Properties of the ferrimagnetic double-perovskite \( \text{A}_2\text{FeReO}_6 \) (A=Ba and Ca)

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Ceramics of \( \text{A}_2\text{FeReO}_6 \) double-perovskite have been prepared and studied for A=Ba and Ca. \( \text{Ba}_2\text{FeReO}_6 \) has a cubic structure \((Fm\bar{3}m)\) with \( a \approx 8.0854(1) \) \( \AA \) whereas \( \text{Ca}_2\text{FeReO}_6 \) has a distorted monoclinic symmetry with \( a \approx 5.396(1) \) \( \AA \), \( b \approx 5.522(1) \) \( \AA \). The barium compound is metallic from 5 K to 385 K, and the calcium compound is semiconducting from 5 K to 385 K. Magnetization measurements show a ferrimagnetic behavior for both materials, with \( T_c = 315 \) K for \( \text{Ba}_2\text{FeReO}_6 \) and above 385 K for \( \text{Ca}_2\text{FeReO}_6 \). A specific heat measurement on the barium compound gave an electron density of states at the Fermi level, \( N(E_F) \) equal to \( 6.1 \times 10^{24} \) eV\(^{-1}\)mole\(^{-1}\). At 5 K, we observed a negative magnetoresistance of 10 % in a magnetic field of 5 T, but only for \( \text{Ba}_2\text{FeReO}_6 \).

Electrical, thermal and magnetic properties are discussed and compared to the analogous compounds \( \text{Sr}_2\text{Fe(Mo,Re)O}_6 \).

I. INTRODUCTION

Perovskite manganites exhibiting a variety of exotic electronic properties \([1]\) that include a spectacular decrease of electrical resistance in a magnetic field \([2]\), the so-called colossal magnetoresistance (CMR) \([3]\), have attracted wide attention in recent years. A significant feature of the electronic structure of the ferromagnetic CMR manganites, revealed by recent experiments \([4,5]\) and theory \([6]\), is that the charge carriers are almost completely spin-polarized at the Fermi level \( E_F \). These materials are half-metallic ferromagnets, where the majority spin states near \( E_F \) are delocalized and the minority spin channel is effectively localized. Since half-metallic ferromagnetism and magnetoresistance (MR), especially at low fields, seem to be intimately related to each other \([7]\) - the latter arising from the former- there is an intense search for half-metallic magnets which could be candidate materials for the realization of MR applications. While several double-perovskite oxides of the kind \( \text{A}_2\text{BB'O}_6 \) (A being an alkaline earth or rare earth ion and B, B' being d-transition metal ions) have been theoretically predicted to be half-metallic antiferromagnets \([8]\), one such material, \( \text{Sr}_2\text{FeMoO}_6 \) \([9]\), has recently \([10,11]\) been shown to be a half-metallic ferrimagnet exhibiting a significant tunneling-type magnetoresistance at room temperature. More recently, Asano et al. \([12]\) have shown that it is possible to have either positive or negative MR in thin films of \( \text{Sr}_2\text{FeMoO}_6 \) grown by pulsed laser deposition.

\( \text{Ba}_2\text{FeReO}_6 \) \([13]\) and \( \text{Ca}_2\text{FeReO}_6 \) are double-perovskites whose structure and properties are quite similar to those of \( \text{Sr}_2\text{FeMoO}_6 \). In both materials a valence degeneracy between the B-site cation occurs, giving rise to the observed metallic and magnetic properties; in the SFMO case, the valence-degeneracy is between \( \text{Fe}^{3+} + \text{Mo}^{5+} \rightleftharpoons \text{Fe}^{2+} + \text{Mo}^{6+} \) states, while in the \( \text{Ba}_2\text{FeReO}_6 \) or \( \text{Ca}_2\text{FeReO}_6 \) case, the degenerate oxidation states are \( \text{Fe}^{5+} + \text{Re}^{6+} \rightleftharpoons \text{Fe}^{2+} + \text{Re}^{5+} \). A major difference between the Mo and Re oxides however, is that \( \text{Mo}^{5+} \) is \( 4d^5 \), whereas \( \text{Re}^{5+} \) is \( 5d^2 \). This would mean that the conducting charge carrier density of the Re compound would be twice as much as in the compound Mo, while the localized spins centered on Fe remain the same in both oxides. We believe that this difference could have an influence on the magnetotransport behavior, especially in view of the recent report \([4]\) that the bulk low field MR in ferromagnetic metals is mainly determined by the charge carrier density. In view of the foregoing, we consider it important to investigate the magnetic and transport properties of \( \text{A}_2\text{FeReO}_6 \) (A=Ba and Ca) and our results are reported in this communication.

II. RESULTS AND DISCUSSION

Polycrystalline samples of \( \text{A}_2\text{FeReO}_6 \) (with A=Ba or Ca) were synthesized by standard solid state methods. First, a precursor oxide of the composition \( \text{A}_2\text{ReO}_5.5 \) (A=Ba or Ca) was prepared by reacting stoichiometric amounts of \( \text{ACO}_3 \) and \( \text{Re}_2\text{O}_7 \) at 1000 °C in air for 2 h. Second, this resultant oxide was mixed with required amounts of \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe} \) powder to obtain the desired composition \( \text{A}_2\text{FeReO}_6 \). Finally, pellets of this mixture were heated in an evacuated sealed silica tube at 910 °C during 4 days, followed by another treatment at 960 °C during the same time, with intermediate grinding. X-Ray powder diffraction (XRD) patterns were taken using a conventional diffractometer with Cu Kα radiation (\( \lambda = 1.5406 \) Å). The XRD patterns of final compounds are shown in Fig.1a and Fig.1b. \( \text{Ba}_2\text{FeReO}_6 \) is indexed on the basis of a cubic cell \((Fm\bar{3}m)\) with \( a \approx 8.054(1) \)
Å, similar to Ba$_2$YRuO$_6$ [15]. Ca$_2$FeReO$_6$ is distorted to a monoclinic symmetry ($P21/n$) with $a \approx 5.396(2) \text{ Å}$, $b \approx 5.522(2) \text{ Å}$, $c \approx 7.688(1) \text{ Å}$ and $\beta = 90.4^\circ$, similar to those of La$_2$CuIrO$_6$ and Nd$_2$MgTiO$_6$ [16]. These results indicate the formation of the double-perovskite (Fig.2) for both compounds, as reported earlier [13] and consistent with recent results [10,11]. One also notes that no impurity phase can be detected in the XRD indicating a clean single phase in each case.

Resistivity ($\rho$) was measured between 5 K and 300 K, on bars with the approximate dimensions of (1x3x8) mm$^3$, using the standard four-probe method. The temperature ($T$) dependence of $\rho$ is shown in Fig.3 at various magnetic fields of 0, 0.2 and 5 T for Ba$_2$FeReO$_6$. The resistivity gradually decreases when the temperature decreases suggesting a metallic behavior below 300 K. The zero-field resistivity was also measured up to 385 K (inset of Fig.3) but no change in the metallic behavior was observed in this region. In contrast, Ca$_2$FeReO$_6$ shows a semiconducting behavior from 5 K to 300 K (Fig.4). While Ba$_2$FeReO$_6$ exhibits magnetoresistance at 5 K, the resistivity of Ca$_2$FeReO$_6$ remains unchanged, even under an applied magnetic field of 8 T. We find, that the latter resistivity does not fit with an activation energy law ($\rho(T) \propto e^{E_a/kT}$). As often found in the manganites [17], the resistivity at room temperature is large (50 mΩ.cm for Ba$_2$FeReO$_6$ and 20 mΩ.cm for Ca$_2$FeReO$_6$), well above the Mott limit, but perhaps reflecting intergrain resistance in these polycrystalline samples. A more detailed understanding of the transport of these materials will require single crystals or oriented films.

To investigate the MR of the Ba$_2$FeReO$_6$, we present the MR at different temperatures in Fig.5. As shown in Fig.3, the Ba$_2$FeReO$_6$ compound exhibits negative MR, with MR defined as $MR(T, H) = [R(H) - R(0)] / R(0)$. The MR is equal to 3 % at 10 K in a 2000 Oe field. This MR under low field at 10K is smaller than that found in Sr$_2$FeMoO$_6$ (10 %) [10]. However, the zero field $\rho(T)$ behavior of Sr$_2$FeMoO$_6$ is rather different at low temperature than Ba$_2$FeReO$_6$ - in Sr$_2$FeMoO$_6$ it tends to increase slightly at 10 K. This behavior might be due to the preparation procedure of the sample which dramatically affects the $\rho(T)$ [10], most probably this is a result of the difference in the structure of these compounds. Indeed, in the series Ba$_2$FeReO$_6$, Sr$_2$FeReO$_6$ [18] and Ca$_2$FeReO$_6$, the crystal symmetry decreases from cubic to tetragonal to orthorhombic (or distorted monoclinic). This is clearly a manifestation of the decreasing Re-O-Fe bond angle from 180 degrees. Accordingly, the conduction band width would be expected to decrease as we go from Ba to Sr to Ca. Thus, it is not surprising that Ba$_2$FeReO$_6$ is metallic and Ca$_2$FeReO$_6$ is not. A similar conclusion occurs when comparing Ba$_2$FeMoO$_6$ and Sr$_2$FeMoO$_6$ [10,19]: Ba$_2$FeMoO$_6$ is metallic (and cubic) whereas Sr$_2$FeMoO$_6$, whose structure is tetragonal, has a resistivity which increases when $T$ decreases [10]. The MR strongly increases at low field with a slower increase at higher field. This effect occurs mainly at low temperature, since at room temperature the MR is very small. The features are characteristic of intergrain magnetoresistance [11]. At low temperature (Fig.5), a small hysteretic behavior also appears but thus is not of relevance to the issues discussed in this paper.
an antiferromagnetic superexchange interaction between spins of Fe$^{3+}$ ($S = 5/2$) and Re$^{5+}$ ($S = 1$). The ferromagnetic Curie temperature ($T_c$) of Ba$_2$FeReO$_6$ was determined as 315 K from the temperature dependence of the magnetization shown in Fig. 6. For Ba$_2$FeReO$_6$, the low temperature saturation magnetization value, taken under a magnetic field of 2 T, is 24.9 emu/g, which is close to the expected value based on Fe$^{3+}$ and Re$^{5+}$ moments (27.3 emu/g). The Ca$_2$FeReO$_6$ compound exhibits a higher $T_c$, above 385 K (not determined). For the Ca$_2$FeReO$_6$ compound, the low temperature saturation magnetization value, measured under a field of 5 T, is calculated to be 40 emu/g which is a little higher than the experimental value (30 emu/g) but in agreement with a previous report [21]. This is probably due to the fact that the full saturation magnetization was not reached even with a 5T magnetic field. The Curie temperature of Ba$_2$FeReO$_6$ is lower than the reported value of $T_c \approx 410$ K for Sr$_2$FeReO$_6$ [18,20] but close to the value of Ba$_2$FeMoO$_6$ ($T_c = 340$ K) [14], whereas the $T_c$ of Ca$_2$FeReO$_6$ seems to be higher (> 385 K). This means that these differences are likely caused by the larger ionic radius of Ba$^{2+}$ (1.47 Å versus 1.31 Å for Sr$^{2+}$ and 1.18 Å for Ca$^{2+}$ [22]) which leads to a larger Re-O-Fe (or Mo-O-Fe) bond length and therefore a smaller exchange and lower Curie temperature.

Magnetization measurements (M) were made with a SQUID (MPMS Quantum Design) magnetometer. These DC measurements were carried out with increasing temperature after the sample was zero field cooled (ZFC). The temperature dependence of M for a magnetic field of 10 Oe is shown in Fig. 6 for Ba$_2$FeReO$_6$. Like several other double-perovskite compounds [18,20], A$_2$FeReO$_6$ (A=Ba and Ca) exhibit ferrimagnetic behavior due to
The specific heat was measured by relaxation calorimetry in the temperature range 2-16 K. The specific heat data for Ba$_2$FeReO$_6$ and Ca$_2$FeReO$_6$ are shown in Fig. 7. In our analysis of the low temperature specific heat we include lattice ($C_{\text{lat}}$), metallic ($C_{\text{cl}}$) and hyperfine ($C_{\text{hyp}}$) contributions. When the temperature decreases below 3 K, the specific heat increases due to the hyperfine contribution $C_{\text{hyp}} = A/T^2$. Since the nuclear spin of Fe$^{56}$ is zero, the hyperfine contribution in our samples arises from the Re$^{56}$ nuclear spin $I = 1$. The experimental values of $A$ are found to be 135±4 mJ-Kmole and 180±5 mJ-K/mole for Ba$_2$FeReO$_6$ and Ca$_2$FeReO$_6$ respectively. In addition, Ba$_2$FeReO$_6$ has the expected metallic contribution, $\gamma T$, with $\gamma = 23.1 \pm 0.2$ mJ/mole-K$^2$. Using $\gamma = \pi^2 k_B^2 N(E_F)/3$, we find the density of states at the Fermi energy $N(E_F)$ to be 6.1×10$^{24}$ eV$^{-1}$mole$^{-1}$. This value is larger than the $N(E_F)$ obtained from the band structure calculation for Sr$_2$FeMoO$_6$ (1.2×10$^{24}$ eV$^{-1}$mole$^{-1}$) [11], probably because Re$^{5+}$ has two electrons on the $d$ orbital (5$d^6$), while Mo$^{5+}$ has only one (4$d^3$).

To achieve a good fit for our Ba$_2$FeReO$_6$ specific heat data two lattice terms are required: $C_{\text{lat}} = \beta_3 T^3 + \beta_5 T^5$, where $\beta_3 = 0.438 \pm 0.003$ mJ/mole-K$^4$ and $\beta_5 = 5.9 \times 10^{-4}$ mJ/mole-K$^6$. Since $\Theta_D = (12\pi^2 p R / 5 \beta_3)^{1/3}$, where $p=10$ is the number of atoms per formula unit, we find the Debye temperature $\Theta_D$ to be 354 K, which is similar to $\Theta_D$ of other perovskites [2].

The best fit for Ca$_2$FeReO$_6$ does not include $\gamma T$ and $\beta_5 T^5$ terms, but requires an additional term $C' \approx \alpha T^a$, where $a$ is close to 2. The absence of the charge carrier term $\gamma T$ is consistent with the insulating resistivity of Ca$_2$FeReO$_6$. The $C' \approx \alpha T^a$ term, or more precisely $C' = C'(\Delta, B, T)$, which is the specific heat of excitations with a dispersion relation $\epsilon = \Delta + Bk^2$ of non-magnetic origin, was also found in the charge-ordered perovskite manganites [24]. In the case of insulating Ca$_2$FeReO$_6$ a charge of 3+ on the Fe site and a charge of 5+ on the Re site create a situation similar to the Mn$^{3+}$-Mn$^{4+}$ charge ordering in manganites. The fit to our Ca$_2$FeReO$_6$ specific heat data gives $\Delta = 7$ K and $B = 22$ meV-Å similar in magnitude to the parameters found in the manganites. We believe that the reasons for the presence of the $C'(\Delta, B, T)$ term in Ca$_2$FeReO$_6$ are similar to those in La$_{0.5}$Ca$_{0.5}$MnO$_3$ [24]. The lattice contribution $\beta_5 T^5$ ($\beta_5 = 0.25 \pm 0.006$ mJ/mole-K$^4$) in Ca$_2$FeReO$_6$ is smaller than in Ba$_2$FeReO$_6$, which can be explained by the different crystal structure (cubic for Ba$_2$FeReO$_6$ and distorted monoclinic for Ca$_2$FeReO$_6$) and smaller Ca mass.

A ferrimagnet has a magnetic contribution to the specific heat, $C_{\text{mag}} = \delta T^{3/2}$, which is similar to that of a ferromagnetic one. However, this contribution, can not be resolved from the specific heat data alone, since our data can be fit well without the magnetic term. Since Ca$_2$FeReO$_6$ and Ba$_2$FeReO$_6$ have a high Curie temperature, and hence, strong exchange interaction ($J$), the magnetic term should be small (since $\delta \propto \frac{1}{J^{3/2}}$).

III. CONCLUSION

In summary, we have investigated the transport, thermal and magnetic properties of two polycrys-
talline double-perovskites Ba$_2$FeReO$_6$ and Ca$_2$FeReO$_6$. Ba$_2$FeReO$_6$ displays a metallic behavior below 385 K whereas Ca$_2$FeReO$_6$ is insulating below this temperature. The specific heat of Ba$_2$FeReO$_6$ gives a low temperature metallic contribution with an electron density of states at the Fermi level close to the band structure value. Insulating Ca$_2$FeReO$_6$ has no metallic term in the specific heat but rather an extra contribution most likely caused by charge ordering of Fe, Re. The Ba$_2$FeReO$_6$ compound exhibits a negative MR at 10K, smaller than the analogous compound Sr$_2$FeMoO$_6$. Magnetic measurements indicate a ferrimagnetic behavior, with a $T_c = 315 K$ for Ba$_2$FeReO$_6$ and above 385 K for Ca$_2$FeReO$_6$. These data have been explained and compared with the analogous compounds Sr$_2$Fe(Re,Mo)O$_6$.

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[1] A.J. Millis, Nature 392, 147 (1998).
[2] R. von Helmholz, J. Weckerg, B. Holzapfel, L. Schultz and K. Samwer, Phys. Rev. Lett. 71, 2331 (1993).
[3] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh and L.H. Chen, Science 264, 413 (1994).
[4] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh and T. Venkatesan, Nature 392, 794 (1998).
[5] R.J. Soulen Jr., J.M. Byers, M.S. Osofsky, B. Nadgorny, T. Ambrose, S.F. Cheng, P.R. Brussard, C.T. Tanaka, J. Nowak, J.S. Moodera, A. Barry and J.M.D. Coey, Science 282, 85 (1998).
[6] W.E. Pickett and D.J. Singh, Phys. Rev. B 53, 1146 (1996).
[7] H.Y. Hwang and S.-W. Cheong, Science 278, 1607 (1997).
[8] W.E. Pickett Phys. Rev. B 57, 10613 (1998).
[9] T. Nakagawa, J. Phys. Soc. Japan 24, 806 (1968).
[10] K.I. Kobayashi, T. Kimura, H. Sawada, K. Terakura and Y. Tokura, Nature 395, 677 (1998).
[11] T.H. Kim, M. Uehara, S. Lee and S.-W. Cheong, Appl. Phys. Lett 74, 1731 (1999).
[12] H. Asano, S.B. Ogale, J. Garrison, A. Orozco, E. Li, V. Smolyaninova, C. Galley, M. Downes, M. Rajeswari, R. Ramesh and T. Venkatesan, preprint.
[13] A.W. Sleight and J.F. Weiher, J. Phys. Chem. Solids 33, 679 (1972).
[14] P. Majumdar and P.B. Littlewood, Nature 395, 479 (1998).
[15] P.D. Battle and C.W. Jones, J. Solid State Chem. 78, 108 (1989).
[16] M.T. Anderson, K.B. Greenwood, G.A. Taylor and K.R. Poeppelmeier, Prog. Solid State Chem. 22, 197 (1993).
[17] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, Y. Tokura, Phys. Rev. B 51, 14103 (1995).
[18] M. Abe, T. Nakagawa and S. Momura, J. Phys. Soc. Jpn. 35, 1360 (1973).
[19] A. Maigan, B. Raveau, C. Martin and M. Hervieu, J. Sol. State Chem. (1999) preprint.
[20] J. Longo and R. Ward, J. Amer. Chem. Soc. 83, 2816 (1961).
[21] A.W. Sleight, J. Londo and R. Ward, Inorg. Chem. 1, 245 (1962).
[22] R.D. Shannon, Acta. Cryst. A32, 751 (1976).
[23] J. J. Hamilton, E.L. Keatley, H.L. Ju, A.K. Raychaudhuri, V.N. Smolyaninova and R.L. Greene, Phys. Rev. B 54, 14926 (1996).
[24] V. N. Smolyaninova, K. Ghosh and R. L. Greene, Phys. Rev. B 58, R14725 (1998).