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Novel methods of synthesis and wet-chemical redox analysis for magnetoresistive double-perovskite Sr_2FeMoO_{6-w}

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An efficient encapsulation synthesis technique and an accurate wet-chemical analysis method for the redox state have been developed for the Sr_2FeMoO_{6-w} double-perovskite compound known as a magnetoresistance (MR) material. Single-phase Sr_2FeMoO_{6-w} samples are reproducibly obtained from Sr–Fe–Mo–O mixtures under very low oxygen partial pressures utilizing an Fe/FeO redox couple as the oxygen trap which is encapsulated together with the starting material mixture in an evacuated synthesis ampoule. Coulometric oxidation titration of the lower-valent iron and/or molybdenum species, formed upon dissolving the sample material in acidic solution, was found to reveal the oxygen content of a Sr_2FeMoO_{6-w} sample with high reproducibility. Furthermore, the initial potential level in the titration is believed to indicate the nature of the reduced species. In the samples synthesized with the present encapsulation technique at 1150 °C the oxygen non-stoichiometry was found to be $w \approx 0.03 \pm 0.02$. No indication of lower-valent molybdenum was observed.

The double-perovskite structure, either A-site ordered $A'A''B_2O_{6-w}$ or B-site ordered $A_2B'B''O_{6-w}$, is derived from the simple perovskite unit, ABO_3, upon co-occupation of the A- or B-site, respectively, with two different metal ions of different sizes and/or charges. For both types, various interesting electronic and magnetic properties are expected including the magnetoresistance (MR) effect.[1] Typically the desired properties are crucially controlled by the oxygen stoichiometry and, further, by the actual valences of the transition metal species at the B-cation site. Depending on the metal composition, degrees of oxygen-deficiency as high as $w \approx 1$ are in general possible for the double-perovskite structure.

The B-site ordered double-perovskite, Sr_2FeMoO_{6-w}, has been known as a ferromagnetic (or ferrimagnetic) conductor with a magnetic transition temperature as high as 420–450 K.[2–5] The phase is obtained under reduced oxygen partial pressures, in the range of about $10^{-9.8}$–$10^{-13.5}$ atm (at 1200 °C).[6] For the unit cell of Sr_2FeMoO_{6-w} both cubic (space group *Fm*3*m*)[2,7] and tetragonal (space group *I*4/*mmm* or *I*4*mm*)[4,5,8] symmetries have been reported. This discrepancy is possibly attributed to the differences in the oxygen content. So far, however, no efforts have been made to accurately determine the oxygen content in Sr_2FeMoO_{6-w} samples by means of chemical analysis or any other techniques.

From electronic-structural calculations half-metallic nature, *i.e.* total spin polarization of conduction electrons, was concluded for Sr_2FeMoO_{6-w}.[9,10] As a most straightforward explanation for the half-metallicity and the other properties known for Sr_2FeMoO_{6-w}, a picture where localized $3d^5$ electrons of high-spin Fe(III) ($t_{2g}^3e_g^2$; $S = 5/2$) and an itinerant $4d^1$ electron of Mo(V) (t_{2g}^1; $S = 1/2$) couple antiferromagnetically has generally been assumed. Consistent with this picture, tunnelling-type negative magnetoresistance was recently observed in polycrystalline[9,11] as well as in thin-film[12–14] samples of Sr_2FeMoO_{6-w} at room temperature. However, even though the trivalent state of iron explains satisfactorily the properties of Sr_2FeMoO_{6-w}, we recently proposed a slightly elaborated picture based on Mössbauer spectroscopy data.[15] The ^{57}Fe Mössbauer spectra obtained for a polycrystalline Sr_2FeMoO_{6-w} sample were best interpreted by assuming a mixed-valence or valence-fluctuating state, formally expressed as $Fe^{2.5+}$, for iron. A similar Verwey-type mixed-valence state had been earlier established for the A-site ordered double-perovskite, $BaSmFe_2O_{5+\delta}$ ($\delta \approx 0$), for which the MR effect was also observed recently.[16,17] In the case of $BaSmFe_2O_{5+\delta}$, the $Fe^{2.5+}$ state separates upon cooling into equal amounts of divalent and trivalent iron at $T_V \approx 200$ K, while for Sr_2FeMoO_{6-w} the mixed-valence state has been confirmed to persist down to 5 K.[15]

In the present contribution, a wet-chemical analysis route is established to accurately determine the oxygen content in Sr_2FeMoO_{6-w} samples. The individual valence states of iron and molybdenum are discussed from the chemical point of view based on the obtained analysis data. Furthermore, during the course of the work, an encapsulation synthesis technique was developed in which the oxygen partial pressure inside the synthesis ampoule is controlled with an Fe/FeO trap to obtain high-quality Sr_2FeMoO_{6-w} samples in a simple and reproducible way.

Experimental

For the synthesis of the polycrystalline Sr_2FeMoO_{6-w} samples stoichiometric amounts of high-purity $SrCO_3$, Fe_2O_3 and MoO_3 powders were used as starting materials. After being thoroughly mixed the starting materials were calcined in an Ar atmosphere at 900 °C for 15 hours. The calcined powders were pelletized and sintered in evacuated and sealed fused-quartz ampoules containing the sample pellets together with Fe grains ($\geqslant$99.9%, under 10 mesh) as the oxygen trap (Fig. 1). The empty space inside the ampoule was filled with a fused-quartz rod. The synthesis was carried out at 1150 °C for 50 hours. Under these conditions the oxygen partial pressure is expected to equilibrate at 2.6×10^{-13} atm due to the redox couple of

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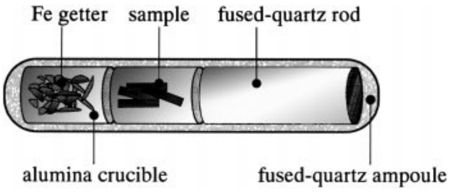

Fig. 1 Schematic representation of the packing of the synthesis ampoule.

Fe/FeO.[18] From the synthesis temperature the ampoule was quenched into liquid nitrogen.

The synthesized samples were checked for phase-purity and lattice parameters by X-ray diffraction (XRD; MAC Science M18XHF[22]; CuKα radiation). The crystal structure and the cation composition of the obtained Sr_2FeMoO_{6-w} phase were investigated by electron diffraction (ED), high-resolution transmission-electron microscopy (HRTEM; Hitachi H-9000) and energy-dispersive X-ray analysis (EDX; Kevex Sigma). In the EDX analysis, $SrMoO_4$ was used as a reference for the Sr/Mo relation.

For determination of the redox state of the Sr_2FeMoO_{6-w} phase, an analysis method based on electrochemical oxidation, *i.e.* coulometric titration,[19] of the lower-valent cation species, formed upon acidic dissolution of the sample, was developed. For this analysis, the sample was dissolved in 1 M HCl solution which had been freed from dissolved oxygen prior to the sample-dissolution by bubbling Ar gas through it for 1 hour. In the coulometric titration both Fe(II) and Mo(V) species introduced in the solution upon the sample-dissolution are oxidized as follows:

$$\mathrm{Fe(II)} \rightarrow \mathrm{Fe(III)} + \mathrm{e}^- \quad (1)$$

$$\mathrm{Mo(V)} \rightarrow \mathrm{Mo(VI)} + \mathrm{e}^- \quad (2)$$

The electrochemical oxidation was performed at a constant current (I) of 3 mA until the potential against the Ag/AgCl electrode reached 820 mV. From the time (t) required for titration the quantity of electrons (n_e) produced and thus the total quantity of the lower-valent Fe(II) and/or Mo(V) species in the sample was calculated as

$$n_e = (I \times t)/F \quad (3)$$

where F is the Faraday constant. The titration was carried out in an inert Ar atmosphere in order to prevent air-oxidation of the species to be oxidized electrochemically. A schematic representation of the titration cell is shown in Fig. 2. A reference Fe(II) solution for establishing the redox characteristics of divalent iron under the present experimental conditions was prepared using $FeCl_2 \cdot 4H_2O$ as the Fe(II) source. The Mo(V) reference was prepared prior to use from the solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ by Zn-reduction.

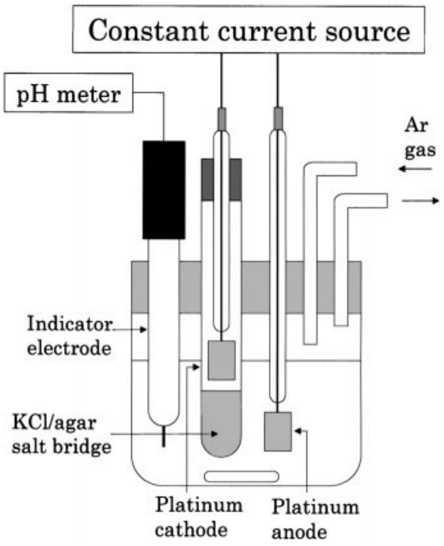

Fig. 2 Schematic representation of the coulometric titration cell.

Results and discussion

The present encapsulation synthesis was found to yield single-phase Sr_2FeMoO_{6-w} samples in a reproducible way, as judged from the X-ray diffraction patterns collected for the synthesized samples (Fig. 3). Also a high-resolution transmission-electron micrograph (Fig. 4(a)), an electron-diffraction pattern (Fig. 4(b)) and EDX analysis data (Table 1) obtained for one of the synthesized samples all together indicate the double-perovskite structure. For the obtained Sr_2FeMoO_{6-w} phase, a cell parameter, $a = 7.880(1)$ Å, was refined from the XRD data in the $Fm3m$ space group of cubic symmetry.

Representative examples of the coulometric titration curves obtained for the Fe(II) and Mo(V) reference solutions are shown in Figs. 5(a) and 5(b), respectively. Both species, Fe(II) and Mo(V), are oxidized quantitatively under the conditions used for the anodic oxidation. This means that the overall redox state, *i.e.* the oxygen content, of a Sr_2FeMoO_{6-w} sample is determined in an unambiguous way by means of the present coulometric titration method. Based on several parallel titrations the degree of oxygen deficiency in the present Sr_2FeMoO_{6-w} sample was established at $w \approx 0.03 \pm 0.02$. This result is consistent with the fact that the ^{57}Fe Mössbauer spectrum presented in ref. 15 for the same sample material was successfully fitted by six-coordinated iron components only, *i.e.* no oxygen-deficiency around Fe atoms was observed within the detection limits of Mössbauer spectroscopy ($\approx 2\%$).

In order to completely understand the electron fine-distribution that applies when the Sr, Fe, Mo and O atoms are arranged into the crystal lattice of Sr_2FeMoO_{6-w}, it is worthwhile to investigate how the valence electrons are distributed when the chemical bond(s) are broken upon the dissolution of the lattice. For identifying the lower-valent species formed the initial potential in the titration is quite indicative. When the solution contains Fe(II)species only, the potential against the Ag/AgCl electrode is between 400 and 600 mV, as in the case of the $FeCl_2 \cdot 4H_2O$ reference solution (Fig. 5(a)). In solution, pentavalent molybdenum is more easily oxidized than divalent iron, and consequently the initial potential is considerably lower for the solutions containing Mo(V)species, *i.e.* in the range of −100 and 100 mV against the Ag/AgCl electrode (Figs. 5(b) and 5(c)). In the solutions containing both Fe(II) and Mo(V), the titration curve for the anodic oxidation exhibits two steps, as shown in Fig. 5(c). In the first step Mo(V) is oxidized into the hexavalent state. The first step is quite well distinguished from the second step in which Fe(II) is oxidized into the trivalent state. This significant difference in the redox potentials of the Fe(II)/(III) and

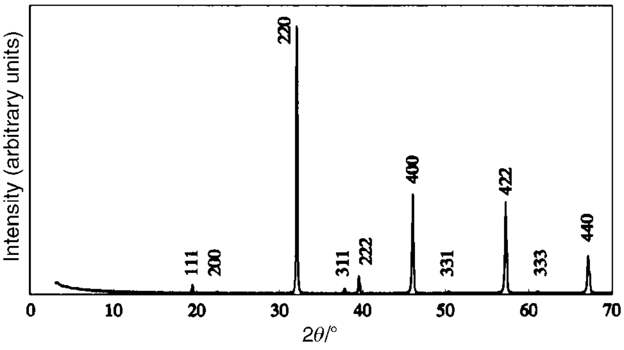

Fig. 3 XRD pattern for a synthesized Sr_2FeMoO_{6-w} sample.

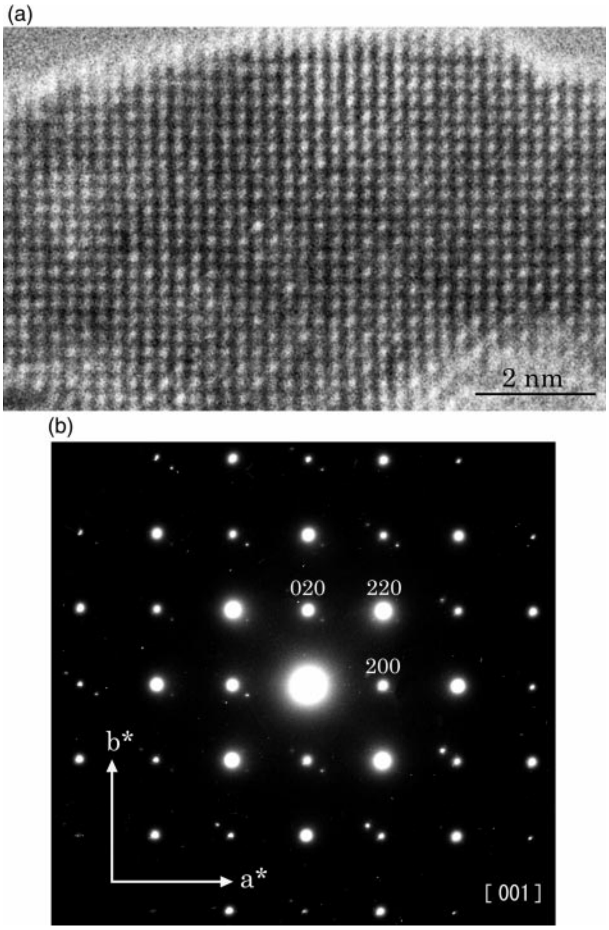

Fig. 4 (a) HRTEM image and (b) ED pattern for a synthesized Sr_2FeMoO_{6-w} sample.

Mo(V)/(VI) couples could in principle be utilized for establishing the distinct valence values of Fe and Mo in Sr_2FeMoO_{6-w}. Unfortunately, it was found that in solution trivalent iron spontaneously oxidizes pentavalent molybdenum. Therefore for samples which might contain Fe(III), quantitative determination of Mo(V) is not unambiguous. However, the initial potential of the solution recorded immediately upon the sample-dissolution should tell qualitatively whether Mo(V) species are formed or not. In the case of the present Sr_2FeMoO_{6-w} samples, the potential remained above 400 mV during the dissolution and titration, indicating that no Mo(V) species are formed but the itinerant $4d^1$ valence electron of molybdenum is adapted by iron when the crystal lattice dissolves. This is consistent with the picture of the mixed-valent $Fe^{2.5+}$ suggested by Mössbauer spectroscopy.[15] An example of the titration curves obtained for the Sr_2FeMoO_{6-w} samples is shown in Fig. 5(d).

Efforts to tune the oxygen stoichiometry of the as-synthesized, nearly oxygen-saturated Sr_2FeMoO_{6-w} samples by means of post-annealing treatments under various inert or reducing atmospheres were unsuccessful. The present encapsulation synthesis route provides interesting possibilities, however. It is believed that by controlling the temperature during the synthesis the oxygen non-stoichiometry of the obtained samples may be tuned. This is due to the fact that the reaction equilibrium between Fe, FeO and O_2 strongly depends on temperature. With decreasing temperature the equilibrium oxygen partial pressure with the Fe/FeO redox couple becomes lower. Consequently, samples synthesized at lower temperatures are believed to be less oxidized than the present Sr_2FeMoO_{6-w} samples with $w \approx 0.03 \pm 0.02$ obtained at 1150 °C. Results of such oxygen-control experiments will be reported elsewhere.[20]

Table 1 Results of EDX analysis for the cation composition in a synthesized Sr_2FeMoO_{6-w} sample

Element (line)	Average atomic concentration (%)
Sr (K_α)	52(3)
Fe (K_α)	24(2)
Mo (K_α)	24(2)

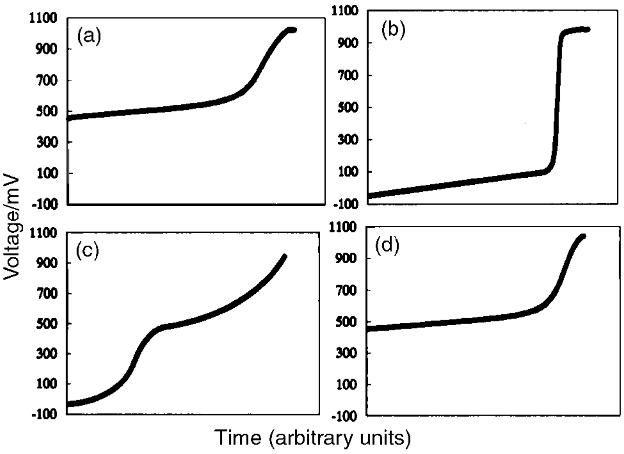

Fig. 5 Typical coulometric titration curves obtained for (a) the Fe(II) reference solution, (b) the Mo(V) reference solution, (c) a mixture of the Fe(II) and Mo(V) reference solutions, and (d) the synthesized Sr_2FeMoO_{6-w} sample.

Conclusions

A novel encapsulation synthesis technique utilizing the Fe/FeO redox couple as the oxygen trap was developed for synthesizing high-quality samples of the Sr_2FeMoO_{6-w} double-perovskite phase. Furthermore, it was verified that coulometric oxidation titration of the total quantity of the lower-valent species, Fe(II) or Mo(V), formed upon dissolving the sample material in acidic solution, provides an accurate means of analyzing oxygen contents in Sr_2FeMoO_{6-w} samples. For the present samples with cubic symmetry the oxygen non-stoichiometry was established at $w \approx 0.03 \pm 0.02$.

Concerning the individual valences of iron and molybdenum, the initial potential level in the coulometric titration is believed to indicate the nature of the reduced species. No indication of lower-valent molybdenum was seen for the present fully-oxygenated samples.

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