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Two-photon interband absorption coefficients in tungstate and molybdate crystals

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ABSTRACT

Two-photon absorption (TPA) coefficients were measured in tungstate and molybdate crystals – $BaWO_4$, KGW, $CaMoO_4$, $BaMoO_4$, $CaWO_4$, $PbWO_4$ and $ZnWO_4$ upon different orientations of excitation polarization with respect to the crystallographic axes. Trains of 25 ps pulses with variable radiation intensities of third (349 nm) harmonics of passively mode-locked 1047 nm Nd:YLF laser were used for interband two-photon excitation of the crystals.

It was suggested that in the case, when 349 nm radiation pumping energy exceeds the bandgap width ($h\nu > E_g$), the nonlinear excitation process can be considered as two-step absorption.

The interband two-photon absorption in all the studied crystals induces the following one-photon absorption from the exited states, which affects the nonlinear process dynamics and leads to a hysteresis in the dependence of the transmission on the excitation intensity. This fact was taken into account under analysis of the experimental dependences of the reciprocal transmission on the excitation intensity. Laser excitation in the transparency region of the crystals caused stimulated Raman scattering (SRS) not for all the crystals studied. The measured nonlinear coefficients allowed us to explain the suppression of SRS in crystals as a result of competition between the SRS and TPA.

1. Introduction

The two-photon absorption (TPA) is of considerable interest for laser, nonlinear optics and spectroscopy. Different applications of TPA technique are considered. The TPA can be used to control energy, temporal, spectral, and spatial parameters of laser radiation, for example, power and duration of laser pulses [1]. The use of TPA technique makes it possible to improve the spatial resolution for experimental microscopy and also for laser microstructuring of materials [2]. The advantages of TPA become apparent in the case of excitation of interband transitions in dielectrics. Upon one-photon excitation of electronic levels in the conduction band, materials are almost nontransparent and the excitation energy is spent on nonradiative losses in the subsurface layer. In this case, the luminescent or absorption characteristics, for example, of tungstate and molybdate crystals, depend on the surface treatment quality [3]. Under two-photon interband excitation of the same level when the energy of each of the two photons corresponds to the transparence region of the material, the mentioned nonradiative losses are negligible and it becomes possible to study the spectral and luminescent properties under homogeneous bulk excitation. The difference in the selection rules for electronic transitions for one- and two-photon excitation also allows one to obtain additional spectroscopic data.

Tungstate and molybdate crystals are promising for application as detectors of ionizing radiation, e.g. as X-ray and γ-detectors, in medical tomography. A list of the crystals applications can be essentially extended. In particular this is connected with a great variety the spectral and luminescent characteristics of both doped and pure crystals [4–9]. The forbidden gap of the different crystals varies within a large range, which implies significant variations in the possible interband electronic excitation energy and luminescence wavelength (from UV to IR). Luminescence in pure and doped tungstate and molybdate crystals has a rather high quantum yield and it can be easily measured even in relatively small volumes. The decay times of intrinsic and impurity luminescence may vary for different crystals from a few nanoseconds to hundreds of microseconds. Slow scintillation decay restricts crystals application to the cases that do not require high counting rate [10].

Activated by trivalent rare-earth ions tungstate and molybdate crystals have good optomechanical properties and are used for laser applications. Recently, these crystals were found to be also promising as objects for Raman spectroscopy and for stimulated Raman scattering (SRS). In particular, linewidths, peak and integral Raman scattering cross sections, and SRS gain coefficients were measured for $PbWO_4$, $BaWO_4$, $CaWO_4$, $PbMoO_4$, $BaMoO_4$, and

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$CaMoO_4$ crystals with the scheelite structure, as well as for $ZnWO_4$ crystals with the wolframite structure [11–14]. Investigations of these crystals as efficient SRS converters in a wide spectral range showed that the interband TPA, which, as well as SRS, is associated with the cubic nonlinearity, may suppress SRS generation in the visible and UV spectral regions [15].

Note, that the TPA coefficients or cross sections have not yet been measured even for many well-known tungstate and molybdate crystals. Previously, we proposed a method to study the interband TPA under laser excitation by train of picosecond pulses with variable intensities [15–17]. In work [15] we measured TPA coefficients in $PbWO_4$, $PbMoO_4$, $CaMoO_4$, and $ZnWO_4$ crystals under 523.5 nm excitation. In this paper we recalculate TPA coefficients for excitation with 523.5 nm wavelength using experimental results [15] and taking into account the divergence of a laser beam.

The purpose of this work is to measure the TPA coefficients in a big number of tungstate and molybdate crystals under picosecond laser excitation with 349 nm wavelength. Based on these results, we will compare the TPA efficiency with the efficiency of another two photon process – stimulated Raman scattering.

2. The theory of two-photon absorption

Let us write the equations for the intensity I of a plane wave propagating in a medium with the length $z=L$ and the linear loss α [1] :

$$dI/dz = -\alpha I - \beta I^2, \tag{1}$$

$$\frac{I_0}{I} = \frac{e^{\alpha L}}{T_F^2} + \frac{(\beta/\alpha)(e^{\alpha L}-1)I_0}{T_F}, \tag{2}$$

here I_0, I are input and output intensities, respectively, $T_F = 4n/(n+1)^2$– transmission caused by Fresnel reflection from the entrance crystal face (n is the refractive index of the crystal), *and* β is the TPA coefficient.

For Gaussian beam and pulse form coefficients β and α are as follows [20–24]:

$$\alpha = \frac{\ln(aT_F^2)}{L} \quad \beta = 2\sqrt{2}\frac{b\alpha T_F}{e^{\alpha L}-1} \quad (\alpha \neq 0), \tag{3}$$

$$\beta = 2\sqrt{2}\frac{bT_F}{L} \quad (\alpha = 0), \tag{4}$$

here $b=\Delta(1/T)/\Delta I_0$ is the tangent or the slope of the linear dependence $1/T(I_0)$, a – coefficient of linear dependence $1/T(I_0)$ for $I_0=0$, where $1/T=E_{in}/E_{out}$ – ratio of input and output laser pulses energy.

We also take into account that for the focused laser beam formulae (3) and (4) need to be corrected due to the variation of cross-section of the laser beam, and hence laser intensity, alongside of the pulse propagation via the sample. Due to this effect for the beam waist in the middle of a crystal we may change the sample length L for effective length L_{eff}:

$$L_{eff} = \arctan\left(\frac{L}{2z_{rel}}\right)\left(\frac{L^2}{2z_{rel}} + 2z_{rel}\right) \tag{5}$$

And in this case of effective input intensity:

$$I_0 = \frac{E_{in}}{\tau S}4\sqrt{\frac{\ln(2)}{\pi}}\left[1+\left(\frac{L}{2z_{rel}}\right)^2\right]^{-1}, \tag{6}$$

here z_{rel} – Rayleigh length is determined as the length within which the beam cross section in the waist doubles (7), E_{in} – input pulse energy, τ is the pulse width at ½ level, S – cross-section beam waist at $1/e^2$, and r_0 – beam waist radius.

$$z_{rel} = \frac{\pi r_0^2 n^2}{\lambda} \tag{7}$$

Simple treatments show that in this case formulae (3) and (4) will be changed:

$$\alpha = \frac{\ln(aT_F^2)}{L} \quad \beta = 2\sqrt{2}\frac{bT_F}{L_{eff}(M_1+M_2+M_3+M_4)e^{\alpha L}} \quad (\alpha \neq 0), \tag{8}$$

$$\beta = 2\sqrt{2}\frac{bT_F}{L_{eff}} \quad (\alpha = 0), \tag{9}$$

here M_i:

$$M_1 = \frac{2-\alpha L}{2}, \tag{10}$$

$$M_2 = \frac{\alpha^2}{8}\left[\frac{L\left(L^2+4z_{rel}^2\right)}{L_{eff}} + \left(L^2-4z_{rel}^2\right)\right], \tag{11}$$

$$M_3 = \frac{\alpha^3 L}{48}\left[\left(12z_{rel}^2 - L^2\right) - \frac{3L\left(L^2+4z_{rel}^2\right)}{L_{eff}}\right], \tag{12}$$

$$M_4 = \frac{\alpha^4}{384}\left[\frac{L\left(L^2+4z_{rel}^2\right)\left(19L^2-12z_{rel}^2\right)}{3L_{eff}} + \left(L^2-4z_{rel}^2\right)^2 - 16L^2z_{rel}^2\right] \tag{13}$$

Formula (8) was obtained for the case when $\alpha L \leq 2$. For small values of $\alpha L \ll 1$, relevant members of the approximation M_i(10)–(13) can be neglected.

3. Experiments and results

3.1. Objects of investigation

We studied tungstate and molybdate crystals $PbWO_4$, $ZnWO_4$, $BaWO_4$, $CaWO_4$, $KGd(WO_4)_2$, $PbMoO_4$, $CaMoO_4$, and $BaMoO_4$. The single crystals in the form of parallelepipeds with polished faces 2–30 mm long were oriented according to crystallographic axes. The crystals were excited by laser radiation with linear polarization parallel and perpendicular to these axes.

Fig. 1(a and b) show the transmission spectra of the crystals in the visible region measured in unpolarized light on a Carry-5000 spectrometer. The transmission value of crystals is restricted by the Fresnel reflection from two faces.

The band-gap widths E_g for the crystals determined in [3–10,25,26] are listed in Table 1.

3.2. Experimental technique

Experimental set up was described in [15,16]. In this work trains of 25 ps pulses with variable radiation intensities of second ($\lambda=523.5$ nm, $LiIO_3$ crystal) and third ($\lambda=349$ nm, KDP crystal) harmonics of passively mode-locked$\lambda=1047$ nm Nd:YLF laser (Fig. 2(a)) were used for interband two-photon excitation of the