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Interaction between $La_{0.7}Sr_{0.3}MnO_3$ and $SrZrO_3$ in CMR composites

Oleg A. Shlyakhtin[a,b] **and Young-Jei Oh***[a]

[a]*Materials Science and Technology Division, Korea Institute of Science and Technology, P. O. Box 131, Cheongryang, Seoul 130-650, South Korea. E-mail: youngjei@kist.re.kr*
[b]*Department of Chemistry, Moscow State University, 119992 Moscow, Russia*

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Annealing of pressed mechanical mixtures of finely grained $La_{0.7}Sr_{0.3}MnO_3$ and coarse-grained $SrZrO_3$ at T = 1000–1300 °C was accompanied by a systematic decrease in $SrZrO_3$ lattice parameters with increasing $La_{0.7}Sr_{0.3}MnO_3$: $SrZrO_3$ ratio and a corresponding decrease in sample magnetization at room temperature. EDX nanoprobe analysis of the composites confirmed substantial out-diffusion of La and Mn from $La_{0.7}Sr_{0.3}MnO_3$ into the $SrZrO_3$ particles. This process, detectable at 1100 °C, leads to an almost uniform distribution of La and Mn (6–8%) in the $SrZrO_3$ grains and the corresponding changes in manganite particle composition at 1300 °C. Zr diffusion backflow is almost absent.

Introduction

The practical application of manganite-based ceramic materials that demonstrate the colossal magnetoresistance (CMR) effect is seriously complicated by their relatively low magnetoresistance (MR) in weak magnetic fields at room temperature. Recent investigations have demonstrated the possibility of substantially enhancing this parameter in manganite–insulator composites, using various insulating components.[1–4] The cause of this effect seems to be related to the increase of MR in the vicinity of the percolation boundary in these systems. At the same time, the published values for the ratios of the components that result in the CMR enhancement are often rather far from the formal percolation boundaries. This discrepancy can result from chemical interaction between the components during the thermal processing of the composites.

In some of these composites, an intensive reaction between the components is accompanied by the appearance of crystalline reaction products,[5] but more often XRD does not detect any new phases. This fact is usually claimed as a proof of the absence of any interaction between the components. At the same time such effects as an abrupt increase in resistivity at rather small insulator content[6] or a shift of components ratio to higher manganite content at higher thermal processing temperatures, corresponding to an MR enhancement,[3] clearly show some kind of chemical reaction in the composites during the thermal processing. However, the details of such interactions have not been studied until now.

One of the largest values of CMR enhancement compared to single phase manganite ceramics (3.5% *vs.* 0.2–0.3% at H = 100 Oe and T = 298 K)[3] was observed for the composites $La_{0.7}Sr_{0.3}MnO_3$(LSM)–$SrZrO_3$. The high temperature interaction of these phases has not been studied, but the reaction of LSM with yttria-doped zirconia (YSZ) during the preparation and processing of solid oxide fuel cells (SOFCs) has been investigated in detail by several groups.[7–13] Depending on the processing conditions and the manganite composition, this reaction results in the appearance of $La_2Zr_2O_7$ and/or $SrZrO_3$, which remain unchanged during further thermal processing. The basic mechanism of this reaction consists of La and Sr out-diffusion into the YSZ, leading to the formation of a $SrZrO_3$–$La_2Zr_2O_7$ layer at the interface between the LSM and the YSZ.[7,11] Along with the crystalline reaction product(s), the formation of amorphous product areas was observed.[8] At the same time these studies gave no evidence of any interaction between LSM and $SrZrO_3$, which could be the reason for the effects observed in the LSM–$SrZrO_3$ composites.

Experimental

The details of the composite preparation are described elsewhere.[3] Preliminary synthesized single phase submicron LSM and pre-annealed micron-sized $SrZrO_3$ powders were mixed in various ratios (20–80% LSM) in a ball mill in ethanol, they were then pelletized, annealed at various temperatures (1000–1300 °C) for 1 h in air and cooled to room temperature at 5 K min^{-1}. The composite samples obtained were crushed in a mortar and studied by XRD (Cu Kα, 1° min^{-1}, Si internal standard), VSM magnetometer (room temperature, $H \leqslant 1.5$ T) and TEM, equipped with a nanoprobe EDX. Additional calibration of EDX in the nanoprobe mode was performed using crushed LSM and $SrZrO_3$ ceramics.

Results and discussion

Several anomalies[3] of the compositional dependence of the magnetoresistance curves of the LSM–$SrZrO_3$ composites showed a possible chemical interaction between the LSM and the $SrZrO_3$ during thermal processing. Initial XRD analysis of the composite samples did not detect the appearance of new phases resulting from a solid state reaction between the components, which correlates quite well with previous results of analysis of LSM–YSZ interaction products.[8–10] It should also be noted that weak field CMR effects are sensitive to even small compositional fluctuations so that even the primary stages of topochemical reaction, which cannot be detected by usual XRD, can result in significant changes in the magnetic properties of the composite.

More detailed investigation of the $SrZrO_3$ lattice parameters for the samples having various LSM content and being processed at different temperatures, confirmed the existence of a chemical reaction between the composite components. Increasing the LSM–$SrZrO_3$ ratio resulted in a monotonous and systematic decrease in both the ***a*** and ***b*** parameters of the tetragonal unit cell, clearly visible even at T = 1100 °C, even though the CMR data indicate no trace of this interaction yet (Fig. 1). In spite of a short reaction time (1 h), a further increase

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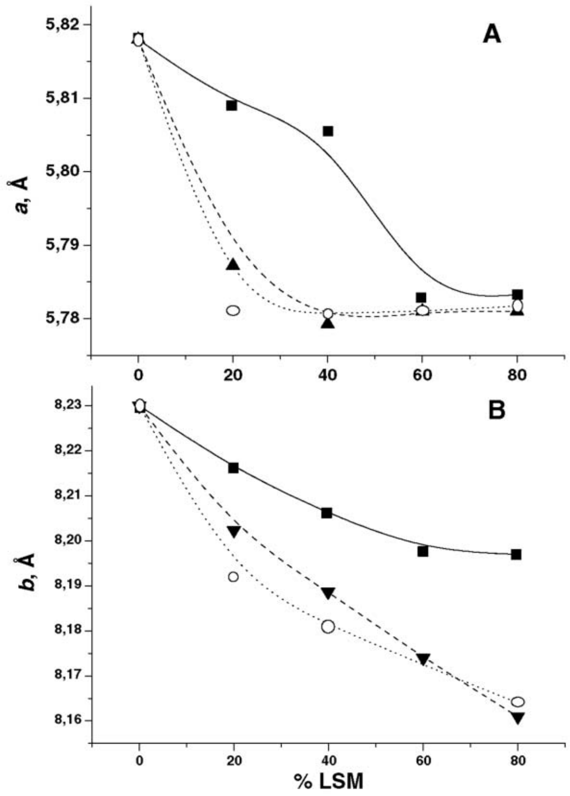

Fig. 1 ***a*** (A) and ***b*** (B) lattice parameters of $SrZrO_3$ unit cell in LSM–$SrZrO_3$ composites annealed at various temperatures: ■, 1100 °C; ▲, 1200 °C; ○, 1300 °C.

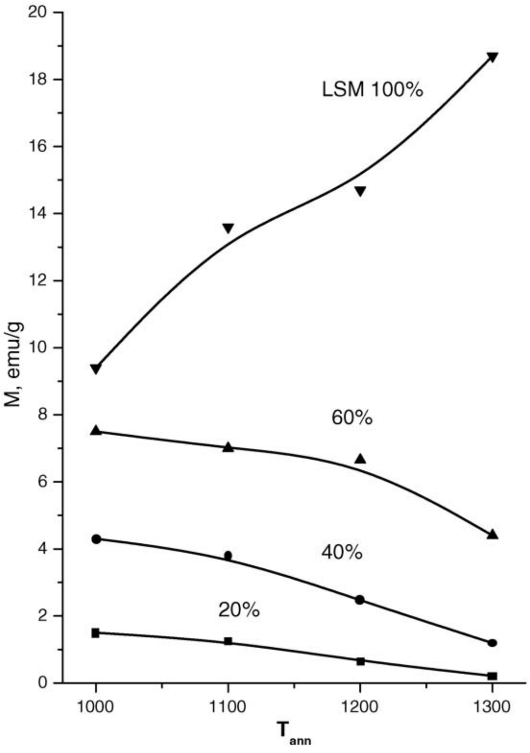

Fig. 2 Magnetization (H = 1.5 T) of composite samples, annealed for 1 h at various temperatures.

in annealing temperature leads to an abrupt decrease in the ***a*** parameter even with a minimal LSM content (20%). Due to the negligible self-nonstoichiometry of the strontium zirconate the most probable reason for this might be diffusion of lanthanum and/or manganese into the $SrZrO_3$ lattice. As mentioned before, the literature[7–12] did not indicate the presence of any La in the $SrZrO_3$ that appeared as a reaction product between the LSM and YSZ, while other authors[13] detected significant amounts of La in Sr-rich regions of the product layer. The solubility limit of La in $SrZrO_3$, as determined by a solid-state reaction method,[14] is about 6 mol%; a further increase in La content was accompanied by the formation of $La_2Zr_2O_7$. Substitution of Sr for La resulted in lattice contraction, but the lattice parameter reduction was ~10 times lower than observed in the present work for LSM–$SrZrO_3$ composites. Hence, the drop in the ***a*** parameter at 1200–1300 °C cannot be attributed only to La diffusion into the $SrZrO_3$. Earlier papers mentioned the possibility of Mn diffusion into $SrZrO_3$,[15] but later investigations did not detect a similar phenomenon. At the same time other authors[7] reported the intensive diffusion of both La and Mn into YSZ during LSM–YSZ interaction.

If the evolution of $SrZrO_3$ lattice parameters is related to the La and Mn diffusion, such changes should be accompanied by simultaneous processes in another component of the LSM–$SrZrO_3$ composite. A precise analysis of the lattice parameters of the lanthanum strontium manganite is complicated by substantial peak broadening, which is especially pronounced at lower annealing temperatures. However, analysis of the magnetic response of the composites obtained, as controlled by the magnetization of the ferromagnetic LSM component, confirmed a substantial evolution of sample magnetization during annealing (Fig. 2). Single-phase LSM ceramics, taken for comparison, demonstrate a monotonous increase in magnetization, in a field of 1.5 T, with increased annealing temperature due to the further crystallographic ordering and grain growth in ferromagnetic La–Sr manganite. At 20% $SrZrO_3$, annealing of the composites at $T > 1100$ °C leads to the reverse effect; after the initial crystallization-related increase, the magnetization manifested a monotonous fall with increasing temperature, which cannot be explained by intrinsic processes within the LSM phase. This process is especially evident at an $SrZrO_3$ content of >40%, when any kind of annealing results in a progressive fall of magnetization. If the change in $SrZrO_3$ lattice parameters is caused by La and/or Mn out-diffusion from the LSM, the magnetization fall observed at elevated processing temperatures can be attributed to the shift of Curie temperature of the LSM in a progressively increasing reaction zone. In which case an ambient temperature magnetization measurement should demonstrate a decreasing amount of ferromagnetic phase.

The most direct evidence of the solid-state chemical interaction of the two phases can be given by local composition analysis. Previous studies of similar interactions have been limited by the size of the EDX microprobe excitation area (1–3 microns), which exceeds the size of the interacting objects in many cases. Application of a nanoprobe with an excitation zone of 15–20 nm provides the possibility of measuring the element distribution within the submicron particles. The analysis of the LSM and $SrZrO_3$ particles contact area after annealing at 1100 °C (Fig. 3a) allows us to conclude, that even at this temperature the character of the elemental distribution points to the mutual diffusion of components, though the interaction is still localized within a 50–70 nm zone. According to TEM studies combined with point-to point EDX analysis, in samples, processed at 1100 °C, large monolithic $SrZrO_3$ particles (continuous area with a clearly defined boundary on the right side of Fig. 4a) are embedded in the mass of disordered LSM crystallites (dark particles on the left side). The mean size of the latter ones being close to 50 nm, so that the interaction is probably limited by a one-crystallite layer of LSM, which covers the $SrZrO_3$ microcrystals, and by surface layers of $SrZrO_3$ particles. Similarly to an LSM–YSZ interaction,[7,11,13] Zr diffusion into LSM can be neglected, and the basic feature of the process is the La and Mn out-diffusion into the $SrZrO_3$.

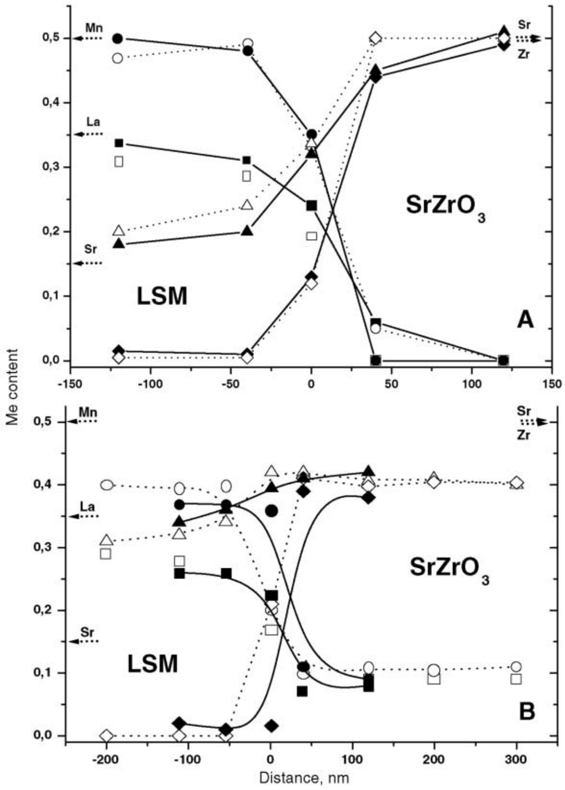

Fig. 3 Composition profiles of elements, measured during point-by-point EDX nanoprobe analysis of the interface between the LSM and $SrZrO_3$ particles in 80% LSM–20% $SrZrO_3$ composites. Annealing temperature: (A) 1100 °C; (B) 1300 °C. ○ and ●, Mn; ■ and □, La; ▲ and △, Sr; ◆ and ◇, Zr. Arrows show the values corresponding to a stoichiometric ratio of cations.

The character of the interaction can be clearly seen at 1300 °C, when the sample is almost paramagnetic and the $SrZrO_3$ lattice parameters are substantially changed compared with the initial phase. While at 1100 °C the elemental ratio outside the contact area is close to the stoichiometric values for both LSM and $SrZrO_3$ (Fig. 3a), at 1300 °C the chemical reaction results in a clearly detectable cation redistribution at least within a zone 200–300 nm from the reaction interface (Fig. 3b).

The most interesting and unusual result of this interaction is the appearance of La and Mn within the $SrZrO_3$ grains. The intensity of their EDX signals substantially exceeds the background level. To ensure statistical plausibility, the measurements were performed at several interaction boundaries at different points in the composite samples (the results of the two measurements are given as filled and empty symbols in Fig. 3a and 3b). The absence of visible gradients for the La and Mn concentrations within at least 300 nm of the reaction boundary makes a uniform distribution rather probable throughout the $SrZrO_3$ grains.

TEM analysis shows that annealing at 1300 °C is accompanied by crystallographic ordering and intensive grain growth of LSM particles (Fig. 4b). The component distribution within these grains is still not uniform; and chemical inhomogeneities are clearly visible in the vicinity of the reaction interface. Short sintering times are characteristic of the LSM materials,[16] while further annealing usually leads to the formation of large grains with uniform composition.[17] The interface for a topochemical reaction is blurred, so that a distinct boundary between LSM and $SrZrO_3$ crystallites is almost absent. At the same time the main reason for the elemental redistribution, easily observable even at 200 nm from the reaction boundary, is the La and Mn out-diffusion, which lead to a decrease in their concentrations, compared to stoichiometric values, and to a corresponding substantial increase in the Sr content over stoichiometry (triangles in Fig. 3b). The single-sided character of this diffusion can also be illustrated by the very low level of Zr EDX signal in the LSM particles, especially outside the area of intensive interaction.

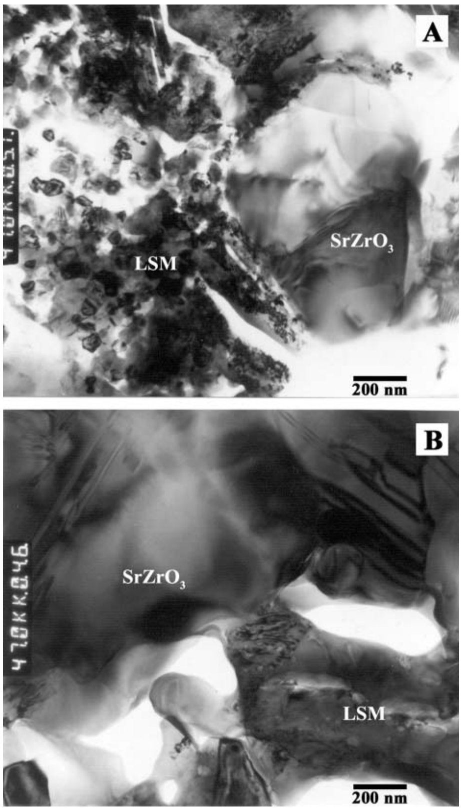

Fig. 4 TEM micrographs of the LSM composites (80% LSM–20% $SrZrO_3$) annealed at: (A) 1100 °C; (B) 1300 °C.

Concluding remarks

The present investigation was aimed at seeking the chemical background for several unusual physical phenomena observed in CMR composites. At the same time the results obtained, which clearly reveal the substantial chemical reactivity of $SrZrO_3$ (even with a rather short reaction time and at moderately high temperatures (1200–1300 °C)), might be of interest for further studies into the processes occurring in SOFCs. The character of the processes occurring during the LSM–$SrZrO_3$ interaction is rather similar to the first stages of the solid-state reaction between LSM and YSZ. However, most of the microprobe studies of this reaction did not detect La or Mn within the $SrZrO_3$ particles. This discrepancy could be due to the higher reactivity of the finely grained LSM powders, used in this work for the preparation of the composite. Another reason might be related to the small size of the $SrZrO_3$ particles, obtained as an LSM–YSZ interaction product and which are comparable in size with the diameter of the microprobe excitation zone, a fact that made it difficult to correctly interpret the EDX results in this case. This last feature makes reasonable the wider application of nanoprobes in solid-state reaction studies, because, as has been demonstrated, some important processes cannot be detected when the usual micron-sized probe is used.

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