Short communication

Hydrothermal synthesis of two perovskite rare-earth manganites, HoMnO$_3$ and DyMnO$_3$

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Abstract

Two perovskite rare-earth manganites RMnO$_3$ (R = Ho, Dy) were synthesized from the hydrothermal redox reactions of KMnO$_4$ and MnCl$_2$ at 250 °C and characterized by means of X-ray diffraction, scanning electron microscopy and SQUID. They are orthorhombic, whereas the hexagonal phases, which were competitive strongly with the orthorhombic phases in solid-state reactions, are avoided in the hydrothermal systems. The pure metastable manganites may serve as a model for understanding the magnetisms of Jahn–Teller distortion and charge ordering. This new synthetic approach leaves many rooms for new doped or undoped RMnO$_3$ compounds.

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Transition-metal oxides with perovskite-related structures show a variety of gigantic-response phenomena such as ferroelectricity, colossal magnetoresistance, oxygen migration and high-temperature superconductivity. Recent extensive efforts to understand their mechanisms have revealed that the local inhomogeneity of the electronic/lattice structure often plays a crucial role in optimizing the properties [1,2]. Tokura [3] believed that the orbital degree of freedom occasionally dominates the magnetic–electronic properties, and its correlation and/or order–disorder transition causes a variety of phenomena through strong coupling with charge, spin, and lattice dynamics. Theoretically, the spin–charge–orbital coupled systems in transition-metal oxides offer the most fascinating and challenging arena to test many theoretical ideas, including quantum liquid, solid, and liquid–crystal states. The extreme compounds, RMnO$_3$ in the perovskite manganites with formula $R_{1-x}A_x$MnO$_3$ (A = alkaline earth) are antiferromagnetic and some of them magnetoelectric, such as

those for R = Sc, Y, Ho–Lu [4]. Solovyev [5] calculated the magnetic interaction parameters of LaMnO$_3$ using the LSDA approach and found strong lattice distortions. It was reported there is a weak ferromagnetism in LaMnO$_3$ when vacancies exist [6–8]. Annealing in oxygen flow will introduce additional vacancies, and thus the solid-state reactions affect the magnetic properties from antiferromagnetic to ferromagnetic with a double-exchange mechanism because of the presence of mixed Mn^{3+}–Mn^{4+} valences [9]. Most of the manganites were synthesized by solid-state reactions [10,11] and sol–gel technique [6,12] at ca. 1200 °C with Ar/O$_2$ or Ar/H$_2$ atmosphere for several days or weeks. In order to obtain pure products, the starting materials must be ground for many times during annealing process. The stoichiometric RMnO$_3$ with 100% Mn^{3+}, could also be prepared by these methods involving annealing under inert atmosphere. For rare-earth cations smaller than Tb^{3+}, the orthorhombic perovskite structure for RMnO$_3$ was no longer the stable phase under ordinary synthetic conditions, since a hexagonal phase (space group P6$_3$cm) with the same stoichiometry strongly competes in stability from Ho, Lu, Y, to Sc, as a

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function of ionic radius [13]. By the citrate method, $HoMnO_3$ and $YMnO_3$ were prepared as metastable phases [14–16]. Synthetic approaches affect properties partially due to the possible variation of morphology, size, the number of vacancies and the surface state [17]. Jeffrey [18] reported the hydrothermal synthesis of the nanocubes of $La_{1-x}Ba_xMnO_3$ with three different doping levels, and the sizes of the nanocubes were ranging from 50 to 100 nm. Here, we report
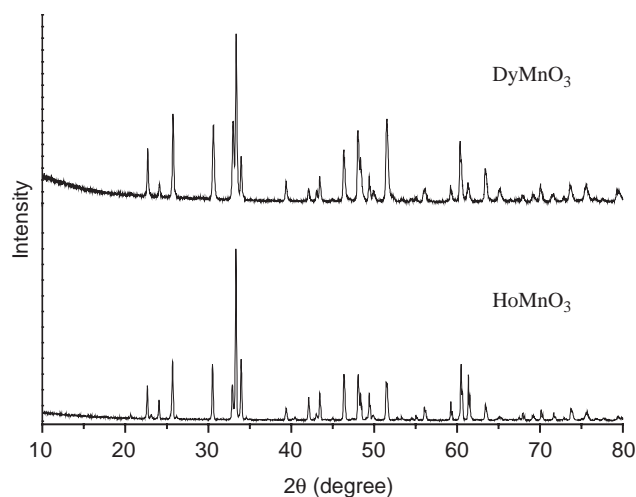

Fig. 1. XRD pattern for $RMnO_3$ (R = HO, Dy) obtained by the hydrothermal synthesis.

the hydrothermal syntheses and magnetic properties of two metastable perovskite rare-earth manganites, $HoMnO_3$ and $DyMnO_3$.

The syntheses were performed in 80-mL Teflon-lined stainless steel autoclaves with filling capacity of 70%. $R(NO_3)_3$ (R = Ho or Dy), $KMnO_4$ and $MnCl_2 \cdot 4H_2O$ were mixed in distilled water on stirring at room temperature. KOH was added to maintain alkalinity. In a typical synthetic procedure, 16 mL HNO_3 solution (0.4 M), 0.17 g $KMnO_4$, 0.84 g $MnCl_2 \cdot 4H_2O$ were mixed with 50 mL H_2O on stirring, and 20 g KOH was added. The reaction mixture was placed in the autoclaves and heated at 250 °C under the autogenous pressure for 2 days. A hydrothermal redox reaction was proposed as follows:

$$5R(NO_3)_3 + KMnO_4 + 4MnCl_2 + 22KOH \rightarrow 5RMnO_3$$
$$+ 15KNO_3 + 8KCl + 11H_2O \ (R = Ho, Dy).$$
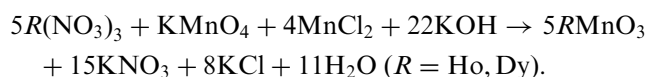
The powder product was washed thoroughly with distilled water and sonicated by a direct immersion titanium horn (Vibracell, 20 kHz, 200 w/cm^2). The dark product crystals were obtained.

Powder X-ray diffraction (XRD) data were collected using a Rigaku D/Max 2500 V/PC X-ray diffractometer (made in Japan) with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) (50 kV, 250 mA) at room temperature by step scanning in the angle range $10 \leqslant 2\theta \leqslant 80°$ with increments of $0.02°$.
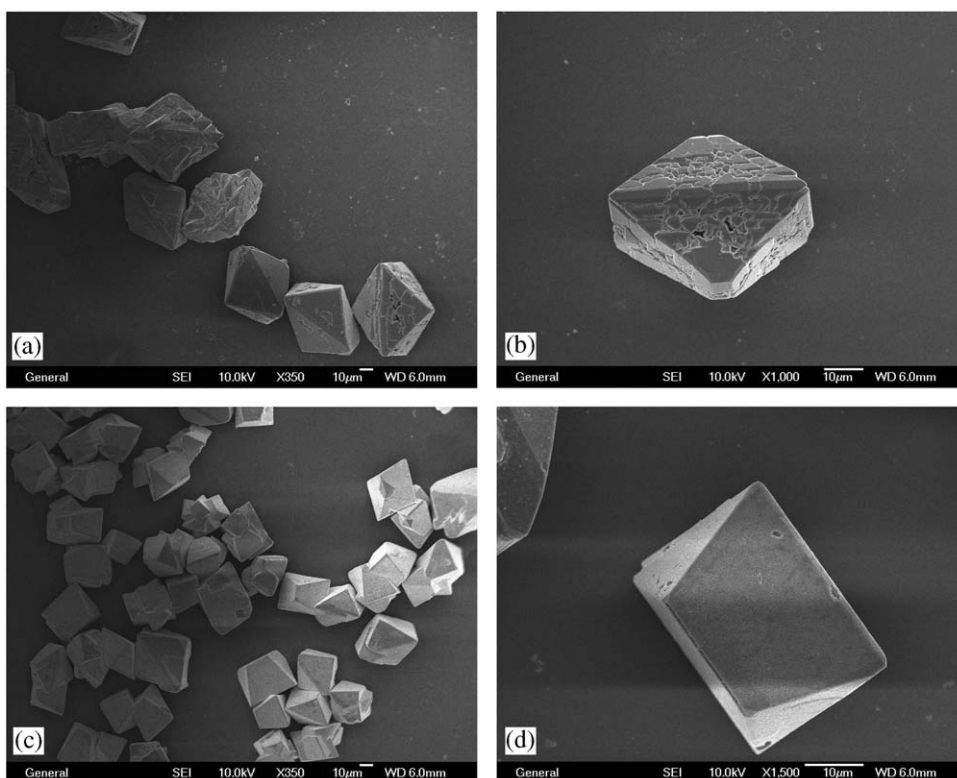

Fig. 2. SEM photos of $RMnO_3$: (a,b) $DyMnO_3$, and (c,d) $HoMnO_3$.

Scanning electron microscopy (SEM) was performed with a Rigaku JSM-6700F microscope operated at 10 kV. The magnetic properties of the $RMnO_3$ (R = Ho, Dy) were studied by measuring the sample magnetization as a function of applied magnetic field using a superconducting quantum interference device magnetometer (Quantum Design, MPMS).

The powder XRD patterns of $RMnO_3$ are shown in Fig. 1 and the lattice parameters were optimized by the least-squares refinement. Two compounds crystallize in orthorhombic system with space group $Pbnm$, $a =$

5.2809(1) Å, b = 5.8385(4) Å, and c = 7.3788(5) Å for $DyMnO_3$; a = 5.2843(9) Å, b = 5.8389(10) Å, and c = 7.3655(13) Å for $HoMnO_3$. The lattice volumes increase with increasing cation radii. All values (a, b, c and V) are similar to those of the corresponding phases synthesized by the citrate method [16]. As a stable phase, hexagonal manganite $RMnO_3$ (R = Ho–Lu, Y, or Sc) strongly competes in stability with the orthorhombic phase, and we noticed that our hydrothermal method did not lead to any hexagonal phase. Perovskite-based structures occasionally show lattice distortion as modifications
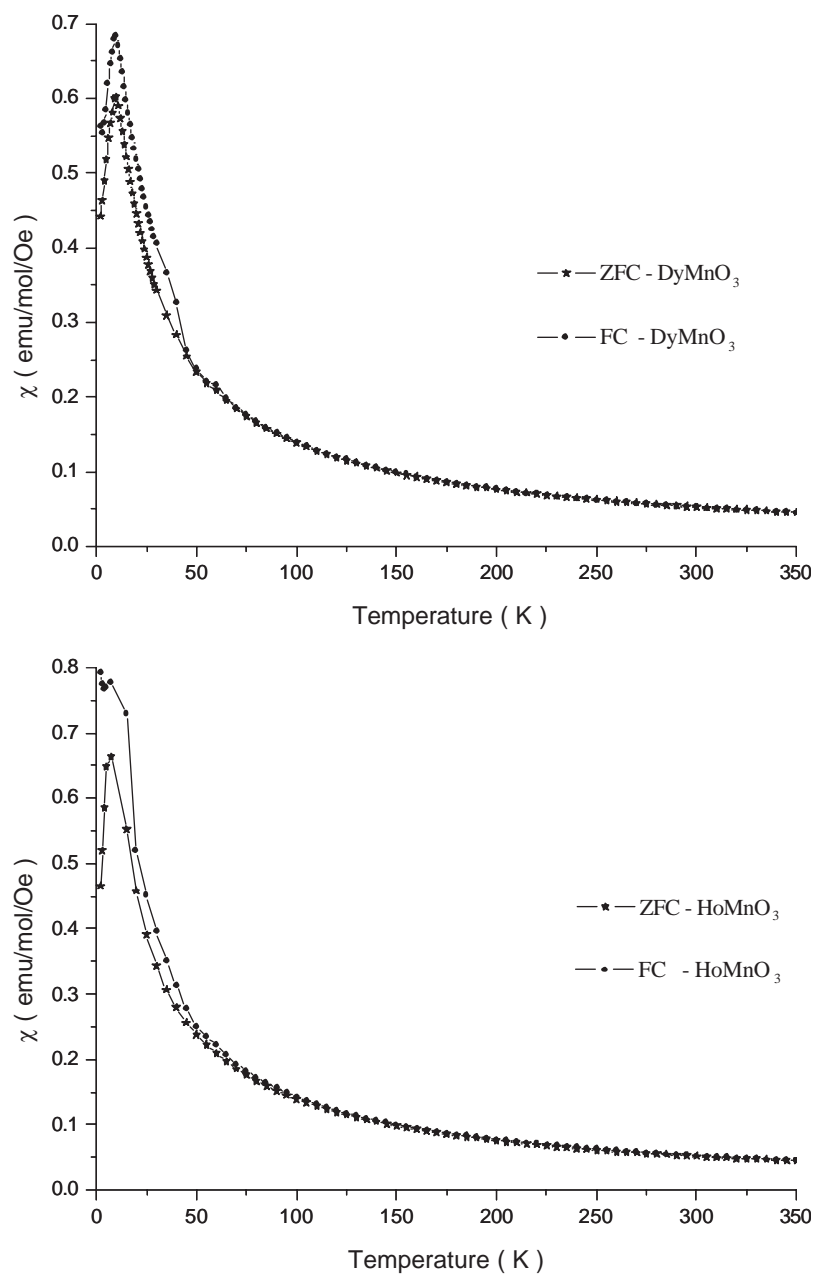

Fig. 3. Plot of susceptibility (χ) against temperature (T) for $RMnO_3$ (R = Dy and Ho) obtained by hydrothermal synthesis with the applied field of 100 Oe.

from the cubic structure. The possible origin for the lattice distortion is the deformation of MnO_6 octahedron arising from the Jahn–Teller effect that is inherent to the high-spin ($S = 2$) Mn^{3+} with double degeneracy of the e_g orbital. Another lattice deformation comes from the connection pattern of MnO_6 octahedra in the perovskite structures, forming the rhombohedral and orthorhombic lattices [19].

SEM photographs of the samples are illustrated in Fig 2. These images clearly revealed the pure phases of perovskite-type $RMnO_3$ (R = Ho, Dy) with 40–50 μm in size, as those for hydrothermally synthesized $ZrSiO_4$ and $ZrGeO_4$ [20,21].

Fig. 3 shows the magnetic susceptibilities (χ) versus temperature (T) for the samples. These curves were recorded by cooling the samples to 2 K, and then heating up to 350 K under the applied field of 100 Oe. In the zero-field-cooled (ZFC) measurements, no anomalies were observed and the magnetic susceptibilities undergo an abrupt increase below 100 K, reaching a maximum value at ca. 10 K, and then decreasing to lower temperatures. It seems a Curie–Weiss behavior at ca. 10 K, although the samples are antiferromagnets under 40 K. This may be due to the strong paramagnetic effects from Ho^{3+} and Dy^{3+}. In the field-cooled measurements, the magnetic susceptibility showed the same behavior as ZFC curve for $DyMnO_3$, but for $HoMnO_3$ the susceptibility underwent an abrupt increase towards a saturation value. This indicates the presence of a weak ferromagnetism effect.

In summary, we have hydrothermally synthesized $RMnO_3$ (R = Ho and Dy) with orthorhombic perovskite structures. $RMnO_3$ crystals were nearly uniform in size with 40–50 μm. Any hexagonal phase, which is competitive strongly with the orthorhombic phase in solid-state method, did not appear in hydrothermal systems. It is respected to synthesize other $RMnO_3$ or doped $RMnO_3$ by this ready method.

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