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The Effect of Preparation Method and Calcination Temperature on the Crystallite Size and Surface Area of Perovskite-Type SrFeO_x

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Abstract. We have investigated the synthesis of perovskite-type SrFeO_x ($2.5 \leq x \leq 3.0$) using three preparative methods: sol-gel, mechanochemical processing and solid state reactions at high temperature of the corresponding oxides. The sample obtained after calcination of the gel from sol-gel method, contained the least amount of strontium carbonate impurity. The amount of strontium carbonate impurity decreased with the increase in calcination temperature. Perovskites obtained have been characterized by X-ray diffraction (XRD) and nitrogen adsorption isotherms. Samples obtained from three methods have been compared with respect to calcination temperature, crystallite size and specific surface area.

Keywords: mechanochemical processing, perovskites, sol-gel, SrFeO_x

Introduction

Since the discovery at Mobil [1, 2] of MCM-41, a mesoporous silica material, there has been an increasing interest to develop new ways to prepare high surface area mesoporous oxide materials including transition metals oxides using wet chemical methods [3–5]. However, relatively little of this work has targeted perovskites. This is surprising since many perovskites are of particular interest as they have many potential commercial applications such as materials for solid oxide fuel cells (SOFC's) [6] and gas sensor devices [7–11]. In order to fully optimize the functionality of these materials, the achievement of controlled porous structures is desirable, since these applications depend to a large extent on the surface area to volume ratio. Moreover, it has been demonstrated that by decreasing the dimensionality of electroceramic materials, including many perovskites, to the 5–100 nm ranges, both the electronic and ionic transport properties may be dramatically affected, leading to improved performance [12–14].

The conventional method for the preparation of hetero-metallic oxides, such as perovskites, is the solid-state reaction at high temperatures of the corresponding binary metal oxides or carbonates. Given that the synthesis occurs at high temperatures, the powders produced with this method are non-porous, coarse, with a non-uniformity of particle size and shape, and have a low specific surface area. The development of innovative processing methods through chemistry permits one to lower the preparation temperature and to improve homogeneity and reproducibility of the ceramic products, with the synthesis of porous, ultrafine and chemically pure powders of mixed metal oxides at low temperatures. Wet chemical methods and mechanochemical processing are two low temperature methods that fall into this category.

In this investigation, we have prepared the non-stoichiometric perovskite, SrFeO_x ($2.5 \leq x \leq 3.0$) [15, 16] using wet chemical methods, mechanochemical processing and solid state reaction in order to compare the crystallite size and specific surface area of the samples. SrFeO_x is a mixed ionic electronic conductor in which the reversible oxygen nonstoichiometry may be exploited for gas sensor applications [11, 17–19].

Experimental Methods

Materials

All reagents were obtained from Aldrich and used as received. The purity of the iron (III) oxide and strontium carbonate starting materials were greater than 99.9% (metals basis), Iron and strontium salts were kept and handled in an inert dry box under argon.

Hardened steel and zirconia vials and balls for mechanochemical syntheses were purchased from ATS Scientific Inc., Burlington, Ontario.

Preparation of SrFeO_x

Solid State Reaction. Strontium and iron oxides were mixed in stoichiometric amounts ($\text{Sr:Fe} = 1:1$), ground together with an agate mortar and pestle and calcined at 1100°C in a muffle furnace. The resulting black product was repeatedly re-mixed, ground and calcined at 1100°C until the XRD pattern indicated the complete conversion to the SrFeO_x perovskite phase.

Mechano-Chemical Method. Strontium oxide and iron (III) oxide (both 99.9%) were mixed in a stoichiometric ratio of Sr:Fe of 1:1 in an agate mortar and pestle under argon in a dry box. The mixture was transferred to a hardened steel vial (size: $2.25'' \times 3.0''$) with steel balls in the dry box. The ball to-powder-weight ratio was kept between 12:1 to 6:1. The contents were agitated on a SPEX 8000 M mixer/mill for two hours at a time. Each time a small amount of sample was removed from the vial in a dry box for XRD investigation. The process was continued until the XRD pattern indicated the least amount of impurity (~ 35 hrs). The reaction was repeated in zirconia vial with zirconia balls, for which a longer reaction time (>40 hrs) was required. This could be a consequence of the more effective sealing of the hardened steel vial versus that of the zirconia vial.

Mechano-Chemical Processing Followed by Calcination. The product obtained from mechanochemical processing contained considerable quantities of SrCO_3 and $\text{Sr}_3\text{Fe}_2\text{O}_{\sim 6.7}$ (Ruddlesden-Popper phase) as impurities. This was calcined at 600°C for 50 hrs.

Sol-Gel Method. For sol-gel, a modified Pechini's method was used [20]. The nitrate salts of strontium and iron in a stoichiometric ratio of iron to strontium of 1:1 were transferred to a round bottom flask under

argon in a dry box. An appropriate amount of water was added to dissolve the two salts. Citric acid in a metal ions to citric acid mole ratio of 1:1 was then added and dissolved by stirring. The pH of the resultant metal citrate solution was adjusted to 6–7 by adding dilute ammonia solution drop wise. The solution was heated in a water bath while stirring with a magnetic stirrer to obtain a viscous solution. At this stage, ethylene glycol was added in a mole ratio of citric acid to ethylene glycol of 1:1.2. Heating and stirring was continued until the solution started solidifying forming a gel-like porous mass. At this stage the temperature was raised to $180\text{--}200^\circ\text{C}$ to obtain a foamy dry mass. This was ground using an agate mortar and pestle using reagent grade acetone. This ground mass was dried and ashed at 400°C in a muffle furnace to completely remove the citrates and ethylene glycol that was left. A reddish brown coloured substance obtained was used as a precursor for SrFeO_x . This precursor was calcined at different temperatures in a muffle furnace to obtain SrFeO_x as a blackish grey powder.

Measurements

The N_2 adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP2000 apparatus. Before measurement, the samples were evacuated overnight at 120°C until the pressure was 10^{-6} torr.

The density of the materials was determined by a pycnometry measurement with helium using Micromeritics Accupyc 1330 apparatus.

X-ray powder diffraction data were collected between $20^\circ \leq 2\theta \leq 80^\circ$ with a scan rate of $2^\circ/\text{min}$ at room temperature on a Scintag XDS 2000 with a theta-theta geometry and a copper X-ray tube. The diffractometer had a pyrolytic graphite monochromator in front of the detector. The samples were mounted on a zero background sample holder made of an oriented silicon wafer. The average crystallite size was determined from a convolution based full pattern fitting using the Topas software package [21]. Peaks were fitted using a simplified integral breadth method to account for both strain and crystallite size effects [22].

Results and Discussion

X-Ray Diffraction

The perovskite SrFeO_x was prepared using four different methods: (1) calcination of strontium and iron

Figure 1. XRD patterns for SrFeO_x , prepared using various methods.

oxides at 1100°C , (2) agitation of strontium and iron oxides on a Spex mixer (mechano-chemical processing), (3) mechanochemical processing followed by calcination at 600°C and (4) sol-gel processing followed by calcination at 600°C . Figure 1 shows XRD patterns for samples prepared from all four methods. The sol-gel processing was the only method yielding a reasonably pure phase of the $\text{SrFeO}_{2.9}$ perovskite phase, as indicated from the XRD spectra shown in Fig. 1. The sample obtained from the solid state preparation method at 1100°C contained considerable amounts of $\text{Sr}_3\text{Fe}_2\text{O}_{6.7}$ impurity. The removal of impurity required repeated re-mixing and calcination cycles. This is apparent from the XRD patterns (Fig. 2) which show that the amount of impurity is reduced considerably after calcination for 100 hrs at 1100°C . However, complete reduction of $\text{Sr}_3\text{Fe}_2\text{O}_{6.7}$ impurity required five

Figure 2. The effect of calcination time at 1100°C on impurity reduction from SrFeO_x .

re-mixing and calcination cycles for a total of 200 hrs at 1100°C . The mechanochemical processing method produced even greater amounts of impurities than the solid-state method. The mechanochemical processing followed by calcination at 600°C reduced these impurities significantly but resulted in additional impurities of SrCO_3 and $\text{Sr}_3\text{Fe}_2\text{O}_{6.7}$ as suggested from the XRD shown in Fig. 1. The remaining impurity could be removed by raising the calcination temperature to 900°C .

Crystallite Size

The average crystallite size of the samples prepared by the four methods was determined from the XRD data and is shown in Table 1. The samples obtained using

Table 1. Textural properties obtained for the SrFeO_x products.

Sample no.	Method of preparation	Crystallite size (nm)	Specific surface area (m^2/g)*	Density (g/cm^3)
1	Solid-state at 1100°C	512	0.1	5.4
2	Mechano-chemical	69.5	3.5	5.0
3	Mechano-chemical followed by calcination at 600°C	73.4	1.6	5.1
4	Sol-gel followed by calcination at 600°C	36 ± 3	18 ± 3	5.0

*By N_2 adsorption/desorption isotherms at 77 K.

solid state reaction of the oxides at high temperature had the greatest crystallite size of all samples. The crystallite size of the samples prepared using sol-gel methodology was the lowest. The samples produced from mechano-chemical processing had approximately double the crystallite size as compared to the samples obtained by sol-gel method. For the solid state method, long periods of calcination at higher temperatures results in a significant growth of crystallites.

Textural Properties

The textural properties of all samples prepared using the four methods were investigated by the N₂ adsorption/desorption isotherms at 77 K and are summarized in Table 1. A type III isotherm was obtained for all samples suggesting a very weak adsorption interaction of which the fundamentals are not very well understood [23]. The data indicate the presence of both micropores and mesopores in these samples.

The samples prepared by sol-gel method exhibit the largest specific surface areas, which decreased with the increase in calcination temperature. This can be explained on the basis of the partial collapse of the micropore structure at higher temperatures [24]. The specific surface areas of the samples prepared by the solid-state method was the lowest.

Density

The density of the samples prepared by various methods did not vary significantly. The sample prepared by the solid-state method had the highest density; the lowest density value was obtained for the samples prepared by sol-gel and mechanochemical processing.

Conclusion

The perovskite SrFeO_x was successfully prepared by sol-gel processing at much lower temperatures than with conventional solids-state methods. Samples prepared by the sol-gel method had greater surface area and lower crystallite size compared to the samples prepared by solid state methods.

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