Structural Stability of CaCuMn$_6$O$_{12}$ under High Pressure and Low Temperature

ZHA NG Wang(张旺)$^1$, YAO Li-De(姚立德)$^1$, YOU Shu-Jie(游淑洁)$^1$, YANG Liu-Xiang(杨留响)$^1$, YANG Hua(杨华)$^1$, LI Feng-Ying(李凤英)$^1$, CHEN Liang-Chen(陈良辰)$^1$, BAO Zhong-Xing(鲍忠兴)$^1$, LI Xiao-Dong(李晓东)$^2$, LIU Jing(刘景)$^2$, JIN Chang-Qing(金常青)$^1$, YU Ri-Cheng(俞日成)$^{1,**}$

$^1$Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, PO Box 603, Beijing 100080
$^2$Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039

(Received 19 October 2006)

In situ high pressure energy-dispersive x-ray synchrotron radiation diffraction and resistance experiments are carried out on CaCuMn$_6$O$_{12}$. Its crystal structure is stable in the measured pressure range. The equation of state of CaCuMn$_6$O$_{12}$ is obtained from the V/$\nu_0$ = $P$ relationship ($V$ and $\nu_0$ are the volumes at pressure $P$ and at atmosphere). The bulk modulus $B_0$ is calculated based on the Birch–Murnaghan equation. Low temperature x-ray diffraction shows no phase transition occurring down to 160 K.

PACS: 75.47.Gk, 91.60.Gf, 41.60.Ap

Manganese perovskite materials have attracted a great deal of attention of scientists because of the interesting interplay among their magnetic, electronic and structural properties.$^{[1-3]}$ Most of the works are about rare-earth manganese perovskites with formula Ln$_{1-x}$A$_x$MnO$_3$ (Ln=rare earth, A=alkaline earth), which show fascinating magnetic, charge and orbital orderings and high magnetoresistance (MR). The colossal magnetoresistance (CMR) can be explained by the applied magnetic field enhanced double-exchange (DE) interaction, which increases the hopping probability of itinerant $e_g$ charges between Mn$^{3+}$ and Mn$^{4+}$. However, these high MR values only occur around the ferromagnetic transition temperature $T_C$, insulator–metal transition temperature $T_{IM}$ and at high magnetic fields. Their low MR values at low magnetic fields and at room temperature limit their practical applications. In order to obtain applicable CMR materials, great efforts have been taken to searching for other new CMR materials, such as double-perovskite structure Sr$_2$FeMoO$_6$,$^{[4]}$ pyrochlore structure Ti$_2$Mn$_2$O$_7$,$^{[5]}$ and CaCu$_x$Mn$_{7-x}$O$_{12}$,$^{[6-9]}$ whose MR mechanism originates from spin polarized inter-grain tunneling.

The CaCu$_x$Mn$_{7-x}$O$_{12}$ ($0 < x \leq 3$) family has a cubic structure with a space group $Im-3$ and represents an $AA'$$_2$B$_3$O$_{12}$ perovskite-like phase with cell parameters of twice the ideal perovskite. Here $A$ is generally a monovalent, divalent or rare earth cation, $A'$ is a Jahn–Teller cation Cu$^{2+}$ or Mn$^{3+}$, and $B$ can be Mn$^{3+}$/Mn$^{4+}$. It is assumed that strong antiferromagnetic exchange interaction exists between Cu$^{2+}$ ions at $A'$ positions and Mn$^{3+}$/Mn$^{4+}$ at $B$ positions. However, the Mn$^{3+}$ ions at the $A'$ position are coupled to Mn$^{3+}$/Mn$^{4+}$ at the $B$ position ferromagnetically, which was confirmed by the experimental observations.$^{[10]}$ The small radii of $A$ and $A'$ lead to a tilted three-dimensional network of BO$_6$ octahedron sharing corners.$^{[11]}$ a slightly distorted 12 oxygen coordinated $A$ site and a grossly distorted icosahedron at $A'$ site. The tilting of the MnO$_6$ octahedra is mainly determined by Cu$^{2+}$ ions versus the cations at $A$ positions, but the Mn-O-Mn angle shows very little sensitivity to the size of the cations at $A$ positions.$^{[12]}$ High pressure can affect the crystal structure, electronic structure and magnetic structures of perovskites and layered perovskites.$^{[13-15]}$ In order to investigate the structural and electrical properties of this perovskite-like structure system under high pressure, we carried out in situ high pressure synchrotron radiation x-ray diffraction (XRD) measurements, high pressure resistance measurements and XRD measurements at ambient temperature and 160 K for CaCuMn$_6$O$_{12}$.

The polycrystalline CaCuMn$_6$O$_{12}$ was prepared by using a traditional solid-state reaction method. CaO, CuO, MnO$_2$, and KClO$_4$ (30% in weight added as mineralizer) were mixed thoroughly with stoichiometric ratios in an agate mortar and pressed into pellets.$^{[7,8]}$ The pellets were sintered at 850°C for 10 h in an oxygen flow. The room-temperature XRD measurements were performed using an M18AHF diffractometer with Cu K$_\alpha$. In situ high pressure synchrotron radiation XRD diffraction experiments on CaCuMn$_6$O$_{12}$ were carried out with a diamond anvil cell (DAC), with a culet of 500 $\mu$m, using synchrotron white radiation at the Beijing Synchrotron Radiation Laboratory (BSRL). The size of the x-ray spot was 30$\times$20 $\mu$m and the diffraction angle was 9° in our experiments. The powder of CaCuMn$_6$O$_{12}$ was loaded, together with a Rudy for internal pressure calibration, into a diameter of 250 $\mu$m hole in a T301 stainless-steel gasket. Methanol:ethanol:water (16:3:1) mixture was used as

---

* Supported by the National Natural Science Foundation of China under Grant Nos 50471053, 10274099, 50321101 and 50332020, and the State Key Basic Research Programme of China under Grant Nos 2005CB623602 and 2005CB724402.

** To whom correspondence should be addressed. Email: rcyu@aphy.iphy.ac.cn
©2007 Chinese Physical Society and IOP Publishing Ltd
the pressure-transmitting medium. The resistances of CaCuMn₆O₁₂ under different pressures were measured in another DAC. The resistances were measured with a ZL5 intelligent LCR meter. The powder sample studied was pre-pressed under 3 GPa before the measurements. The technologic details used for the DAC and the measurements were the same as those used previously.¹⁶,¹⁷

Figure 1 shows the XRD pattern of CaCuMn₆O₁₂ and the inset is the structure of CaCuMn₆O₁₂ indicating the MnO₆ polyhedral structure. No impurity was detected in the sample and all the peaks can be indexed with a space group of Im3, and crystal lattice constant a = 7.342 Å, which is double lattice constant of an ideal perovskite. Mineralizer KClO₄ was decompounded to KCl and O₂ at 600°C, and all the KCl vaporized away during sintering at 850°C for 10 hours in oxygen flow. A series of electric diffraction (ED) patterns was obtained from the sample, and the ED patterns from three main zones [100], [110], [111] are shown in figure 2. High-resolution transmission electron microscopy (HRTEM) image of the CaCuMn₆O₁₂ taken along the [111] zone axis is presented in figure 2 too. Both ED patterns and HRTEM image show the characteristics of a cubic structure, which accords with the result of the XRD experiment.

![Fig. 1. XRD pattern of CaCuMn₆O₁₂. Inset: the structure of CaCuMn₆O₁₂ indicating the MnO₆ polyhedral structure.](image)

In the measured pressure range of 0–31.24 GPa though an electronic structural change occurs at 1.1 GPa,¹⁸

![Fig. 2. Electron diffraction patterns of CaCuMn₆O₁₂ and high-resolution transmission electron microscopy image of CaCuMn₆O₁₂ along the [111] zone axis.](image)

![Fig. 3. Energy-dispersive x-ray diffraction patterns of CaCuMn₆O₁₂ at different pressures.](image)

The crystal lattice parameter decreases gradually with pressure and the V/V₀ − P relationship is presented in the pressure range of 0–31.24 GPa, as shown in Fig. 4. The experimental data are fitted by the Birch–Murnaghan (BM) equation

\[
P = \frac{3}{2} B₀ \left[ \left( \frac{V}{V₀} \right)^{-7/3} - \left( \frac{V}{V₀} \right)^{-5/3} \right] \times \left\{ 1 - \frac{3}{4} (4 - B₀) \times \left[ \left( \frac{V}{V₀} \right)^{-2/3} - 1 \right] \right\}
\]

by assuming its first-order derivative B₀'' = 4 for CaCuMn₆O₁₂, the bulk modulus B₀ is obtained to be B₀ = 230 ± 2 GPa.

Figure 5 depicts the XRD patterns recorded at 160 K and 300 K. No difference is observed between the two patterns expect little lattice parameter change from a = 7.342 Å to 7.334 Å, indicating that there is
no crystal structural change occurring at low temperature down to 160 K.

**Fig. 4.** Characteristics of volume ratio $V/V_0$ versus pressure $P$ for CaCuMn$_6$O$_{12}$. The circles represent the experimental data and the solid line represents the fitted curve.

**Fig. 5.** XRD patterns of CaCuMn$_6$O$_{12}$ under different temperatures.

**Fig. 6.** Dependence of resistance $R$ on pressure $P$ for CaCuMn$_6$O$_{12}$.

Figure 6 presents the pressure dependence of the resistance of the CaCuMn$_6$O$_{12}$ at room temperature. The resistance of the sample remains nearly a constant at first ($0 \leq P \leq 2$ GPa), because the powder sample was pre-pressed at 3 GPa. Then the resistance decreases abruptly in the range of $2 \leq P \leq 4$ GPa due to the compact connection of the sample grains under pressure. With further increase of pressure up to 20 GPa, the resistance decreases slowly and no abrupt change appears, indicating that there is no phase transition occurring in the measured pressure range. The concluded results from the resistance measurements agree with those from the high pressure synchrotron radiation XRD experiments.

The crystal structural stability of the sintered cubic CaCuMn$_6$O$_{12}$ with a space group of $Im-3$ has been studied by the energy-dispersive x-ray diffraction carried out with synchrotron radiation under high pressures up to 31.24 GPa. The electrical properties have also been studied by the measurements of its resistance under high pressure. Both the experiments indicate that the crystal structure of the compound is stable in the measured pressure range. Low temperature XRD experiments suggest that there is no phase transition in CaCuMn$_6$O$_{12}$ but little decrease of the lattice parameter down to 160 K. The equation of state of CaCuMn$_6$O$_{12}$, based on the BM equation, is obtained from the $V/V_0 - P$ relationship, and the bulk modulus and its pressure derivative are also obtained.

**References**

[1] Zener C 1951 Phys. Rev. 82 403