Magnetoresistive 'necked-grain' $CaCuMn_6O_{12}$ ceramics prepared by ultrasonic aerosol spray pyrolysis

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Ultrasonic aerosol spray pyrolysis was applied to obtain $CaCuMn_6O_{12}$ bulk ceramics with a microstructure consisting of necked submicron particles demonstrating advanced functional properties due to a large contribution of intergrain tunneling magnetoresistance.

The effect of negative colossal magnetoresistance in mixed-valence perovskites is known since pioneering works on $LaMnO_3$-based materials.[1] These compounds experience a ferromagnetic phase transition accompanied by a sharp decrease of resistance. The application of an external magnetic field shifts this transition to higher temperatures widening the existance range of a conducting phase. As a result, the effect of colossal magnetoresistance is most pronounced in the vicinity of the Curie temperature.[2] To describe this phenomenon in manganites, the concepts of Jahn–Teller distortion and double exchange interaction are used. Recently, double distorted perovskites $Ca(Cu_xMn_{3-x})Mn_4O_{12}$ possessing a negative magnetoresistance in a wide temperature range of ferromagnetic state have attracted special attention due to an unconventional character of magnetoresistance in this class of compounds.[3,4] The physics of this phenomenon involves not only microscopic mechanisms of magnetic and magnetoelastic interactions but also the processes of intergranular tunneling in ceramics.[5,6] The application of a magnetic field to ceramics consisting of fine particles coupled by tunnel junctions leads to the alignment of grains magnetic moments, which in case of substantial spin polarization of current carriers results in diminishing the resistivity. In this work, ultrasonic aerosol spray pyrolysis, an advanced preparation method of fine-grain ceramics, was developed to enhance the colossal magnetoresistance effect of the $CaCuMn_6O_{12}$ mixed-valence manganite[6] by the design of a microstructure built from a network of necked submicron particles.

To synthesise the $CaCuMn_6O_{12}$ by a standard ceramic technique, the application of high oxygen pressures seems necessary[3,4] to prevent the instability of an Mn^{4+} oxidation state at high temperatures. An expected way to overcome this problem under ambient oxygen pressure is the reduction of interaction temperatures accompanied by an increase in the reaction ability of starting reagents. To follow this idea, the CuO and Mn_2O_3 high-quality oxides and $CaCO_3$ were mixed in a stoichiometric ratio and dissolved in an excess of nitric acid at 40–80 °C with 10–20% H_2O_2 added to reduce Mn_2O_3 into a soluble manganese nitrate. After complete dissolution of the reagents, the acid nitrate solution was placed in an internal bath inside of an ultrasonic nebulizer separated from its metallic vibrating membrane by a Teflon film and a layer of pure water. Inside the bath, the solution converts into submicron mist transferring by flowing air into a hot-wall reactor preheated to 700 °C. At the reactor outlet, the oxide dust of thermally decomposed nitrate solution was collected on the surface of a hot microporous glass filter. The collected dark readily reacting oxide precursor powder with a small amount of low-melting residual nitrates was pressed into small pellets 5–8 mm in diameter. The final thermal treatment was performed in pure flowing oxygen at 850 °C for 48 h.

Powder X-ray diffraction patterns for phase identification were collected in the 2θ range 20–70° (Stoe XRD diffractometer, $CuK\alpha_1$). The unit cell parameters were determined by the least-squares fit of the peak positions obtained with a focusing FR-552 Guinier camera ($CuK\alpha_1$, germanium as an internal standard). The morphology of the products obtained both prior and after heat treatment was studied by scanning electron microscopy and electron probe microanalysis using a Leo Supra 50 VP digital scanning electron microscope (SEM) equipped with an Inca (Oxford) energy-dispersive X-ray detector

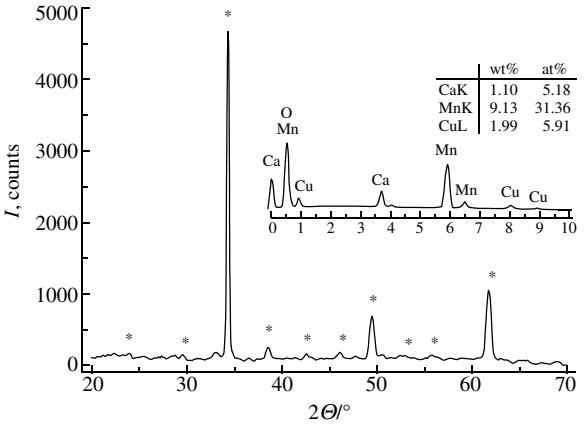

Figure 1 XRD pattern of the fully heat-treated $CaCuMn_6O_{12}$ ceramic sample prepared using ultrasonic aerosol spray pyrolysis. The inset shows EDX analysis data (area scan) for the sample.

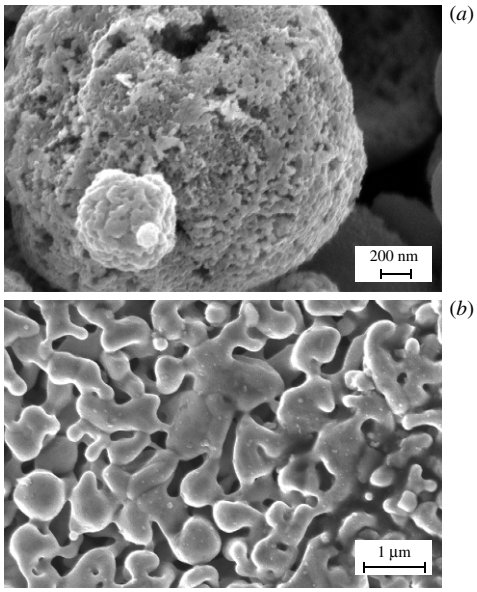

Figure 2 Micromorphology of the $CaCuMn_6O_{12}$ sample prepared by ultrasonic aerosol spray pyrolysis: (*a*) as prepared ASP powder (T = 750 °C in a hot zone); (*b*) 'necked' ceramic microstructure formed in pellets sintered at 850 °C in oxygen for 48 h.

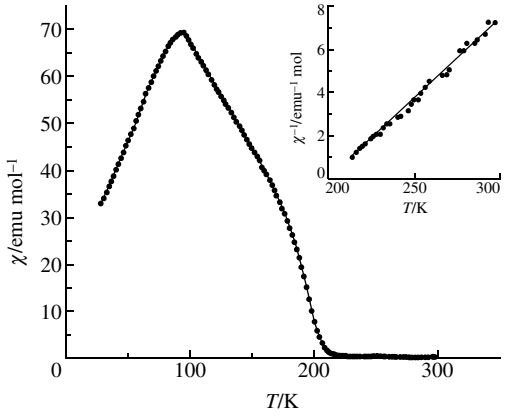

Figure 3 The temperature dependence of the ac susceptibility of $CaCuMn_6O_{12}$. The temperature dependence of the inverse magnetic susceptibility is shown in the inset.

(EDX) having a spot size of < 3 μm. To confirm chemical composition, EDX spectra were collected from about 10 randomly selected grains or using area scans. Magnetic susceptibility was measured by an ac magnetometer in the temperature range 25–300 K. The temperature and field dependence of the resistance was measured by a standard four-probe technique at 77–300 K in magnetic fields up to 1 T.

The X–ray pattern of $CaCuMn_6O_{12}$ after final heat-treatment is shown in Figure 1. The sample is a single-phase matching well the compositional dependence of cell parameters for the cubic solid solution $CaCu_xMn_{7-x}O_{12}$ and also appropriately corresponding to the recent results of structure refinement of the $CaCuMn_6O_{12}$ phase.[6] According to electron probe microanalysis, the $CaCuMn_6O_{12}$ sample had the expected Ca:Cu:Mn ratio of 1:1:6.

The SEM images of $CaCuMn_6O_{12}$ before and after thermal treatment are shown in Figure 2. It is evident that initial hollow microspheres consisting of 10–50 nm nanoparticles, building the core shells, transform into ~0.5 μm grains interconnected with elongated necks that provide percolation of electric current through this ceramic structure having weak links responsible for tunneling magnetoresistance of this material.

The temperature dependence of the ac susceptibility χ of $CaCuMn_6O_{12}$ (Figure 3) demonstrates a sharp increase of χ at $T_C = 200$ K. At about 90 K, the ac susceptibility reaches a maximum and decreases with lowering the temperature. This behaviour suggests the formation of a spin glass state below 90 K, as could be expected for the compound with randomly distributed Cu^{2+} and Mn^{3+} ions in same crystallographic positions. At high temperatures, the ac susceptibility of $CaCuMn_6O_{12}$ obeys the Curie–Weiss law $\chi = N_A g^2 \mu_{eff}^2 \mu_B^2 / 3k_B(T - \Theta)$ with $\mu_{eff} = 10.5\mu_B$ and $\Theta = 200$ K. On the assumption of frozen orbital motion, the spin – only part of magnetic susceptibility is estimated at $11.4\mu_B$ ($g = 2$), which is consistent with the experimentally observed values. The coincidence of the absolute

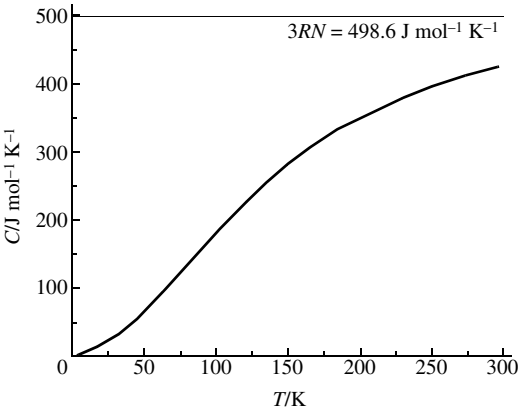

Figure 4 The temperature dependence of the specific heat of a $CaCuMn_6O_{12}$ phase.

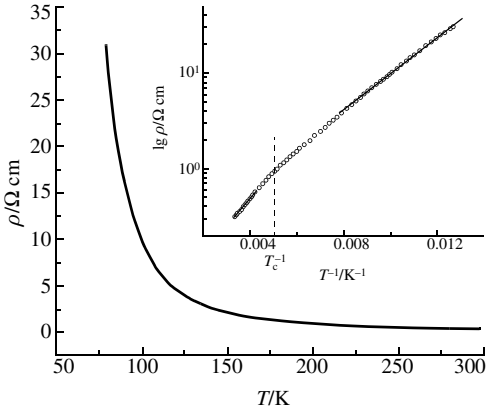

Figure 5 The temperature dependence of the resistance of $CaCuMn_6O_{12}$ ceramics.

values of Curie temperature T_C and Weiss temperature Θ points to the absence of frustration effects in the structure of $CaCuMn_6O_{12}$.

The temperature dependence of the specific heat C of $CaCuMn_6O_{12}$ is shown in Figure 4. The absence of any anomaly in the $C(T)$ dependence indicates that no structural transformation occurs in the sample in the test temperature range. Moreover, the smoothness of the $C(T)$ dependence around the magnetic phase transition can be understood only on the assumption of the itinerant type magnetism in this compound. The $C(T)$ dependence at low temperatures can be approximated by a sum of $\alpha T^{3/2}$ and βT^3. The former term corresponds to a magnon contribution to the specific heat, the latter is a lattice contribution. The estimate for the upper limit of the Debye temperature obtained from the lattice contribution amounts to $\Theta_D = 730$ K.

The temperature dependence of the specific resistance of $CaCuMn_6O_{12}$ in the range 77–300 K is shown in Figure 5. Two activation regions are clearly seen in the $\rho = \rho_0 \exp(-E/k_BT)$ dependence, *i.e.*, $E_1 = 60$ meV at $T > T_C$ and $E_2 = 40$ meV at $T_C > T$. It was conjectured[5] that these activation energies are relevant to interband transitions. In this case, the reduction of activation energy at the transition into a ferromagnetic state is due to splitting of spin-up and spin-down subbands, which results from spontaneous magnetization. The rapid increase of the absolute resistance at cooling prevents the measurements at low temperatures.

The field dependence of the resistance $[\rho(H) - \rho(0)]/\rho(0) \times 100\%$ is shown in Figure 6. Clearly, at the transition into a ferromagnetic state, the type of magnetoresistance curves changes from superlinear to sublinear. Since the magnetoresistance is the odd effect with respect to a magnetic field, the $\rho(H)$ dependence is symmetrical with respect to changes in magnetic field direction. At $T > T_C$, the magnetoresistance $\rho(H)$ is proportional to χH^2. The effect increases when approaching the

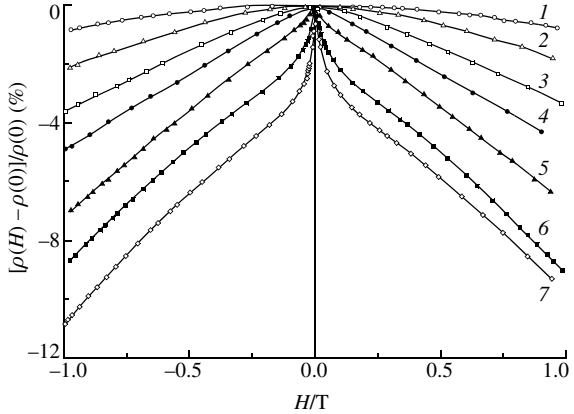

Figure 6 The set of field dependencies of magnetoresistance of $CaCuMn_6O_{12}$ ceramics at various temperatures: (*1*) 224, (*2*) 211, (*3*) 201, (*4*) 191, (*5*) 150, (*6*) 90 and (*7*) 88 K.

Curie temperature as corresponding to the increase of magnetic susceptibility in a paramagnetic state. At $T < T_C$, the magnetoresistance is determined by the internal magnetic field, which is proportional to magnetization M. The $M(H)$ curves are nonlinear rapidly increasing at a low magnetic field. This leads to sublinear field dependencies of magnetoresistance in a ferromagnetic state.[7] In general, the absolute values of MR are greater than published data for the same system[4] by a factor of 1.5–2; this can be attributed[6] to the discussed microstructural features of our samples.

In conclusion, the application of ultrasonic aerosol spray pyrolysis allowed us to obtain a colossal magnetoresistance material, which exhibits ~10% effect under magnetic fields of about 1 T at $T \leq 200$ K. The fact that colossal magnetoresistance in $CaCuMn_6O_{12}$ is observed in a wide temperature range below the Curie temperature indicates that the processes of intergranular tunneling are important for this class of materials and this necessarily demands the control of a ceramic microstructure.

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