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LaSr-manganate powders and bulk material by crystallization of a glass

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Abstract

LaSr-manganate (LaSr)MnO_3 with perovskite structure was prepared in the basic system MnO_2–SrO–La_2O_3–B_2O_3(–SiO_2) by a modified glass crystallization method. X-ray diffraction, magnetic measurements, EDX and particle size investigations (specific surface) were carried out. The influence of the annealing conditions on the phase composition and the magnetic properties of the powders are discussed. In the silicate-free system manganate powder samples show values of specific saturation magnetization up to 53 Am^2/kg, a Curie temperature between 369 and 389 K and a mean particle size in the order of 100 nm. The powders reveal the magneto-resistive effect. In the silicate system the borate phase was leached out to get a manganate-SiO_2 mixture which could be sintered to bulk samples. The sintering conditions have been varied to avoid a decrease of the magnetization due to the formation of non-magnetic phases. Sintered samples show a superposition of the CMR and the GMR effect due to grain boundaries.

Keywords: Electrical properties; Glass crystallization; Magnetic properties; Perovskites

1. Introduction

Sr-doped La-manganate (LSMO) is an interesting material for magneto-resistive sensor applications, especially because of its high Curie-temperature allowing room temperature applications of the colossal magneto-resistive effect (CMR) of this material.[1] The achievable magnitude of the CMR-effect strongly depends on the crystallographic quality of the material.[2] Compared with epitaxial thin films the technology for the preparation of screen printed thick films from powder pastes is much cheaper. For applications a ceramic material consisting of small manganate particles which shows a large grain boundary effect at low temperatures could also be interesting. Therefore the applicability of glass crystallization for the LSMO powder preparation was checked for the first time in a previous work,[3] because this technique is a proven method for preparation of high-quality ferrite powders.[4] The method also enables the preparation of bulk glass ceramics with a high content of the desired particles by sintering of glass crystallized SiO_2-containing powder mixtures at lower temperatures compared with usual ceramics.[5]

2. Experimental

A glass MnO_2–SrO–La_2O_3–B_2O_3 (–SiO_2) was melted in air at ~1430°C in a Pt-crucible according to a composition $La_{0.7}Sr_{0.3}MnO_3 + SrB_2O_4$. A La–Sr-ratio of about 7:3 leads to a maximum of the Curie-temperature.[6] In the case of the SiO_2-containing system SiO_2 was added to the initial melt mentioned above, according to 10 wt.% of the theoretical LSMO yield of the melt. The raw materials used are: MnO_2, $MnCO_3$, $SrCO_3$, La_2O_3, H_3BO_3, SiO_2.

The melt was quenched between two rotating steel rollers to get nearly amorphous flakes. The flakes were heat treated at certain temperatures from 600 to 950°C (the melting temperature of the flakes) for some hours to reach crystallization of manganate within the matrix.

2.1. The borate system

The manganate powders were isolated by dissolving the complete matrix with hot diluted acetic acid and afterwards rinsed and dried.

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2.2. The silicate–borate system

Besides the formation of the manganate particles in the SiO_2-containing system a segregation of the matrix into Sr-borate and SiO_2 takes place. The borate phase was removed by dissolving in acetic acid and the remaining material was afterwards rinsed. To avoid losses of SiO_2 the slurry had to be centrifuged and freeze dryed. After this step a homogenous mixture of LSMO crystals in the order of about 100 nm and much finer SiO_2-particles (diameter about 5 nm) was achieved without any additional, mechanical homogenization treatment. The LSMO crystallites are covered by the much finer SiO_2-particles. The powder mixture was pressed isostatically at 150 MPa and sintered between 850 and 1000 °C.

X-ray diffraction (CuK_α), EDX investigations and specific surface measurements (BET-method) were carried out to characterize the powders. For comparison with the SEM investigations[3] mean particle sizes assuming a spheric particle shape and $\rho(\mathrm{LaSr})\mathrm{MnO_3} = 6.5$ g/cm^3 [7] were estimated from the specific surface values. The specific saturation magnetization σ_∞ (extrapolated) and the coercivity H_c were measured by VSM (PMC) ($H_{max} =$ 1200 kA/m). The Curie temperature was measured by VSM in a field of ≈ 875 kA/m. The electric resistance for determination of the magnetoresistance effect was measured with a standard four-point method. Contacts were made with silver paste. Factors of geometry were not taken into account.

3. Results and discussion

3.1. Structure and magnetic properties

All the powders prepared from the borate system by annealing at temperatures below 900°C consist of perovskite phase and a second MnO_x phase, probably Mn_3O_4, as low temperature measurements of the magnetization vs. T reveal a step at ≈45 K corresponding to the Curie-temperature T_c of Mn_3O_4[8] as shown in Ref. 3.

With increasing annealing temperature the MnO_x-impurity concentration decreases and the specific saturation magnetization σ_∞ (at room temperature) increases up to 53 Am^2/kg, comparable with magnetization values of single-crystal $La_{0.7}Sr_{0.3}MnO_3$ [9] (Fig. 1). These samples show an X-ray diffraction pattern of nearly single phase LSMO (Fig. 2, curve a). The mean particle size of this optimized powder estimated by the BET-method (≈ 10 m^2/g) is of the order of 100 nm in accordance with the SEM-investigations.[3]

The nearly single phase powders have a composition (EDX) $(La_{1-x}Sr_x)_{1-y}Mn_{1+y}O_3$ with a La-content $1-x$ between 0.57 and 0.70 and a Mn-content $1+y$ from 0.95 to 1.15. The Curie-temperature determined from $M_s(T)$-measurements has a value between 370 and 390 K in accordance to $M_s(T)$-measurements of LSMO-single crystals.[9] No significant dependence of T_c on the La/Sr-ratio was found in the range of composition mentioned above.

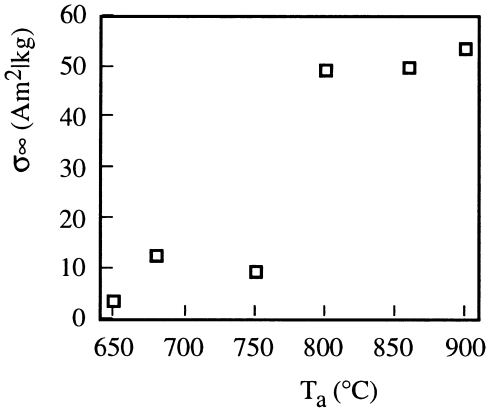

Fig. 1. Specific saturation magnetization (at room temperature) of powders from borate glass as a function of annealing temperature (time: 24 h).

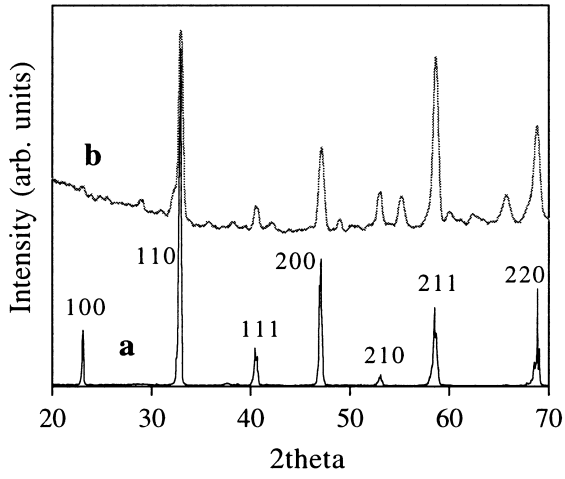

Fig. 2. X-ray diffraction patterns of LSMO powder from borate glass annealed at 930°C/8 h (a) and of SiO_2-containing ceramics (b) with $T_{sint} = 950$°C.

The manganate-SiO_2-powder mixtures prepared from the silicate–borate system by leaching the borate show an analogous dependence of the LSMO phase formation on the annealing conditions of the flakes. Pure perovskite-SiO_2-powders with no or a neglectible amount of other Mn-compounds can be prepared at $T \geqslant 900$°C. The comparison of magnetic measurements (σ_∞) and EDX analysis indicates a higher content of SiO_2 than expected from the initial melt composition due to leaching out soluble Mn-compounds. The content of nonmagnetic Mn-phases in the powder is up to 5%. The processing of ceramic samples was done with powders from glass samples annealed at 900°C.

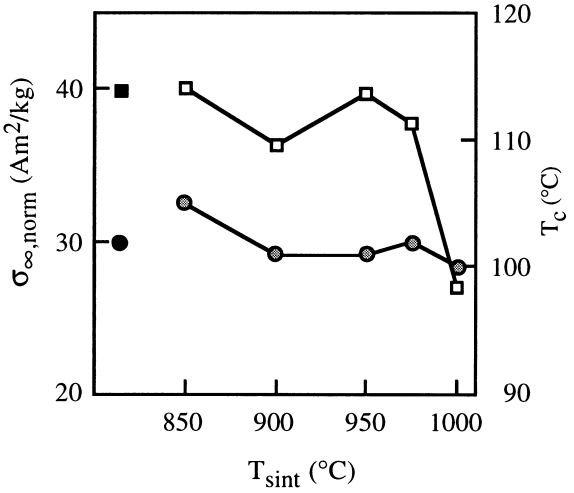

Fig. 3. Normalized specific saturation magnetization of sintered samples taking SiO_2-content (from EDX) into account (squares) and Curie temperature (circles) vs. sintering temperature; black: non-sintered samples.

With increasing sintering temperature a strong decrease of the saturation magnetization can be observed above 950°C (Fig. 3 shows σ_∞ of the LSMO powder fraction calculated from the powder composition by EDX) due to a transition from perovskite LSMO to non-magnetic phases like Mn-oxide or braunite $MnMn_6SiO_{12}$ which is known from X-ray diffraction patterns (Fig. 2, curve b), whereas the Curie temperature of the LSMO is nearly constant.

The normalized specific saturation magnetization of the sintered samples taking the SiO_2-content into account (Fig. 3, see above) is only $\approx$ 75% of the value of pure LSMO from the borate system of 53 Am^2/kg.

3.2. Magnetoresistance

Measurements of the resistance and their temperature and magnetic field dependence were carried out on pressed powder samples and sintered compacts, respectively. During the heating of the samples a magnetic field $B=1$ T was switched off and on, so that the temperature and field dependence of the resistance could be measured simultaneously. The magnetoresistance ratio $\Delta R/R = (R(0) - R(H))/R(H)$ for $B=1$ T clculated from these curves shows for pressed powders from the borate system the typical behaviour of polycrystalline LSMO,[10] consisting of a grain boundary effect, caused by tunneling processes between the grains via grain boundaries, increasing with decreasing temperature and a CMR-effect near the Curie-temperature [11] (which corresponds with T_c measured by VSM)[3] with a maximum value of 9% (Fig. 4).

Pressed LSMO–SiO_2 powder mixtures behave like high-ohmic material. A CMR-effect near T_c couldn't be measured.

The magnetoresistance ratio $\Delta R/R$ of sintered material for $B=1$ T shows also the above mentioned behaviour

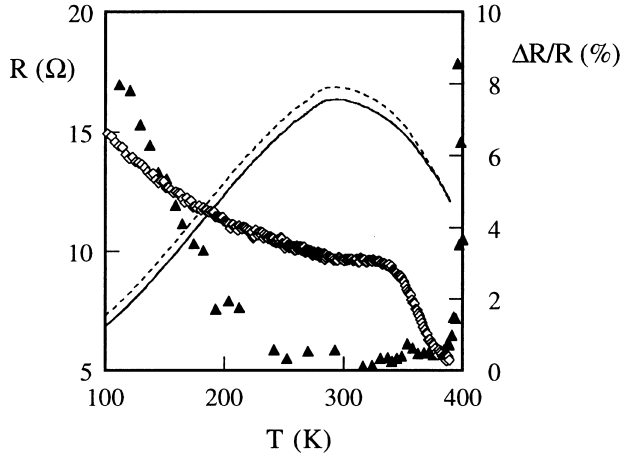

Fig. 4. Magnetoresistance $\Delta R/R$ of a powder compact from borate glass (triangles) and of sintered material (squares) for $B=1$ T and resistance of the sintered sample (dotted line: $B=0$) vs. temperature; SiO_2-content: $\approx$ 23 wt.%; $T_{sint}=950$°C.

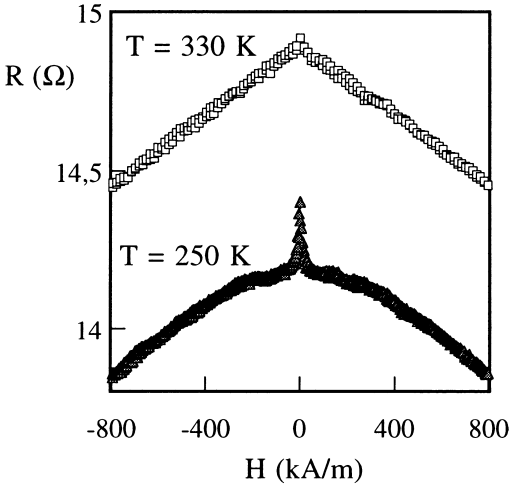

Fig. 5. Field dependence of the resistance of the sintered sample of Fig. 4 at 250 and 330 K.

but the CMR-effect near the Curie-temperature is not so significant. The grain boundary effect, increasing with decreasing temperature, and the CMR-effect lead to a plateau at ~330 K with a value of $\approx$ 3% (Fig. 4). The $R(T)$-maximum at 290 K can be explained from T_c-deviations of material at the grain boundaries.[12] In Fig. 5 the field dependence of the resistance can be seen. The $R(H)$-curve at 250 K shows a superposition of the low field GMR-effect with higher field sensitivity and the CMR-effect which is dominating in the high field range. At 330 K the CMR-effect is dominant and the $R(H)$-dependence is nearly linear.

4. Conclusions

Nearly single phase powders of LSMO can be prepared successfully by the glass crystallization method.

The magnetic properties of the powders from borate glasses are comparable with the properties of LSMO single crystals concerning their magnetization and Curie-temperature. The powders show a CMR-effect with a maximum value of 9% at $B = 1\ T$ at $T \approx 380$ K typical for high quality LSMO materials. LSMO-ceramic samples with a high manganate content were prepared from a silicate glass system. The sintering conditions have to be optimized to avoid a decrease of the magnetization due to the formation of non-magnetic Mn-compounds. Sintered samples show a superposition of the CMR and the GMR effect due to grain boundaries. The Curie temperature is about 330 K. An optimized SiO_2-content has to be found in future.

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