Comment on ''Magnetoresistance and phase composition of La-Sn-Mn-O systems''

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In a published paper by Li *et al.* [Phys. Rev. B **60**, 10 284 (1999)] the transport properties and phase composition of the manganites $La_{1-x}Sn_xMnO_{3+\delta}$ ($x=0.1$–0.5) are studied. The authors analyze their results assuming the existence of two phases: a perovskite $LaMnO_{3+\delta}$ and a pyrochlore $(La_{0.5}Sn_{0.5})_2Mn_2O_7$. We consider that they misinterpret the x-ray diffraction data and we conclude that the manganites $La_{1-x}Sn_xMnO_{3+\delta}$ are in fact a multiphase material composed by $LaMnO_{3+\delta}$, $La_2Sn_2O_7$, Mn_3O_4, and SnO_2. The magnetic transition observed by Mössbauer experiments around 65 K attributed by Li *et al.* to that of the $(La_{0.5}Sn_{0.5})_2Mn_2O_7$ pyrochlore phase would correspond to that of the paramagnetic-ferrimagnetic one of Fe-doped Mn_3O_4.

In the paper by Li *et al.*,[1] the transport properties of both $La_{1-x}Sn_xMnO_{3+\delta}$ with $x=0.1$–0.5 and Fe-doped samples are studied by means of magnetoresistance measurements, ^{57}Fe and ^{119}Sn Mössbauer spectroscopy, and x-ray diffraction.

These samples are prepared by solid-state reaction at 1200 °C. Concerning their phase compositions, the authors indicate that samples with $x<0.5$ consist of two phases: an ABO_3 perovskite and an $A_2B_2O_7$ pyrochlore of chemical formulas $LaMnO_{3+\delta}$ and $(La_{0.5}Sn_{0.5})_2Mn_2O_7$, respectively.

With respect to the sample with $x=0.5$, they report the existence of a single-phase material of $(La_{0.5}Sn_{0.5})_2Mn_2O_7$ composition.

Their interpretation of the magnetoresistance measurements and the Mössbauer spectroscopy results of the La-Sn-Mn-O system is based on the assumption of the existence of only these two phases: $LaMnO_{3+\delta}$ and $(La_{0.5}Sn_{0.5})_2Mn_2O_7$. They indicate that the magnetoresistance observed in the $La_{0.7}Sn_{0.3}MnO_{3+\delta}$ sample[1] would correspond to that of the $LaMnO_{3+\delta}$ with La and/or Mn ion deficiency. For the $x=0.5$ sample, they find an insulator material whose properties are assigned to those of the pyrochlore material of $(La_{0.5}Sn_{0.5})_2Mn_2O_7$ composition.[1]

From the ^{57}Fe Mössbauer spectra of the sample with nominal $La_{0.5}Sn_{0.5}Mn_{0.985}Fe_{0.015}O_{3+\delta}$ composition, the authors observe the existence of a paramagnetic doublet from room temperature to $T=65$ K. This doublet begins to disappear and becomes a sextet between $T=65$ and 50 K. They conclude that a magnetic ordering temperature is present between $T=65$ and 50 K which is attributed to that of $(La_{0.5}Sn_{0.5})_2Mn_2O_7$ pyrochlore phase.

In another paper,[2] we report results on the solubility of Sn in the $LaMnO_{3+\delta}$ perovskite for samples with nominal composition: $La_{1-x}Sn_xMnO_{3+\delta}$ ($x=0.00$, 0.10, 0.30, and 0.5). The samples are prepared by two different routes: the LMM (liquid-mix method) and NDM (nitrate decomposition method). These methods are chosen because they give more homogeneous samples than those obtained by the usual solid-state reaction.[3] Both synthesis routes lead to identical results, confirming that the observed phases correspond to the stable ones of the ternary La_2O_3-Mn_3O_4-SnO_2 phase diagram.

Our x-ray diffraction data for samples with nominal $La_{0.7}Sn_{0.3}MnO_{3+\delta}$ and $La_{0.50}Sn_{0.50}MnO_{3+\delta}$ compositions prepared at high temperature (1200 °C), are identical to those of Refs. 1 and 4–6. The x-ray diffraction data of the $x=0.30$ sample are indexed as a mixture of four phases: $LaMnO_{3+\delta}$, SnO_2, $La_2Sn_2O_7$ and Mn_3O_4. The presence of such phases is confirmed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis. These results are not in agreement with those of Ref. 4, where the authors claim the existence of a single-phase material. Although we agree with the results of Refs. 1, 5 and 6 on the fact that $La_{0.7}Sn_{0.3}MnO_{3+\delta}$ is a multiphase material, we disagree with the phase identification. The main difference between our results and those or Refs. 1, 5 and 6 is the pyrochlore identity, $La_2Sn_2O_7$ instead of $(La_{0.5}Sn_{0.5})_2Mn_2O_7$. Our sample with nominal $La_{0.50}Sn_{0.50}MnO_{3+\delta}$ composition is also characterized as a multiphase material composed of $La_2Sn_2O_7$ and Mn_3O_4 as majority phases and $LaMnO_{3+\delta}$ and SnO_2 as minority ones. Figure 1 displays our x-ray diffraction data of the sample with nominal $La_{0.50}Sn_{0.50}MnO_{3+\delta}$ composition. Despite the fact that the main reflections of this diffractogram are those of the pyrochlore phase $La_2Sn_2O_7$, the weaker ones belong

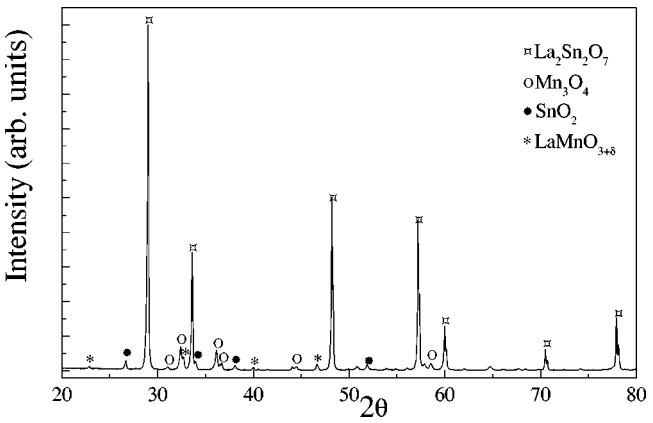

FIG. 1. X-ray diffraction data of the sample with nominal composition $La_{0.50}Sn_{0.50}MnO_{3+\delta}$.

to Mn_3O_4. Our SEM observations confirm the existence of the phases assigned to our x-ray diffractogram.[2]

In Ref. 1 the authors show the x-ray diffraction patterns of $La_{1-x}Sn_xMnO_{3+\delta}$ for different x values. They index their x-ray data for samples $x=0.1$, 0.2, and 0.3 as a mixture of an ABO_3 phase and an $A_2B_2O_7$ one. They observe that reflections assigned to $A_2B_2O_7$ phase increase as x increases while those of ABO_3 decrease. Therefore, they conclude that the sample with $x=0.5$ is a single-phase material of $(La_{0.5}Sn_{0.5})_2Mn_2O_7$ composition. However, they neglect the small reflections of the diffractogram of their Fig. 1 which are mainly those of Mn_3O_4.

We have determined the concentrations of the four phases present in the sample by means of a quantitative analysis of our x-ray diffractogram using the Rietveld method with the FULLPROF program.[7] The use of this method allows the quantitative analysis of a multiphase material with a very high accuracy.[8]

This analysis indicates that the material with nominal $La_{0.5}Sn_{0.5}MnO_{3+\delta}$ composition consists of four phases with the following coefficients :

$$La_{0.5}Sn_{0.5}MnO_{3-\delta} \simeq 0.221\ La_2Sn_2O_7 + 0.321\ Mn_3O_4 + 0.051\ LaMnO_{3+\delta} + 0.051\ SnO_2$$

Therefore, Mn_3O_4 is the phase with higher molar concentration of the multiphase material.

Concerning the ^{57}Fe Mössbauer study for the $La_{0.50}Sn_{0.50}MnO_{3+\delta}$ sample,[1] where they indicate a paramagnetic doublet from room temperature to 65 K, and magnetic ordering temperature between $T=65$ and 50 K, we suspect that this magnetic transition corresponds to that of Mn_3O_4. This is due to the fact that in the $La_{0.50}Sn_{0.50}MnO_{3+\delta}$ sample we detect a magnetic transition around $T=45$ K which is assigned to the paramagnetic-ferrimagnetic one of the Mn_3O_4.[2] In order to explore this possibility, we prepare two samples: a pure Mn_3O_4 sample and a Fe-doped one of $(Mn_{0.985}Fe_{0.015})_3O_4$ composition, and compare their magnetic behavior by dc magnetization measurements.

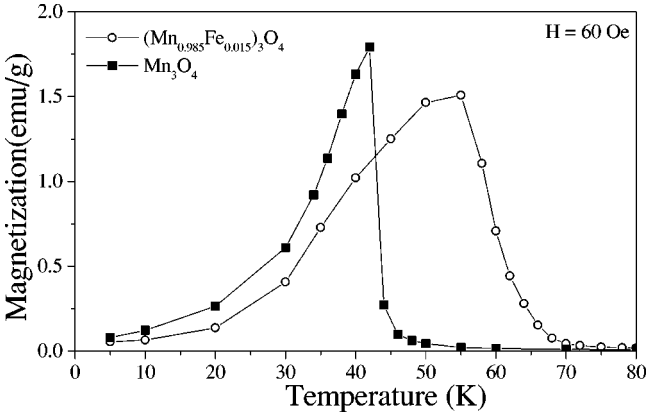

FIG. 2. dc magnetization as a function of temperature [zero-field-cooled (ZFC) measurements] under an applied magnetic field of 60 Oe for Mn_3O_4 and $(Mn_{0.985}Fe_{0.015})_3O_4$.

Figure 2 shows the dc magnetization as a function of temperature (ZFC measurements) under an applied magnetic field of 60 Oe for Mn_3O_4 and $(Mn_{0.985}Fe_{0.015})_3O_4$. The presence of Fe increases the magnetic order temperature from $T=45$ K for the undoped sample to 60–65 K for the Fe-doped material. This magnetic order temperature agrees with that reported by Li *et al.* for $La_{0.5}Sn_{0.5}Mn_{0.985}Fe_{0.015}O_{3+\delta}$.[1] But it should correspond to that of the Fe-doped Mn_3O_4 phase instead that of the single-phase material of composition $La_{0.5}Sn_{0.5}Mn_{0.985}Fe_{0.015}O_{3+\delta}$ as held in Ref. 1.

Therefore, based on our x-ray diffraction data, SEM, EDS, and dc magnetization of a $(Mn_{0.985}Fe_{0.015})_3O_4$ sample, we conclude that the sample with nominal composition $La_{0.50}Sn_{0.50}MnO_{3+\delta}$ is a multiphase material composed mainly of $La_2Sn_2O_7$ and Mn_3O_4 which is not in agreement with a single-phase one of composition $(La_{0.5}Sn_{0.5})_2Mn_2O_7$ as reported in Refs. 1, 5 and 6.

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