High-pressure Raman study of MgV_2O_6 synthesized at high pressure and high temperature*

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A new structural phase of MgV_2O_6 was obtained by a high-pressure, high-temperature (HPHT) synthesis method. The new phase was investigated by the Rietveld analysis of X-ray powder diffraction data, showing space group *Pbcn* (No. 60) symmetry and $a = 13.6113(6)$ Å (1 Å = 0.1 nm), $b = 5.5809(1)$ Å, $c = 4.8566(3)$ Å, $V = 368.93(2)$ Å^3 ($Z = 4$). High pressure behavior was studied by Raman spectroscopy at room temperature. Under 22.5 GPa, there was no sign of a structural phase transition in the spectra, demonstrating stability of the HPHT phase up to the highest pressure.

Keywords: high-pressure and high-temperature, MgV_2O_6, Raman spectroscopy, high-pressure

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1. Introduction

Vanadium oxide compounds have attracted considerable attention in recent years because their unique electronic and ionic characteristics have potential applications in catalysts and are suitable for cathode materials in batteries and electrochromic devices.[1–5] As rechargeable divalent metal battery cathode materials, the electrochemical properties of vanadium-based oxides depend heavily on the synthesis and processing methods.[6,7] So far, several synthesis methods have been reported for MV_2O_6 (M = Mg, Ca, Mn, Co, Cu, Zn), such as a rheological phase reactions method,[8] solid-state reactions,[9–11] a sol–gel method,[12] a high-pressure, high-temperature (HPHT) method,[13] and wet chemical reactions at low temperatures.[14] A variety of structural symmetries can be found in MV_2O_6 synthesized at ambient pressure, from orthorhombic to triclinic, and all of them belong to the brannerite or thorutite ($ThTi_2O_6$) structure category. In brannerite structures, the M^{2+} ions are octahedrally coordinated and the V^{5+} ions have a $5+1$ coordination. The vanadium ions are occasionally described as 5-coordinated because the sixth oxygen atom is only weakly bonded at distances of 2.4 Å–2.8 Å.[15,16] Except for M = Mn, MV_2O_6 will transform at high pressure synthesis to the orthorhombic columbite ($FeNb_2O_6$) structure. The transition from a brannerite structure to a columbite structure involves an increase of V^{5+} coordination from $5+1$ to 6, a change in oxygen packing from cubic close-packed to hexagonal close-packed, a retention of the partial structure of the VO_6 sheets and a collapse of the MO_6 rutile-like chains into α-PbO_2 chains. High-pressure polymorphs are usually denser (6%∼10% for MV_2O_6 phases) than their ambient pressure counterparts, and often have layered or close-packed structures. Layered structures are quite promising for applications as cathode materials. Therefore, the investigation of the high-pressure MV_2O_6 polymorphs in addition to their ambient pressure modifications will be useful for their possible applications. However, the crystal structures of the HPHT synthesis of MV_2O_6 compounds at high pressure have not been investigated yet, although their ambient X-ray patterns have been reported.[13] In this paper, we report the preparation of a single phase of a high-pressure modified MgV_2O_6 and its resolved crystal structure. In addition, *in situ* Raman spectra were obtained in a diamond anvil cell (DAC) up to 22.5 GPa. Better understanding of the structural properties and electrical transport properties of MgV_2O_6 under pressure could contribute to improving the designs of electrode devices in the future.

2. Experiments

Samples of MgV_2O_6 were synthesized by HPHT. The samples were prepared from MgO (99.99% in purity) and V_2O_5 (99.99%) powders, weighed according to the stoichiometric ratio. After being uniformly mixed in an agate mortar, the mixtures were pressed into a disk with a diameter of 8 mm and a height of 2 mm. The sample disks were positioned for HPHT synthesis in a cubic anvil high-pressure apparatus on an edge at 1273 K and 5 GPa. The temperature and pressure were kept for 60 min. An X-ray diffraction system (Rigaku) with Cu Kα radiation ($\lambda = 1.5418$ Å) was used to determine the crystal structure.

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For high-pressure Raman experiments, the DAC was utilized to generate high pressure and the T301 stainless steel gasket was pre-indented to 50-μm thickness. MgV_2O_6 (HPHT) was loaded into the DAC with chips of ruby for measuring the chamber pressure by the ruby fluorescence technique.[17] High-pressure Raman experiments were carried out at room temperature up to 22.5 GPa. A mixture of 16:3:1 (methanol/ethanol/water) was chosen as the pressure transmitting medium. The measured pressure difference of various ruby fluorescence signals remained well separated throughout the experiment, indicating that a good quasi-hydrostatic condition was maintained even when the pressure medium was solidified. A commercial spectrometer (Renishaw inVia Raman microscope) in combination with a charge-coupled device (CCD) detector was used to collect all the Raman spectra in backscattering geometry. The sample was excited by the 514.5 nm of an argon–ion laser with a power of 10 mW. Pressure-induced shifts of overlapping Raman bands were analyzed by fitting the spectra with Lorentzian functions to determine the line shape parameters.

3. Results and discussion

The crystal structure data were refined by Rietveld analysis of the X-ray powder diffraction data with GSAS software.[18] The observed and calculated XRD patterns along with the difference plot are shown in Fig. 1. The typical refined unit cell and profile parameters along with the refinement indices are summarized in Table 1. The refined atomic position coordinates are given in Table 2. The typical bond lengths of various atoms are given in Table 3. The crystal structure of the HPHT phase of MgV_2O_6 shows that Mg and V cations are situated at the center of the octahedra surrounded by six oxygen atoms. The MgO_6 and VO_6 octahedra form independent zigzag chains by sharing edges, and the chains are connected by sharing corners in the order of MgO_6 chain–VO_6 chain–VO_6 chain,[19] as shown in the inset of Fig. 1.

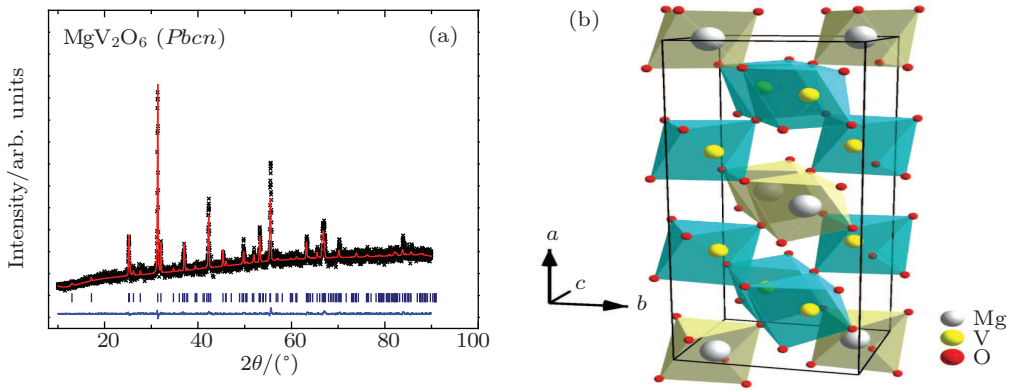


Fig. 1. (color online) (a) Rietveld refinement of the room temperature XRD pattern of MgV_2O_6 (HPHT) with a columbite structure. The cross mark is the observed data and the solid line is the calculated pattern. The vertical bars mark all possible Bragg reflections. The difference between the observed and calculated patterns is shown at the bottom. (b) Crystal structures of MgV_2O_6 (HPHT) with orthorhombic *Pbcn* symmetry. Blue polyhedra represent the VO_6 octahedra and yellow polyhedra the MgO_6 octahedra.

Table 1. Crystallographic data for MgV_2O_6 (HPHT).

Color	Black
Chemical formula	MgV_2O_6
Space group	*Pbcn* (No. 60)
Z	4
a/Å	13.6113(6)
b/Å	5.5809(1)
c/Å	4.8566(3)
Volume/Å^3	368.93(2)
Density/g·cm^{-3}	4.0
2θ range/(°)	10–90
R_p/%	8.44
R_{wp}/%	11.27

Table 2. Refined atomic coordinates for MgV_2O_6 (HPHT).

Atom	Site	*x*	*y*	*z*
Mg	4*c*	0	0.1596(9)	0.25
V	8*d*	0.1603(1)	0.3183(5)	0.7716(1)
O1	8*d*	0.0788(2)	0.3783(5)	0.4122(5)
O2	8*d*	0.0847(8)	0.1149(1)	0.9198(6)
O3	8*d*	0.2539(9)	0.1312(2)	0.6146(9)

Table 3. Typical inter-atomic distances d_{1-2}/Å in MgV_2O_6 (HPHT).

Atom 1	Atom 2	Count	d_{1-2}/Å
Mg	O1	2x	1.805(9)
	O2	2x	1.991(6)
	O2	2x	2.088(3)
V	O2	1x	1.692(3)
	O3	1x	1.815(5)
	O3	1x	2.053(8)
	O1	1x	2.094(7)
	O1	1x	2.135(6)
	O3	1x	2.234(4)

Figure 2(a) shows the room temperature Raman spectra of MgV_2O_6 (HPHT) for selected pressures in the spectral range of 100 cm^{-1}–1200 cm^{-1}. In our Raman measurements at ambient pressure, 15 Raman-active modes can be observed. The Raman spectra collected for MgV_2O_6 (HPHT) exhibit a common feature: two major Raman modes with strong intensity appear at 596.3 cm^{-1} and 915.7 cm^{-1}, and the rest of

the modes have relatively weak intensity. The lack of lattice dynamics studies of MgV_2O_6 (HPHT) make it somewhat difficult to discuss the behavior of Raman modes at high pressure without knowing the mode assignments. Since MgV_2O_6 transforms at HPHT synthesis to the orthorhombic columbite ($MgNb_2O_6$) structure, one might expect some similarities in the Raman spectra. In this case, some Raman modes could remain unchanged in $MgNb_2O_6$, as noted by Husson *et al.*[20,21] who studied the Raman spectra of the columbite structure. Therefore, the modes were due to the V–O stretching and covered a wide range from about 400 cm^{-1} to 950 cm^{-1}. From about 100 cm^{-1} to 400 cm^{-1}, O–V–O bending vibrations were observed, and they contributed to the deformation of both the octahedra and the chains and also contributed to the inter-chain vibrations.

With increasing pressure, it was found that MgV_2O_6 (HPHT) remained stable up to 22.5 GPa. Figure 2(b) shows the pressure dependence of Raman shifts of MgV_2O_6 (HPHT) at room temperature. All the observed phonon modes show monotonous increases in frequency under increasing pressure. Although some Raman modes of MgV_2O_6 (HPHT) merge into one band above 13.1 GPa, the behavior could be interpreted as one Raman band crossing over another band. Our Raman result is in close agreement with the report of Husson *et al.*,[22] i.e. that the columbite structure is very stable.

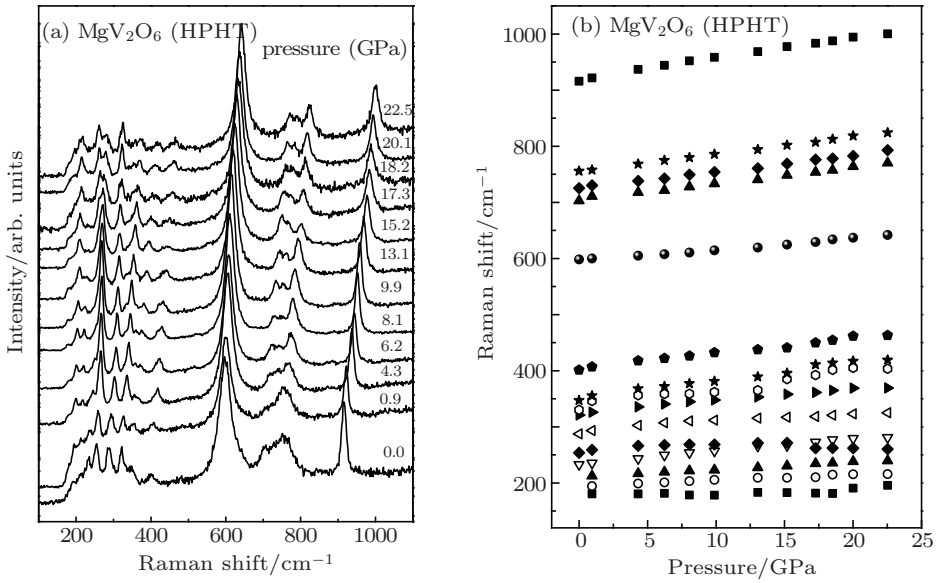


Fig. 2. (a) Representative room temperature Raman spectra of MgV_2O_6 (HPHT) at various pressures. (b) Pressure dependence of the shifts of Raman active modes for MgV_2O_6 (HPHT).

4. Conclusions

Rietveld refinement of X-ray powder diffraction data reveals a new crystal structure of MgV_2O_6 prepared by high-pressure, high-temperature synthesis, and the new phase has a columbite-type layered structure. Furthermore, we carried out a Raman scattering study of MgV_2O_6 (HPHT) under high pressures. The high pressure Raman measurements show that the new structure remains stable up to 22.5 GPa. These results should be helpful for understanding the physical properties of MgV_2O_6 (HPHT) and future investigations. Further work on the investigation of the possibility of pressure-induced phase transition from the ambient phase to the HPHT phase in MgV_2O_6 is in progress.

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