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THE STUDY OF BARIUM-GADOLINIUM, BARIUM-YTTRIUM AND BARIUM-BISMUTH DOUBLE MOLYBDATES AS A POTENTIAL ACTIVE MEDIA FOR MICROCHIP RAMAN LASERS

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Abstract. In this work, $BaR_2(MoO_4)_4$ compounds (where R = Gd, Y, Bi) have been synthesized, and a comparative study of the Raman spectra of these compounds has been carried out for the first time, to the best of our knowledge. It has been shown that these compounds, potentially, are the promising active media for conversion of laser radiation on the stimulated Raman scattering effect, in particular, for a microchip self-Raman laser. The peak and integral cross sections of the most intense bands in the Raman spectrum (around 850 cm^{-1} and 950 cm^{-1}) of the compounds under consideration are comparable in magnitude with the cross sections of barium tungstate – the well-known highly efficient stimulated Raman scattering crystal. It has been found that the peak intensities of the vibration around 850 cm^{-1} decrease with decreasing radius and mass of the R^{3+} cation. The optical damage threshold of $BaBi_2(MoO_4)_4$ and $BaGd_2(MoO_4)_4$ crystals on cleaved (non-polished) surface was estimated at about 500 MW/cm^2.

Keywords: Raman, optical materials and properties, crystal structure.

Introduction

The effect of stimulated Raman scattering (SRS) gives an effective and relatively simple way to obtain new wavelengths from existing lasers. At present, oxide single crystals are intensively studied as Raman active media [1]. Among the variety of latter, tungstates and molybdates with a scheelite or scheelite-like structure should be distinguished: they allow to convert the wavelength of solid-state pulsed lasers with an efficiency of tens of percent, both in the nano- and picosecond pulse durations [1–3]. In the practical implementation of SRS-devices, Raman- and self-Raman lasers are of considerable interest due to their compactness, simplicity of design and, as a result, high reliability and low cost of the final device. Currently, medium and high average power Raman lasers with a pulse energy of 0.025–15 mJ have been developed on the basis of neodymium laser media and Raman-active tungstate and molybdate crystals [1,2,4]. Along with this, attention is drawn to the idea of creating low-power Raman lasers in a microchip configuration with unique characteristics inherent in microchip lasers: subnanosecond pulse duration and high repetition rate (up to hundreds of KHz), high beam quality ($M^2 \approx 1$) [5]. For example, microchip Raman lasers based on Nd:LSB and Nd:YAG crystals with passive Q-switching on YAG:Cr^{4+} were investigated in [6,7]. Plates 2 mm thick of $Ba(NO_3)_2$ and $KGd(WO_4)_2$ crystals were used as the Raman media. The conversion efficiency of the pump energy to the Stokes component reached 8%, and the duration of the Stokes pulses was 48-118 ps, with a peak power of up to 48 kW. For the further development of such devices, the implementation of the Raman conversion inside the microchip laser gain medium itself is attractive, but it requires an active medium with special laser properties (high quantum efficiency and strong absorption at the pump wavelength), and at the same time with high cross section bands in the Raman spectrum. We found such properties in scheelite-like double molybdate crystals with the formula $BaR_2(MoO_4)_4$ (where

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R = Ce-Lu, Y, Bi). The crystal structure of these compounds is represented by layers of $[R_2O_2]$ units and BaO_{10} polyhedra surrounded by isolated MoO_4 tetrahedra, and belongs to the monoclinic C2/c space group [8–10]. The possibility of mutual isomorphic substitution of R^{3+} ions in these compounds makes it possible to obtain highly concentrated laser media with a concentration of active centers up to 100 at. % (for example, $BaNd_2(MoO_4)_4$). The concentration quenching effect in this case is relatively weak due to the large interionic $R^{3+} – R^{3+}$ distances [11]. On the other hand, the presence of isolated $[MoO_4]^{2-}$ anionic complexes in combination with large and heavy Ba^{2+} and R^{3+} cations allows predicting small line widths and high cross sections for internal Raman oscillations of the anionic complex, which implies a significant SRS effect [1].

Due to the layered structure, $BaR_2(MoO_4)_4$ crystals tend to cleave on plane-parallel plates with a thickness of tenths to a few mm. The surfaces of these cleaved plates have a sufficiently high optical quality and do not require additional polishing, which greatly simplifies the process of microchip manufacturing. In [12, 13] lasing was obtained on plates cleaved from a Nd-doped $BaGd_2(MoO_4)_4$ (BGM) crystal. The results of these studies show that the spectroscopic and laser properties of Nd:BGM crystal are very suitable for diode-pumped miniature lasers. As for the other $BaR_2(MoO_4)_4$ compounds, their laser characteristics have not yet been investigated, to the best of our knowledge; apparently, this is due to the difficulty of growing single crystals, since, with the exception of R =Ce-Gd, $BaR_2(MoO_4)_4$ compounds melt incongruently [10, 14] and require complicated high temperature solution growth methods. The SRS properties of $BaR_2(MoO_4)_4$ were also not studied to date. Recently, we have demonstrated the possibility of growing $BaBi_2(MoO_4)_4$ crystals from self-flux [14]. The study of the Raman spectra showed that the compound is a promising SRS-active medium. In the present work, a comparative study of the Raman characteristics of $BaGd_2(MoO_4)_4$ (BGM), $BaY_2(MoO_4)_4$ (BYM) and $BaBi_2(MoO_4)_4$ (BBiM) was carried out.

1. Experimental

BGM, BYM and BBiM powdered samples were synthesized by solid phase reaction. The starting materials $BaCO_3$, Gd_2O_3, Y_2O_3, Bi_2O_3, MoO_3 with a purity not lower than 4N were mixed in the required proportions in an agate mortar and annealed at 550 °C for 24 hours. The completeness of the reaction was controlled by XRD on SHIMADZU XRD–7000 diffractometer using Cu Kα radiation. BGM single crystal was grown by the Czochralski method under conditions similar to [11]. BBiM crystals were obtained by spontaneous crystallization from a high-temperature solution, as described in [14]. The Raman spectra were recorded using a DFS-24 LOMO Photonics double monochromator, a copper vapor laser was the excitation source (yellow line at 578.2 nm). The spectral resolution of the setup was about 1 cm^{-1}.

2. Results and discussion

The XRD patterns of the sintered compounds are presented in Fig. 1. It can be seen that the BGM, BYM, BBiM diffraction patterns correspond to monoclinic $BaR_2(MoO_4)_4$ (JCPDS # 00-036-0192) with slight variations in peak positions. Thus, solid-phase synthesis was almost completed, as far as we can see.

Fig. 2 shows the Raman spectra of BBiM and BGM single crystals, and solid-phase sintered BYM compound. Since the structure of the studied compounds is ordered, and the symmetry is low, the spectra are represented by a large number of well-resolved sharp lines. The low-frequency and high-frequency regions of Raman vibrations are clearly separated by a gap of 200–250 cm^{-1}. This behavior is due to the heterodesmic nature of the chemical bonds in these compounds: their structure is composed of $[MoO_4]^{2-}$ anionic complexes with a strong internal Mo-O covalent bond and a relatively weak external bond with Ba^{2+} and R^{3+} cations, which is typical in scheelite crystals [15]. Thus, the internal high-frequency vibrations of the $[MoO_4]^{2-}$ complex and the external low-frequency vibrations of the cations and the complex as a whole can be distinguished in the Raman spectra.

As a rule, internal vibrations of the anionic complex are SRS-active in scheelites [1–4]. In the case of the considered compounds, two high-intensity bands around 850 and 950 cm^{-1} are found in the high-frequency region. It is known that the SRS efficiency of a medium can be estimated by comparing the parameters of Raman bands (line widths $\Delta\nu_R$, peak intensity Σ_{peak}, and integral intensity Σ_{int}) [1]. We com-

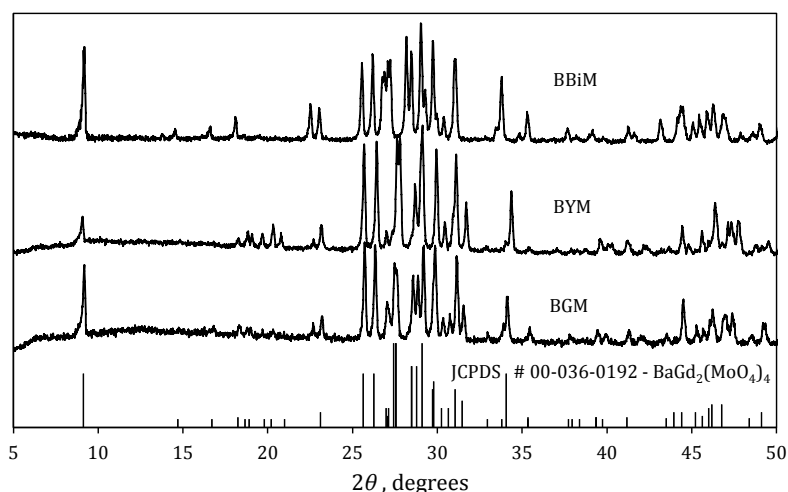Figure 1. Experimental XRD patterns of sintered BGM, BYM and BBiM powders, and reference pattern of $BaGd_2(MoO_4)_4$ from JCPDS # 00-036-0192
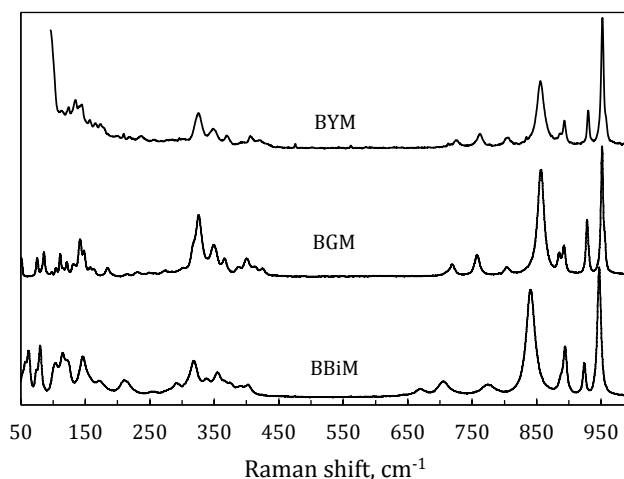

Figure 2. Spontaneous Raman spectra of BBiM and BGM single crystals, and solid-phase sintered BYM compound

pared the parameters of the Raman bands of BBiM, BGM and BYM compounds with the parameters of SRS active $\nu_1(A_g)$ vibration of the well-known SRS material $BaWO_4$ *via* the following procedure.

The mechanical mixtures of each $BaR_2(MoO_4)_4$ (R = Gd, Y, Bi) and $BaWO_4$ sintered powders were prepared by grinding in an agate mortar. $BaWO_4$ powder was synthesized in our previous work [14]. Weights of $BaR_2(MoO_4)_4$ and $BaWO_4$ were taken in the proportion, which corresponds to the equal volumes of the crystals (densities of the crystals were calculated from XRD data [8,10]). Thus, a comparison of the Raman vibration intensities in mixtures of $BaWO_4$ and the compounds under study makes it possible to estimate the ratio

of the intensities for the corresponding single crystals. To reduce the error introduced by our measuring setup, due to its relatively low resolution (about 1 cm^{-1}), the deconvolutions of the observed spectra and the instrumental function were performed through the approximation of the real spectra by the sum of Lorentzians, as we described in details in ref. [14]. As a result, the parameters of the individual Raman bands of the deconvolved spectrum were obtained. The parameters of the most intensive high-frequency Raman bands of BBiM, BGM and BYM, and the SRS-active band of $BaWO_4$ are presented in Table 1. One can see that the integral intensities of the Raman bands in BBiM compound are several times higher than in BGM, BYM and $BaWO_4$. This should

Table 1. Comparative parameters of the most intensive high-frequency Raman bands of the BBiM, BGM and BYM compounds and the SRS-active $\nu_1(A_g)$ band of $BaWO_4$

	Raman shift, cm^{-1}	$\Delta\nu_R$, cm^{-1}	Σ_{int}, arb. units.	Σ_{peak}, arb. units.
$BaWO_4$	925	2.7	1	1
$BaBi_2(MoO_4)_4$	945	4.9	2.41	1.13
	839	13.2	5.49	0.95
$BaGd_2(MoO_4)_4$	951	4.0	1.00	0.63
	856.5	10.6	1.62	0.38
$BaY_2(MoO_4)_4$	952	4.2	1.21	0.72
	855.5	13.0	1.81	0.34

have a positive effect on SRS-gain in the transient regime, when the pump pulse duration is comparable to the phase relaxation time of the SRS-active mode [1, 3]. The latter is no more than several tens of picoseconds for oxide crystals [3]. For longer pump pulse durations in the stationary SRS regime, in particular, in the case of Q-switched microchip lasers with the pulse duration 0.1–1 ns, the Raman peak intensity is the main parameter, which determine the SRS gain [1]. Table shows that BBiM, BGM and BYM compounds demonstrate approximately the same peak intensities of the Raman mode around 950 cm^{-1}, comparable to the intensity of the SRS-active mode of $BaWO_4$ (which has excellent SRS characteristics among scheelite-like crystals). The peak intensities of the vibration around 850 cm^{-1} decrease with decreasing radius and mass of the R^{3+} cation. It should be noted that the most intense oscillations around 950 cm^{-1} in the considered compounds provide the largest Stokes shift among all known scheelite Raman crystals, which is interesting for new laser wavelength generation.

Since high pump intensity is required to exceed the SRS threshold, and, therefore, SRS material should have a high radiation resistance, we estimated the optical damage threshold of the BBiM and BGM crystals. A Nd:YAG Q-switched laser with 10 ns pulse duration was used as the light source. The optical damage threshold of both BBiM and BGM crystals on cleaved (non-polished) surface was estimated at about 500 MW/cm^2.

Conclusions

A comparative Raman study showed that the BBiM, BGM and BYM crystals are potential SRS-active media for the stationary SRS regime, and in addition, the BBiM crystal may be of interest for the transient SRS due to the high integral cross section of Raman modes. Presumably, in the case of doping with laser ions, BBiM, BGM and BYM compounds are attractive as active media for microchip Raman lasers with self-Raman conversion.

Acknowledgement

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