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Experimental and theoretical studies of optical and nonlinear optical properties for $MnTeMoO_6$ crystal

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ABSTRACT

$MnTeMoO_6$ crystal was obtained by top-seeded solution growth method. Optical and nonlinear optical properties of $MnTeMoO_6$ crystal were measured. Band structures, DOS, optical properties of $MnTeMoO_6$ were calculated. Both calculated and experiment results of the optical properties show that a transitional absorption band is exhibited in $MnTeMoO_6$ crystal. Second harmonic generation measurements show that the SHG response with fundamental wavelength 1.06 μm decreases to a quarter of that with fundamental wavelength 2.05 μm. The transitional absorption band has a great effect on the nonlinear optical property of $MnTeMoO_6$ crystal. The formation of the transitional absorption band in $MnTeMoO_6$ crystal would be attributed to the internal transitions of transition-meta ions with incomplete electron shells (Mn^{2+} $3d^3 4s^2$). In addition, the transitional absorption band plays an important role in the coloration of $MnTeMoO_6$ crystal, and the crystal can be made into selective optical oscillators and laser wavelength recognizing device by utilizing the characteristic of the transitional absorption band.

1. Introduction

$MnTeMoO_6$ crystal is a preponderant candidate for near-mid-IR nonlinear optical material. $MnTeMoO_6$ was first synthesized by Forzatti and Trifiro [1] in the 1970s, through the traditional solid-state reaction technique. It was first focused on its catalytic properties and used to be a highly selective catalyst for the oxidation of butene to butadiene and of propylene to acrolein [2,3]. After about three decades, the structure and magnetic properties of $MnTeMoO_6$ were reported by Doi et al. [4]. Our previous work reported the crystal growth of $MnTeMoO_6$ crystal [5]. It is found that a transitional absorption band in $MnTeMoO_6$ crystal, which could affect the second harmonic generation (SHG) efficiencies and application of this material [6–16]. Therefore, it is necessary to study the original of the transitional absorption band, which is beneficial to the application of $MnTeMoO_6$ crystal. In addition, the theoretical studies of electronic structures in $MnTeMoO_6$ can be better to explain the formation of the transitional absorption band.

In this study, we report band structure and density of states (DOS) of $MnTeMoO_6$ for the first time. Both experimental and theoretical studies were performed to investigate the optical properties of $MnTeMoO_6$ crystal. The measured nonlinear optical properties with different fundamental wavelength in $MnTeMoO_6$ crystal were reported. Furthermore, the original of the transitional absorption band, and the effect of the transitional absorption band on nonlinear optical properties for $MnTeMoO_6$ crystal were discussed.

2. Experimental and computational details

2.1. Crystal growth

$MnTeMoO_6$ crystal has been grown by the top-seeded solution growth (TSSG) method. The TeO_2–MoO_3 mixture was chosen as self-flux system. The temperature decreasing rate is 0.2–0.5 °C per day in the crystal growth process. The period of growth is about 50 days. Fig. 1 shows the as-grown $MnTeMoO_6$ crystal. The size of as-grown crystal is 15 × 10 × 3 mm^3. The crystal is rufous and transparent.

2.2. Characterizations

The single crystal structure of $MnTeMoO_6$ was determined by the single crystal X-ray diffraction on a Bruker SMART APEX-II

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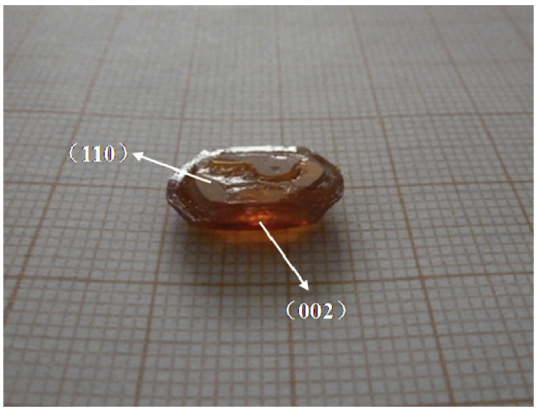

Fig. 1. As-grown $MnTeMoO_6$ crystal. Note that the size of crystal is 15 × 10 × 3 mm^3.

diffractometer equipped with a CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298(2) K. A rufous and transparent crystal with dimensions of 0.05 × 0.02 × 0.02 mm^3 was chosen for structure determination. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Data integration and cell refinement were done by the INTEGRATE program of the APEX-2 software [17], and multi-scan absorption corrections were applied using the SCALE program for the area detector [17]. The structure was solved in the space group $P\bar{4}2_1m$ (No.113) by direct methods and refined by full matrix least-squares methods on F^2, and the refinements converged for $I > 2\sigma$ (I). All calculations were performed using the SHELXTL crystallographic software package [18]. A symmetry analysis on the model using PLATON [19] revealed that no obvious space group change was needed. Details of crystal parameters, data collection and structure refinement are summarized in Table 1. The final refined atomic coordinates and isotropic displacement parameters are summarized in Table S1 in the supplementary material. The selected bond distances (Å) and angles (deg) are given in Table S2, and the anisotropic displacement parameters are listed in Table S3. Additional information in the form of CIF (Depository number: CCDC 1403672) is available in the supplementary material.

Table 1
Crystallographic data and structural refinements for $MnTeMoO_6$.

Formula	$MnTeMoO_6$
Formula weight (g/mol)	374.48
Temperature (K)	298(2)
Radiation, wavelength (Å)	Mo Kα, 0.71073
Crystal system	Tetraganol
Space group	$P\bar{4}2_1m$ (No.113)
Unit cell dimensions (Å)	a = 5.227(2)
	b = 5.227(2)
	c = 8.969(8)
Unit cell volume ($Å^3$)	245.0(3)
Z	2
D_c (g/cm^3)	5.075
Absorption coefficient (mm^{-1})	10.916
F(000)	334
Crystal size (mm^3)	0.05 × 0.02 × 0.02
Theta range for data collection (°)	2.27 to 30.91
Index ranges	$-7 \le h \le 7$, $-7 \le k \le 6$, $-9 \le l \le 12$
Reflections collected	1828
Independent reflections	432 [R(int) = 0.0607]
Completeness to theta = 30.91	98.5%
Absorption correction	None
Max. and min. transmission	0.8112 and 0.6113
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	432/6/30
Goodness-of-fit on F^2	1.315
Final R indices $[F_o^2 > 2\sigma(F_o^2)]$	R_1 = 0.0584, wR_2 = 0.1464
R indices (all data)	R_1 = 0.0650, wR_2 = 0.1510
$R_1 = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$, $wR_2 = \{\sum w[(F_0)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$	

UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV-2550 spectrometer in the range of 240–850 nm at room temperature. $BaSO_4$ was used as a reference material. The crystal sample with a thickness of about 1 mm was cut from the as-grown crystal and parallel to {001} plane.

Powder second harmonic generation measurement was carried out on the modified method of Kurtz and Perry [20]. Crystal powder samples of $MnTeMoO_6$ were ground and sieved into 150–200 μm. The fundamental wavelength, 1.06 μm or 2.05 μm, was generated by Q-switched lasers. Sieved KDP or KTP powder (150–200 μm) was used as a reference.

2.3. Computational details

Single-crystal structural data of $MnTeMoO_6$ was used for the theoretical calculations. Band structure, DOS, optical property calculations were performed with the commercial software CASTEP code in Materials Studio of Accelrys Inc. [21,22] by using the first-principles calculations based on density functional theory (DFT) [23,24]. The ultrasoft pseudo-potential [25] is adopted to describe the ion–electron interaction. The generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) functional [26] is used to describe the exchange and correlation energy in our calculations. The following orbital electrons were treated as valence electrons: Mn $3d^54s^2$, Te $5s^25p^4$, Mo $4d^55s^1$ and O $2s^22p^4$. In order to consider the localized states in the transition elements Mn and Mo, the DFT + U [27] method with an additional on-site d orbital dependent correlation Hubbard U was adopted to calculate the electronic structure in $MnTeMoO_6$ as well. Kinetic energy cutoff 300 eV and Monkhorst–Pack [28] k-point meshes with a density of 4 × 4 × 2 points in the Brillouin zone were chosen. Our convergence tests show that the choice of the above computational parameters is sufficiently accurate for this study.

3. Results and discussion

3.1. Theoretical studies

To understand electronic structures of $MnTeMoO_6$, band structures as well as DOS calculations based on the DFT method are

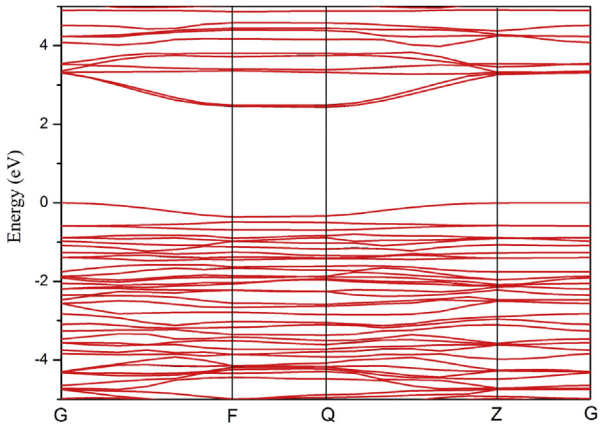

Fig. 2. Band structure of $MnTeMoO_6$ (bands are shown only between −5 and 5 eV for clarity).