| | |
|---|---|
| INTERNAL RAMAN MODES OF MULTIFERROIC MnWO4 | MODE RAMAN NỘI CỦA VẬT LIỆU TỔ HỢP SẮT TỪ/SẮT ĐIỆN MnWO4 |

ABSTRACT
We have studied Raman spectra of multiferroic monoclinic MnWO4 single crystals as a function of temperature. A polarization analysis of the spectra collected from oriented single crystals allows us to completely assign the symmetries of the 18 observed peaks, as expected from theoretical analysis. The six internal modes have been identified by their weak temperature dependence. Characteristic second-order Raman peaks have been assigned to overtones and combination of phonons with different symmetries.

TÓM TẮT
Chúng tôi nghiên cứu phổ Raman của đơn tinh thể MnWO4 multiferroic cấu trúc đơn tà theo nhiệt độ. Phân tích tính chất phân cực của phổ thu thập được từ các đơn tinh thể định hướng cho phép chúng ta xác định đặc tính đối xứng của 18 peak quan sát được phù hợp với dự đoán lý thuyết. Chúng tôi đã xác định được sáu mode nội từ tính chất phụ thuộc nhiệt độ yếu của chúng. Các peak Raman bậc hai đặc trưng đã được ấn định cho các overtone và sự kết hợp của các phonon với các đối xứng khác nhau.

Overtone: dao động bậc cao

Multiferroic: vật liệu có cả tính chất sắt từ và sắt điện

INTRODUCTION

MnWO4 is one member of magnetoelectric multiferroics materials, which currently attract considerable attention [1,2]. MnWO4 shows ferroelectric and magnetic order simultaneously and display coupling between these properties. The coupling between ferroelectric and magnetic order has show a strong interplay between electric polarization and magnetic order. Detailed studies of the magnetic of the magnetic ordering in this material [3] have shown that its Curie-Weiss constant 9 is —75 K, while magnetic order appears only below TN3 » 13.5 K. Below TN3, there are two more magnetic transitions at TN2» 12.5 K and TN1 » 6.5-8 K, and three magnetic ordered phases; AF1 (T <TN1), AF2 (TN1< T < TN2), and AF3 (TN2 < T < TN3) phases [4].

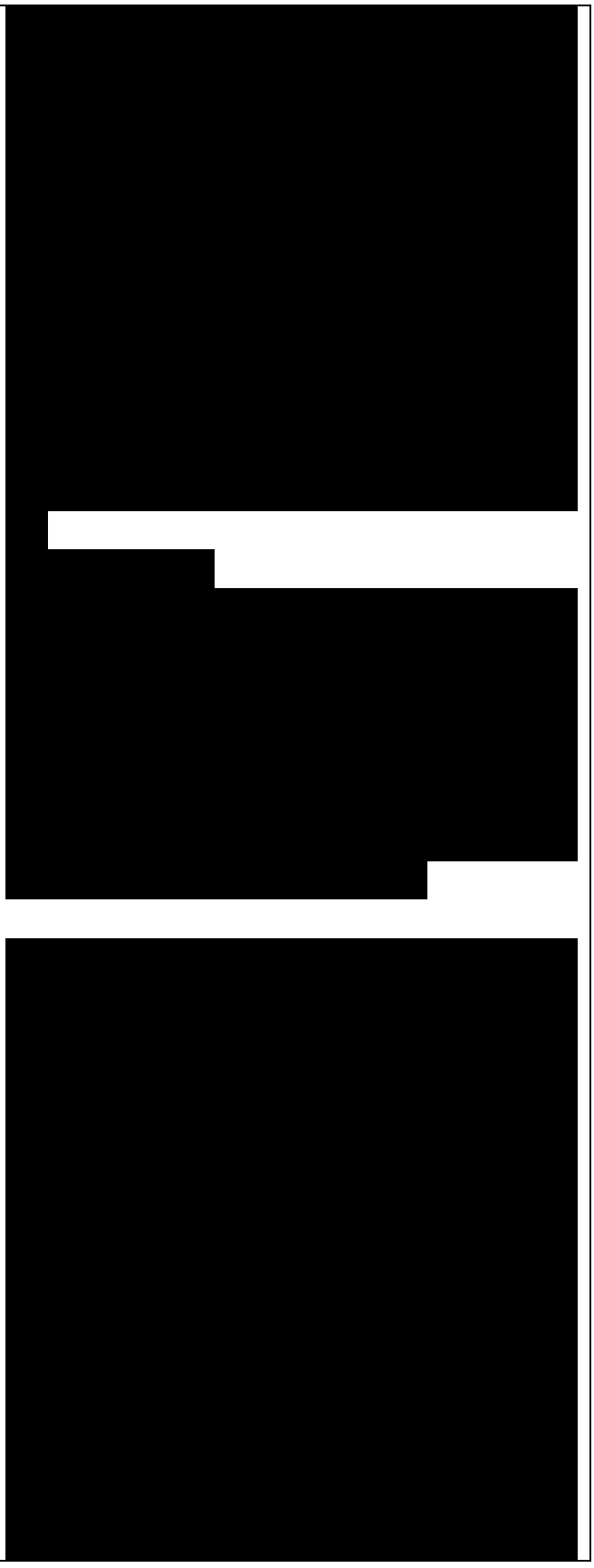
MnWO4 is isomorphic to those of a

group of tungstates (Zn, Fe, Hg...) that contain octahedral WO6 group. While studies of the optical properties and Raman spectra of ZnWO4 [5, 6], HgWO4 [7] has been reported in literatures, there have not been any worked related to Raman spectra of MnWO4 in our knowledge. In this paper, a complete assignment of the lattice modes of MnWO4 is done for the first time. The temperature dependent of frequency, line width of internal Raman modes, characteristic second-order Raman peak are discussed.

EXPERIMENT

Single crystals of MnWO4 were grown by the floating zone method. The resulting crystals appear to be blood red and transparent in thin section. The crystals were oriented using Laue x-ray photographs then cut and polished into a rectangular block of 2.5x2x1 mm3 with edges were parallel (within 10) to the crystallographic axes.

The Raman spectra were excited with the 647.1 nm line of Kripston laser in different back scattering geometries. In all cases, the laser power at the sample surface was about 2 mW. The micro-Raman measurements were performed using the Jobin-Yvon T64000 triple-mate instrument with a LN2-cooled charge-coupled device (CCD) detector. Full range spectra were obtained in the single mode of the spectrometer with 80 mm slit. The triple additive configuration with 50 mm slit was utilized to obtain the low frequency modes. A closed cycle helium cryostat was used to vary the sample temperature from 13 to 300K.



For each measurement, the temperature was stabilized for 20 min before acquiring a spectrum.

RESULTS AND DISCUSSION

MnWO4 is crystallized in a wolframite structure, which belong to monoclinic space group P2/c and C2h point-group with two formula groups per primitive cell. By making the correlation between site group and factor group for each site, then eliminating the acoustic mode, we obtain the proper vibrational modes of MnWO4: T(k=0) = 8Ag+ 10Bg +8Au + 10Bu,. Among them, all of the even (g) vibration (8Ag and 10Bg) are Raman active and the odd (u) vibrations (8Au+10Au) are IR active. The Raman tensors for each of these modes are given by:

As derived from the Raman tensors of the respective modes, all Ag and Bg modes can be distinguish observed in Z (XX) Z and Z(XY) Z configuration, respectively. Figure 1 shows polarized Raman spectra of MnWO4 obtained at 13 K in two different configurations that allow the observation of all the Raman active modes.

Fig.1. Raman spectra of MnWO4 in scattering geometries corresponding to Ag and Bg symmetries.

Although all Raman bands are strongly polarized, some of the Ag bands show weekly in the spectra for the Bg modes and vice versa. The frequency of all the Raman active modes in MnWO4 at 300K and 13K are listed in table 1, with their modes symmetry. It should be noted that the Bg mode at 179 cm-1 (peak 5) can be observed at temperature

lower than 180 K only.

For classifying the Raman active modes, a good approximation is to label vibration as internal or external. First of all, we separate the internal vibration modes associated with W-O from those associated with Mn-O bond.

This is reasonable since the strong electronegativity of hexavalent tungsten would result in highly covalent W-O bond and in more ionic Mn-O bond [7]. The internal vibrations of the tightly bound ions are expected in general to higher frequency than the external vibration. Moreover, the internal modes should have weak temperature dependence.

Table 1. Frequency of 18 Raman mode of MnWO4 at

The frequencies temperature dependence of 18 vibration modes of MnWO4 are shown in figure 2.

Fig.2. Frequency temperature dependence of the Raman modes of MnWO4.

It is clearly seen from figure 2 that the frequencies of the modes 12 (Ag), 15(Bg), 16 (Ag), 17 (Bg) and 18 (Ag) are weekly dependent on temperature. Therefore, we can assign these modes to internal modes. Base on the data of neutron diffraction of MnWO4 [7], we may consider the MnWO4 lattice interactions, which can be separated into internal vibrations in which an octahedral vibration WO6 as a unit. This assumption has been successful in applying to assign the internal mode of ZnWO4 [8]. The correlation diagram between the Oh symmetry of WO6

octahedral, C2 site symmetry and P2/c space group are shown in table 2.

Table 2. Correlation diagram for the internal modes of WO6 [8].

Group theoretical analysis confirms that 4Ag and 2Bg are internal modes. Since 3Ag and 2Bg modes have been assigned to internal mode of WO6 in MnWO4, there is one more Ag mode should be found. Among the remaining Ag modes, the mode 14 (548 cm-1) has lowest frequency temperature dependence; we may therefore assign this mode to the internal modes.

The linewidth of each internal mode at different temperatures was obtained by assuming a convolution of two lorentzians. In second order perturbation, the temperature dependence of linewidth arises only through cubic anharmonic interactions corresponding to decay and combination process. The best fit to the data of six internal modes are obtained by assuming only the combination of the observed phonon with another phonon of frequency w' to create a third excitation frequency w'', where, w''=w+w'. The linewiths of six internal modes are fitted with functions of the form [8].

(1)

Where, r0 is the linewidth at 0K, B is a temperature independent factor that reflect the strength of the cubic anhamornic interaction. n(w) is the Bose-Einstein occupation number:

Where, h is Planck's constant, c is the speed of light, kB is Bonltsmann's constant, and T is absolute temperature.

The best fit in the case of mode 12 (Ag),

13 (Bg) and 18 (Ag) are shown by solid lines in fig. 3.

Fig. 3. Temperature dependence of the linewidth of mode 12 (a), 15 (b) and 18 (c).

The resulting parameters for internal modes are listed in table 3.

Table 3. Best values of the parameter obtained form fitting equation (1) for linewidth of internal modes.

It can be seen from table 3 that the fitting values of w' and w'' for each internal modes contain two of the observed Raman frequencies that fitter by an average lower than 10% except the value w'' of the mode 18. However, the Raman frequency corresponds to such long wavelength (1094 cm-1) is not restricted to the wave vectors near the center of Brillouin zone [8].

We therefore prove that the temperature dependence of the linewidths of the internal modes of MnWO4 can be expressed in terms of anharmonic interactions.

Second order Raman scattering spectra of MnWO4 in different scattering configurations at 15 K and 300 K are shown in fig.4.

Fig. 4. Second-order polarized Raman spectra of MnWO4 at 13 and 300 K.

It is noticed that the overtones of Ag or Bg in the Brillouin zone always contribute to Ag symmetry, which can be observed in (xx) configuration. In contrary, the combinations of phonons belonging to different symmetries will never contain Ag representation.

The highest frequency of the two-phonon is expected to be at the double frequency

of the mode 18 (2 x 884 = 1768 cm-1). It can be clearly seen that, the bands at 1762 and 1399 cm-1 can be detected in both (xx) and (yx) polarized spectra. These bands therefore not only contributed by overtone of the highest frequency mode 18 (Ag, 884 cm-1) and mode 16 (Ag, 997 cm-1), respectively but combinations of phonon with different symmetries. The other bands at 1720, 1652, 1440, 1293 and 1076 cm-1, which are appeared in the (yx) polarized spectra (probe the Bg symmetry excitations), are probably due to combination of phonons with different symmetries.

CONCLUSION

The phonon excitations in monoclinic MnWO4 single crystals are studied by means of Raman scattering spectroscopy. The 18 zone-center vibration modes are assigned based on their polarization properties as expected from group theory analysis. The six internal modes have been identified by their weakly temperature dependent. The anharmonic broadening of the internal modes were studied as a function of temperature. Characteristic second-order Raman peak have been assigned to overtones and combination of phonons with different symmetries.