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LETTER TO THE EDITOR

Synthesis of Doped Rare Earth Manganate Perovskite Crystals Using Fused Salt Electrolysis

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A facile method for the synthesis of doped lanthanum manganate crystals, suitable for the measurement of electrical and magnetic properties, is presented. Mixtures of sodium molybdate and molybdenum(VI) oxide are used as a solvent to which La_2O_3, $MnCO_3$, and $SrMoCO_4$ are added as solutes which are then electrolyzed at 800–1040°C for varying lengths of time with Pt electrodes. Well-formed cubic crystals, with edge dimensions up to 1.5 mm, form at the anode. Magnetization measurements show a transition to the ferromagnetic state in the temperature range ~250–320 K, depending on the amount of aliovalent doping at the La sites. An insulator-to-metal transition is also observed in the vicinity of the ferromagnetic ordering temperature. © 1997 Academic Press

The detailed study of the interesting magnetic and electronic properties of doped rare earth manganates has been limited by the availability of suitable single-crystal specimens, which have been difficult to prepare (1, 2). Although fused salt electrolysis (FSE) is used to grow large single crystals of low valent oxides by cathodic reduction, relatively little attention has been paid to the use of FSE for preparing high valent oxides, particularly manganates.

Kostiner and Banks prepared Al-substituted Mn_2O_3 in the pseudo-cubic bixbyite form by anodic oxidation in sodium tungstate–tungsten trioxide melts containing manganese oxide (3). Ternary oxide formation in the form of hollandite-related oxides of the type M_xMnO_2 (M = K, Rb) was reported by Strobel and LePage, who used M_2O–MoO_3 or M_2O–V_2O_5 eutectics as solvents for MnO (4). It seemed to us that single crystals of mixed valent rare earth manganates might be grown at temperatures below 1000°C, using similar solvents to which rare earths had been added. In this paper we describe our initial experiments using molybdate melts and present preliminary data on the physical properties of the products.

The crystals were grown using melts obtained from mixtures of sodium molybdate and molybdenum(VI) oxide to which $MnCO_3$, La_2O_3, and $SrMoO_4$ or $SrCO_3$ were added. Electrolyses were carried out with Pt electrodes, in air, from 800 to 1040°C in high density (MacDanel) alumina crucibles for 30 min to 48 h using currents between 10 and 40 mA. Products were washed in warm, dilute solutions of potassium carbonate containing a small amount of ethylenediaminetetraacetic acid.

Chemical analyses were made with a Baird Atomic Model 2070 inductively coupled plasma emission spectrometer (ICP). X-ray powder diffraction data were obtained using a Rigaku D-Max 2 system (graphite monochromatized Cu$K\alpha$ radiation). Electrical resistivity measurements were made in a four-probe configuration, and magnetic measurements were carried out on batches of randomly oriented crystals using a Quantum Design SQUID magnetometer (MPMS) between 4 and 300 K.

The results of several FSE runs are summarized in Table 1. The oxidized products grow directly on the anode spiral in the form of highly reflecting, black crystals with a cubic-like habit whose edge dimensions are typically between 0.3 and 1.5 mm. Formation of the rare earth manganate phase occurs exclusively above about 950°C. Lower temperatures result in a mixture of the manganate and Mn_2O_3, with the latter being the exclusive product at 850°C. Typically, we ran between 980 and 1000°C. Even under these conditions, complete solubility of the MnO is not achieved. This may actually aid crystal growth since the excess solid helps maintain a steady-state concentration of Mn in the melt. An unexpected result was the formation at the cathode of small, weakly magnetic, dendritic crystals. The X-ray powder diffraction pattern of this product shows that a phase of the rhombohedral $LaMnO_3$ type is always

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TABLE 1
Conditions for Crystal Growth of Substituted Rare Earth Manganates and Description of Products Obtained

Sample ID	Starting molar ratios: Na_2MoO_4:MoO_3:La_2O_3:MnO:$SrMoO_4$	Time (h)	I (mA)	Temperature (°C)	Description of products
7-17	2.31 : 1.00 : 0.173 : 0.394 : 0.000	12	30	825	Anode: bixbyite-type crystals approx. 1 mm on edge Cathode: MoO_2
7-20	2.31 : 1.00 : 0.280 : 0.390 : 0.000	4.5	30	1035	Anode: $LaMnO_3$-type weakly magnetic black cubes 0.2–0.4 mm on edge Cathode: $LaMo_5O_8$ + weakly magnetic dendritic powder
21-2	2.54 : 1.00 : 0.312 : 0.420 : 0.000	17	20	1015	Anode: magnetic black cubes, some 1 mm on edge Cathode: magnetic dendritic powder
7-22	2.31 : 1.00 : 0.280 : 0.390 : 0.156	22	20	990	Anode: strongly magnetic black cubes, 0.5–0.7 mm on edge Cathode: weakly magnetic dendritic powder.
130-6	2.40 : 1.00 : 0.300 : 0.300 : 0.335	47	25	975	Anode: strongly magnetic black cubes, 0.5–1.5 mm on edge Cathode: $LaMo_{8-x}O_{14}$

present, sometimes mixed with MoO_2 or other ternary molybdenum oxides. Apparently, soluble, oxidized Mn-containing species are produced at the anode which then migrate to the cathode where compound formation takes place.

Table 2 gives a summary of unit cell data for the various compounds formed, along with their chemical formulas as determined by ICP analysis. We have chosen to present the chemical formulas on a full oxygen stoichiometry basis since this convention is supported by crystallographic evidence (5–9). Although deviations of oxygen stoichiometry from the ideal value of 3 are all within the estimated accuracy of 1–2% for the metal determinations, the consistent small negative bias observed on average is probably real.

The presence of significant amounts of sodium in the anode products was not unexpected, since alkali rare earth manganates are well established (10). The presence of Al, which was not anticipated, and which is apparently abstracted from the crucible, has a significant effect on both the degree of magnetization and the Curie temperature. The amount of Sr incorporated relative to the formal La/Sr ratio is unexpectedly low, indicating that the limit of formation of Mn^{4+} in these phases is largely determined by the amount of sodium that can be incorporated.

Figure 1 shows the temperature dependence of the magnetic susceptibility of crystals with the nominal composition $La_{0.859}Na_{0.096}Sr_{0.022}Mn_{0.948}Al_{0.066}O_3$ (sample 7-22A) in the range 2–375 K. A sharp increase in the susceptibility observed below ~265 K, followed by near-saturation behavior down to 2 K, is characteristic of a transition to the ferromagnetic state. The ferromagnetism in the manganates is attributed to the well-known double-exchange correlations between the Mn^{3+} and Mn^{4+} ions mediated by the oxide ions (11). The ordering temperature T_c, among other

TABLE 2
Unit Cell Data and Chemical Compositions of Substituted Lanthanum Manganate Crystals Prepared by Fused Salt Electrolysis

Sample	Analyzed composition	a (Å)	α^0	V_{cell} (Å^3)	V_F (Å^3)[a]
7-20A	$La_{0.872}Na_{0.084}Mn_{0.951}Al_{0.039}O_3$	5.4676(3)	60.56(1)	117.04(2)	58.52(1)
21-2A	$La_{0.844}Na_{0.094}Mn_{0.924}Al_{0.050}O_3$	5.4646(3)	60.54(1)	116.80(2)	58.40(1)
7-22A	$La_{0.859}Na_{0.096}Sr_{0.022}Mn_{0.948}Al_{0.066}O_3$	5.4579(2)	60.504(5)	116.28(1)	58.14(1)
130-5A	$La_{0.859}Na_{0.093}Sr_{0.028}Mn_{0.917}Al_{0.047}O_3$	5.4610(3)	60.49(1)	116.48(2)	58.24(1)
130-6A	$La_{0.819}Na_{0.113}Sr_{0.033}Mn_{0.930}Al_{0.053}O_3$	5.4609(5)	60.49(1)	116.44(3)	58.22(2)
7-16A	$Mn_{1.876}Al_{0.124}O_{2.96}$	9.3768(6)		824.4(1)	

[a] Volume per formula unit.

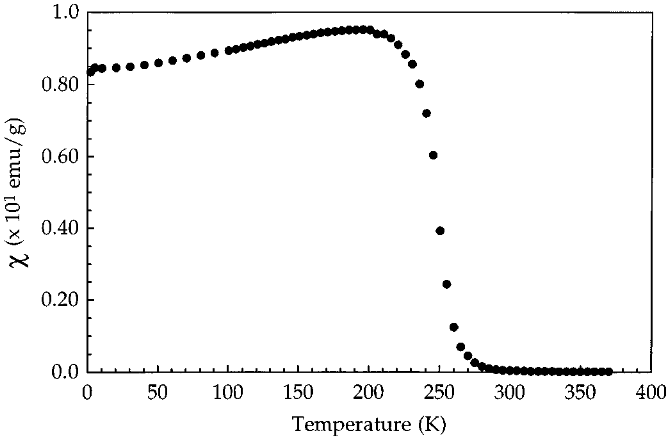

FIG. 1. Magnetic susceptibility of a batch of randomly oriented single crystals of doped lanthanum manganates (sample 7-22A) as a function of temperature.

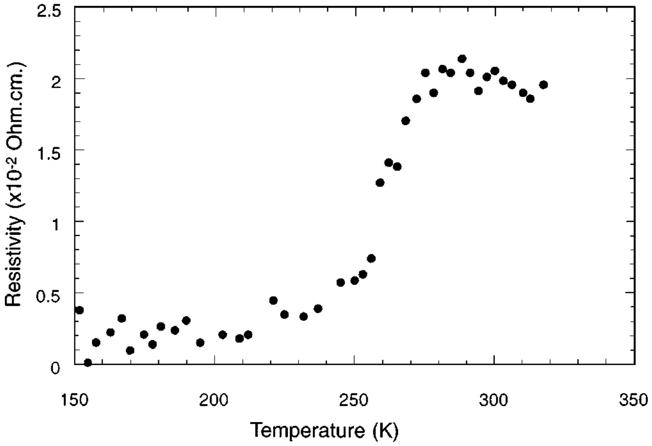

FIG. 2. Temperature variation of the electrical resistivity of a (La, Sr, Na)MnO_3 single crystal (sample 7-22A).

factors, has been shown to depend sensitively on the unit cell volume and the degree of hole doping in the samples. In general, T_c increases with increasing size of the cations substituted at the La site at an optimum hole doping of ~30% (12). From the compositional analysis data we find the Mn^{4+} content in these crystals to be ~25%. Based on ionic radius considerations [Na^+(153 pm), Sr^{2+}(158 pm), and La^{3+}(150 pm); CN = 12], the average size at the La site is 147 pm, comparable to the corresponding value of 150 pm in $La_{0.7}Ca_{0.3}MnO_3$. Thus, the T_c of ~265 K observed in our crystals is in good agreement with the T_c's ~250–260 K reported for $La_{0.7}Ca_{0.3}MnO_3$ samples (13). The small negative curvature of the susceptibility below T_c is most likely due either to the presence of isolated antiferromagnetic domains in the crystals or to local distortions induced by Al^{3+} ions on the manganese sites, resulting in a weak coupling of ferromagnetic domains.

Typical temperature-dependent electrical resistivity behavior of a single crystal chosen from the batch used in the magnetization measurements is shown in Fig. 2. The broad semiconductor–metal transition, T_{im}, observed near ~260 K corresponds well with the T_c (265 K) from the magnetization studies. Thus, the simultaneous observation of transitions in electrical resistivity (T_{im}) and magnetization (T_c) in our crystals is consistent with the general behavior of hole-doped rare earth manganates. The room-temperature resistivity of ~2×10^{-2} ohm-cm observed in this study is comparable to the literature reports on $La_{1-x}Sr_xMnO_3$ single crystals for $x = 0.175$ (2); the Al^{3+} impurity centers present in our crystals may also be partly responsible for the observed high resistivity.

We are now examining methods of achieving more controlled doping, including the use of other containers for the melt and other solvents, as well as pursuing a more detailed examination of their electrical and magnetic properties.

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