

Raman spectra and elastic properties of KPb_2Cl_5 crystals

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Raman scattering spectra and elastic constants of KPb_2Cl_5 crystals have been studied. The results obtained are interpreted in terms of the *ab initio* lattice dynamics model taking into account multipole moments of ionic electron envelopes. The experimental results have been found to be in good agreement with numerical simulation; the narrow phonon spectra are shown to be due to a considerable contribution of heavy cations into the eigenvectors of the higher frequency lattice modes.

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1 Introduction

Progressive development of nonlinear solid state optics and infrared photonics calls for new materials with a wide transparency window in the IR range (down to 30 μm). The phonon spectra of complex halides with heavy cations are shorter than those of traditional oxide systems and this attracts a great deal of interest.

Crystals of the $\text{Me}^I\text{Pb}_2\text{Hal}_5$ family (where Me^I is an alkaline ion and Hal is a halogen) are found to have a wide IR window of interest. Unlike many other halides these crystals are rather tolerant to environmental changes and can be grown as bulk single crystals [1]. Fairly loose packing of bulky ions makes possible to vary composition and properties of the crystals to have a suitable matrix for active laser media [2].

The paper studies phonon spectra and elastic properties of the KPb_2Cl_5 crystal of that family to understand the physical nature of such low-lying phonon frequencies. Elastic properties studied in parallel provide information on their correlation with the crystal structure, which is of interest for material science, for potential applications of these crystals in IR acoustooptic devices, in particular.

To simulate phonon spectra and to establish correlation between spectral frequencies and structural units and ionic interactions, we used the *ab initio* approach [3–5] since conventional methods (see e. g. [6,7]) employ too many unknown fitting parameters for such a low symmetry complex structure.

2 Experimental

KPb_2Cl_5 crystals belong to the $P2_1/c$ space group, $Z = 4$, $a = 8.854(2)$ Å, $b = 7.927(2)$ Å, $c = 12.485(3)$ Å, $\beta = 90.05(3)$, $V = 876.3(4)$ Å³. The atomic coordinates as per [8] are given in Table 1; details of crystal synthesis can also be found in [8].

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Table 1 Atomic coordinates ($\times 10^4$) for KPb_2Cl_5 crystal.

	X	Y	Z
K(1)	5092(5)	514(6)	1696(4)
Pb(1)	65(1)	58(1)	1742(1)
Pb(2)	2547(1)	4359(1)	9937(1)
Cl(1)	9585(4)	1655(5)	4023(3)
Cl(2)	2218(4)	405(4)	9986(3)
Cl(3)	5401(5)	1798(6)	4186(4)
Cl(4)	2355(5)	3117(5)	2204(3)
Cl(5)	7702(6)	3449(5)	1885(3)

Optical quality samples for the experiments were selected under a polarizing microscope. The samples have been oriented with an accuracy of $\pm 5'$ and cut as parallelepipeds with the edges running along crystallographic axes and with the flatness better than $\pm 2 \mu\text{m}/\text{cm}$. The Raman spectra were obtained with a U-1000 double-grating spectrometer (I.S.A. Jobin Yvon) and 514.5 nm 0.5 W Ar^+ polarized laser for excitation. Elastic constants $C_{\lambda\mu}$ have been measured with the pulsed bulk acoustic wave method [9,10] at 29.5 MHz.

3 Results and discussion

The vibrational representation at the center of the Brillouin zone looks as follows:

$$\Gamma = 24A_g(xx, yy, zz, xy, yx) + 24B_g(xz, zx, yz, zy) + 24A_u + 24B_u, \quad (1)$$

where the respective components of the Raman scattering tensor are given in brackets. The low symmetry and the complex structure of the crystal denies separating vibrations of various ionic sublattices by the group theory analysis.

The experimental Raman spectra are shown in Fig. 1.

All the lines observed are found to be below 250 cm^{-1} . The spectra are strongly anisotropic, all the lines are well polarized. The number of well-defined peaks turns out to be less than predicted in (1), and to assign them to structural units the peaks should be compared to the numerical simulation results.

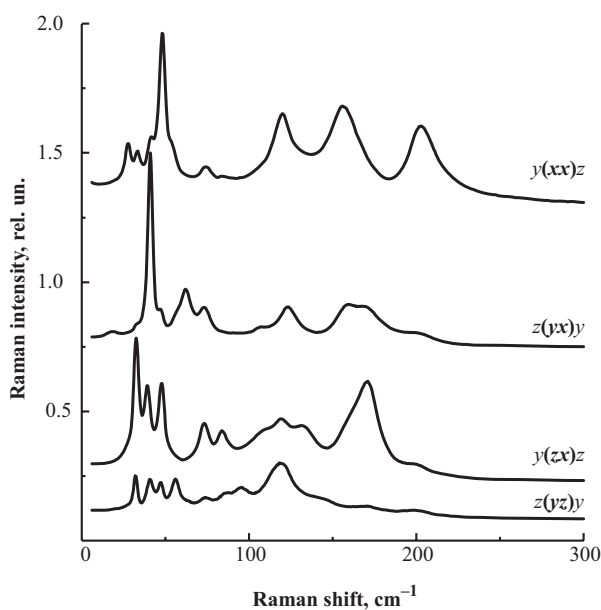


Fig. 1 Polarized Raman scattering spectra of KPb_2Cl_5 crystal under ambient conditions.

A modified Gordon-Kim approach [3,4] used for the simulation takes into account higher multipole distortions of the ionic charge densities. This is particularly important for the low-symmetry structure of KPb_2Cl_5 where interactions of these multipoles are strongly involved in the lattice dynamics. Details of the simulation procedure and the symmetry analysis of the normal modes are described in [5]. Table 2 shows the experimental frequencies and their respective calculated modes. The frequencies are found to agree best in the middle part of the spectrum. Calculation results for the lower frequencies (including a few imaginary values) strongly depend on the initial structural data: their variation within the experimental accuracy can change the values by 100%.

Table 2 Experimental and calculated frequencies (in cm^{-1}) of Raman active modes in KPb_2Cl_5 .

A_g		B_g	
Calculated	Experimental	Calculated	Experimental
34 <i>i</i>		38 <i>i</i>	
26 <i>i</i>		28 <i>i</i>	
25 <i>i</i>		6	
21	18	28	33
34	27	39	40?
41	35	45	42
45	43	46	48
53	50	57	
57	} 56	64	} 57
58		67	
60	62	71	
67		74	75
73	73	80	85
76		84	
86	85	90	88
91		95	95
92		100	
101		103	108
106	108	107	119
110	120	115	132
123	124	120	144
129	127	129	158
134	132	140	173
159	200?	161	202

Figure 2 shows relative displacements of ions in the eigenvector of the highest mode in the spectrum, which determines the boundary of the transparency window in the crystal. From the figure it is apparent that while chlorine ions still form the main part of the eigenvector, the heavy cations are also involved in the mode. This may be the reason for such a low frequency of this mode and explain the more narrow spectra of the crystal than in high symmetry perovskite-like chlorides [5].

Table 3 presents the measured elastic constants versus the calculated ones in the same Gordon-Kim approach. The constants were calculated with the same dynamic matrix by the well known procedure (see e. g. [6]). The calculated results are in a fairly good agreement with the experimental measurements.

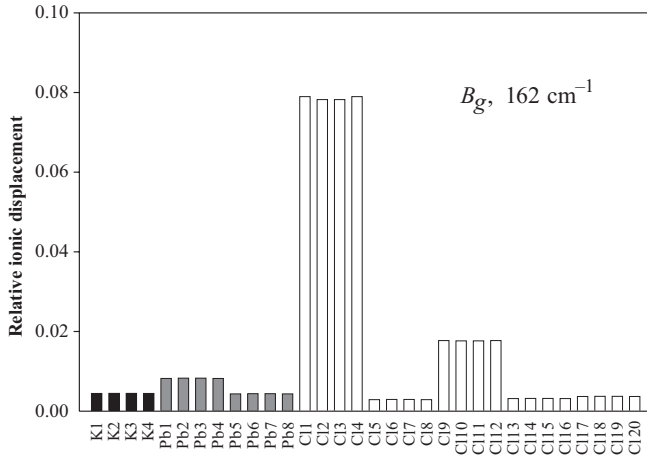


Fig. 2 Relative amplitudes of ionic displacements in the eigenvector of the highest phonon mode of KPb_2Cl_5 crystal.

Table 3. Experimental and calculated nonzero elastic constants of KPb_2Cl_5 crystal (10^{10} N/m^2)

Constant:	C_{11}	C_{12}	C_{13}	C_{15}	C_{22}	C_{23}	C_{25}	C_{33}	C_{35}	C_{44}	C_{46}	C_{55}	C_{66}
Experimental:	4,34	1,93	1,77	-0,05	3,53	1,52	0,05	3,62	0,06	1,11	0,03	1,10	1,43
Calculated:	4.00	1.30	1.37	-0.03	3.87	1.42	0.01	3.47	0.01	1.30	0.03	1.30	1.24

4 Conclusion

We have obtained experimental Raman spectra of the KPb_2Cl_5 crystal and interpreted them with the *ab initio* lattice dynamics model. The modified Gordon-Kim model yielded phonon frequencies in good agreement with the experimental data even for this low-symmetry crystal. Analysis of the phonon eigenvectors has shown that the low phonon frequencies are due to considerable involvement of heavy cations in all lattice modes including the highest frequency ones. The same approach yielded good results for the crystal elastic constants, too.

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