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Enhanced magnetoresistance in Sr_2FeMoO_6 by combustion synthesis

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A novel method of producing magnetoresistive oxides is described, which involves low temperature combustion synthesis from a mixture of nitrates and fuel, as applied to Sr_2FeMoO_6. The method yields ceramics with a fine crystallite size of 100–200 nm and a room temperature resistivity of 200 µΩ m. Low field magnetoresistance (6.5% in 0.1 T) is enhanced dramatically compared to samples prepared by conventional solid-state reaction due to the efficient intergrain tunnelling arising from the high density of grain boundaries. Magnetoresistance in low fields is essentially independent of temperature from 5–300 K, and it persists up to 350 K, providing the prospect of sensor applications in an extended temperature range.

Sr_2FeMoO_6 is an ordered double perovskite of the $A_2BB'O_6$ type in which the Fe and Mo order on alternate octahedral B and B′ sites.[1,2] Band structure calculations by Kobayashi *et al*[3] and others[4,5] indicate that the compound is a type I_B half-metallic ferromagnet,[6] according to a recent classification scheme. The Curie temperature of about 415 K is higher than for any mixed-valent manganite.[7] Low field room temperature magnetoresistance in this compound raises the possibility of practical applications. Polycrystalline ceramics produced by conventional solid-state reaction[3,8–11] exhibit a room temperature magnetoresistance ratio, $[\rho(0) - \rho(H)]/\rho(0)$, of about 5–7% in a 1.0 T magnetic field and 1–2% in 0.1 T. However, for potential sensor applications, it is necessary to improve the low field magnetoresistance, which depends, essentially, on intergranular contacts. The intergrain magnetoresistance is strongly dependent on the number and nature of the grain boundaries. This led us to the idea of decreasing the grain size and improving low field magnetoresistance by adopting a new synthesis route. Combustion synthesis is a novel technique for producing ceramics with ultrafine crystallites which offers fine tuning of composition and high chemical homogeneity in multicomponent ceramics.[12] Here, we report the synthesis of the double perovskite Sr_2FeMoO_6, and the observation of enhanced low field intergrain magnetoresistance in samples synthesised by this method.

Single-phase Sr_2FeMoO_6 was prepared using a mixture of metal nitrates [$Sr(NO_3)_2$, $Fe(NO_3)_3{\cdot}9H_2O$, and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (dissolved in nitric acid)] as 'oxidisers' in the presence of a fuel to induce highly exothermic redox reactions. Oxalic acid dihydrazide (ODH) was used as fuel. The oxidiser–fuel ratio was calculated based on the valencies of the oxidisers (*O*) and fuel (*F*), as defined in propellant chemistry,[13] keeping $O/F = 1$ in order to release the maximum energy in the reaction. Strontium and iron nitrates are dissolved in water separately, while ammonium molybdate is dissolved in nitric acid, and the three solutions are mixed in decreasing order of solubility. ODH solution is added finally to the saturated solution. The light green gel is then introduced into a preheated furnace at 350 °C for 5 min for the combustion reaction. As-combusted powder is heat treated at 400 °C to decompose the unreacted nitrates and at 700 °C to remove any organic traces. The powders are then pressed into pellets and sintered at 1200 °C in 1% H_2–Ar atmosphere to obtain single-phase Sr_2FeMoO_6. Since the reaction time is very short, the resulting crystalline phases nucleate, but do not grow, thus yielding crystallites of about 100–200 nm. Reference samples are prepared by solid-state reaction,[8,9] heating stoichiometric mixtures of $SrCO_3$, Fe_2O_3 and MoO_3 in air followed by sintering at 1200 °C in 1% H_2–Ar. The grain size is 2–5 µm. Phase analysis was carried out using powder X-ray diffraction and ^{57}Fe Mössbauer spectrometry. Resistivity measurements were performed using a linear four probe method with and without magnetic field. Magnetisation measurements were made using a 5 T SQUID magnetometer.

Fig. 1 illustrates the effect of the different reaction steps. The powder X-ray diffraction pattern of as-combusted powder [Fig. 1(a)] reveals the presence of $SrMoO_4$, $Sr(NO_3)_2$ and poorly crystallised $Fe_2(MoO_4)_3$. Decomposition at 400 °C leads to the elimination of $Sr(NO_3)_2$ [Fig. 1(b)]. Further heat treatment at 700 °C leads to the appearance of the perovskite phase $SrFeO_3$ [Fig. 1(c)], in addition to the phases already identified. Single phase, tetragonal Sr_2FeMoO_6 (space group *I4/mmm*) with $a = 5.576$ and $c = 7.893$ Å ($a = 5.573$ and

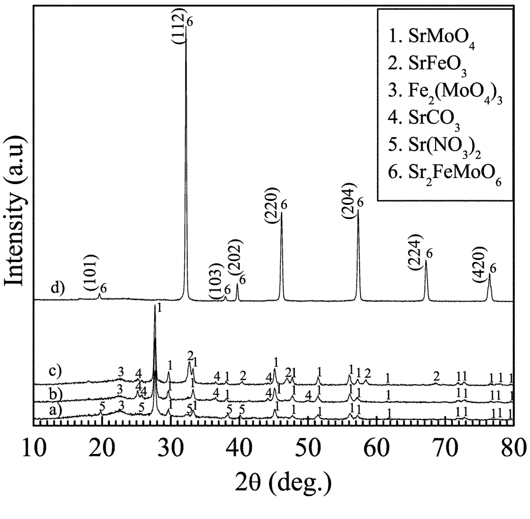

Fig. 1 X-Ray diffractograms of (a) as-combusted powders, (b) after 400 °C treatment, (c) after 700 °C treatment and (d) single phase Sr_2FeMoO_6.

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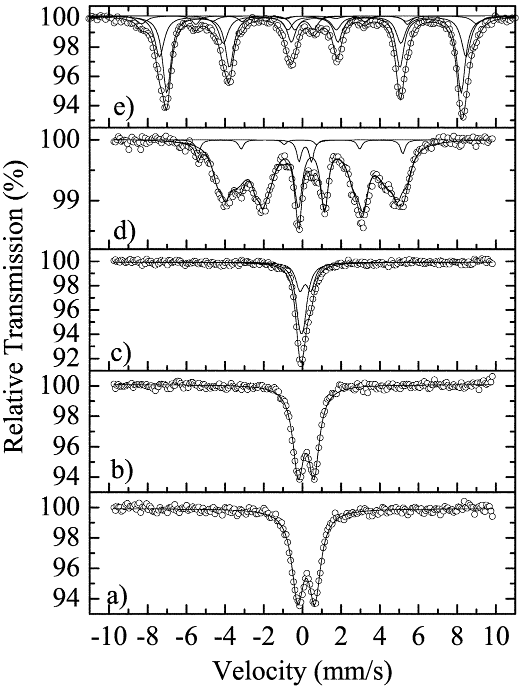

Fig. 2 Room temperature Mössbauer spectra of (a) as-combusted powders, (b) after 400 °C treatment, (c) after 700 °C treatment, (d) single phase Sr_2FeMoO_6 and (e) Mössbauer spectra of Sr_2FeMoO_6 at 15 K.

b = 7.897 Å for solid-state-synthesised sample) is obtained after heating to 1200 °C, as shown in Fig. 1(d).

The phase analysis was supported by Mössbauer spectra of samples taken after each reaction step. Room temperature spectra are shown in Fig. 2. The spectra [Fig. 2(a), (b)] of the as-combusted precursor and after the 400 °C treatment indicate that iron is in a Fe^{3+} high spin state, probably in the poorly-crystallised $Fe_2(MoO_4)_3$ phase, which is observed by X-ray diffraction [Fig. 1(a), (b)]. After heat treatment at 700 °C, the presence of $SrFeO_3$ is indicated by the characteristic room temperature Mössbauer spectrum [Fig. 2(c)], which shows the presence of Fe^{4+} ions.

The Mössbauer spectra at 300 [Fig. 2(d)] and 15 K [Fig. 2(e)] of the sample sintered at 1200 °C in an H_2–Ar atmosphere confirm the formation of Sr_2FeMoO_6 with minor paramagnetic and iron metal impurities. The spectrum at 15 K shows the presence of three different environments in the double perovskite structure of Sr_2FeMoO_6. The main component with the large absorption area and higher isomer shift (Table 1) is attributed to iron ions which have a well-ordered first-neighbour Mo environment in the B crystallographic sites. The secondary component with a lower absorption area and isomer shift values is attributed to iron ions with a disordered first-neighbour Mo environment (5 Mo, 1 Fe). There is a small component (7% of total area) with the largest hyperfine splitting (54 T) which corresponds to iron ions in B′ sites with six iron neighbours.[14,15]

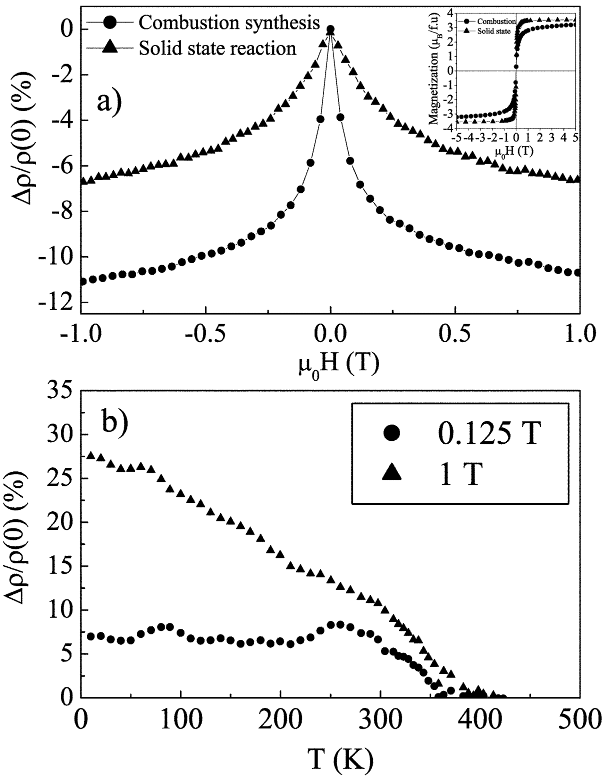

Fig. 3 (a) Room magnetoresistance of Sr_2FeMoO_6 for samples produced by combustion synthesis and solid-state reaction; the 5 K magnetisation curves are shown in the insert. (b) Temperature dependence of magnetoresistance in the range 10–400 K.

The Curie temperature, determined by thermogravimetry, is 400 K, slightly lower than that of the reference sample (T_C = 415 K). The insert in Fig. 3(a) compares the low temperature magnetisation curves of Sr_2FeMoO_6 prepared by combustion reaction and solid-state reaction. The magnetisation is unsaturated at low temperatures, even in a 5 T magnetic field. The saturation magnetic moment, determined by extrapolating to $1/H^2 = 0$, is always less than the half-metallic value of 4 μ_B per formula unit anticipated for a ferrimagnetic configuration of Fe^{3+} ($3d^5$) and Mo^{5+} ($5d^1$), which reflects the antisite disorder. The extrapolated value of 3.20 μ_B per f.u. at 5 K is lower than that of the reference sample (3.51 μ_B per f.u.). The reduction and lack of saturation of magnetic moment may be attributed to (i) antisite defects[14,16] resulting from the partial disorder of Fe and Mo ions, (ii) antiphase boundaries,[15,17,18] (iii) atom cation deficiency or (iv) surface spin disorder.[19] From the intensity of the second and third components of the Mössbauer spectra, we deduce that $p = 6 \pm 1\%$ of the cations are misplaced in antisite defects in the combustion synthesis

Table 1 Hyperfine parameters of Sr_2FeMoO_6 at 300 and 15 K

T/K	Component	$\delta^a \pm 0.02$/mm s^{-1}	$B_{hf} \pm 0.5$/T	A (%)	$3d^n$	p (%)
300	Main	0.58^b	26.0^b	92		
	Fe-metal	0	33.0	5	—	—
	Paramagnetic	0.11		3		
15	Main	0.72	47.3	53		
	Secondary	0.62	49.2	32		
	Third	0.46	53.8	7	5.3	6
	Fe-metal	0.11	34.0	4		
	Paramagnetic	0.20		4		

^{a}Relative to α-Fe at 300 K. ^{b}Average values.

material, which is the same as the antisite defect concentration in the reference samples.[15] The magnetic moment per formula unit is given by $M = (4 - 8p)$ or $(4 - 10p)$ μ_B, according to whether the misplaced Mo atom has its moment parallel or antiparallel to the majority iron moment.[15] The value of p deduced from the intensity of the secondary component in the Mössbauer spectra leads to moment of 3.52 μ_B, assuming $M = (4 - 8p)$ μ_B. The extra moment reduction and lack of saturation in the combustion-synthesised sample may be due to a low concentration of antiphase boundaries[15,17,18] rather than surface spin disorder, which would tend to destroy the low field magnetoresistance.

Fig. 3(a) compares the room temperature magnetoresistance $[\Delta\rho/\rho(0)]$ for Sr_2FeMoO_6 synthesised by combustion reaction and conventional solid-state reaction. The effect of the field on resistivity is much stronger in combustion-synthesised Sr_2FeMoO_6 than in the reference sample. A room temperature magnetoresistance ratio of 6.5% is obtained in 0.1 T and 12% in 1.2 T. The MR ratio at any given field is enhanced by a factor of about two. The room temperature MR ratio at 0.1 T is the highest of the samples prepared by solid-state reaction reported in the literature so far.[3,8–11] The enhancement of low field magnetoresistance in combustion-synthesised samples is related to the increased intergrain tunnelling which appears to arise from the large number of grain boundaries. There is no hysteresis.

For sensor applications, it is important to minimise the temperature dependence of the magnetoresistance and to maintain it above room temperature. Fig. 3(b) shows the temperature dependence of the magnetoresistance in 0.125 and 1.0 T. The important observation is that the low field magnetoresistance is almost independent of temperature from 5 to 300 K and it collapses at around 360 K, 0.9 T_C.

In summary, we have synthesised ceramics with fine crystallites of Sr_2FeMoO_6 by a novel combustion synthesis method. The enhanced low field magnetoresistance is attributed to the abundance of intergrain tunnel barriers. Magnetoresistance persists up to 360 K and it is almost independent of temperature below 300 K. The method can be extended to doped materials with high Curie temperatures,[20] leading to the prospect of sensor applications in an extended temperature range.

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