ISSN 1027-5495. Functional Materials, 24, No.4 (2017), p. 635-639.
doi:https://doi.org/10.15407/fm24.04.635

Growth of $SrWO_4$ and $CaMoO_4$ single crystals and their characterization by means of Raman spectroscopy

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Received September 9, 2017

The $SrWO_4$ and $CaMoO_4$ crystals grown under different conditions by the Czochralski method were studied by means for Raman spectroscopy. Raman spectra of the crystals were measured and peaks were identified. For $SrWO_4$ crystals 2nd and 3rd Stokes were observed for the first time.
Keywords: $SrWO_4$ and $CaMoO_4$ crystals, Raman spectroscopy

Методом рамановской спектроскопии исследованы монокристаллы $SrWO_4$ и $CaMoO_4$ выращенные в различных технологических условиях методом Чохральского. Определены, проанализированы и идентифицированы линии в рамановских спектрах этих кристаллов. В кристаллах $SrWO_4$ впервые получена ВКР генерация не только первой, но второй и третьей стоксовых компонент.

Вирощування монокристалів $SrWO_4$, $CaMoO_4$ та їх характеризація методом раманівської спектроскопії. *М.Б.Космина, О.М.Шеховцов, І.О.Ходасєвіч, С.В.Войтіков, В.А.Орлович*.

Методом раманівської спектроскопії досліджено монокристали $SrWO_4$ і $CaMoO_4$, вирощені у різних технологічних умовах методом Чохральського. Визначено, проаналізовано та ідентифіковано лінії у раманівських спектрах цих кристалів. В кристалах $SrWO_4$ вперше отримано ВКР генерацію не тільки першої, але другої і третьої стоксових компонент.

1. Introduction

The application area of discretely tunable lasers is wide and covers spectroscopy, remote sensing, 3D imaging, nuclear physics and others. Nonlinear optic effects like Raman scattering, optical parametric amplification are applied successfully for tuning of laser wavelength. It is worth to be noted that the utilization of media combining lasing oscillation and the function of nonlinear optic converter has a number of advantages (higher stability of functional characteristics, simple design, lower price) in comparison with laser apparatus containing the gain medium and the nonlinear optic medium.

It was shown recently, that the tetragonal tungstate and molybdate single crystals with divalent cations (sheelite mineral family with the space group C^6_{4h}) are promising gains media for Raman lasers [1]. For these crystals the generations of Stoke and anti-Stoke harmonics were observed, multi-wave

Stoke and anti-Stoke parametric amplification were obtained. Simultaneous lasing oscillation and Raman conversion were achieved under different pumping conditions for Nd doped crystals.

However, there are problems to be solved for effective application tungstate and molybdate single crystals for Raman lasers. For the effective Raman conversion the single crystals should be free of color centers and contain lowest concentrations of point defects and uncontrolled impurities [2–5]. These specifications are conditioned by crystal growth technology. It is known that the quantum yield of Raman scattering is low. But the quantum yield can be achieved to 40–60 %. Thus, for the effective Raman conversion the single crystals should own the high optical breakdown also. The study is aimed to the crystals growth of $CaMoO_4$ and $SrWO_4$ single crystals and their characterization by means of Raman spectroscopy.

2. Experimental

The dried initial components $CaCO_3$ (99.99 %), $SrCO_3$ (99.99 %), WO_3 (99.99 %) and MoO_3 (99.95 %) were taken. To compensate losses due to evaporation of melt during the crystal growth 1 wt.% of WO_3 (99.99 %) or MoO_3 was added to the mixture of initial reagents over stoichiometric ratio of $SrWO_4$ and $CaMoO_4$, respectively. A solid state synthesis was carried out in air according to the regimes presented in Table. The formation of $SrWO_4$ and $CaMoO_4$ compounds carried out according to the reactions:

$$SrCO_3 + WO_3 \rightarrow SrWO_4 + CO_2\uparrow, \quad (1)$$

$$CaCO_3 + MoO_3 \rightarrow CaMoO_4 + CO_2\uparrow. \quad (2)$$

Pure $SrWO_4$ and $CaMoO_4$ single crystals were grown by the Czochralski method in iridium crucibles in argon. For the crystal growth apparatus an automatic "Kristall 3M" growth equipped weight control system was used. The growth was performed on an oriented seed along the [001] direction. The growth parameters of crystals were: temperature gradient T_z = 50–70 K/cm, rotation speed ω = 20–30 min^{-1}, and pulling rate V_z = 1–3 mm/h. The crystals had a diameter up to 20 mm and a length to 100 mm (Fig. 1). The crystal-melt interface was convex. The grown single crystals were free of impurity phases and macroscale defects (gas bubbles, cracks, inclusions of crucible material). According to the chemical analysis data, the total concentration of uncontrolled impurities in each crystal did not exceed 30–50 ppm.

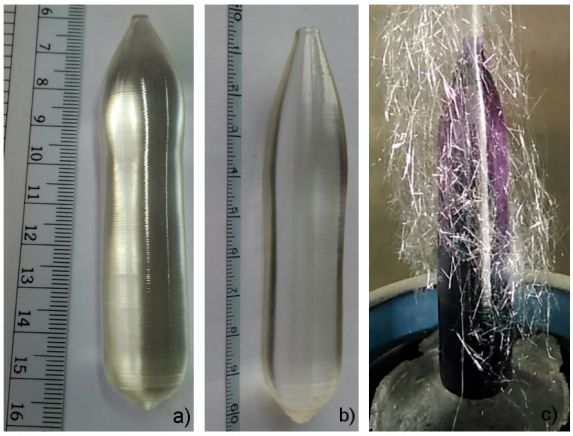

Fig. 1. The photos of the crystals: after annealing in air $SrWO_4$ (a) and $CaMoO_4$ (b); $CaMoO_4$ (c) covered by white "fog".

To minimize thermoelastic stresses, after the detachment of crystals the ingots were kept above the melt for 2 h and cooled down to the room temperature for 24 h. Additionally, the crystals were annealed in air at 1000°C for 12 h at the heating/cooling rate 30°C/h.

Raman spectra were measured by the laboratory Raman spectrometer including the helium-cadmium laser HCL-40I, monochromator-spectrograph (MS3504I) and CCD-camera (Spec-10:256) with automatic control of the recording and processing of spectra by software "WinSpec/32 v.2.5.15.5". Raman spectra have been registered in 45°-geometry. Crystals were excited by linearly polarized continuous wave laser radiation at the wavelength of 441.6 nm and power of 25 mW. The scattered radiation was focused through a notch filter with a stop band of 442 nm on the 100 μm en-

Table. Parameters of solid state synthesis

	Duration, h	Temperature, °C	Phase content, wt.%
$SrWO_4$	96	1000	98
$CaMoO_4$	96	1100	96

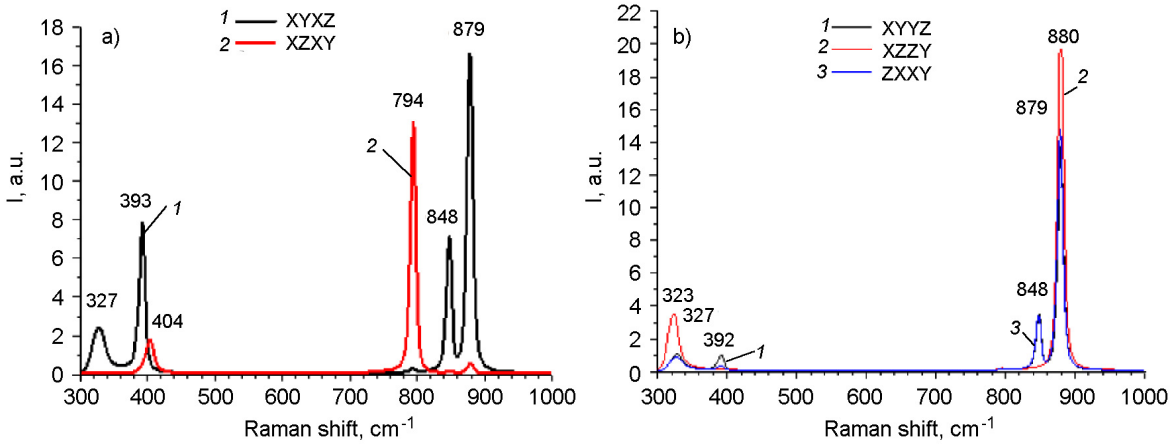

Fig. 2. Polarized Raman spectra of $CaMoO_4$ crystal: a — π-polarization, b — σ-polarization.

trance slit and was dispersed by a diffraction grating with the 2400 lines per mm. Raman spectra were recorded in the range of frequency shifts from 200 to 1600 cm^{-1} with spectral resolution of 1.5 cm^{-1}.

Polarized Raman spectra were measured in a 90° geometry when the scattered radiation was expanded by a diffraction grating of 2,400 pcs/mm of a monochromator-spectrograph MS3504i with a CCD camera Spec-10:256. The spectral resolution was about 1.5 cm^{-1}. The samples were excited by continuous linearly polarized radiation of an argon laser with a wavelength of 514.5 nm and a power of ~ 60 mW. The scattered radiation was focused by a two-lens objective, a thin-film polarizer was placed between the lenses, and a 515 nm non-stop filter was fed to an input slit 200 μm wide. The Raman spectra were recorded in the frequency shift range 300–1000 cm^{-1} in such a way that one of the crystallographic axes coincided with the direction of polarization of the incident beam, and for the scattered light two components with polarization parallel and perpendicular to the direction of the incident beam were fixed. The investigated crystals $CaMoO_4$ and $SrWO_4$ had the shape of regular parallelepipeds with the following dimensions: 6×5×4 mm^3 ($CaWO_4$), 5×5×5 mm^3 ($SrWO_4$).

3. Results and discussion

One of the growth problems of tungstate and molybdate crystals is evaporation of tungsten and molybdenum oxides, respectively, leading to deviation from stoichiometric composition and affecting optical quality. One of the decisions is crystal growth from enriched by tungsten and molybdenum oxides melts. Generally, 0.5–1.5 wt.% of tungsten (molybdenum) oxide is added over stoichiometric composition. The appearance of $CaMoO_4$ single crystal is presented in Fig. 1. It is seen that the single crystal is covered by white "fog" containing needle and strip like particles. According to X-ray analysis "fog" consists of needle type single crystals of molybdenum oxide. Unfortunately, such approach doesn't lead to the crystals completely free of vacancies of molybdenum. According to the data of X-ray diffraction, molybdate crystals grown from enriched by molybdenum oxide melt have vacancies of molybdenum. Another decision of the problem is related to minimization of melt evaporation. It is achieved at growth of crystals with a diameter close the diameter of the crucible because no covered by the growing crystal surface of melt is minimal. Such approach was successfully applied for the growth of high quality $CdWO_4$ crystals with volume of ~ 350 cm^3. Both approaches were applied at crystal growth of $SrWO_4$ and $CaMoO_4$ single crystals.

For the characterization of the crystals Raman spectra have been studied. The spectra of spontaneous Raman scattering for $SrWO_4$ and $CaMoO_4$ crystals are presented in Figs. 2 and 3.

The observed oscillations in the Raman spectra of $CaMoO_4$ and $SrWO_4$ crystals are in good agreement with those known from the literature [1–5]. The crystals $CaMoO_4$ and $SrWO_4$ possess similar Raman spectra [1, 2], which indicates a weak connection between the anion group $[XO_4]^{2-}$ (X = Mo, W) and cations. This peculiarity of the crystals allows to divide the oscillations into external and internal ones. Internal vibrations include the motion relative to the sta-

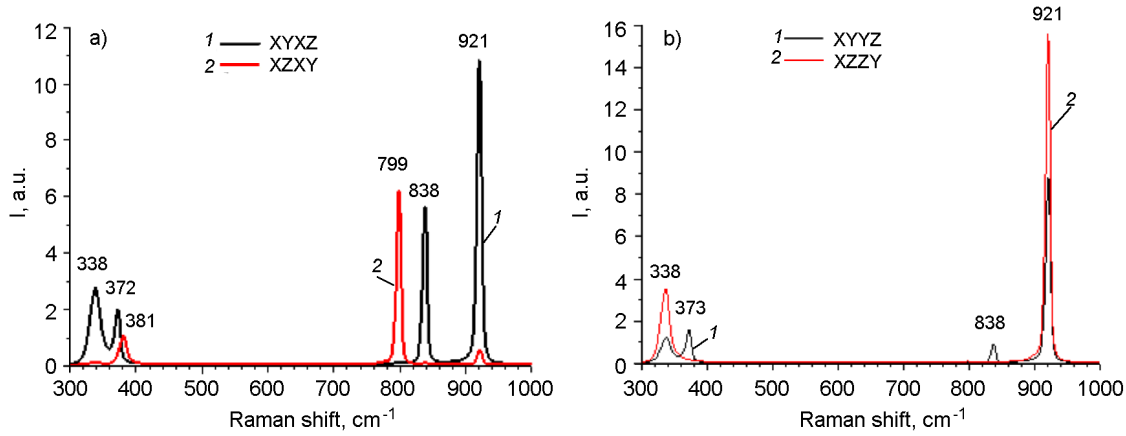

Fig. 3. Polarized Raman spectra of $SrWO_4$ crystal: a — π-polarization, b — σ-polarization.

tionary center of mass of the ion $[XO_4]^{2-}$, located in the frequency range 700–1000 cm^{-1}, and to the outer ones — the movements of the ion itself, as a whole unit, ranging from 100 to 500 cm^{-1}. In the Raman spectra of the $CaMoO_4$ crystal (Fig. 2), the bands with frequencies 393 (B_g) and 404 (E_g) cm^{-1} correspond to the asymmetric bending of the $[MoO_4]^{2-}$ ion or to the ν_4 oscillation, the splitting of which depends on the direction of polarization of the incident radiation.

The 327 cm^{-1} band is the sum of overlapping oscillations of 318 cm^{-1} for ν_4 (E_u) and 333 cm^{-1} of the angular bending of O–Mo–O ν_2 (A_g). The bands of about 794 (E_g) and 848 (B_g) cm^{-1} refer to the asymmetric bending of the Mo–O bond (ν_3). The symmetrical stretching of this bond ν_1 (A_g) manifests itself in the form of an intense band at a frequency of about 879 cm^{-1}. Comparison of the spectra obtained for the excitation configurations-observation of X(YY)Z and Z(XX)Y shows the difference in the scattering intensity of the peak at 392 cm^{-1} and the equality of the intensities of the other peaks, which shows that they are not completely polarizable. A fully polarized peak of 794 cm^{-1} is dominant in the exciting radiation polarized perpendicular to the Z axis. A peak of 880 cm^{-1} dominates when the polarization of the laser radiation is parallel to this axis.

The Raman spectra of the $SrWO_4$ crystal have the same character as described above (Fig. 3). The bands of about 838 (B_g) and 799 (E_g) cm^{-1} refer to the asymmetric bending of the W–O bond (ν_3). The intense band at a frequency of about 921 cm^{-1} corresponds to the symmetric stretching of this bond ν_1 (A_g). The bands with frequencies of about 372 (B_g) and 381 (E_g) cm^{-1} correspond to the asymmetric W–O–W bend in the $[WO_4]^{2-}$ ion. As in the case of the $CaMoO_4$ crystal, the splitting of the vibration ν_4 depends on the direction of polarization of the incident radiation. The 338 cm^{-1} band is the symmetric bending of the ν_2 (A_g) W–O–W chain.

Oscillations with frequencies of about 799, 372, and 381 cm^{-1} are completely polarized. While the oscillations near 338, 838, and 921 cm^{-1} are manifested with any polarization, but with different intensities. The difference in the vibration frequencies ν_1 (A_g) in the measured spectra and in the data of [6–10] can mean that there are differences in the form of $[WO_4]^{2-}$ tetrahedra in the investigated sample and in crystals whose spectra are reported in [6–10].

4. Conlusions

The $SrWO_4$ and $CaMoO_4$ crystals grown under different conditions by the Czochralski method were studied by means for Raman spectroscopy. It was determined, that intensities and FWHMs depend strongly upon growth conditions. Most intensive peaks with small values of FWHM were observed for the crystals grown at minimized evaporation and deviation from stoichiometric composition of melt. For $SrWO_4$ crystals 2nd and 3rd Stokes were observed for the first time.

Acknowelegment. This work is supported by the Ukraine-Belarus grant (F73/2016) of State Fund for Fundamental Research of Ukraine and Belarusian Republican Foundation for Fundamental Research.

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