

Pb₂FeReO₆: new defect pyrochlore oxide with a geometrically frustrated Fe/Re sublattice†

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Received 11th April 2003, Accepted 27th May 2003

First published as an Advance Article on the web 12th June 2003

Nominal Pb₂FeReO₆ adopts a defect pyrochlore structure at ambient pressure unlike the other A₂FeReO₆ (A = Ca, Sr, Ba). Rietveld refinement of the crystal structure of one of the compositions Pb₂FeReO_{6.1} from powder XRD data shows that the structure is cubic pyrochlore ($a = 10.382$ Å; space group: $Fd\bar{3}m$) where oxygen vacancies occur at O2 (8b) sites. The divergence between the ZFC and FC magnetic susceptibility data and the non-Arrhenius resistivity behaviour of Pb₂FeReO₆ compositions are characteristic of the underlying geometrically frustrated Fe/Re cation sublattice in the pyrochlore structure.

Introduction

Magnetic double perovskites, A₂BReO₆ (A = Ca, Sr, Ba; B = 3d transition metal) and their molybdenum analogs, which have been known for a long time,¹ attract current attention^{2–6} following the reports of tunnelling type magnetoresistance in the M = Fe compounds at room temperature.^{7,8} The magnetoresistive properties arise from a special electronic structure consisting of localized majority spin ($S = 5/2$) Fe and itinerant minority spin Re/Mo d electrons, that give rise to ‘half-metallicity’ to these materials.^{7,8} Recent investigations^{2–6} have uncovered quite a variety of electronic properties in these materials, whose origin has not been fully understood. For instance, among the A₂FeReO₆, the A = Ba and Sr members are metallic and ferrimagnetic, while the A = Ca member is insulating;³ nevertheless, the ferrimagnetic T_c increases in the series:⁹ Ba < Sr < Ca, the T_c of 540 K for Ca₂FeReO₆ being the highest value reported yet for a ferrimagnetic double perovskite.¹⁰ Ca₂FeMoO₆, on the other hand, is a metallic ferrimagnet⁴ ($T_c = 380$ K), albeit having the same monoclinic structure as Ca₂FeReO₆.

To probe further the influence of A-site cations on the structure and properties of magnetic double perovskites, we explored the A = Pb members of the A₂BReO₆ series. Not only does the radius of Pb²⁺ (1.49 Å in 12 CN), being similar to that of Sr²⁺ (1.44 Å in 12 CN), make it appropriate for the A site of perovskite oxides, but also the presence of a 6s² lone pair provides additional avenues for chemical bonding¹¹ which influences the structure and properties of ABO₃ compositions. Indeed our investigations revealed that Pb₂FeReO₆ adopts a pyrochlore structure instead of the expected perovskite structure. We describe the synthesis, structure and electrical/magnetic properties of pyrochlore Pb₂FeReO₆ in this paper.

Experimental

We synthesized polycrystalline Pb₂FeReO₆ by the following method. A precursor oxide of composition Pb₂ReO_{5.5} was first prepared by reacting stoichiometric quantities of PbO and Re₂O₇ in flowing Ar at 550 °C for 12 h. This oxide was then

mixed with the required quantities of Fe₂O₃ and Fe powder to obtain the composition Pb₂FeReO₆. Pellets of this mixture were heated in evacuated sealed tubes at elevated temperatures for varying durations with grindings in between. Powder XRD patterns (recorded with a Bruker C2 Discover X-ray diffractometer with an area detector and CuK_α radiation) showed the formation of a pyrochlore phase instead of the expected perovskite phase. The conditions for the formation of single-phase pyrochlore were optimized by trial and error. It was found that when the reaction was carried out in an evacuated ($\sim 10^{-5}$ Torr) sealed silica tube at 600 °C for two days with a grinding in between, a homogeneous single-phase product was obtained and its XRD pattern could be indexed on a FCC cell with $a = 10.384$ Å. The oxygen stoichiometry of the sample (determined by thermogravimetric reduction in 1 : 1 hydrogen : argon atmosphere using a Cahn TG-131 system) was found to correspond to the composition Pb₂FeReO_{6.09 ± 0.01}. We prepared another sample of nominal composition Pb₂FeReO_{5.9} by the same method. Powder XRD showed the formation of a single phase pyrochlore oxide with $a = 10.374$ Å, but its oxygen stoichiometry turned out to be Pb₂FeReO_{5.81 ± 0.01}. The variation in oxygen stoichiometry is likely due to the residual oxygen content in the sealed reaction tube.

We determined the structure of Pb₂FeReO_{6.1} by Rietveld refinement of powder XRD data. The XRD data were collected using a Bruker C2 Discover X-ray powder diffractometer (CuK_α radiation) in the 2θ range 3 to 100° in steps of 0.02 in 7 frames with 1800 seconds exposure time for each frame. Refinements were carried out using the FULLPROF program¹² using the standard refinement procedure. The refinement was carried out in $Fd\bar{3}m$ space group with Pb at 16d, Fe/Re at 16c, O1 at 48f and O2 at 8b crystallographic positions. The position parameter x for O1 at 48f was refined first, keeping a fixed occupancy and thermal parameters for all the other atoms. Then the occupancies of Pb and Fe/Re were refined followed by refinement of thermal parameters. At the end, oxygen occupancies were allowed to refine alternately with the thermal parameters. Final refinements gave x for O1 as 0.3243 and the occupancy of O2 as 0.10 in agreement with TG data. Zero-field cooled (ZFC) and field cooled (FC) magnetic measurements were carried out using a SQUID MPMS Quantum Design magnetometer in the 5–300 K range. DC electrical resistivity on bars of $1 \times 2 \times 8$ mm³ dimension was

†Electronic supplementary information (ESI) available: powder XRD patterns of pyrochlores Pb₂FeReO_{6.1} and Pb₂FeReO_{5.81}. See <http://www.rsc.org/suppdata/jm/b3/b304118m/>

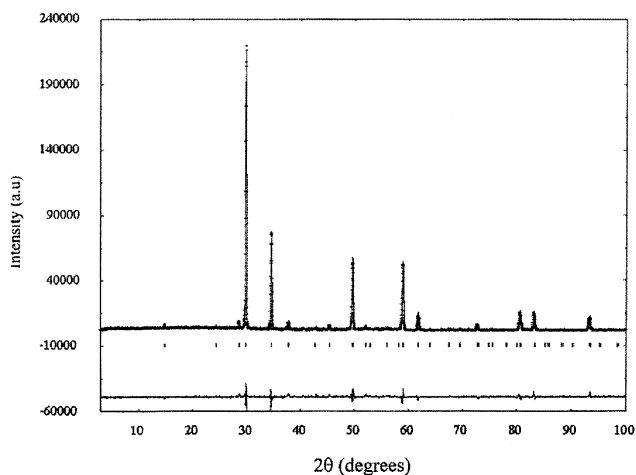


Fig. 1 Observed (+), calculated (–) and difference (bottom) Rietveld refined powder XRD profiles of pyrochlore $\text{Pb}_2\text{FeReO}_{6.1}$. The vertical lines mark the allowed Bragg reflections.

measured in the same temperature range using a standard four-probe method.

Results and discussion

The Rietveld refinement confirmed the anion-deficient pyrochlore structure of $\text{Pb}_2\text{FeReO}_{6.1}$. Refinement results are shown in Fig. 1 and Table 1 and the structure is drawn in Fig. 2. In general, for anion-deficient $\text{A}_2\text{B}_2\text{O}_{6+x}$ pyrochlores,¹³ the B atoms occupy 16c sites and six oxygen atoms (O1) 48f sites forming a corner shared B_2O_6 octahedral network (Fig. 2) wherein the large A cations reside at eight-coordinated 16d sites. The O2 (8b) sites are either empty ($x = 0$) or partially occupied ($x > 0$). The refinement results of $\text{Pb}_2\text{FeReO}_{6.1}$ (Table 1) are consistent with this model, showing a statistical distribution of Fe/Re atoms at 16c sites, full occupancy for O1 at 48f and an occupancy of 0.1 at 8b sites. The position parameter for O1 ($x = 0.3243$) is within the range reported¹³

Table 1 Crystallographic data^a for pyrochlore $\text{Pb}_2\text{FeReO}_{6.1}$ together with selected bond lengths and bond angles

Atom	Site	x	y	z	$B/\text{\AA}^2$	Occupancy
Pb	16d	0.5	0.5	0.5	0.60(5)	1.00
Re/Fe	16c	0	0	0	0.73(4)	1.00
O1	48f	0.3243(3)	0.1250	0.1250	0.91(6)	1.00
O2	8b	0.3750	0.3750	0.3750	0.15(2)	0.10(2)

^aSpace group: $Fd\bar{3}m$, $a = 10.382(1) \text{ \AA}$; $R_p = 7.9$, $R_{wp} = 8.3$, $R_{Bragg} = 8.0$, $R_F = 7.9$, $\chi^2 = 2.4$. Bond lengths (\AA) and angles ($^\circ$): Re/Fe–O1 ($\times 6$) = 1.991(1), Pb–O1 ($\times 6$) = 2.588(2), Pb–O2 ($\times 2$) = 2.248, Re/Fe–O1–Re/Fe = 134.41(1), O1–Re/Fe–O1 = 85.40(1), O1–Re/Fe–O1 = 94.60(1)

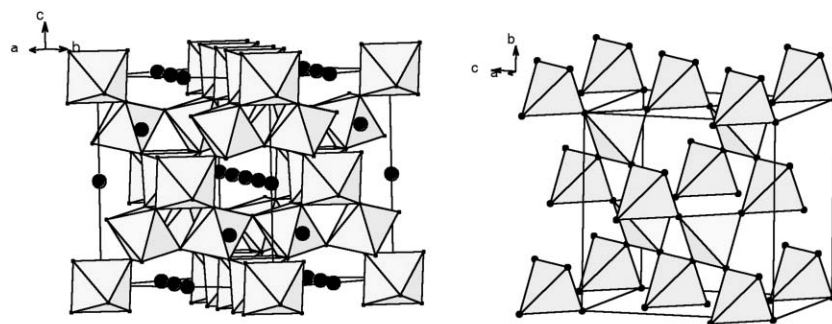


Fig. 2 (a) Crystal structure of pyrochlore $\text{Pb}_2\text{FeReO}_6$ showing the octahedral network. (b) Fe/Re cation sublattice of interconnected tetrahedra at the 16c position.

for pyrochlore oxides in general. The Fe/ReO₆ octahedron is nearly regular and the Fe/Re–O distance (1.991 \AA) is consistent with a random distribution of Fe/Re atoms at the octahedral sites. Considering the close similarity of XRD patterns of both $\text{Pb}_2\text{FeReO}_{6.1}$ and $\text{Pb}_2\text{FeReO}_{5.81}$, we believe the latter also adopts a similar defect pyrochlore structure wherein there are likely additional oxygen vacancies (0.19 per formula unit) at 48f sites.

Although one would have expected $\text{Pb}_2\text{FeReO}_6$ to form a double perovskite structure similar to $\text{Sr}_2\text{FeReO}_6$ on the basis of size considerations (Goldschmidt tolerance factors are 0.989 and 0.972 for the Pb and Sr oxides respectively), stabilization of the pyrochlore structure instead suggests the role of the Pb^{II} : $6s^2$ lone pair. Longo *et al.*¹¹ argued that formation of a A–A bond through polarisation of the $6s^2$ core mediated by the 8b anion vacancy is the prime reason for the occurrence of several ABO_{3+x} oxides containing $6s^2$ lone pair A cations in the defect pyrochlore structure.¹³ Alternatively, Sleight¹⁴ suggested that it could be due to the preference of oxygen for a tetrahedral coordination of metal atoms in the pyrochlore structure, instead of a six fold coordination ($4A + 2B$) in the perovskite structure, when both A and B cations are not highly electropositive.

Unlike the perovskite structure, the pyrochlore structure has geometrically frustrated cation sublattices¹⁵ which preclude long range ordering of Fe/Re atoms in $\text{Pb}_2\text{FeReO}_6$. This lack of long range ordering of Fe/Re is reflected in the magnetic properties of $\text{Pb}_2\text{FeReO}_6$.

Both the pyrochlore compositions show similar magnetic susceptibility and electrical resistivity behaviour. The strong divergence between FC and ZFC magnetic data (Fig. 3) below 150 K suggests a spin glass ground state.¹⁵ While the data for the $\text{O}_{5.81}$ composition show a distinct two peak pattern below 150 K, the peaks are much less pronounced in the data for $\text{O}_{6.1}$ composition, although the peak positions remain nearly the same. The susceptibility above 150 K also is not quite Curie–Weiss like; $\theta = \sim -170 \text{ K}$ (estimated by extrapolation of the high temperature susceptibility data for the $\text{O}_{5.81}$ composition) likely suggests short range antiferromagnetic correlations between the transition metal atoms in the disordered FeReO_6 array, the Fe–Fe antiferromagnetic interaction being the strongest among them. The M vs. H plot (Fig. 4) for $\text{Pb}_2\text{FeReO}_{6.1}$ shows a saturation moment of $0.9 \mu_B$ at 10 K which is much less than the expected value of $\sim 3.0 \mu_B$ for an antiferromagnetic coupling of $\text{Fe}^{2+}/\text{Re}^{6+}$ (or $\text{Fe}^{3+}/\text{Re}^{5+}$) moments. The smaller than expected saturation moment is consistent with short-range antiferromagnetic correlations in a frustrated FeReO_6 sublattice of the pyrochlore structure. Between the two pyrochlore compositions investigated, $\text{Pb}_2\text{FeReO}_{6.1}$ shows a higher saturation moment at low temperatures than $\text{Pb}_2\text{FeReO}_{5.81}$: a higher moment for the more oxidized sample (higher oxygen content) is consistent with a smaller d electron count on the FeReO_6 framework and short range antiferromagnetic interaction between Fe and Re

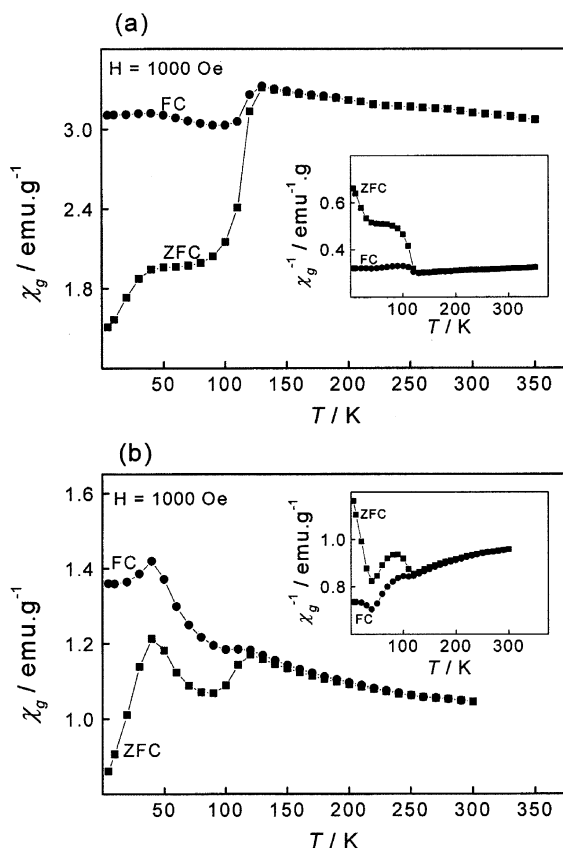


Fig. 3 Temperature dependence of magnetic susceptibility (χ_g) for pyrochlore (a) $\text{Pb}_2\text{FeReO}_{6.1}$ and (b) $\text{Pb}_2\text{FeReO}_{5.81}$. Insets show the corresponding inverse susceptibility as a function of temperature.

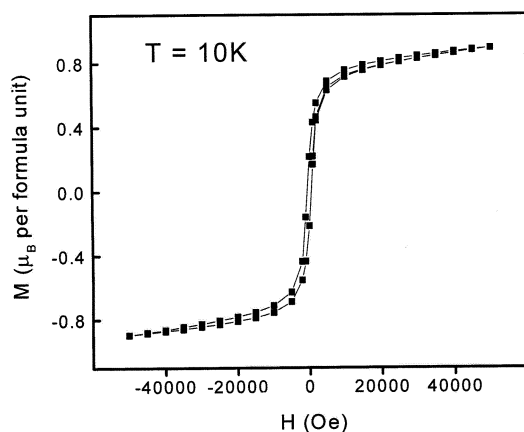


Fig. 4 Magnetisation (M) vs. field (H) plot for $\text{Pb}_2\text{FeReO}_{6.1}$.

ions. Regardless of the oxidation state assignments, ($\text{Fe}^{2+}/\text{Re}^{6+}$, d^6-d^1 or $\text{Fe}^{3+}/\text{Re}^{5+}$, d^5-d^2), oxidation will increase the net magnetization for both these antiferromagnetic couples.

Many transition metal pyrochlore oxides,¹⁵ for example¹⁶ $\text{Y}_2\text{Mo}_2\text{O}_7$, show a FC/ZFC divergence characteristic of spin glass freezing that has been attributed to a frustrated Mo^{IV} sublattice with competing magnetic interactions. But what is unusual for $\text{Pb}_2\text{FeReO}_6$ is the presence of two peaks in the magnetic data (Fig. 3) one at ~ 125 K and the other at ~ 50 K. The DC electrical resistivities of both the samples (Fig. 5) are also typical of spin glass pyrochlores¹⁷ ($\text{R}_2\text{Mo}_2\text{O}_7$) showing a non-Arrhenius temperature dependence. Further physical investigations of the oxidation states of Fe/Re and magnetic interactions are essential to understand the spin dynamics of $\text{Pb}_2\text{FeReO}_6$ pyrochlore.

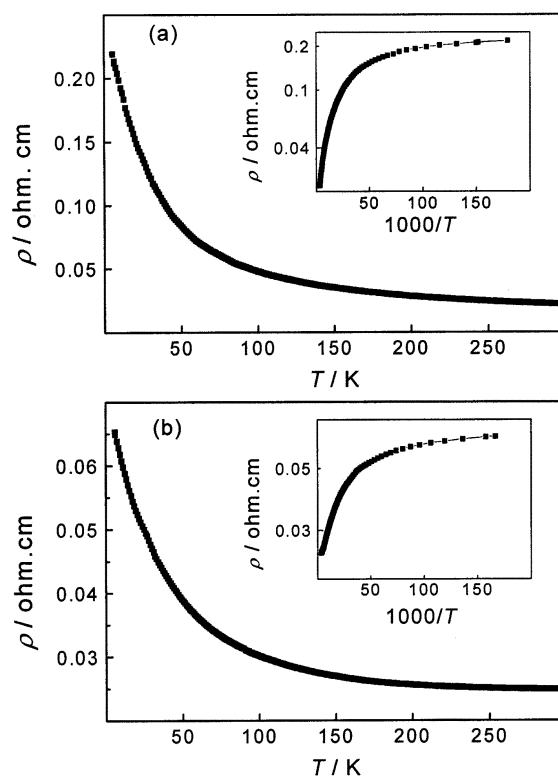


Fig. 5 Electrical resistivity (ρ)–temperature (T) plots for pyrochlore (a) $\text{Pb}_2\text{FeReO}_{6.1}$ and (b) $\text{Pb}_2\text{FeReO}_{5.81}$. Insets show the corresponding $\log(\rho)$ – $1/T$ plots.

Since defect pyrochlore ABO_{6+x} oxides containing $\text{Pb}^{II}/\text{Bi}^{III}$ are known to transform to a perovskite structure at high pressure,^{18,19} we expect that pyrochlore $\text{Pb}_2\text{FeReO}_6$ also would transform under pressure to a perovskite structure, where Fe/Re would likely order in the long range with attendant changes in electronic properties from a spin glass semiconductor to a ferrimagnetic ‘half-metal’.

Conclusions

Unlike A_2FeReO_6 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) which adopts ordered double perovskite structures showing ferrimagnetic and metallic properties ($\text{Ca}_2\text{FeReO}_6$ is insulating), $\text{Pb}_2\text{FeReO}_6$ is stabilized in a defect-pyrochlore structure at atmospheric pressure. The frustrated Fe/Re sublattice of the pyrochlore structure precludes a long range ordering of the magnetic cations, resulting in a spin-glass behaviour for $\text{Pb}_2\text{FeReO}_6$.

Acknowledgements

We thank NSF (DMR - 0076460) and DST, New Delhi for support of this work. L.S. thanks the Council of Scientific and Industrial Research, New Delhi for the award of a research fellowship. We thank Mr. Chad Stoltz for assistance with the magnetic measurements.

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