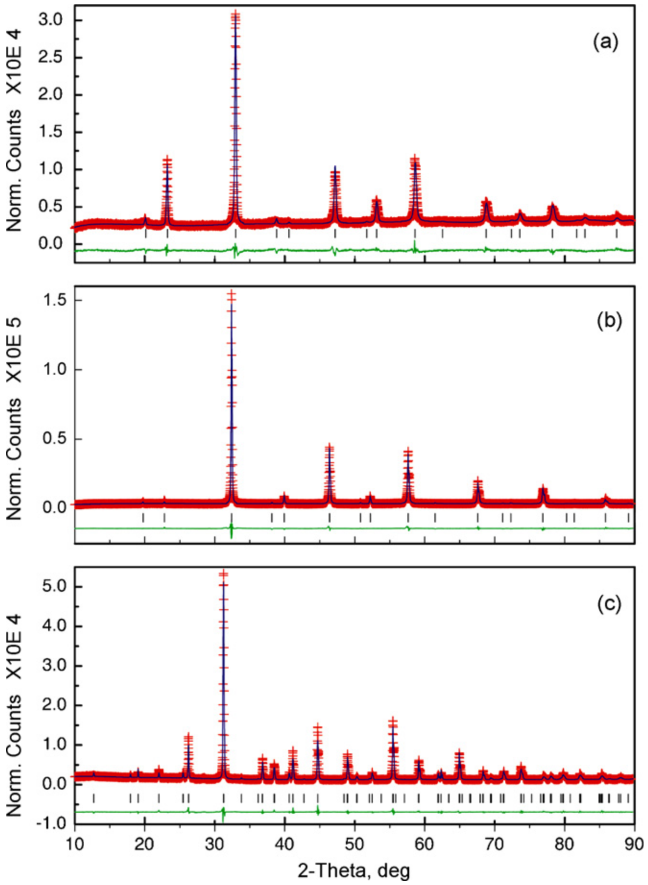

Fig. 1. XRD Rietveld fit for $A_2FeMn_{0.5}W_{0.5}O_6$ compounds: (a) A = Ca, (b) A = Sr and (c) A = Ba.

electric $BaTiO_3$. Several Mn based compounds, for example $BiMnO_3$ and rare-earth manganites of the type $RMnO_3$ and RMn_2O_5 (where R = Y, Ho, Tb, Eu) are multiferroic [10–14] reflecting that Mn cation play a role in inducing the behavior. It has been shown that $MnWO_4$, a compound containing Mn and W cations exhibits simultaneous ferroelectric polarization and spiral magnetism below 13 K [22]. Also, Mn is known to modify properties of ferroelectric materials; small amount of Mn substitution significantly suppresses the dielectric loss of ferroelectric $BaTiO_3$ [23]. First principle calculations have shown that difficulties in finding good insulating ferromagnets for multiferroic applications could be overcome by introducing ferrimagnetism through B-site cation ordering in perovskite structures [24].

In view of foregoing we prepared $A_2FeMn_{0.5}W_{0.5}O_6$ (A = Ca, Sr, Ba) compositions and investigated their structure, magnetic and dielectric properties. Since ferromagnetism and ferroelectric property are mutually exclusive and that there are only few multiferroic materials, our present work shows a way out for realizing the magneto-dielectric effect by integrating magnetic and ferroelectric ions in an ordered perovskite lattice.

2. Experimental

$A_2FeMn_{0.5}W_{0.5}O_6$ (A = Ca, Sr, Ba) compounds were prepared by ceramic method. Stoichiometric quantities of ACO_3, Fe_2O_3, MnO_2 and WO_3 were mixed thoroughly and heated in air at 1100 °C for 1 day followed by heating at 1400 °C for 4 days with intermediate grindings and palletizing. Furnace heating and cooling was programmed with a ramp rate of 300 °C per h during the heat treatment cycles. In the final step, pellets were annealed in oxygen atmosphere at 800 °C for 1 day and then slowly cooled (60 °C per h) to room temperature. The cation stoichiometry was confirmed by EDX analysis and the oxygen content was estimated through iodometric titrations. X-ray powder diffraction (XRD) patterns were recorded using Bruker D8 X-ray diffractometer with CuKα radiation operating in the Bragg–Brentano geometry. Rietveld quality data were collected with a step size of 0.02° 2θ over 12 h. We have determined the crystal structure and lattice parameters by carrying out Rietveld refinements of powder XRD data using General Structure Analysis System (GSAS) code [25]. Magnetization measurements were carried out using PPMS (Quantum Design) magnetometer. A capacitor for ferroelectric measurement was made by sputtering gold on both sides of the pellet by DC sputtering. Capacitance and dissipation of the sample were measured using Agilent impedance analyzer between 350 and 50 K range in a frequency range of 100 Hz to 1 MHz.

3. Results and discussion

Powder XRD reveals the formation of single phase $A_2FeMn_{0.5}W_{0.5}O_6$ compounds (Fig. 1). XRD patterns indicate that A = Ca, Sr compounds are cubic while the A = Ba compound adopts a hexagonal perovskite type structure. Oxygen content estimated through iodometric analysis is close to the expected value of 6.0 for all the three compositions (Table 1) indicating that oxygen vacancies are not present in the structure. XRD Rietveld analysis shows that $Ca_2FeMn_{0.5}W_{0.5}O_6$ and $Sr_2FeMn_{0.5}W_{0.5}O_6$ crystallize in cubic DP structure (space group *Fm*-3*m*), the refined lattice parameters are

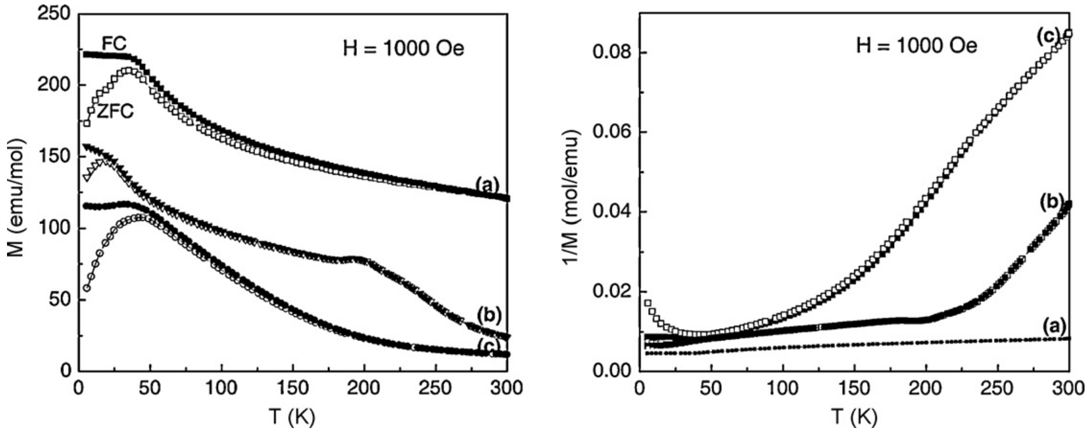

Fig. 2. Temperature (*T*) variation of magnetization (*M*) behavior for $A_2FeMn_{0.5}W_{0.5}O_6$ double perovskites (a) A = Ca, (b) A = Ba and (c) A = Sr. Closed symbols (FC) and open symbols (ZFC). Inverse *M* vs. *T* plots (FC) shown on right hand side figure.