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LETTER TO THE EDITOR

Single-crystal growth and properties of the double-layered manganese oxidesG Balakrishnan, M R Lees and D M^cK Paul

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Abstract. The giant-magnetoresistance cubic perovskite oxides of the type RMnO_3 ($\text{R} =$ rare earth) can be tailored by layering with additional MnO_2 sheets. The layered manganese oxides, $(\text{R}, \text{Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$, produce variants that adopt the K_2NiF_4 structure for $n = 1$ and $n = 2$ similar to that of the high- T_c cuprates, and exhibit interesting properties. Single crystals of the two-layer ($n = 2$) perovskites of the type $(\text{R}, \text{Sr})_3\text{Mn}_2\text{O}_7$ ($\text{R} = \text{Nd}, \text{Pr}$) have been grown by the floating-zone method using an infra-red image furnace. Large crystals could be cleaved from the boules grown.

The perovskites of the type RMnO_3 have been extensively studied because of their giant or colossal magnetoresistance (GMR/CMR) properties [1–3]. They can be substituted for with divalent atoms such as Sr, Ba and Ca to provide Mn^{3+} and Mn^{4+} in the lattice. The parent compounds (undoped) are usually insulating and antiferromagnetic (LaMnO_3 for example), while the doped compounds exhibit a wide variety of magnetic structures. Layered variants of RMnO_3 structure can be produced by tailoring the structures, i.e. by adding additional layers of MnO_2 . This is similar to the structures of the high-temperature superconductors with the CuO_2 layers. The single- and double-layered compounds in the series, $(\text{R}, \text{Sr})_{n+1}\text{Mn}_n\text{O}_{3n+1}$, for $n = 1$ and $n = 2$ adopt the K_2NiF_4 structure and are tetragonal. The $n = 1$ compound is similar to the La_2CuO_4 structure, and the $n = 2$ compound is analogous to the $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure [4, 5]. The $n = \infty$ phase is the three-dimensional perovskite. A number of the $(\text{R}, \text{Sr})_3\text{Mn}_2\text{O}_7$ compounds have been synthesized in polycrystalline form earlier by Battle *et al* [6], and their magnetoresistance properties have also been reported. The $\text{R}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ compounds for $\text{R} = \text{Nd}, \text{Pr}$ and La have been also been synthesized in polycrystalline form by Seshadri *et al* [7].

The floating-zone method [8] is an ideal method for the single-crystal growth of most oxides. Single crystals of the $n = \infty$ compound can be grown as large boules for most compositions [9], either doped or undoped. Moritomo *et al* [5] have previously reported the single-crystal growth and the magnetoresistance properties of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$. While in the $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ compound the magnetoresistance observed is coupled with the onset of long-range ferromagnetic ordering, the magnetoresistance observed in some of the polycrystalline $(\text{Nd}, \text{Sr})_3\text{Mn}_2\text{O}_7$ compounds by Battle *et al* [6] is not necessarily associated with the presence of magnetic order. The magnetoresistance of all of the double-layered compounds may not therefore be qualitatively explained using the double-exchange model [10], which has been widely invoked to explain the behaviour of the RMnO_3 type of compounds ($n = \infty$). In this letter we describe the single-crystal growth of a few of the $n = 2$ series of the Nd- and Pr-based manganese perovskites by the floating-zone method. Initial characterization of the crystals is also presented.

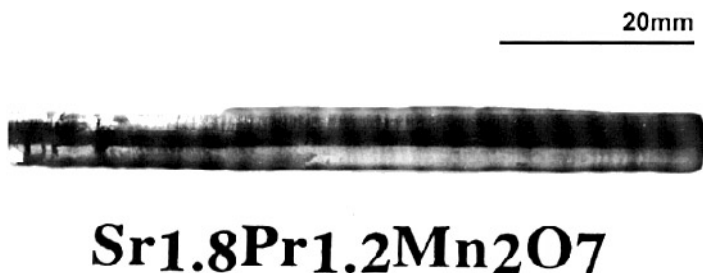


Figure 1. A photograph of a crystal of $\text{Sr}_{1.8}\text{Pr}_{1.2}\text{Mn}_2\text{O}_7$ grown using the infra-red image furnace. (Growth rate: 7 mm h^{-1} ; rotation: 25 rpm, in air.)

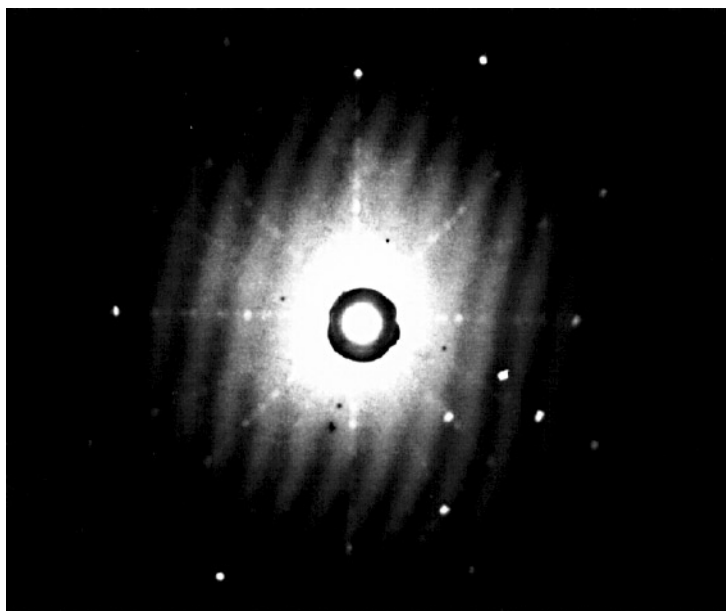


Figure 2. An x-ray Laue back-reflection photograph of the cleaved surface (001) of a crystal of $\text{Nd}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$.

Polycrystalline powders of all of the starting compositions, $\text{Pr}_{1+x}\text{Sr}_{2-x}\text{Mn}_2\text{O}_7$ and $\text{Nd}_{1+x}\text{Sr}_{2-x}\text{Mn}_2\text{O}_7$ ($x = 0, 0.2$ and 0.5), were synthesized starting from high-purity Nd_2O_3 or Pr_6O_{11} , SrCO_3 and MnO_2 . The powders were ground well together, calcined at 1100 and 1200 °C for 24 h, and then fired at 1350 °C for 24 h. The resulting powder was then isostatically pressed in the form of rods, and sintered at 1350 °C for 24 h. The rods were typically 80 mm long and 6 to 8 mm in diameter. The crystal growth was carried out using a double-ellipsoidal infra-red image furnace (NEC, SC-N35HD) in air. The growth rate was 6 to 8 mm h^{-1} and the rods were rotated at 25–30 rpm. In some cases, the growth was carried out at 2 mm h^{-1} and 15 rpm to compare the quality of the resulting crystals. Alternating-current susceptibility measurements were made using a standard mutual-inductance technique.

Large crystals with extended flat facets along the length of the boule were obtained for both the Nd- and the Pr-based compounds. There was not much difference in the

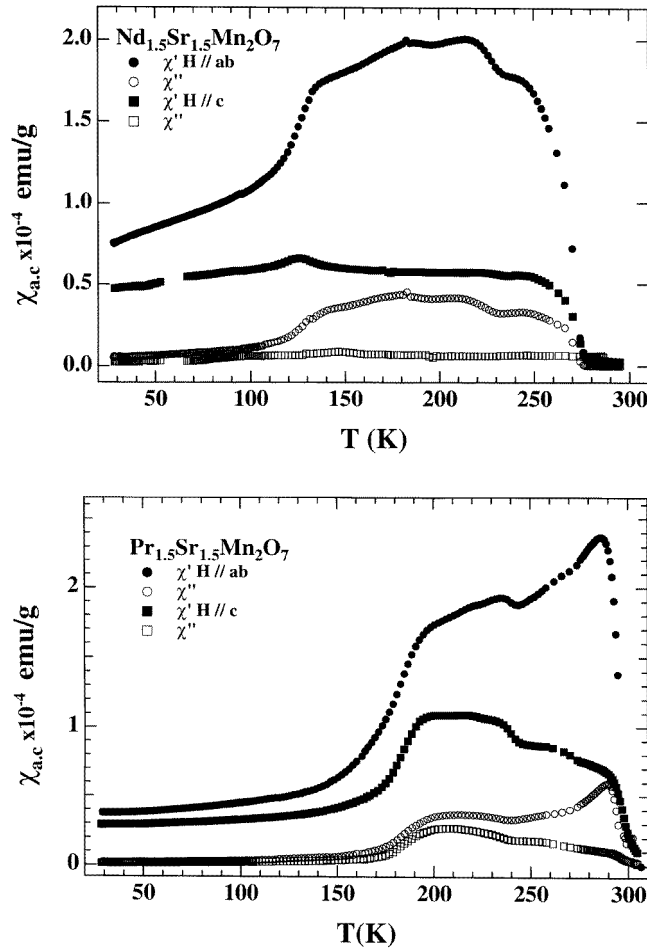


Figure 3. The measured ac susceptibility, χ' (the real part) and χ'' (the imaginary part), for single crystals of $\text{Nd}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ and $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ for the ac field parallel and perpendicular to the ab -plane. ($H_{ac} = 7$ Oe.)

quality of the crystals obtained for the two different growth rates used. The crystals obtained adopted the required growth orientation easily when a seed crystal was used. A photograph of one of the crystals grown is shown in figure 1. The boules could be cleaved easily along the growth axis, to reveal flat shiny surfaces; this is particularly true of the $\text{Nd}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ crystals. The boule grown could be cleaved to produce large platelets. Crystals as large as $20 \text{ mm} \times 5 \text{ mm} \times 3 \text{ mm}$ could easily be obtained from the boules grown. The quality of the crystals grown has been checked using x-ray Laue photographs and by neutron diffraction techniques as well. An x-ray Laue photograph of one of the cleaved crystals is shown in figure 2 and shows that the surface of the cleaved crystals is the (001) plane. Initial x-ray powder diffraction analysis carried out by us on the Nd- and Pr-based compounds shows that the patterns could be indexed to the tetragonal space group $I4/mmm$, and the lattice parameters obtained are in general agreement with previously published data [6, 7]. The lattice parameter a decreases with increasing x while the parameter c increases. Battle *et al* [6] report the observation of two different phases for

compositions of $\text{Nd}_{1+x}\text{Sr}_{2-x}\text{Mn}_2\text{O}_7$, for x less than 0.5. High-resolution diffraction work needs to be carried out on our single-crystal specimens to check whether they show similar biphasic properties.

The ac susceptibility was measured on the crystals grown, and the results for two of the crystals grown, for $x = 0.5$, are shown in figure 3. The measurements were done with the ac field parallel and perpendicular to the ab -plane of the crystal. From the plot of the measured ac susceptibility for the $\text{Nd}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ and the $\text{Pr}_{1.5}\text{Sr}_{1.5}\text{Mn}_2\text{O}_7$ crystal, it can be seen that the properties of these crystals are highly anisotropic. This is also reflected in the resistivity measured for single-crystal $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ by Moritomo *et al* [5]. The onset of antiferromagnetic correlations can be seen at around 100 K and the ferromagnetic ordering sets in at 280 K and 305 K respectively in the Nd and the Pr crystal. Initial confirmation of these magnetic features has been provided by neutron diffraction studies on the above crystals [11]. Detailed investigations of the magnetic and magnetotransport properties of all the crystals grown are under way, and will be published separately.

In conclusion, we have successfully grown single crystals of the double-layer manganese perovskites of the type $(\text{R}, \text{Sr})_3\text{Mn}_2\text{O}_7$, $\text{R} = \text{Nd}$ and Pr , for $x = 0, 0.2$ and 0.5 . Due to the large anisotropy exhibited by these compounds, single-crystal specimens will prove essential in examining their physical properties in any detail. The layered perovskites provide the ideal system in which to investigate the strengths of the various exchange interactions present. It is thought that the intra-layer interactions are much stronger than the inter-layer interactions in these anisotropic materials. The role played by the reduced dimensionality of the layered compounds in determining the magnetic and magnetoresistive properties needs to be understood.

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