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Comparative study of TITiOPO₄ and KTiOPO₄ crystals by Raman spectroscopy

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Phonon spectra of TITiOPO₄ and KTiOPO₄ have been measured in a few scattering geometries. A comparative analysis of the difference in the line positions has been performed. It has been shown that a strong relative shift of lines in the frequency range $<100 \text{ cm}^{-1}$ can be explained well by the mass ratio of the ions involved into vibration. At higher frequencies the mechanism of these shifts is more complicated and can be explained by the combined effect of a few factors.

Key words: phonon spectrum, thallium titanyl phosphate, potassium titanyl phosphate.

Introduction

The family of titanyl orthophosphates, to which TITiOPO₄ (TTP) and KTiOPO₄ (KTP) belong, is of great interest because many members demonstrate high electro-optical and nonlinear optical properties. It is known that isomorphous cation substitution of Rb, Cs or Tl for K in the near surface regions of KTP is possible via an ion exchange reaction [1, 2]. As a result the formation of an optical waveguide layer with increased refractive index is observed. To understand the optical and structural properties of such complex layered structures the best starting point is to define initially the properties of individual compounds from the family. Here the transformations of phonon spectra when the K ion in the KTP lattice is changed to a heavy Tl ion are followed by Raman spectroscopy. A previous study [3] reveals that KTP and TTP Raman spectra are similar, while there are phonon line shifts and intensity redistributions. So, we focus our attention on the analysis of the distinctions in Raman spectra of the two crystals.

Experimental Setup

TTP crystals were grown from a flux of the ternary system Tl_2O_3 - TiO_2 - P_2O_5 by spontaneous nucleation. X-ray analysis shows that the crystals are orthorhombic with lattice parameters a=12.89 Å, b=6.49 Å and c= 10.60 Å. KTP crystals were grown by the top seeded

solution growth (TSSG) method from $K_4P_2O_7$ self flux. The Raman spectra were recorded at room temperature with a double - grating monohromator DFS-24 and a He-Ne laser (λ =632.8 nm, W=30 mW). The spectral resolution was ~2 cm⁻¹. The Raman scattering experiments were carried out at room temperature and backward and right angle geometries of the light scattering were used.

Results and Discussion

Experimental spectra of A_1 phonons are presented in Fig. 1a, b. The polarization geometry in Fig. 1a is Z(YY)Z ($\Theta=0^{\circ}$, $\Psi=90^{\circ}$, where Θ and Ψ are the angles between the Z and Y axes respectively and the direction of the phonons). In Fig. 1b the spectra are presented when $\Theta=90^{\circ}$. The spectra in Z(YY)Z and X(ZZ)X scattering geometries are similar to the spectra in Z(YY)Z and Y(ZZ)Y scattering geometries respectively and are not presented in Fig. 1a, b. Raman spectra for the scattering geometries, where A_2 phonons are allowed, are presented in Fig. 2. The comparison of our results with experimental data obtained earlier by other authors is presented in Table 1.

The effect of the change of a K atom to Tl is different for different phonon modes. It is evident from the data presented above, that the phonon lines can be separated into three groups.

1. Low-frequency lines $(<100 \text{ cm}^{-1})$ with a strong relative shift of the phonon line position. The line at 90 cm⁻¹ (KTP Fig. 1a) shifts to 50 cm⁻¹ in TTP. The experimental frequency ratio is 1.8.

2. Lines in 200-350 and 600-800 cm⁻¹ spectral ranges shift to lower energies in the case of TTP crystals in comparison to KTP. The line at 768 cm⁻¹ shifts to 731

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Fig. 1. Raman spectra for A_1 phonons in TTP in Z(YY)Z geometry: (a) Θ =0° and (b) Θ =90°.

cm⁻¹ (Fig. 1a), the line at 693 cm⁻¹ to 649 cm⁻¹ (Fig. 1b) and 797 cm⁻¹ to 731 cm⁻¹ (Fig. 2). For the 600-800 cm⁻¹ spectral range the lines in KTP shifts to lower energy in TTP whereas the typical frequency ratio



Fig. 2. Raman spectra for A₂ phonons in TTP.

between spectra of two crystals is 1.05-1.09. Typical shifts in the range 200-350 cm⁻¹ correspond to the frequency ratio 1.02-1.04. These results do not depend on the values of the angles Θ and Ψ .

3. Phonon lines in the spectral range $400-600 \text{ cm}^{-1}$ have the same frequencies in KTP and TTP.

The lines in the low-frequency range with a strong relative shift of phonon line position can be explained by the ratio of masses involved in the vibrations. The shift of the line 90-50 cm⁻¹ can be ascribed to a vibration involving K(Tl) and Ti atoms [4]. The predicted frequency

ratio is
$$\sqrt{\frac{(m_{\rm Tl}+m_{\rm Ti})}{(m_{\rm K}+m_{\rm Ti})}} \approx 1.7$$
 which agrees well with the

experimental one being ~1.8 (here m_{Tl} , m_{Ti} , m_{K} are the atom masses of Tl, Ti, K respectively).

According to Ref. [4] the phonon lines in the 200-350 and 600-800 cm⁻¹ frequency ranges correspond to vibrations involving mainly TiO_6 octahedra. It is impossible

Table 1. Measured Raman frequencies of $A_1(LO)$ modes in present paper (column "experim.") and in [3, 5]. The spectrum in [3] was obtained at 110 K

KTP, A ₁ (TO), X(ZZ)Y				KTP, A ₁ (LO), Z(YY)Z			
experim.	[5]	experim.	[5]	experim.	[3]	experim.	[3]
56.3	56.7	307.4	308.3	_	31.0	271	266.2
73.5	74.1	349.4	319.4	39	41.7	294	289.8
_	86.5	_	340	_	44.7	324	317.0
100.4	101.3	369.1	369.2	48	51.9	_	337.5
112.4	112.9	399.9	400.1	-	54.3	365	361.8
119.4	120.5	429.8	429.6	61	62.3	396	388.6
153.2	152.5	459.6	461.6	_	70.6	479	482.0
-	176.5	-	545.5	91	92.6	545	545.6
202	202.8	-	569.5	127	129.3	_	568.1
212	212.1	-	596.6	154	156.5	582	582.2
-	228.6	628.8	627.7	-	161.7	_	588.8
267.6	267.4	692.4	693	200	202.4	_	614.5
288.5	289.8	-	832	205	207.5	732	736.3
				231	232.8	815	818.8
				237	238.8		

to explain the experimental shift of the high-frequency lines in TTP relative to the KTP lines by the ratio of atom masses. Other possibilities for the experimental shift of phonon lines can be considered:

- the change of the effective potential for the vibration considered when atom K had been replaced by Tl (which is 5.2 times heavier than K);
- the shift is caused by different values of the LO-TO splitting in the crystalline electric field for the two crystals. The different values of the splitting or the change of crystalline electric field can result by replacement of K by Tl.

The second possibility can be checked by analysis of LO-TO splitting for two crystals. According to Ref. [4] the value of the $A_1(LO)$ to $A_1(TO)$ mode frequency ratio for the line 736 cm⁻¹ is 1.1. In our experiments LO-TO splitting in both TTP and KTP crystals is the same, so the different position of phonon mode lines between KTP and TTP in the 200-350 and 600-800 cm⁻¹ spectral ranges can not be ascribed to different values of LO-TO splitting in the crystalline electric field. Therefore, this frequency shift in the experimental spectra between TTP and KTP is caused by a change of the effective potential for the vibration, whereas the frequency shift under LO-TO splitting in TTP is equal to the corresponding shift in KTP.

According to Ref. [4] phonon lines in the 400-600 cm^{-1} range correspond to phonons involving mainly PO₄

tetrahedra. Therefore, it appears that PO_4 tetrahedra are the same for KTP and TTP crystals, since the phonon positions are the same for these two crystals.

Conclusions

Raman spectra of TITiOPO₄ were measured and compared with that of KTiOPO₄. The strong relative shift of lines in the low-frequency range, $<100 \text{ cm}^{-1}$, can be explained by the mass ratio of the ions involved in the vibrations. The line shift in the ranges 200-350 and 600-800 cm⁻¹ can be attributed to TiO₆ octahedra vibrations and can be explain by the combined effect of a few mechanisms.

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