Synthesis of CMR manganate compounds:

the consequences of the choice of a precursor method

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Abstract

We have studied the electrical transport properties of manganate samples synthesized by different precursor methods. Differences in the synthesis process of the materials can result in samples with similar grain size but very different physical properties, contrary to what happens in samples prepared by the same method.

Keywords: Electroceramics ; grain boundaries ; microstructure ; perovskites

1. Introduction

In the past years, perovskite manganates like $Ln_{1,x}A_xMnO_3$ (Ln = lanthanide; A = alkaline earth) have attracted considerable attention, owing to the Colossal MagnetoResistance (CMR) properties of some compounds. Those materials have been studied in different forms [1-3]: thick or thin films, single crystals and polycrystalline materials. In this latter case, the solid state reaction is certainly the most often used processing method. Although the solid state reactivity of the starting materials and the poor homogeneity of the final product. For those reasons, alternative low-temperature processing techniques (i.e. sol-gel, combustion, freeze drying, etc.) have been developed in solid state chemistry [4]. It turns out that the experimental conditions can strongly affect several parameters [5,6] that influence the physical properties of manganate compounds. The oxygen content depends on the temperature of the thermal treatment and on the annealing atmosphere. It affects the physical properties by modifying the charge carrier content. The grain size (or, more generally, the microstructure) does not depend on the chemical composition but only on the experimental procedure. However, it is now obvious that the grain size can influence the physical properties.

Several research groups have reported results comparing samples prepared either by the solid state reaction or by a soft solution-processing method. A difference in grain size (which can reach several orders of magnitude) is generally put forward in order to explain the broadening of the transition in the R(T) curve in the case of low-temperature-prepared samples [5,7]. However, until now, there has been no comparative study of different low-temperature methods. In this work, we show that, depending on the chosen precursor method, the final products can display highly different electrical properties: in some samples, the resistance vs. temperature curve display a double peak, which has been attributed to the existence of a disordered shell at the surface of the grains.

2. Experimental

Samples of calcium-doped manganate $La_{0.7}Ca_{0.3}$ MnO₃ were prepared by two different precursors methods: either sol-gel with acetic acid or combustion with urea. In the acetate sol-gel method [8], a solution of metallic acetates in a mixture of water and acetic acid (85:15, v/v) is dried for 3 days in an oven at 383 K, yielding a glassy gel. In the urea combustion method [9], the solution of metallic nitrates and urea is heated in a sand bath until combustion occurs, thanks to urea decomposition into gaseous products. In each method, the precursors are formed by heating the combustion products or the gels to 873 K, in order to remove most of the organics. Those precursors are either amorphous or very badly crystallized. A subsequent thermal treatment is necessary to improve the crystallinity Label, synthesis method and thermal treatment of each sample are summarized in Table 1.

Alumina crucibles are used below 1273 K, platinum crucibles are necessary above this temperature. Intermediate grindings are performed in an agate mortar. The powders are pelletized before the last step in the thermal treatment.

The crystal structure was checked by X-ray diffraction with a Siemens D5000 powder diffractometer. IR spectra were recorded on KBr pellets, with a Bruker IFS 66 spectrometer. Thermal analysis was performed with a Netzsch STA 449C apparatus. Pellet pieces were put into resin and polished in order to perform optical microscopy (Olympus AH3-UMA), scanning electron microscopy (Hitachi S-2500) and energy dispersive X-ray

(EDX) analysis (Oxford Link Pentafet). No striking deviation from the nominal composition was observed by EDX analysis. The micro structure was evidenced by scanning electron microscopy on unpolished pellets. The average grain size values are listed in Table 1. Density measurements were carried out with the Archimedes' method. Resistance measurements as a function of temperature were performed by the standard four-probe method, with a Quantum Design Physical Properties Measurement System (PPMS).

Label	Synthesis method	Thermal treatment	Mean grain size (µm)
LCA1	Sol-gel with	5 h, 873 K	1
	acetic acid	5h, 1173 K	
LCA2	Sol-gel with	5 h, 873 K	2
	acetic acid	5 h, 1323 K	
LCA3	Sol-gel with	5 h, 873 K	6
	acetic acid	5 h, 1523 K	
LCA4	Sol-gel with	5 h, 873 K	5-10
	acetic acid	4 h, 1523 K	
		10 h, 1523 K	
LCU	Combustion	5 h, 873 K	2
	with urea	4 h, 1523 K	
		10 h, 1523 K	

Table 1 Label, synthesis method, thermal treatment and mean grain size

3. Results and discussion

Three samples (LCA1, LCA2 and LCA3) were prepared by the sol-gel method with acetic acid and annealed at 1173, 1323 and 1523 K, respectively. The temperature dependence of the electrical resistance of those samples is shown in Fig. 1. The resistance data are normalized at 300 K rather than transformed to resistivity data because of the inaccuracy in the measurement of the geometrical factor. The low-temperature-annealed sample displays a broad peak at low temperature. The two samples annealed at higher temperatures show single peaks at high temperature, but the resistive transition of the sample annealed at the highest temperature is noticeably sharper. As expected, the mean grain size increases with the increase in annealing temperature (see Table 1). Similar results were obtained by Zhang et al. [10], who prepared some polycrystalline samples of La_{0.82}Sr_{0.18}MnO₃ by a precursor method. The 1723 K-annealed sample displays a sharp single peak whereas a broad single peak is observed at a lower temperature for the 1173 K-annealed sample. Samples treated at intermediate temperatures display a double-peak behaviour. The mean grain size increases when the annealing temperature is increased. From the results of such studies, it is now well established that samples prepared at low temperature often display additional features (such as a broadening of the transition or the apparition of a low temperature peak). Those phenomena are attributed to the small size of the grains and can be prevented by a higher annealing temperature and/or a longer thermal treatment, which yield materials with bigger grains.



Fig. 1. Temperature dependence of R/R (300 K) for the samples LCA1, LCA2 and LCA1.

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However, the comparative studies have been up to now restricted to samples prepared by the same precursor method. Therefore, we have decided to compare two samples prepared by different techniques but with the same thermal treatment. The resistance vs. temperature curves of the samples LCA4 (prepared by sol-gel with acetic acid) and LCU (prepared by combustion with urea) are shown in Fig. 2. The two curves are strikingly different, with a double peak for the LCU sample and a sharp single peak for the LCA4 sample. This difference in the resistance behaviour is coupled to a difference in grain size: once again, the double-peak sample is characterized by a small grain size (see Table 1). The interesting point in this case is that those samples with very different grain sizes are obtained by the same thermal treatment. Therefore, the origin of the grain size difference can be attributed to the different precursor methods.



Fig. 2. Temperature dependence of R/R (300 K) for the samples LCU and LCA4.

Fig. 3. Scanning electron micrographies of the powders obtained after: (a) drying of the acetic acid gel; (b) decomposition of a citrate gel; (c) combustion of the urea mixture.



In Fig. 3, we compare the microstructures of $La_{0.7}Ca_{0.3}MnO_3$ precursors obtained (a) by decomposition of an acetic acid gel, (b) by decomposition of a citrate gel and (c) by combustion of a urea mixture. Besides, it turns out from X-ray diffraction experiments that the acetic acid precursor remains amorphous even after drying up to 773 K, whereas the peaks of the manganate phase are already present in the diffractogram of the combustion product. Given such dissimilarities between the powders at the different stages of the synthesis, it is not at all astonishing that materials with different grain sizes can be obtained with the same thermal treatment.

A corollary to this observation is that it is possible to obtain samples with similar grain size by different thermal treatments if different precursor methods are used. The samples LCA2 and LCU have the same grain size $(2 \mu m)$ and porosity (evaluated from the density measurements and electronic and optical micrographies). Besides, no significant difference of grain size variance was noticed. Therefore, we might expect that the resistance behaviours would be similar. On the contrary, Fig. 4 shows that the resistance curves are very different, with a double peak for the LCU sample and a single peak for the LCA2 sample. We can conclude that the grain size is not the only parameter that has to be taken into account in order to explain the resistance behaviour.

Fig. 4. Temperature dependence of R/R (300 K) for the samples LCU and LCA2.



First, we have to examine how the presence of a double peak can be related to a small grain size. In a doublepeak feature, the broad peak appears at a lower temperature than the $T_{\rm c}$ expected from the chemical composition of the sample. Two explanations are possible. The depressed T_c can be due to a compositional inhomogeneity: a modification of the chemical composition affects the charge carrier density and, thus, $T_{\rm c}$. Following the Zener theory [11,12], the T_c value depends also on the exchange interactions between manganese ions. A lowered T_c can result from an alteration of the orbital overlapping, consequence of a modification of the Mn-0 distances and Mn-O-Mn angles. The broadening of the low-temperature peak might indicate a distribution of those structural parameters and, thus, a nonnegligible fraction of disordered material. Indeed, it is generally accepted that there is strain at the surface of small grains [13,14]. The idea that the appearance of the low-temperature broad peak is related to the disorder at the grain surface is corroborated by very interesting results of Akther Hossain et al. [15]. Those authors studied the influence of thermal treatments at low O_2 partial pressure on the behaviour of polycrystalline pellets of La_{0.67}Ca_{0.33}MnO₃. A low-temperature broad peak was induced by those treatments. Besides their "intrinsic" effect, the oxygen vacancies are likely to introduce some additional disorder at the grain surfaces. Indeed, the deoxygenating process is more likely to create oxygen vacancies at the grain boundaries because grain boundary diffusion coefficients for oxygen exceed bulk diffusion by more than one order of magnitude [15]. However, oxygen vacancies cannot explain most of the double peaks: the thermal treatments were generally carried out in air, what has been shown to lead to oxygen-stoichiometric samples [3].

We have shown that there is convincing experimental evidence that the double-peak feature is related to disorder (compositional or structural) at the surface of the grains. The fact that different resistance behaviours can be observed for samples with similar grain size must thus be related to a difference in the extent of disorder. In fact, the expression "disorder at the grain surface" is misleading: of course, the disorder happens in a 3D volume, and it is better to speak about a "disordered shell". Given the striking differences observed during the formation of the manganate phase by different precursor methods, it is to be expected that the volume fraction of disordered phase or the degree of disorder can be different for the same grain size. It is interesting to note that IR spectroscopy as well as thermal analysis indicate that the crystallization begins at temperatures where carbonaceous residues are still present.

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Before concluding, we would like to mention the existence of double peaks of another type, occurring in samples prepared by the solid state reaction method. Sun et al. [16] used a mixture of lanthanum oxide and hydroxide to synthesize their samples. They have shown that the oxygenation inhomogeneity leads to a double-peak behaviour. In this case, the compositional disorder occurs on the scale of the whole sample and not in each grain as in the case of the low-temperature-prepared samples. It is likely that most of the double peaks reported for high-temperature-prepared samples are of this type. Araujo-Moreira et al. [17] have shown that in the case of a La_{0.7}Ca_{0.3}MnO₃ film with such a chemical inhomogeneity, several peaks are present in the χ'' component of the AC susceptibility. The AC susceptibility behaviour of our La_{0.7}Ca_{0.3}MnO₃ samples (shown in Fig. 5) confirms that no macroscopic inhomogeneity is present, despite the double-peak behaviour of the temperature dependence of the electrical resistance.

0.12 3e-3 0.10 (arbitrary units) 0.08 2e-3 0.06 0.04 0.02 0.00 0 200 250 150 300 350 T(K)

Fig. 5. Temperature dependence of the real and imaginary parts of the AC susceptibility for the sample LCA2.

4. Conclusion

By studying the electrical transport properties of samples synthesized by different precursor methods, we have confirmed that the appearance of a low-temperature broad peak is related to the existence, at the grain surface, of a disordered shell of a non-negligible depth. We have shown that this parameter is strongly influenced by the synthesis conditions. In particular, the choice of the precursor method has important consequences. Striking differences in microstructure and crystallization appear during the synthesis process. Therefore, samples prepared with the same thermal treatment can have very different grain sizes. More importantly, we have also shown that differences in the "history" of the materials can result in samples with similar grain size but very different physical properties. Therefore, it is not enough to check the similarity in grain sizes before comparing results for two samples. This is a usual practice, based on observations in samples prepared by the same method, where the quality of the samples is directly related to the grain size. We have shown here that this statement cannot be extended to samples prepared by different methods: if samples of similar grain size are obtained by different precursors methods and thermal treatments, the fractions of disordered material are probably very different, and thus strongly influence the electrical resistance properties.

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