Optical Materials 52 (2016) 203–211

Contents lists available at ScienceDirect

Optical Materials

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

Phase equilibria diagrams, crystal growth peculiarities and Raman investigations of lead and sodium-bismuth tungstate–molybdate solid solutions

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ARTICLE INFO

Article history:
Received 17 October 2015
Received in revised form 23 December 2015
Accepted 27 December 2015
Available online 31 December 2015

Keywords:
Stimulated Raman scattering
Dual-wavelength laser
Solid solution
Phase diagram
Tungstate
Molybdate

ABSTRACT

In this paper a comprehensive study of lead and sodium-bismuth tungstate–molybdate solid solutions was carried out, including the clarification of their structural peculiarities and phase diagrams of $PbMoO_4$–$PbWO_4$ and $NaBi(MoO_4)_2$–$NaBi(WO_4)_2$ systems, the study of spontaneous Raman spectra of these compounds, as well as preliminary experiments on single crystals growth of lead tungstate–molybdate. The linewidths, peak and integral intensities of the totally symmetric Raman vibrations of solid solutions were estimated in comparison with known SRS-active crystals. The conditions of the Czochralski growth of optically transparent lead tungstate–molybdate mixed crystals were found and SRS effect was observed in these crystals when pumping by 12 ns 1064 nm laser pulses.

1. Introduction

Dual-wavelength laser radiation has some unique applications in the devices like differential absorption lidars, dual-wavelength laser probes, dual-wavelength interferometers, terahertz radiation sources, medical instrumentation. Dual-wavelength laser beam can be obtained from optical parametric oscillator [1] or laser, emitting simultaneously on two wavelengths. In the latter case dual-wavelength regime can be reached by creating appropriate output mirror coatings, using the intracavity etalon, or optimizing the gains of active medium on two different Nd^{3+} transitions [2–9]. In spite of successful usage of the above devices nowadays, their main problem is low reliability due to complexity of the design and necessity of precision tuning of the optical scheme. Furthermore, the applications of dual-wavelength lasers are limited by discrete set of Nd^{3+} radiative transitions.

An another approach is the conversion of single-wavelength emission of conventional lasers to multi-wavelength beam by means of stimulated Raman scattering (SRS) effect in the appropriate single crystals [10–17]. The output radiation of solid-state Raman converters and Raman lasers usually contains pump wavelength and one or several Stokes components simultaneously. However, in this case, pump and Stokes pulses are nonsynchronous due to pump depletion effect that greatly limits an applications. For example, difference frequency generation becomes ineffective. One can assume that SRS pulses will be synchronous if they are generated on different Raman vibrational modes within the Stokes of the same order, since, in this case, Raman oscillations are not a pump sources for each other. Simultaneous SRS on different vibrational modes has been observed in several papers [11,18–21], when SRS was exited by picosecond pump pulses. At the same time, in the nanosecond range, which is often indispensable in practice, SRS occurs, as a rule, at only single vibrational mode with the highest peak intensity.

It is known that totally symmetric vibration $\nu_1(A_g)$ in tungstate–molybdate solid solutions with scheelite structure $M(MoO_4)_x(WO_4)_{1-x}$ (M = Ca, Sr, Ba, Pb; $0 < x < 1$) demonstrates two-mode behavior [22–24]. In these media, two Raman bands that belong to the $\nu_1(A_g)$ vibrations of the $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ anionic complexes are observed simultaneously, and intensity ratio of these bands is related to concentration ratio of tungsten and molybdenum in crystal. Since $\nu_1(A_g)$ vibration is SRS-active in scheelites [10], in Ref. [24] dedicated to studying of $Ba(MoO_4)_x(WO_4)_{1-x}$ we made an assumption that in solid solutions with equal peak intensities of $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ $\nu_1(A_g)$ bands it is possible to obtain

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http://dx.doi.org/10.1016/j.optmat.2015.12.043
0925-3467/

simultaneous SRS on the complexes of both types. Afterwards this assumption was confirmed by direct SRS experiments with Ba$(MoO_4)_{0.45}(WO_4)_{0.55}$ crystal [25]. Generation of dual-wavelength laser emission by such way seems attractive mainly because of simplicity and reliability of final apparatus construction: SRS does not require the achievement of the phase-matching conditions and appropriate fine adjustment of optical scheme, and there is no necessity in an additional optical elements for compensating amplification on two vibrational modes if the solid solution chemical composition has been chosen correctly.

The concentration of SRS-active $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ anionic complexes and, therefore, the Raman gain in tungstate–molybdate solid solutions proved to be less than in appropriate nominally pure tungstates and molybdates. For example, measured values of the Raman gain coefficients in $Ba(MoO_4)_{0.45}(WO_4)_{0.55}$ crystal was approximately twice less than in $BaWO_4$ [25]. This fact must be taken into account, when searching for a new SRS-active media based on solid solutions, since the SRS can be obtained only when the pumping intensity difference between the optical damage and SRS thresholds is positive. Based on the foregoing, solid solutions $Pb(MoO_4)_x(WO_4)_{1-x}$ (PMW_x) and $NaBi(MoO_4)_{2x}(WO_4)_{2-2x}$ (NBiMW_x) were selected as the objects of the present study, because, along with the barium tungstate [26], lead and sodium-bismuth tungstates and molybdates are known as the most effective SRS-active medium in a series of scheelite-related compounds [27–30]. In addition, it is known that PMW_x and NBiMW_x solid solutions single crystals could be grown by Czochralski technique in form of large size and good optical quality boules [23,31,32], which are necessary for SRS applications. The aims of the present work were: clarifying the fusibility curve of $PbMoO_4$–$PbWO_4$ system [33] and the study of the phase equilibria in the $NaBi(MoO_4)_2$–$NaBi(WO_4)_2$ system for determination of the growth conditions of PMW_x and NBiMW_x solid solutions crystals; investigations of the spontaneous Raman spectra of these compounds; the study of a peculiarities of PMW_x single crystals growth and carrying out preliminary SRS experiments with them.

2. The experimental procedures and calculations

2.1. Synthesis of the samples

The samples were synthesized *via* solid-phase reaction. Chemical purity of the raw materials was not less than 99.9%. The starting powders of PbO, Bi_2O_3, Na_2CO_3, $BaCO_3$, $SrCO_3$, MoO_3, and WO_3 were mixed in the required proportions and subjected to a multistep high temperature annealing in air. PMW_x compounds were synthesized sequentially at 500, 650, and 900 °C, NBiMW_x – at 500 and 700 °C, the time of annealing at each temperature stage was 24 h, the values of x lay in $0 \leqslant x \leqslant 1$ range. $BaWO_4$, $SrWO_4$ and $SrMoO_4$ compounds were annealed at 1000 °C for 24 h. The raw powders of $CaCO_3$, TeO_2, $LiNbO_3$, $NaNO_3$ were used in addition to the synthesized compounds (see Section 2.4).

2.2. Growth of PMW_x single crystals

PMW_x crystals were grown by the Czochralski method in platinum crucible of 50 mm in diameter and 45 mm in height, in air atmosphere. The crucible was inductively heated from 8 kHz generator, and, besides that, the active afterheater with resistive heating was used in the annealing zone, which allowed to adjust temperature gradients within the growth chamber. The pulling and rotation rates were 1.5–3 mm/h and 35 rpm, respectively. At the end of the growth process the crystal was detached from the melt surface and cooled down to room temperature over 15 h by linearly decreasing the power supplied to the inductor and active afterheater. The seeds were cut along the [100] crystallographic direction from nominally pure $PbWO_4$ or $SrWO_4$ crystals. The latter gave the best result since $PbWO_4$ is extremely brittle material, and seed produced from it is often destroyed, causing a drop of the crystal during the aftergrowth cooling down. Axial temperature distribution inside the growth chamber was measured by Pt/Rh thermocouple installed instead of the seed holder.

2.3. X-ray diffraction and differential thermal analysis

The X-ray diffraction (XRD) patterns were obtained on SHIMADZU XRD–7000 diffractometer using Cu Kα radiation. Data were collected in $10° \leqslant 2\theta \leqslant 70°$ angular range with 0.02° step. The unit cell parameters of the investigated compounds were refined by the Le Bail method in Jana2006 software [34].

Differential thermal analysis (DTA) was carried out on Q-1500D derivatograph. The signal from the thermocouples was digitized using a 24-bit ADC OWEN MV110-2A and recorded on a PC. The weights of the batches were about 1 g. Heating and cooling rates were 5 °C/min, each sample was taken through at least two heating and cooling cycles. The accuracy of the solidus and liquidus temperatures estimation was about ±2 °C.

2.4. Raman spectroscopy

Raman spectra were recorded at 180° scattering geometry using DFS-24 LOMO Photonics double monochromator and pulsed copper vapor laser as the excitation source with emission wavelength of 578.2 nm and 16 kHz pulse repetition. The average excitation power at the sample did not exceed 1 W. Signal was detected by photomultiplier with multialkali photocathode, photon counting with synchronous detection method was applied. The spectral resolution of the system was about 1 cm^{-1}. The resulting spectra were corrected according to the spectral sensitivity of the photocathode.

In Ref. [10,29] the relationship between the Raman gain and the parameters of the bands in the spontaneous Raman spectrum was shown. It was found that the highest Raman gain in transient SRS regime is observed in crystals with relatively high integral intensity Σ_{int} of the SRS-active vibration. In steady-state SRS regime, in addition to the Σ_{int} value, the Raman linewidth $\Delta\nu_R$ is important, which is minimal in the most effective SRS media. Thus, in steady-state regime of SRS, crystals with the highest peak intensity of the SRS-active vibration Σ_{peak} in the spontaneous Raman spectrum are the primary interest. The steady-state or transient SRS regime is realized when the pump pulse duration τ_p is much greater than the dephasing time of SRS-active vibrational mode, or comparable with the latter, respectively. The dephasing time for the majority of the known SRS-active crystals did not exceed a few tens of picoseconds [35], thus, when the SRS was excited by nanosecond laser pulses, the SRS regime can be considered as steady-state with high accuracy.

In the present work the following method was applied to estimate the parameters of spontaneous Raman bands. At first, the mechanical mixture of powdered test and reference samples was prepared. $BaWO_4$ compound was used as a reference, and the values of its Σ_{peak} and Σ_{int} taken as units. Test and reference samples were weighted in proportion, which corresponds to equal volumes of the crystals. Then, the Raman spectrum of the mixture was recorded, and parameters Σ_{peak} and Σ_{int} of the individual lines related to the test and reference sample were compared.

Because the spectral resolution of our measurement system was comparable to the Raman linewidths of the examined compounds, a considerable errors arisen in determination of the Raman band parameters on the basis of the observed spectrum, which, as known, is the convolution of the instrumental function and the real spectrum. To minimize these errors, we carried out the deconvolution