

Vibrational spectra of KPb_2Cl_5 and KPb_2Br_5 crystals

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Received 14 July 2004; received in revised form 18 January 2005; accepted 20 February 2005

Abstract

Lattice dynamics of KPb_2Cl_5 and KPb_2Br_5 crystals is simulated in the framework of ab initio model, taking into account multipole moments of electron envelopes of ions. Results are compared with experimental polarized Raman spectra; good agreement with results of simulations is shown. Extremely low frequencies of phonon spectra are explained by big mass of anions together with considerable participation of heavy cations in the eigenvectors of upper frequency lattice modes.

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PACS: 63.20.Dj; 77.84.Bw; 78.30.Hv

Keywords: KPb_2Cl_5 ; KPb_2Br_5 ; Lattice dynamics; Ab initio simulations

1. Introduction

Nowadays development of solid state nonlinear optics and infrared photonics stimulates exploration of new materials with wide transparency window in the IR range (down to 30 μm). This problem attracts interest to crystals of complex halides with heavy cations possessing shorter phonon spectra, as compared to traditional oxide systems. Crystals of $\text{Me}^+\text{Pb}_2\text{Hal}_5$ family (Me^+ —alkaline ion, Hal—halogene) demonstrate this wide IR window. They are rather stable to environmental conditions (in contrast to many other halide crystals) and could be grown in bulk single crystal samples [1]. Quite loose packing of bulky ions makes it possible to vary crystals' compositions and properties and provides a means to use them as a matrix for active laser media (see e.g. [2–4]).

In this work we have studied phonon spectra of KPb_2Cl_5 and KPb_2Br_5 crystals of this family, trying to understand physical nature of so low-lying phonon frequencies. To simulate phonon spectra and to connect spectral frequencies with structural units and interionic interactions, we have used ab initio approach [5–7], since traditional empirical methods (see e.g. [8,9]) employ too many unknown fitting parameters for such low symmetry complex structures.

2. Method of simulations

Crystals under investigations belong to $P2_1/c$ space group, with $Z = 4$ formula units per unit cell. Parameters of KPb_2Cl_5 structure: $a = 8.854(2) \text{ \AA}$, $b = 7.927(2) \text{ \AA}$, $c = 12.485(3) \text{ \AA}$, $\beta = 90.05(3)$, $V = 876.3(4) \text{ \AA}^3$, parameters of KPb_2Br_5 structure: $a = 9.256(2) \text{ \AA}$, $b = 8.365(2) \text{ \AA}$, $c = 13.025(3) \text{ \AA}$, $\beta = 90.00(3)$, $V = 1008.4(4) \text{ \AA}^3$ [10] (see also [11,12]). Atomic coordinates are given in Tables 1 and 2. The unit cell structure of the KPb_2Cl_5 crystal is shown in Fig. 1.

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Table 1
Relative coordinates of atoms ($\times 10^4$) of 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)

Table 2
Relative coordinates of atoms ($\times 10^4$) of KPb_2Br_5 crystal

	X	Y	Z
K(1)	5099(6)	542(6)	1692(5)
Pb(1)	108(1)	25(1)	1750(1)
Pb(2)	2559(1)	4329(1)	9937(1)
Br(1)	9578(2)	1648(2)	4022(2)
Br(2)	2220(4)	391(2)	9981(2)
Br(3)	5419(2)	1819(2)	4210(4)
Br(4)	2366(2)	3130(2)	2199(2)
Br(5)	7677(3)	3463(2)	1881(2)

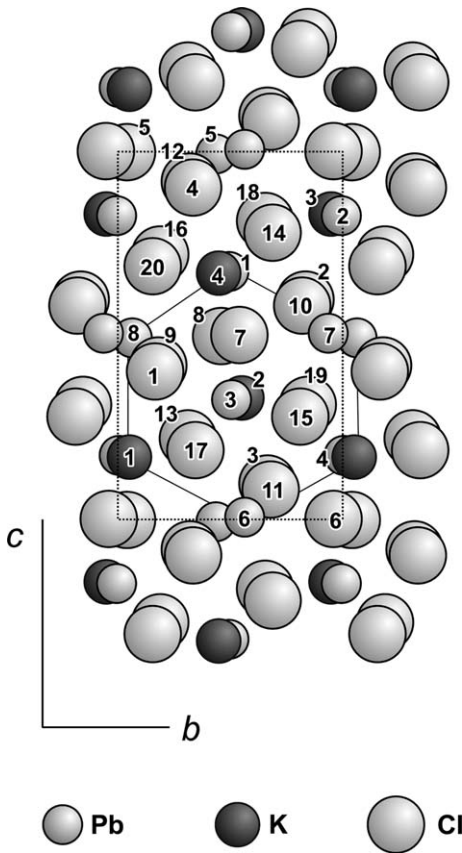


Fig. 1. Unit cell structure of KPb_2Cl_5 crystal.

Phonon spectra were simulated in the framework of generalized Gordon–Kim model [5,6], where distortions

of electronic envelopes of the ions are taken into account. This is crucial for low symmetry structures, since interactions of induced multipoles can participate considerably in total lattice energy and dynamics.

According to [5,6] electron density distribution of every ions under external field was calculated as

$$V_{\text{ext}}^{(l)} = r^{(l)} P_l(\cos \theta), \quad (1)$$

where $P_l(\cos \theta)$ are Legendre polynomials. Potential of Watson sphere

$$V_{\text{W}} = \begin{cases} -Z_{\text{ion}}/R_{\text{W}}, & r < R_{\text{W}} \\ -Z_{\text{ion}}/r, & r > R_{\text{W}} \end{cases} \quad (2)$$

was used for a spherical component of the field. Dipole ($l=1$) and quadrupole ($l=2$) distortions were taken into account. Total crystal energy was calculated as a sum of long range multipole–multipole and short range (calculated using density potential approach) interactions. Radii of Watson spheres, induced dipole and quadrupole moments were found by minimization of total crystal energy (details are given in [5,6]).

Expression for dynamical matrix, that follows from this energy, is given in [7]. Its diagonalization, as usual, provides frequencies and eigenvectors of lattice vibration modes. Obtained eigenvectors at the center of Brillouin zone (active in first order optical processes) have been attributed to irreducible representations of crystals' point group:

$$\Gamma = 24A_g(xx, yy, zz, xy, yx) + 24B_g(xz, zx, yz, zy) + 24A_u + 24B_u. \quad (3)$$

Components of Raman scattering tensor, where corresponding modes should be active, are given in brackets.

To perform such attribution, vibrational representation $P(g)$ of the group was built and projective operators [11] obtained as

$$\Gamma_{\rho} = \frac{N(\rho)}{N(g)} \sum_{g \in G} \chi_{\rho}^*(g) \Gamma(g). \quad (4)$$

Here, $N(\rho)$ is dimension of the ρ th irreducible representation of symmetry operation, $N(g)$ is dimension the group, $\chi_{\rho}(g)$ is a character of irreducible representation matrix, $\Gamma(g)$ is vibrational representation for g operation of symmetry, Γ_{ρ} is projective operator, summation is done over all symmetry operations of the group. Eigenvector \mathbf{f} transforms according to the ρ th representation of the group, if it satisfies to the criterion [13]:

$$\Gamma_{\rho} \mathbf{f} = \frac{N(g)}{N(\rho)} \mathbf{f}. \quad (5)$$

This attribution was used to compare results of simulation with experimental data.

3. Experiment

Samples for experiments of $2 \times 2 \times 4 \text{ mm}^3$ size were cut along crystallographic axes of their lattices. Raman spectra have been obtained with U-1000 (I.S.A. Jobin Yvon, France) double grating spectrometer and Ar^+ laser (514.5 nm, 500 mW) for excitation.

Experimental spectra are given in Figs. 2 and 3. As it was supposed, spectra are limited to extremely low fre-

quencies; all observed lines are well below 250 cm^{-1} for chloride and below 200 cm^{-1} —for bromide crystals. Strong anisotropy and high polarization of Raman components are clearly seen. Number of well determined lines in all scattering geometries is below of the one, predicted by (3).

4. Results of simulations and discussion

Simulated frequencies of Raman active lines for KPb_2Cl_5 crystal are given in Table 3 together with the values from experimental spectra (Fig. 2). Best agreement observed in the middle part of the spectra. At the lowest (below 20 cm^{-1}) frequencies calculated values depend strongly on minor deviations of atomic coordinates—their variation within experimental precision brings considerable (up to 100%) changes of these frequencies, leaving middle and upper frequencies (that are of interest for our investigation) practically unchanged.

Very similar results, with slight downward shift due to the bigger mass of bromine ions, have been obtained for KPb_2Br_5 crystal. Complete set of its calculated frequencies is given in Table 4.

Relative displacements of ions in the eigenvectors of highest modes (after accounting for atomic masses), that

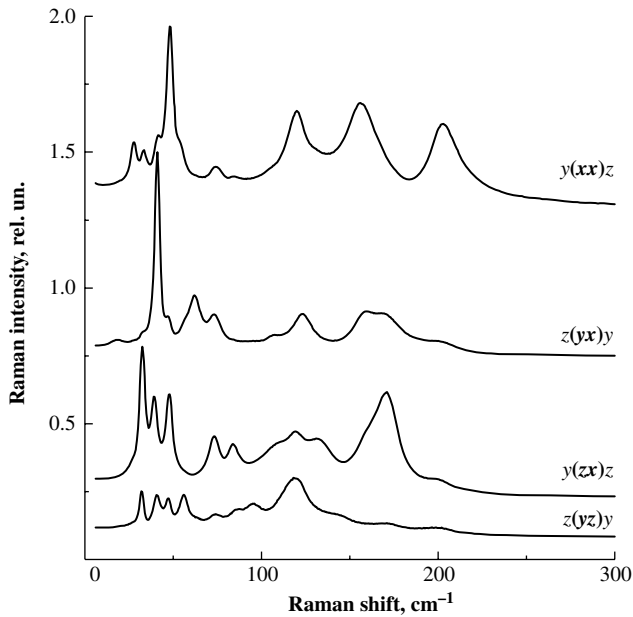


Fig. 2. Polarized Raman scattering spectra of KPb_2Cl_5 crystal.

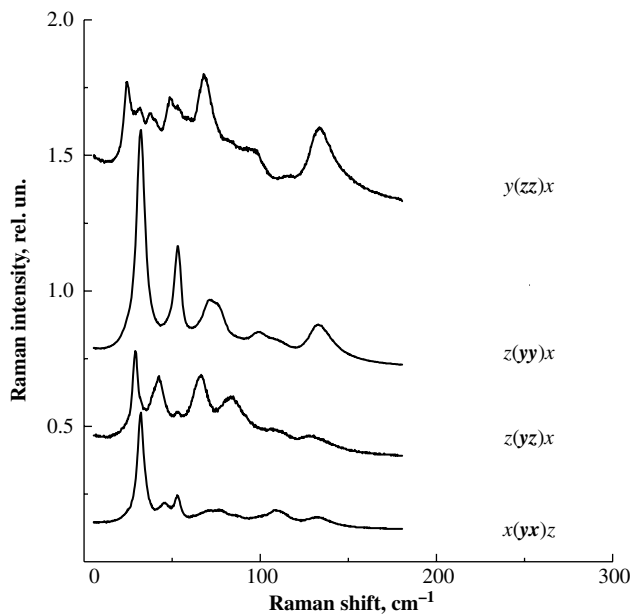


Fig. 3. Polarized Raman scattering spectra of KPb_2Br_5 crystal.

Table 3

Simulated and experimental (from Raman spectra) frequencies (cm^{-1}) of KPb_2Cl_5 crystal

A_g		B_g	
Simulation	Experiment	Simulation	Experiment
34i		38i	
26i		28i	
25i		6	
21	18	28	33
34	27	39	40
41	35	45	42
45	43	46	48
53	50	57	57
57	56	64	
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	162	202

Table 4
Calculated frequencies (cm^{-1}) of $\text{K}\text{Pb}_2\text{Br}_5$ vibrational spectrum

A_g	B_g	A_u	B_u
10i	11i	26i	20i
22i	23i	0	27i
9	10	2	0
17	21	15	0
31	30	20	6
32	33	22	24
36	38	30	27
39	42	37	40
41	45	41	42
44	46	46	45
46	50	47	48
53	60	49	54
53	62	53	57
59	65	58	62
65	68	61	67
68	73	66	69
73	74	67	71
75	77	74	76
78	82	81	82
81	85	84	85
85	91	86	89
89	96	91	91
94	99	93	101
108	110	109	110

define the low frequency boundary of transparency window, are shown at Figs. 4 and 5. It is seen from these figures that, in spite of dominating part of halide ions, contribution of heavy cations stays considerable. Such complex mixture of different sublattices displacements results from low symmetry of crystal structures (in contrast for example to high symmetry perovskite-like halides [7]). This contribution of heavy cations increases effective masses of upper lattice modes and moves their frequencies down.

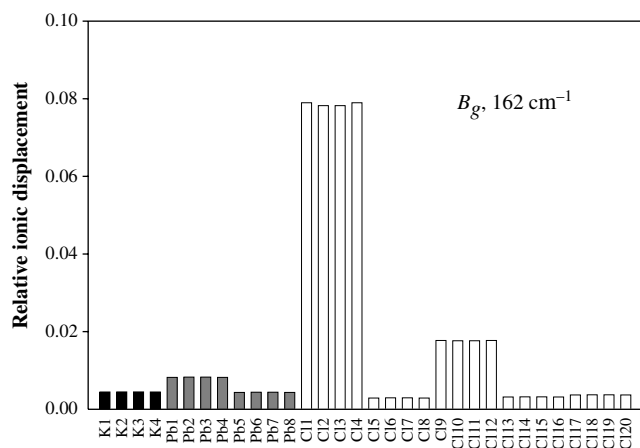


Fig. 4. Relative amplitudes of ionic vibrations in the highest lattice mode of $\text{K}\text{Pb}_2\text{Cl}_5$ crystal. Atomic numbering corresponds to Fig. 1.

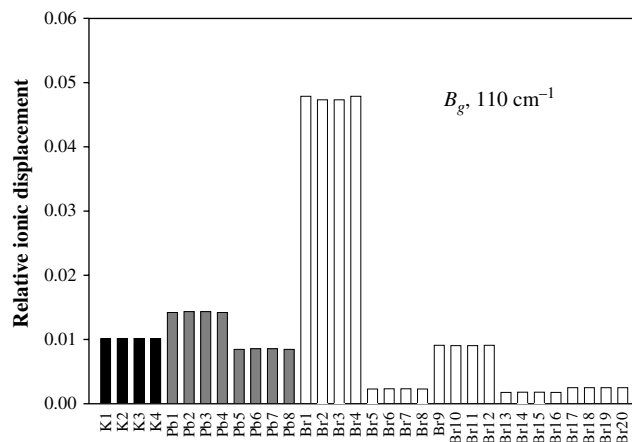


Fig. 5. Relative amplitudes of ionic vibrations in the highest lattice mode of $\text{K}\text{Pb}_2\text{Br}_5$ crystal.

5. Conclusion

So we can conclude that used ab initio approach simulates phonon spectra of investigated crystals reasonably good, and together with developed symmetry approach provides a means to describe their lattice dynamics in reasonable agreement with experimental data. Obtained information on eigenvectors of lattice modes show that extremely narrow phonon spectra of these crystals is due to considerable contribution of heavy cations into upper lattice modes, as a results of complex crystal structure and its low symmetry.

Acknowledgments

Helpful discussions with Prof. V.I. Zinenko and Prof. K.S. Aleksandrov are gratefully acknowledged.

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