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Novel method of synthesis for double-perovskite Sr_2FEMoO_6

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Polycrystalline double perovskite Sr_2FeMoO_6 nanosized powders have been prepared using a wet chemical coprecipitation method of synthesis. The products were ignited in nitrogen at different temperatures in order to examine thermal evolution of precursors. Powders that were fired at an above 850°C for two hours have almost a single-phase structure. Some intermediate phases have been found at low temperatures. Powder X-ray diffraction linewith measurements show an average particle size in the order of 40 nm for samples annealed in 600–1000°C. It is suggested that the samples annealed at these temperatures were both simultaneously paramagnetic and ferromagnetic in nature. The advantages of this method are the low temperature involve in the sample preparation and the use of a non-reducing atmosphere.

1. Introduction

Sr_2FeMoO_6 is an ordered double perovskite of the $A_2BB'O_6$ type with alternately ordered Fe^{3+} ($3d^5$, $S = 5/2$) and Mo^{5+} ($4d^1$, $S = 1/2$) ions [1–3]. The structure of the Sr_2FeMoO_6 is suggested to be either tetragonal |4/m [1, 4–6] or cubic [7]. This compound displays a half-metallic behavior with a ferromagnetic Curie temperature of 410–450 K [3]. The low temperature saturation magnetization, Ms, varies from ~2.6 to 3.7 μ_B/f.u with the sintering conditions [9]. The Fe/Mo ordering has a profound impact on the saturation magnetization of the material [8, 9]. Low field room temperature magnetoresistance (MR) of this compound raises the possibility of practical applications. Electrical resistivity, MR and magnetic susceptibility data for this perovskite are widely reported [8–11]. The intergrain magnetoresistance (IMR) is strongly dependent on the number and nature of the grain boundaries [12, 13]. 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 tunneling arising from the high density of grain boundaries [14].

Standard solid state reaction, usually needs a elevated sintering temperature in a stream mixture of H_2 and Ar. Sol-gel methods have been reported for preparing nanometers oxides which nanometer-scale grain size. Thermal treatment involves a stream mixture of H_2 and Ar [15, 16]. In order to avoid the use of hydrogen during the thermal treatment novel methods of synthesis with an efficient encapsulation technique have been reported [17].

The aim of the present work is to present an alternative chemical route for producing ultrafine crystallites of mixed oxides with chemical homogeneity. The inclusion of iron in a low valence state makes unnecessary a stream mixture of H_2 and Ar during thermal treatment.

Precursors are calcined for two hours in a nitrogen atmosphere.

2. Experimental

2.1. Sample preparation

A requirement for achieving maximum homogeneity in a chemically coprecipitated powder is to maintain on a microscopic level, the same chemical environment at the interface between the constituents being mixed. Oxalates were prepared following approximately the procedure of Wickham [18]. The iron powder (0.0800 mol, assayed for iron content), ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and Sr $(OH)_2\cdot nH_2O$ (recently prepared from $Sr(NO_3)_2$ and Na(OH)) were mixed stoichiometrically in a Pyrex three-necked Wolff bottle. One neck is fitted with a reflux condenser, another with a gas inlet tube, and the third with a separator funnel. A Teflon-covered magnetic stirring bar rests in the bottle, which is set on an electric hot plate equipped with a magnetic stirring device. The acetic acid solution is added, and air is replaced by nitrogen gas led into the bottle through the delivery tube and out through the condenser. The mixture is stirred continuously until the state of quantitative dissolution is reached. After that, precipitation was carried on using oxalic acid solution (2 M) with the aid of the separator funnel. To improve the precipitation of the oxalates, acetone was added. After precipitation, the mixture was stirred for few minutes, digested for ten minutes and then cooled. The light green precipitate was filtered off, thoroughly washed with ethanol and acetone. It was dried overnight at 100°C in a vacuum oven.

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The resulting light green (or even light blue) mixed solid solution of oxalates and molybdic products was decomposed in nitrogen at 650–1050°C for two hours (labeled S2). Several thermal conditions were tried to get samples with differing amounts of disorder. The samples of Sr_2FeMoO_6 were annealed at 1050°C, 1150 and 1250°C for eight hours (labeled S8-1050, S8-1150 and S8-1250).

2.2. Powders characterization

Thermogravimetric Studies (TG) and differential thermal analysis (DTA) of precursors were carried out in a DTG50 Shimadzu Thermoanalyzer, in the temperature range of room temperature to 1000°C in nitrogen atmosphere, with a heating rate of 5°C/min. Initially, a 5.0×10^{-3} g of sample was weighed.

The resulting complex oxides were characterized by X-ray powder diffraction analysis (XRD). XRD patterns were recorded by a Rigaku X-ray diffractometer, using Cu K_α radiation and then analyzed. The data were analyzed using the Rietveld refinement program FULLPROF [19]. The average particle sizes of the samples can be estimated by X-ray linewidths according to classical Scherer formula.

Precursors and calcined samples morphology were examined by scanning electronic microscopy (SEM) and energy dispersive X-ray analysis (EDAX).

Magnetic properties were measured in a SQUID magnetometer's magnetic fields varied between $1\ T \geq H \geq 0$ at 10 K for sample S2-1050. Samples S8-1050, S8-1150 and S8-1250 were measured at 300 K (RT).

A ^{57}Co source (Rh matrix) was used to record the Mössbauer spectra (MS) of the samples in constant acceleration mode at room temperature (RT) and at 22 K.

3. Results and discussion

TG and DTA (Fig. 1) indicate that sample precursors powders contain relatively large amounts of water although they have been dried overnight at 80°C in a

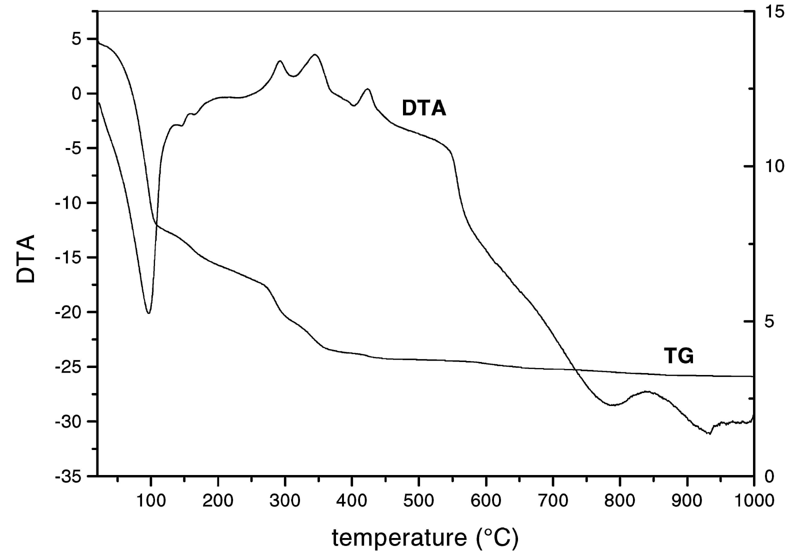

Figure 1 Thermogravimetric profiles (DTA and TG) of precursors (heating rate 10 K min^{-1}) in nitrogen.

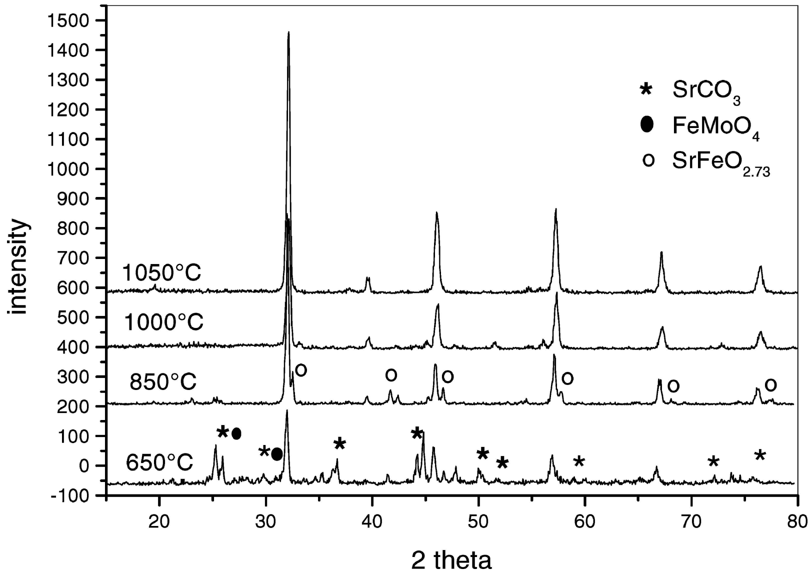

Figure 2 Thermal evolution of precursors seen by X-ray diffraction diagrams. Precursors treated at each temperature for two hours

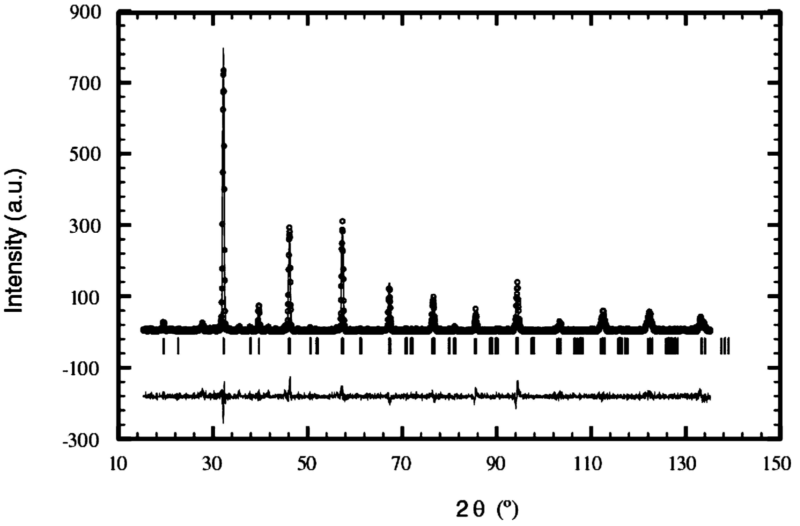

Figure 3 X-ray pattern of polycrystalline Sr_2FeMoO_6 sample calcined at 1050°C for two hours in nitrogen. The vertical bars indicate the expected reflection positions from space group P4/m.

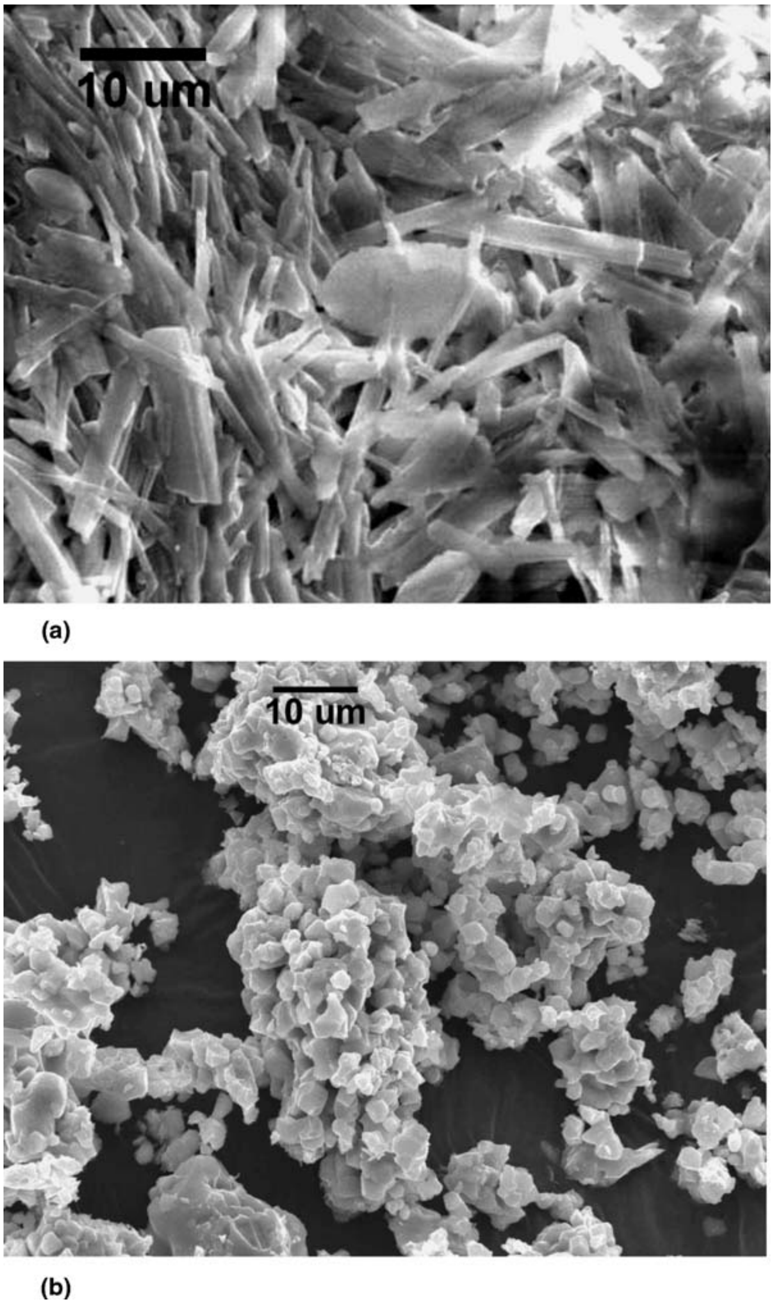

Figure 4 (a) Microstructure obtained by SEM: precursors as prepared. (b) Microstructure obtained by SEM: precursors calcined for two hours at 1050°C.

vacuum oven. The total weight loss of water (40%) at 100°C depends on the relative dehydration while the precipitate is being washed with alcohol and acetone. We can observe three exothermic peaks centered at 290°C, 340 and 425°C corresponding to strontium or iron oxalates and molybdenum compounds respectively. Weight loss up to 700°C is near 70%.

Fig. 2 shows X-ray diffraction patterns of precursors of Sr_2FeMoO_6 annealed in nitrogen for two hours at different temperatures. In the sample of precursors treated at 650°C most of the characteristic peaks of the perovskite phase appear with others attributed to $SrCO_3$ and $FeMoO_4$. At 850°C some weak lines attributed to a mixed oxide of Sr and Fe ($SrFeO_{3-x}$) are observed. At higher temperatures crystalline structure improves. The average crystalline size for the (200) peak for samples sintered at 850–1050°C (Fig. 2) is 40, 50 and 55 nm respectively. The refined data of a sample of Sr_2FeMoO_6 treated at 1050°C for two hours (space group |4/m) are shown in Fig. 3. The unit cell parameters are $a = b = 5.5583(2)$ Å and $c = 7.8861(5)$ Å. A small amount of alkaline earth molybdates impurity phase ($SrMoO_4$), which is estimated to be less than 1.2% on the basis of XRD data can be appreciated. This second phase was not observed in samples with longer thermal treatment.

Fig. 4a shows SEM imagine of precursors with some inhomogeneity in morphology and composition confirmed by Edax analysis. We can appreciate large needle particles as long as 10 μm, which seem to be rich in iron and strontium, and coarse spherical particles.

Fig. 4b corresponds to calcined powders, which consist in small and irregular homogeneous shaped particles, mostly agglomerated <1–2 μm.

In MS spectra at RT of sample S2-1050 (Fig. 5a) the central paramagnetic signal is much more noticeable than that of samples annealed for longer periods (Fig. 5b), comprising 28% of the total area. We assign the paramagnetic signals as arising form the superparamagnetic regime of the ≈55 nm particles that constitute this sample, which at 22 K still display a relatively high degree of relaxation comprising more than 10% of the total area. The low temperature spectra of S2-1050 has better resolution. The three magnetic sextets at 22 K were assigned to Fe atoms whose first neighbors have well-ordered Mo environments, disordered Mo environments, and Fe ions in B′ sites with six Fe neighbors. The hyperfine parameters have been recently published [20].

However, longer annealing time can improve cationic ordering and consequently its saturation magnetization. MS spectra at RT for samples S8-1050, S8-1150 and S8-1250 (Fig. 5b) have rather broad and complicated absorption lines, reflecting the effect of multiple metal neighbor environments on the magnetic field of iron ions, as also the effect of temperature in the vicinity of Tc. These spectra's were fitted by means of a discrete distribution of hyperfine fields, two or three sextets and a paramagnetic component. The ratio of the sites can be seen to change with the annealing temperature. Longer annealing time decreases the amount of disorder as S8-1050 MS spectra in Fig. 5b indicates two crystalline sites, completely absent in S2-1050 (Fig. 5a). Extensive data analysis will be reported separately.

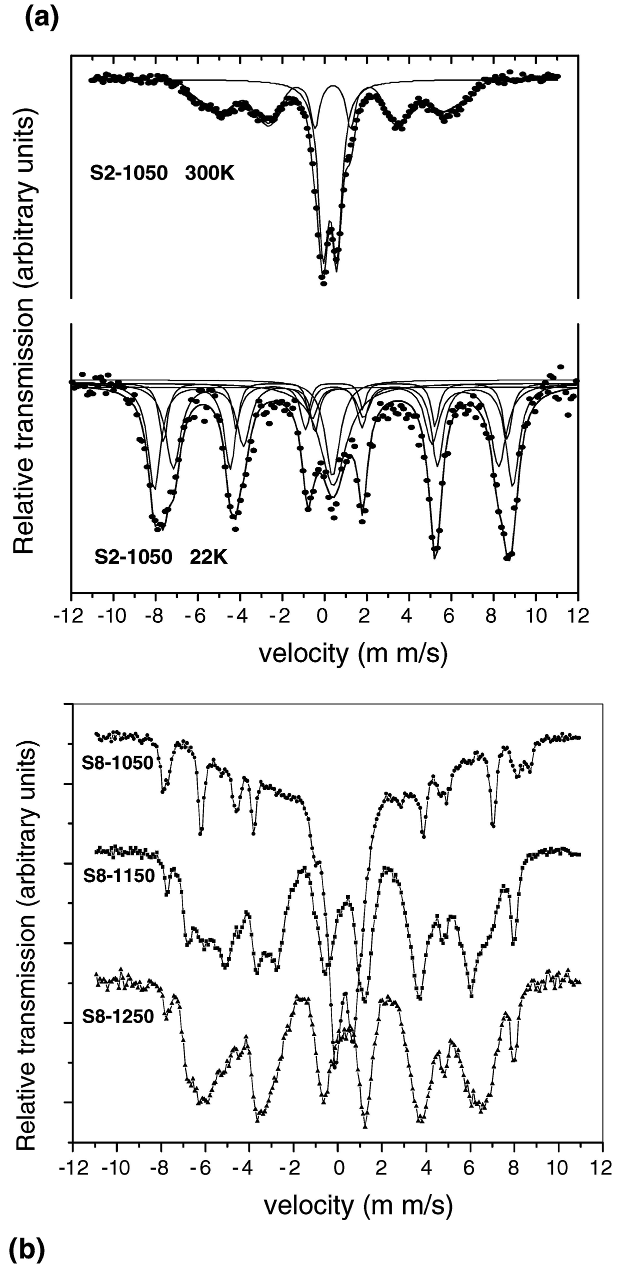

Figure 5 (a) Mössbauer spectra of S2-1050 at RT and at 22 K. (b) Mössbauer spectra of S8-1050, S8-1150 and S8-1250 at RT.

Low temperature (10 K) saturation magnetization of Sr_2FeMoO_6 prepared by this method and annealed at 1050°C for two hours (S2-1050) is close to 2.0 μ_B/f.u. which is lower than that of samples prepared by solid-state reaction [1]. The reduction on saturation can be originated from the strong disorder effect due to more grain boundaries of nanometer samples and short thermal treatment. It was found that the intensity of superstructure line (101) which reflects the extend of Fe/Mo ordering at B/B′ sites [9], decreases upon lowering the annealing temperature. The magnetization data also shows a significant reduction of the saturation magnetic moment (RT) with decreasing annealing temperature (Fig. 6). These results indicate that there is a correlation between the defect concentration and the magnetic properties.

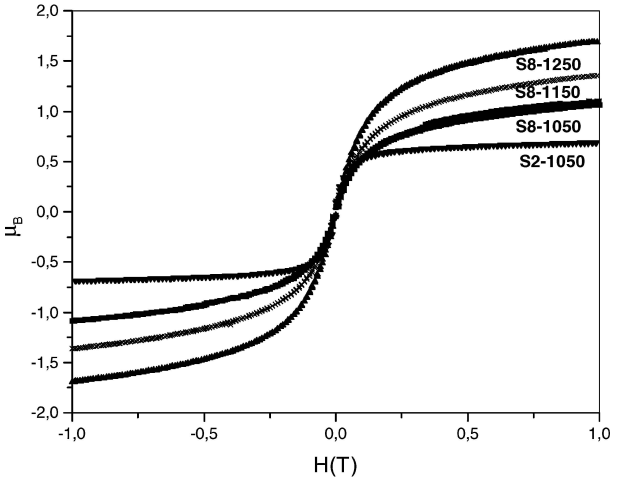

Figure 6 Magnetization curves at 300 K of samples prepared at different temperatures.

4. Summary

Double perovskites nanocrystallites were prepared by coprecipitation from metal acetate solution with oxalic acid. The reactant is a mixture of mixed oxalates and molybdenum compounds. During the thermal decomposition in nitrogen the precursor become the mixture of the metal oxides. Thus the sintering temperature can be effectively decreased (850°C) and nanometer-scale grain size can be obtained. The advantages of this method are the low annealing temperature and the use of a non-reducing atmosphere during annealing.

To gain knowledge about the structure in detail, Mössbauer spectroscopic investigations and electric and magnetic measurements of these samples are being carried on and will be soon published.

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