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Lead pyrovanadate single crystal as a new SRS material

T.T. Basiev, Yu.K. Voron'ko, V.A. Maslov, A.A. Sobol, V.E. Shukshin

***Abstract*. Lead pyrovanadate $Pb_2V_2O_7$ single crystals of optical quality suitable for laser experiments are obtained. Vibrational modes are identified based on the analysis of the polarised Raman spectra of the single crystals. The main parameters (width at half maximum, peak and integral intensities) of the spectral lines most promising for SRS conversion in this material are estimated. These parameters are compared with the corresponding parameters of the most frequently used lines of known Raman materials: yttrium and gadolinium vanadates, potassium and lead tungstates, and lead molybdate.**

Keywords: *Raman light scattering, lead pyrovanadate $Pb_2V_2O_7$, SRS lasers.*

1. Introduction

The high efficiency of yttrium and gadolinium orthovanadate crystals as SRS-active media was previously demonstrated in [1 – 5]. It is of interest to evaluate the possibility of SRS conversion in other vanadate crystals, in particular, lead pyrovanadate, which is known as a natural mineral chervetite.

The study of this material also allows one to estimate the effect exerted by the Pb^{2+} cation, which has a strong bond covalency, on the cross section of Raman scattering on the internal vibrations of the $[V_2O_7]$ complex. Studying the stimulated Raman scattering in MWO_4 and $MMoO_4$ single crystals of the scheelite structure with M = Ba, Sr, Ca, and Pb, the authors of [6] found that the cross sections of Raman scattering on the internal vibrations of the $[WO_4]$ and $[MoO_4]$ complexes are anomalously large in the $PbWO_4$ and $PbMoO_4$ crystals.

In the present work, we comparatively estimate the cross sections of the most intense Raman lines of the internal vibrations of the $[VO_4]$, $[V_2O_7]$, $[WO_4]$, and $[MoO_4]$ complexes in the $Pb_2V_2O_7$, YVO_4, $GdVO_4$, $PbWO_4$, $PbMoO_4$, and $CaWO_4$ single crystals. Since the literature contains no data on the Raman spectra of $Pb_2V_2O_7$ crystals, we studied them in polarised light and identified the vibrational spectra.

T.T. Basiev, Yu.K. Voron'ko, V.A. Maslov, A.A. Sobol, V.E. Shukshin
A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia;
e-mail: sobol@lst.gpi.ru, shukshinve@lst.gpi.ru

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2. Studied crystals and experimental technique

The $Pb_2V_2O_7$ single crystals were crystallised from a congruent melt [7]. The raw materials (PbO and V_2O_5, high purity grade 2 – 3 for microelectronics) with a total mass of 60 g were melted in a platinum crucible 40 mm in diameter. After homogenisation of the melt at a temperature of 750 °C in a resistance furnace, lead vanadate was spontaneously crystallised on a platinum rod 2 mm in diameter as the melt was cooled with a rate of 0.8 °C h^{-1}. The temperature gradient did not exceed 2 °C cm^{-1}. To decrease the number of forming centres, the seed holder was pulled with a rate of 5 mm h^{-1}. The $Pb_2V_2O_7$ single crystals had a sheet form and reached dimensions of $3 \times 8 \times 1$ mm.

The size of the single crystals allowed us both to reliably measure the Raman spectra in polarised light and to estimate the scattering cross sections for individual lines. The YVO_4, $GdVO_4$, $PbWO_4$, $PbMoO_4$, and $CaWO_4$ single crystals studied previously in [1, 6, 8 – 10] were grown by the Czochralski method. The relative scattering cross sections were measured on identically thick plates under the same conditions of excitation and recording of Raman spectra using the 180° scattering geometry as in works [6, 8, 9]. The spectra were recorded with a SPEX Ramalog 1403 spectrometer with a resolution better than 1 cm^{-1} under excitation by the 514.5-nm argon laser line. The line with $\lambda = 488$ nm was not used due to its strong absorption by the $Pb_2V_2O_7$ crystal.

3. Experimental

According to [11, 12], the $Pb_2V_2O_7$ crystal structure corresponds to the monoclinic space group $P2_1/a$ (C_{2h}^5) with four formula units per unit cell. The structure contains the pyrovanadate anions $[V_2O_7]^{4-}$. The following atomic positions are identified in the lattice: Pb(l), Pb(2), V(l), V(2), and O(1–7). All the 11 positions have the local symmetry C_1. Based on this, we calculated the vibrational spectrum Γ of the crystal for the Brillouin zone centre as

$$\Gamma = 33A_g + 33B_g + 33A_u + 33B_u.$$

The active vibrations in the Raman spectra are $33A_g + 33B_g$, and the active vibrations in the IR absorption spectra are $32A_u + 31B_u$. We managed to separate the A_g and B_g

vibrations using the polarised Raman spectra in different scattering geometries. The Raman tensors for the monoclinic structure have the form

$$\begin{vmatrix} \alpha_{xx} & \cdot & \alpha_{xz} \\ \cdot & \alpha_{yy} & \cdot \\ \alpha_{zx} & \cdot & \alpha_{zz} \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} \cdot & \alpha_{xy} & \cdot \\ \alpha_{yx} & \cdot & \alpha_{yz} \\ \cdot & \alpha_{zy} & \cdot \end{vmatrix}$$

for the A_g and B_g vibrations, respectively.

This form of the Raman tensors corresponds to the case when the second-order axis C_2 is parallel to the y axis of the Cartesian coordinate system and to the crystallographic axis b. The axes of the single crystal were oriented with respect to the axes of the Cartesian coordinate system as $a||x$, $b||y$, and $c'||z$. In this case, the c' axis was perpendicular to the ab plane. The experiments were performed in the scattering geometries $x(zz)\bar{x}$, $x(yy)\bar{x}$, and $z(xx)\bar{z}$ (in Porto notations) for identification of the A_g vibrations and in the $x(yz)\bar{x}$ and $z(xy)\bar{z}$ geometries for identification of the B_g vibrations. The choice of these geometries allowed us to avoid the birefringence effects of monoclinic crystals and to maximally separate the A_g and B_g vibration lines. The polarised Raman spectra are shown in Fig. 1. The spectra in the region of 20–100 cm^{-1} are presented in Fig. 2. The results of identification of the symmetry of the observed vibrations are listed in Table 1. We reliably identified 29 A_g vibrations and 8 B_g vibrations. The considerably smaller number of recorded B_g vibrations compared to the set found from the theoretical group analysis for the C_{2h}^5 structure is explained by the extremely low intensity of most B_g vibrations. As a result, it is difficult to separate these lines on the background of intense lines of A_g vibrations even in polarised spectra. Attention is drawn to the most intense high-frequency A_g line ($\Delta\nu = 878$ cm^{-1}) and to the line with $\Delta\nu = 579$ cm^{-1} of the same symmetry. According to [13], these lines can be assigned to the symmetric internal vibrations of the end VO_3 group and of the bridging V–O–V bond of the pyrovanadate anion, respectively.

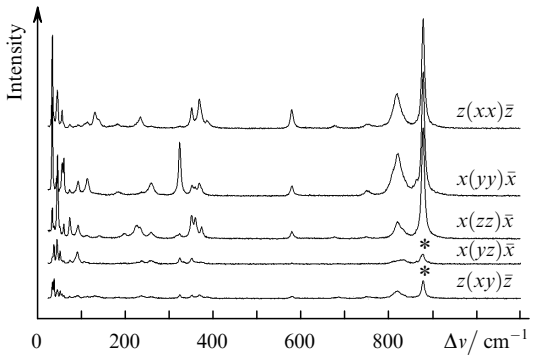

Figure 1. Polarised Raman spectra of a lead pyrovanadate single crystal at a temperature of 300 K. The A_g vibrations are observed in the scattering geometries $x(zz)\bar{x}$, $x(yy)\bar{x}$, and $z(xx)\bar{z}$, while the B_g vibrations are observed in the geometries $x(yz)\bar{x}$ and $z(xy)\bar{z}$. The asterisks denote the frequencies of vibrations forbidden in the given scattering geometry.

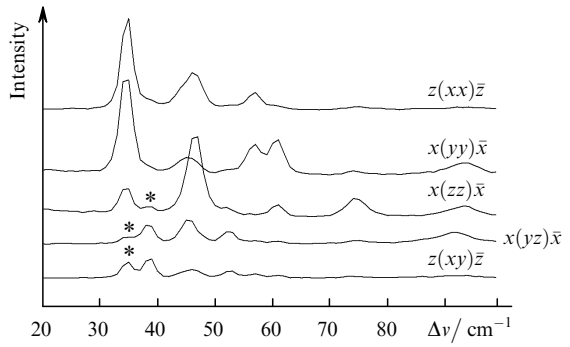

Figure 2. Polarised spectra from Fig. 1 in the region of 20–100 cm^{-1}.

Table 1. Frequencies and symmetries of vibrations in the lead pyrovanadate crystal at a temperature of 300 K.

Frequency shift/cm^{-1}		Notations
A_g	B_g	
34		
	38	
45		
	46	
47		
	53	
57		
61		
74		
	91	
94		
107		
114		
132		
141		
185		
201		
226		
236		
	240	
260		
314		
324		
	335	
352		
360		
369		
373		
387		
579		vibration ν_s (V–O–V)
678		
	685	
750		
810		line wing
820		
830		line wing
	833	
878		vibration ν_s (VO_3)

Table 2 lists the spectroscopic parameters of the most intense Raman lines in the studied crystals at a temperature of 300 K. Of particular interest are the line half-widths $\delta_{1/2}$, the optical dephasing times T_2, and the peak (σ_{peak}) and integral (σ_{int}) line intensities, which allow one to evaluate the potential of the use of materials in Raman lasers [14–19]. One can see that σ_{int} for the line with $\Delta\nu = 878$ cm^{-1} of the ν_s (VO_3) vibration of the pyrovanadate anion in $Pb_2V_2O_7$ is higher than for the totally symmetric vibration ν_1 of the [VO_4] tetrahedron in $GdVO_4$ (by 30 %) and YVO_4 (by 15 %). The small optical dephasing time and the large

linewidth of the v_s (VO_3) vibration (8 cm^{-1}) compared to the vibration v_1 of [VO_4] (2.6–2.9 cm^{-1}) result in a smaller σ_{peak} for the studied line in lead pyrovanadate than for the lines v_1 in gadolinium and yttrium pyrovanadates, but these parameters are important for realisation of stationary SRS. Table 2 also shows that the integral intensity of Raman lines in vanadate systems increases when the crystal lattice contains the Pb atom as a structural element, although this intensity in the orthomolybdate and orthotungstate structures is even higher. The intensity σ_{int} for the v_1 line in $PbWO_4$ and $PbMoO_4$ is higher than in $CaWO_4$ by a factor of 3.3 and 7.5, respectively (Table 2).

Table 2. Spectroscopic parameters of the most intense Raman lines of the studied crystals at 300 K.

Crystal	Δv/ cm^{-1}	T_2/ps	$\delta_{1/2}$/cm^{-1}	σ_{peak}	σ_{int}
$PbMoO_4$	871	1.8	6.0	6.7	7.5
$PbWO_4$	904	2.6	4.1	5.4	3.3
$Pb_2V_2O_7$	820*	0.5	20.0	0.3	0.7
$Pb_2V_2O_7$	878	1.3	8.0	1.7	2.2
YVO_4	891	4.1	2.6	4.5	1.9
$CaWO_4$	911	1.8	5.9	1.0	1.0
$GdVO_4$	884	3.5	3.0	3.9	1.7

Note. Intensities σ_{peak} and σ_{int} are normalised to those for the line with $\Delta v = 911$ cm^{-1} in $CaWO_4$ and are given for the geometries corresponding to the maximum scattering intensities.
* Data in this line are given for the total profile with a maximum at $\Delta v = 820$ cm^{-1}.

The large half-widths of the lines of the A_g symmetry in the Raman spectrum, $\delta_{1/2} = 8$ cm^{-1} ($\Delta v = 878$ cm^{-1}) and 20 cm^{-1} ($\Delta v = 820$ cm^{-1}), can be of special interest in quantum electronics for realisation of the stationary SRS and parametric scattering of pico- and subpicosecond laser pulses [14–18].

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