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To cite this article: D V S Muthu et al 2012 J. Phys.: Conf. Ser. 377 012025

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High-pressure synchrotron x-ray diffraction study of RMnO₃ (R = Eu, Gd, Tb and Dy) up to 50 GPa

D V S Muthu¹, A E Midgley², P R Scott², M B Kruger², J R Sahu³, A K Sood¹ and C N R Rao³

¹Department of Physics, Indian Institute of Science, Bangalore – 560012. India
²Department of Physics, University of Missouri, Kansas City 64110 USA
³Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore – 560064. India

Abstract. We have carried out synchrotron based high-pressure x-ray diffraction study of orthorhombic EuMnO₃, GdMnO₃, TbMnO₃ and DyMnO₃ up to 54.4, 41.6, 47.0 and 50.2 GPa, respectively. The diffraction peaks of all the four manganites shift monotonically to higher diffraction angles and the crystals retain the orthorhombic structure till the highest pressure. We have fitted the observed volume versus pressure data with the Birch-Murnaghan equation of state and determined the bulk modulus to be 185 ± 6 GPa, 190 ± 16 GPa, 188 ± 9 GPa and 192 ± 8 GPa for EuMnO₃, GdMnO₃, TbMnO₃ and DyMnO₃, respectively. The bulk modulus of EuMnO₃ is comparable to other manganites, in contrast to theoretical predictions.

1. Introduction
Rare-earth manganites RMnO₃ (R = Eu, Gd, Tb, and Dy) have attracted a lot of interest due to their coupling between ferroelectric and anti-ferromagnetic properties [1]. RMnO₃ compounds which contain large R ions crystallize in the orthorhombic structure while those with smaller R ions crystallize in hexagonal structure. The boundary between these structures is present between Dy and Ho. At room temperature, R = Eu, Gd, Tb and Dy are paraelectric and paramagnetic with a distorted perovskite structure (due to tilting and deformation of MnO₆ octahedra) of orthorhombic symmetry with space group Pbnm [2 - 4]. In comparison to many studies under temperature and magnetic field, only a few experimental studies have been reported under pressure in perovskite RMnO₃, R = Tb and Dy [5, 6] and R = La, Pr and Sm [7-10]. Theoretical calculations [11] have shown that the bulk moduli in RMnO₃ (R = Dy-La) decreases with increasing molar volume with an anomalous dip for EuMnO₃. This motivated us to perform high pressure synchrotron based x-ray diffraction measurements on Eu, Gd, Tb and DyMnO₃ to determine the equation of state and look for possible phase transitions.

2. Experimental
High-pressure x-ray experiments were performed at room temperature at beamline X17C of the National Synchrotron Light Source at Brookhaven National Laboratory. Powder samples were loaded along with ruby chips, into a hole of ~100 µm diameter drilled in a pre-indented steel gasket. A Mao-Bell type diamond-anvil cell (DAC) was used with methanol:ethanol (4:1) mixture as pressure-transmitting medium. Pressure was monitored using the ruby fluorescence technique [12].
experiments were carried out up to ~50 GPa using monochromatic x-rays (\(\lambda = 0.4066\) Å) and a two-dimensional (2D) imaging plate. The sample to imaging plate distances were 209.22 mm for EuMnO\(_3\), 185.02 mm for Gd (Tb) MnO\(_3\) and 185.09 mm for DyMnO\(_3\). The 2D images were transformed into plots of intensity versus 20 by radial integration using the FIT2D software package. Since the ambient structure is known, the lattice parameters and unit cell volumes were determined at each pressure by profile refinement of all four samples using Jana2000 package [13] without doing structural refinement. The equation of state was determined from the observed volume versus pressure using Igor Pro software.

3. Results and discussion

Eu, Gd, Tb and DyMnO\(_3\) crystallize in the orthorhombic structure (space group Pbnm -no. 62). With increasing pressure the diffraction peaks shift monotonically to higher diffraction angle value till the highest pressures without any phase transition. The lattice parameters and unit cell volumes at each pressure were determined. The zero pressure bulk modulus is found to show a small increase with decreasing ionic radius (molar volume also decreases).

3.1. EuMnO\(_3\)

Figure 1a shows x-ray diffraction patterns, after background subtraction at selected pressures of EuMnO\(_3\). With increasing pressure the diffraction peaks shift to higher angular values (decrease in d-spacing). The decompressed sample (from 54.4 GPa) with little broadening of peaks compared to the lowest starting pressure diffraction peaks. Profile fitting of the diffraction peak taken at 0.2 GPa yields the lattice parameters \(a = 5.3479\) Å, \(b = 5.8459\) Å, and \(c = 7.4578\) Å and the unit cell volume \(V = 233.2\) Å\(^3\) which matches with an earlier report [2]. The cell parameters and the unit cell volume were subsequently determined for each pressure. The pressure versus unit cell volume is shown in figure 1b. The experimental data were fitted using the Birch-Murnaghan equation of state (EOS) (\(P = 1.5K_0[(V/V_0)^{7/3} - (V/V_0)^{5/3}] [1 + 3/4 (K_0 - 4) [(V/V_0)^{-2/3} - 1]]\), where \(V_0\) is the unit cell volume, \(K_0\) is the bulk modulus and \(K_0'\) is the first pressure derivative of bulk modulus under ambient pressure) [14]: yields a bulk modulus of \(K_0 = 185 \pm 6\) GPa, and its first pressure derivative \(K_0' = 3.7 \pm 0.5\).

3.2 GdMnO\(_3\)

The lattice parameters and the unit cell volume of GdMnO\(_3\) at the lowest pressure were determined to be: \(a = 5.3202\) Å, \(b = 5.8627\) Å, \(c = 7.4291\) Å and \(V = 231.7\) Å\(^3\) which are in good agreement with the reported values [2]. Figure 2a shows the variation of the unit cell volume with pressure. The solid line

![Figure 1(a) Diffraction patterns of EuMnO\(_3\) at a few representative pressures, (b) Pressure versus unit cell volume. Solid (open) circles represent unit cell volumes for compression (decompression) pressure. The solid line represents the Birch-Murnaghan equation of state.](image_url)
represents the Birch-Murnaghan EOS fit to the experimental data. This yields a bulk modulus of $190 \pm 16$ GPa and a first pressure derivative of $3.2 \pm 1.6$.

### 3.3 TbMnO$_3$

Profile refinement of the diffraction peaks collected at 0.2 GPa yields the lattice parameters: $a = 5.2939$ Å, $b = 5.8407$ Å, $c = 7.3886$ Å and $V = 228.5$ Å$^3$ which match with previously reported values [3]. Chen et al. have reported pressure-induced variations of the electronic state as well as structural distortion of Tb and DyMnO$_3$ but the equation state was not measured [5, 6]. The pressure dependence of the unit cell volume for TbMnO$_3$ is shown in Figure 2b. The bulk modulus and its pressure derivative were determined by fitting the Birch-Murnaghan EOS to the data. The results are $K_0 = 188 \pm 9$ GPa and $K_0' = 8.9 \pm 1.2$.

![Figure 2](image1.png)

Figure 2 (a) Pressure dependence of unit cell volume for GdMnO$_3$. (b) Pressure dependence of unit cell volume for TbMnO$_3$. Solid (open) circles represent unit cell volumes for compression (decompression) pressure. The solid line represents the Birch-Murnaghan EOS.

### 3.4 DyMnO$_3$

The lattice parameters and unit cell volume ($a = 5.2713$ Å, $b = 5.8335$ Å, $c = 7.3786$ Å and $V = 226.9$ Å$^3$) were determined from the profile refinement of the diffraction pattern recorded at the lowest pressure (0.7 GPa). Figure 3 shows the pressure dependence of the unit cell volume. The Birch-Murnaghan EOS fit to the pressure versus volume data yields a bulk modulus of $K_0 = 192 \pm 8$ GPa and its first pressure derivative $K_0' = 1.6 \pm 0.6$.

![Figure 3](image2.png)

Figure 3. Pressure dependence of unit cell volume for DyMnO$_3$. Solid (open) circles represent unit cell volumes for compression (decompression) pressure. The solid line represents the Birch-Murnaghan EOS.

Figure 4 shows the molar volume dependence of bulk modulus of RMnO$_3$. As the ionic radius decreases from La-Dy more distortion is introduced because the buckling of Mn-O-Mn angle increases
and the structure deviates from orthorhombic to distorted orthorhombic. The unit cell volume decreases as the distortion increases correspondingly the bulk modulus increases. A noteworthy observation from figure 4 is that the experimental value of the bulk modulus for EuMnO₃ does not show an anomalous decrease as compared to the theoretical predictions [11].

![Figure 4](image_url)

**Figure 4.** Molar volume dependence of bulk modulus for various RMnO₃. Filled squares represent experimental values. The values for La, Pr and SmMnO₃ are taken from Ref. 7 and 8. Open squares represent the theoretical values from Ref. 11.

4. Conclusion

In conclusion, we have performed a synchrotron based high-pressure study on rare-earth manganites, RMnO₃ (R = Eu, Gd, Tb and Dy) up to 54.4, 41.6, 47.0 and 50.2 GPa, respectively. Our studies do not reveal any phase transition, and structure remains orthorhombic till the highest pressures. The fit to the experimental data using the Birch-Murnaghan EOS yields the zero pressure bulk modulus to be 185, 190, 188 and 192 GPa in Eu, Gd, Tb and DyMnO₃, respectively. These values are compared with the theoretical predictions [11].

5. Acknowledgments

AKS thanks Department of Science and Technology, India for financial assistance. This work was partially supported by NSF Contract Number DMR-0605493, NSF COMPRES EAR 10-43050. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

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