Vibrational Spectroscopy 84 (2016) 127–132

Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Investigation of band gap effect and dephasing on Raman line broadening for the highest-frequency A_g mode in comparison with $SrWO_4$ and $SrMoO_4$

Jun Suda[a,*], Petr G. Zverev[b]

[a] Department of Electrical and Electronic Engineering, School of Engineering, Chukyo University, Japan
[b] A.M. Prokhorov General Physics Institute Russian Academy of Sciences, Vavilov str. 38, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form 8 March 2016
Accepted 9 March 2016
Available online 10 March 2016

Keywords:
Raman spectra
Linewidth
Phonon dispersion
Lattice dynamical perturbative approach
Dephasing effect

ABSTRACT

The phonon dispersions of $SrWO_4$ crystal were calculated using the lattice dynamical calculations approach. Spontaneous Raman spectra in $SrWO_4$ were measured in the temperature range from 15 K to 295 K, and the temperature dependence of the linewidth of the A_g (921-cm^{-1}) Raman mode was analyzed using the lattice dynamical perturbative treatment. The experimental temperature dependence of the linewidth was well described by the calculated one which included both the cubic and the dephasing relaxation terms. The bands for internal modes in $SrWO_4$ are broader than that in $SrMoO_4$. The number of the up-conversion relaxation processes in $SrWO_4$ is determined by the interaction between higher vibronic bands with lower bands. So the relative impact of the dephasing process in the linewidth broadening on $SrWO_4$ crystal is smaller than that in $SrMoO_4$.

1. Introduction

In recent years, scheelite crystals (e.g., $SrWO_4$, $BaWO_4$, $PbWO_4$ and $SrMoO_4$) have attracted the interest of several research groups as promising and efficient nonlinear and laser materials in the Raman laser development [1,2]. Basiev et al. [3] showed that $SrWO_4$ and $SrMoO_4$ crystals had high Raman gain coefficient of 4.7 cm/GW and 5.6 cm/GW at 1.06 μm, which are close to that in the most efficient $BaWO_4$ Raman scheelite crystal. The frequency shifts in $SrWO_4$ and $SrMoO_4$ Raman lasers are 921 cm^{-1} and 888 cm^{-1}, respectively. In contrast to $BaWO_4$ crystal $SrWO_4$ and $SrMoO_4$ crystals can be doped with laser active rare earth ions. This allows one to consider $SrWO_4$ and $SrMoO_4$ as efficient crystals for Raman lasers with self-frequency-conversion. The steady-state Raman gain coefficient is inversely proportional to the Raman mode linewidth [1]. During the operation of a Raman laser, its nonlinear medium is heated due to the Stokes losses, which results in the thermal instability of the Raman laser operation due to the Raman mode broadening and frequency shift [1].

Long before the recent report on classical lattice dynamical calculations in $CaMoO_4$ by Senyshyn et al. [4], phonon dispersions and phonon anharmonicities in $PbMoO_4$ had been calculated by Shinagawa et al. [5]. Phonon dispersion relations for $PbMoO_4$ were determined by the lattice dynamical calculations [5], and the temperature dependences of spontaneous Raman spectra for several phonon modes in this crystal were investigated using the lattice perturbative approach, which well correlated with the experimental data on the line broadening and the frequency shift. Our earlier lattice dynamical calculations also led to a high precision in the determination of the phonon dispersions in the low-frequency range and to a good description of the acoustic phonon images in $CaWO_4$ [6,7].

Very recently, we clarified that the highest frequency A_g Raman mode strongly depends on dephasing processes in the scheelite crystals [8–10]. By the lattice dynamical calculations approach it was found that there was an energy gap of more than 350 cm^{-1} between the high- and low-frequency bands in $BaWO_4$ and $SrMoO_4$. The experimental temperature dependence of the linewidth of the highest frequency A_g Raman mode was well described by the calculated one that considered both cubic and dephasing relaxation terms. The relative impact of the dephasing process on the relaxation process for this mode in $SrMoO_4$ was greater than that for $BaWO_4$ [8]. This indicated that the impact of the dephasing process was related with the band gap width [8–11]. The obtained results allowed us to predict the temperature dependence of the Raman gain during operation of Raman lasers with scheelite crystals [8–10]. However, the dependence of the dephasing process probability on the difference between Mo-O and W-O vibrations in

* Corresponding author.
E-mail address: suda@sist.chukyo-u.ac.jp (J. Suda).

http://dx.doi.org/10.1016/j.vibspec.2016.03.011
0924-2031/

tungstate and molybdate scheelite crystals has not been clarified up to now. The result of this investigation will help to find efficient scheelite Raman laser materials with better thermal Raman properties.

The aim of this study was to investigate the anharmonicity of the highest-frequency A_g Raman mode (921-cm^{-1} peak) in $SrWO_4$ crystal by both the lattice dynamical calculations and spontaneous Raman spectroscopy and to compare it with those in $SrMoO_4$.

2. Experimental procedures

The unit cell of $SrWO_4$, as shown in Fig. 1(a) is composed of twelve atoms. The specimen used in the experimental study was doped with Nd^{3+} ions (1 wt%), cut perpendicular to the c axis, optically polished, and had dimensions of $5 \times 5 \times 6\,mm^3$.

The experimental setup for spontaneous Raman spectroscopy utilized excitation by a single-longitudinal-mode cw argon ion laser ($\lambda = 514.5$ nm) and registration by a Spex-1403 double-spectrometer. A cooled photo-multiplier tube recorded Raman scattering signals from the sample on a PC. The laser intensity on the sample was about 0.5 W. The absorption of the excitation beam in the sample and cryostat was negligible. A back scattering scheme was used to increase the signal-to-noise ratio. The spectral resolution of the whole system with 10-μm slits was 0.16 cm^{-1}. The spectral profiles of all Raman modes were well described by a Lorentzian function. The sample was attached to the cold tip of a closed-cycle helium optical cryostat with temperatures variable from 15 K to 295 K. The temperature controller allowed us to maintain the crystal temperature with an accuracy of ±1 degree during the experiment.

3. Results and discussion

The unit cell of $SrWO_4$, which contains two Sr^{2+} ions and two WO_4^{2-} anions, is composed of twelve atoms (see Fig. 1(a)). The first Brillouin zone of $SrWO_4$ is shown in Fig. 1(b). The phonons with the wavevector $\boldsymbol{q} = \mathbf{0}$, according to the group theory analysis, are presented with the irreducible representation of the space group C_{4h}^6 as follows [12]:

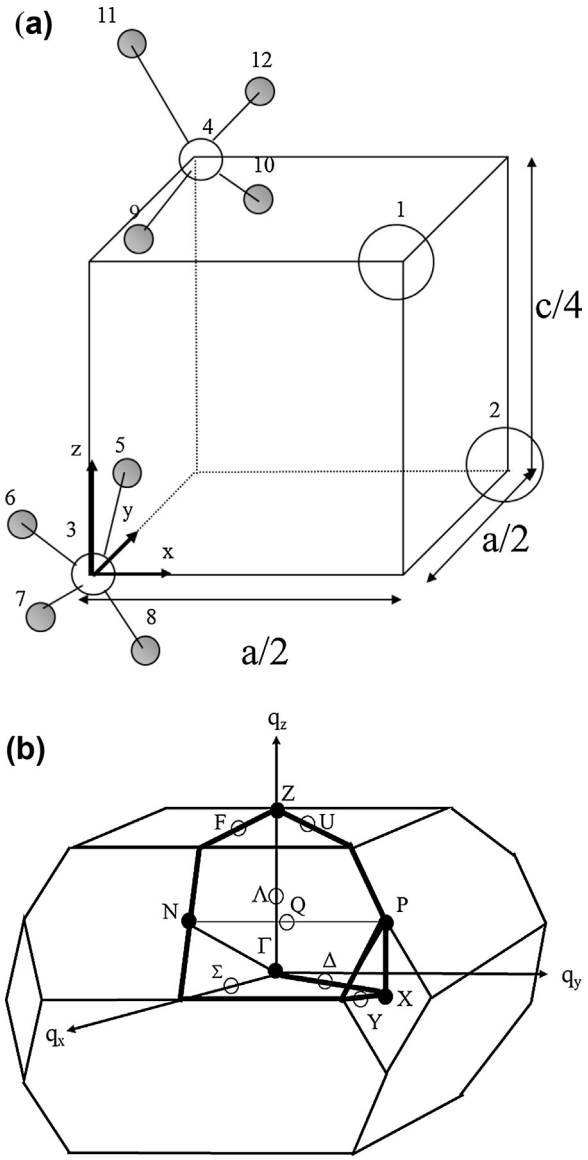

Fig. 1. (a) The body-centered tetragonal unit cell for $SrWO_4$ crystal. The open large, open small, and shaded circles represent Sr, W, and O atoms, respectively. The *a*,*b*, and *c* axes are parallel with the direction of x, y, and z, respectively. (b) The first Brillouin zone for a body-centered tetragonal system. The thick solid line represents the irreducible Brillouin zone.