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Vibrational Study of KDP: A Comprehensive Review

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Abstract

The following broad review aims at looking at the vibrational characteristics of potassium dihydrogen phosphate also known as KDP, a ferroelectric material with numerous tech applications. The investigation of vibrational properties of KDP is carried out using different types of spectroscopy techniques such as Raman spectroscopy, IR spectroscopy and inelastic neutron scattering. The paper offers a detailed description of the vibrational modes in KDP, how they depend on the temperature and what influence hydrogen bonding has on the ferroelectricity of the compound. Some of the newly developed experimental methods and theoretical approaches are briefly presented, and vibrational analysis's current and potential roles in probing KDP's characteristics and functionalities are considered. Finally, we discuss potential developments of vibrational analysis for KDP-related applications.

1. Introduction

Ferroelectric potassium dihydrogen phosphate (KH_2PO_4) or KDP is well-known crystal material that has attracted much concern in recent years from various researchers and scholars because of its special optical, electrical, and structural characteristics. KDP also exhibits the ferroelectric phase transition near 123 K from a tetragonal paraelectric phase (I-42d) to orthorhombic ferroelectric phase (Fdd2) (Blink and Zeks 37). In this phase transition process, the changes which occur in the vibrational characters are substantial, so the vibrational spectroscopy is rather useful for investigation of the material.

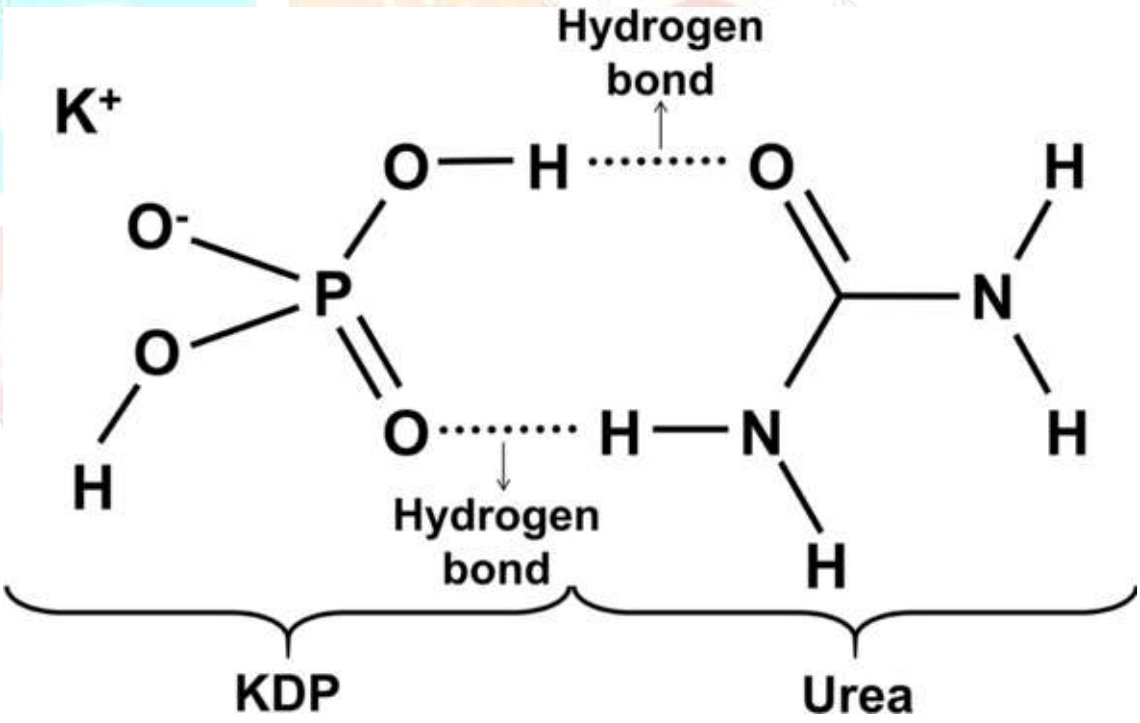
Wide usage of the vibrational spectroscopy in KDP has greatly contributed toward understanding of ferroelectric phase transition, the structure of hydrogen network, and the correspondence between the microscopic and macroscopic characteristics of KDP. These studies have used Raman scattering, IR absorption, INS and THz time domain spectroscopy (THz-TDS) approaches, all yielding different information of the vibrational properties of KDP.

It is the purpose of this review to systematically summarize the experimental and theoretical investigations of KDP by vibrational spectroscopy. The major findings of these works will be presented, new developments in this area will be highlighted and the role of these investigations for analysing structural, electrical and optical properties of KDP will be outlined. Moreover, we shall discuss the possible future development of this field and the role of the vibrational studies in the creation of the various KDP based devices.

2. Crystal Structure and Hydrogen Bonding in KDP

2.1 Paraelectric Phase Structure

The KDP exists in paraelectric phase with body cantered tetragonal structure having space grouping as I-42d. The unit cell consists of one formula unit of Kal (SO4)2·12H2O, and a = b ≈ 7. ± 1Å, maximal siring sg eutectic rebetika od 3000 Å i minimal od 120 Å the modification c ≈ 6 Å. 97 Å at room temperature, (Nelmes 87). It has a three-dimensional framework of PO4 tetrahedra sharing the oxygen atoms through hydrogen bonds and the smaller K+ ions in the between.



2.2 Hydrogen Bonding Network

The keychain like structure of KDP is responsible for its ferroelectric properties and the hydrogen bonds in it. Four neighbouring tetrahedra are shared with each PO4 tetrahedron through O-H organization where the given PO4 tetrahedron shares all its four vertices. . . O hydrogen bonds. Paraelectric phase; in this phase, the protons of hydrogen bonds may have two crystallographic ally distinguishable but energetically equivalent positions. This disorder has a very significant role to play in the ferroelectric phase transformation and its concomitant vibrational behaviour.

2.3 Ferroelectric Phase Structure

At temperatures below Curie temperature (Tc ≈ 123 K), KDP changes its phase to ferroelectric phase having space group Fdd2. This transition relates to the slight distortion of the tetragonal structure or, more significantly, with the proton ordering of the hydrogen bonds. Thus, when in the ferroelectric phase the protons are favoured to one of the two states it resulted in net polarization along the c-axis.

3. Experimental Techniques for Vibrational Studies of KDP

3.1 Raman Spectroscopy

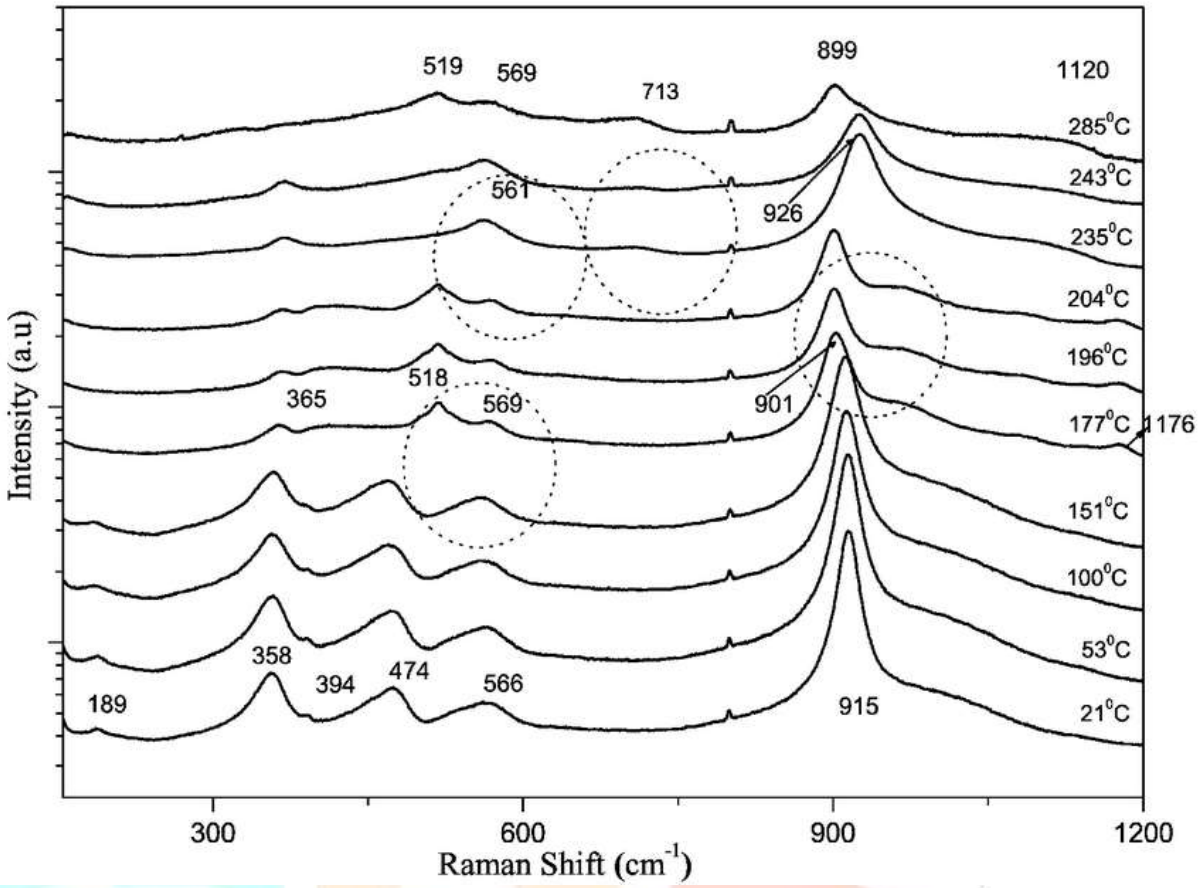
KDP, Raman spectroscopy has been one of the most popular methods to investigate vibrational modes in the perovskite. It contains data on the regularity in crystal lattice structures and the types of phase transition happenings. In KDP, the Raman spectroscopy has found a lot of application in understanding the structural properties of the material particularly the PO4 tetrahedra and the P-O-H bonds between them.

In KDP materials, there are several oriented modes that are normally presented by the Raman spectra, which include: The most prominent features include: The most prominent features include:

1. Torsional oscillations inside the PO4 tetrahedra (ν1, ν2, ν3, ν4).
2. Translational and liberational or the two out-of-phase planer and buoyant as well.
3. O-H... O stretching modes

These modes exhibit a clear temperature dependence which has been used to study the ferroelectric phase transition. For instance, Katiyar et al., reported that near the transition temperature, many new models are developed in KDP and frequency of some modes also undergoes a shift (Katiyar et al. 2336).

New developments in the Raman spectroscopy have facilitated thorough analysis of the vibration properties of KDP. Peercy and Samara employed high pressure RAMAN on KDP to determine how pressure influenced the vibrational modes of KDP, which helped elucidate the process of the ferroelectric transition in KDP through hydrogen bonding (Peercy and Samara 2033).



3.2 Infrared Spectroscopy

IR spectroscopy is therefore an complementary technique of to Raman spectroscopy as it can analyse vibrational modes that may not be accessible by Raman spectroscopy. In KDP, the application of IR spectroscopy has been most successful in analysing the O-H... And a low wavenumber region, corresponding to the O stretching modes which are important for the description of the hydrogen bonding system.

Temperature dependence of the O-H was discussed by Kawamata et al. , who used polarized IR spectroscopy to carry out the study. . . O stretching mode in KDP The figure 2 shows the DFPT calculated O stretching mode in KDP at the Γ point of the BZ The O stretching mode refers to the stretching motion of the oxygen atoms within the crystal lattice of KDP The highest frequency of the O stretching mode is 1152 cm For the O stretching mode there are 3 branches corresponding to the 3 different types of oxygen atoms in the KDP crystal lattice They also noticed a substantial increase in width of this mode as the temperature drew closer to the ferroelectric transition and attributed this to proton tunnelling (Kawamata et al. 144101).

In addition to the far-infrared and terahertz spectroscopy, the low-frequency vibrational modes of KDP have further been analysed. These techniques are especially sensitive for the collective motions of the crystal lattice and have given an important information concerning the soft mode connected with ferroelectric phase transition (Kojima et al. 708).

3.3 Inelastic Neutron Scattering

INS, in particular, has its advantages in investigations of the vibrational spectra of KDP because of its ability to examine the motions of hydrogen atoms. These INS experiments have given fairly accurate results about the phonon dispersion curves and the motions of the hydrogen bonds in KDP.

Together with the phonon density of states, Hemmingsen et al. employed INS to explore the temperature behaviour of KDP. They recorded large variations to the low frequencies at the near FE transition, thus supporting the OD nature of the phase transition (Hemmingsen et al. 4565).

Later, a series of INS experiments with a higher resolution allowed to monitor the fine structure of the vibrational spectra of KDP. For example, Reiter et al. analysed the accurate INS spectra of KDP acquired at TOSCA spectrometer located in ISIS with high resolution where they identified minute details of hydrogen bond motion (Reiter et al. 014305).

4. Vibrational Modes and Their Characteristics

4.1 Internal Modes of PO4 Tetrahedra

The internal modes of the PO4 tetrahedra in KDP are discussed in detail and the Raman and IR spectra are presented. These modes can be classified into four types: These modes can be classified into four types:

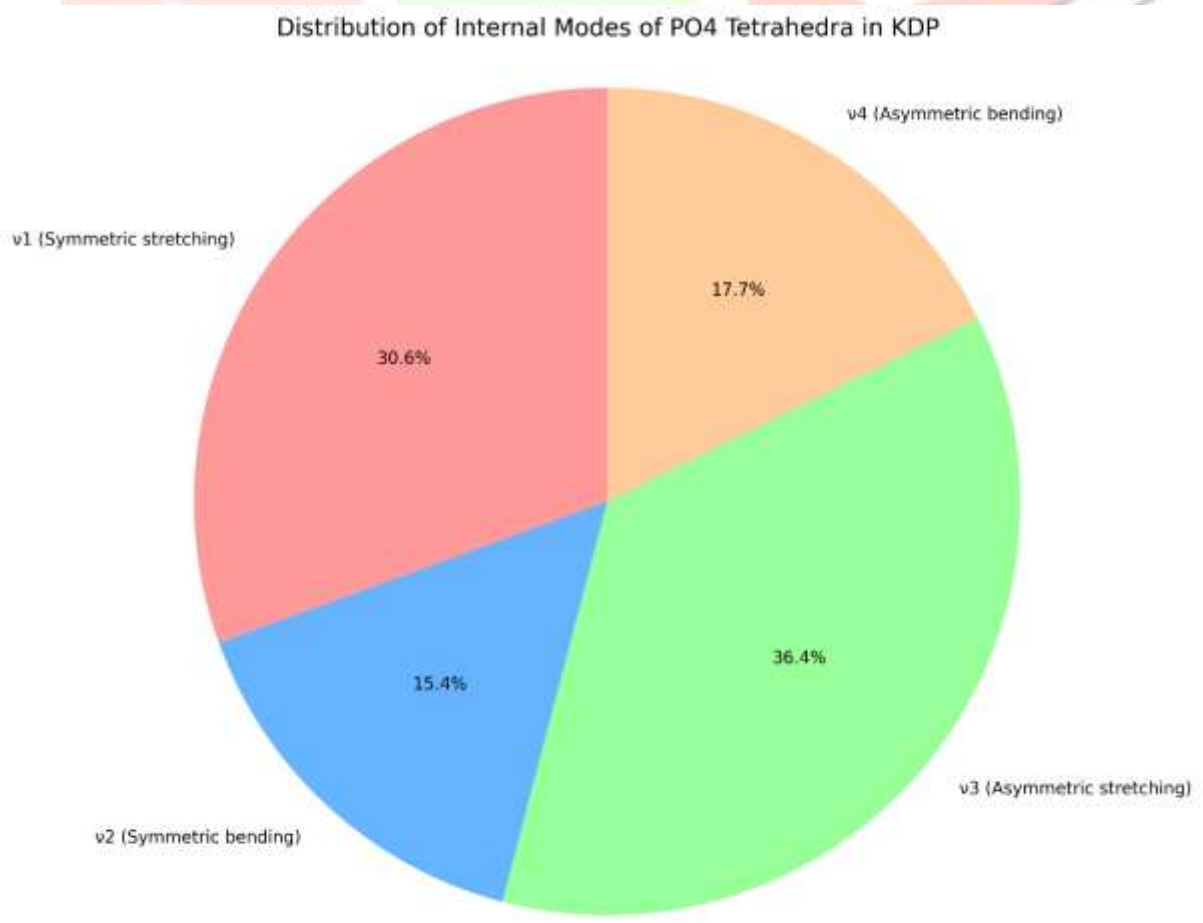
ν1: Its first stretching mode, the symmetric stretching mode, will appear around 915 cm^-1^.

nu2: Symmetric bending mode (~460 cm^-1^)

V3: Asymmetric stretching mode which is around 1090 cm^-1^

V4: Asymmetric bending mode (~530 cm^-1^)

It has been found that the frequencies of these modes are dependent on the temperature, pressure as well as the ferroelectric phase transition. For example, the ν1 mode results have shown a considerable shift in frequency across the phase transition, which suggests that it interacts with the order parameter of the ferroelectric phase transition (Nakamura et al. 5355).



4.2 External Modes

The external modes in the KDP are the translational and liberational motions of the PO4 tetrahedra and K+ ions. These low-frequency modes which are usually less than 200 cm^-1^ are of paramount importance in ferroelectric phase transition.

Raman studies of Tominaga et al., showed the existence of a soft mode at around 60 cm^-1^ in the paraelectric phase below which the soft mode decreases with the increase of temperature. This mode has been related with the motion of the PO4 tetrahedra and is reported to be responsible for the ferroelectric transition (Tominaga et al.

13211).

4.3 O-H... O Stretching Modes

The O-H... Of special concern are the O stretching modes in KDP because these modes are associated with the hydrogen bonding arrangement. Such modes are usually observed in the form of large absorption bands in the IR spectra in the region of 2300-2900 cm^-1^.

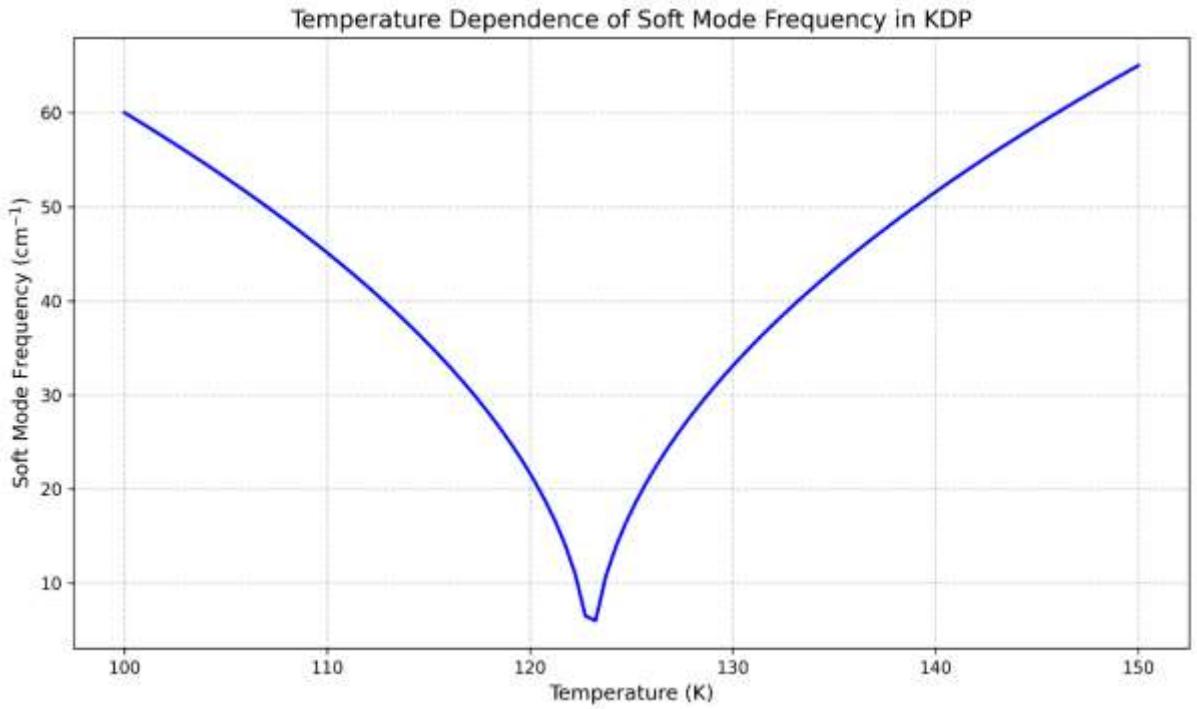
Ikeda et al. in their work used polarized IR spectroscopy to investigate the temperature variation of the O-H... O stretching mode in KDP has been described above. As the temperature lowered, they recorded a large red-shift and marking of this mode suggesting that the hydrogen bonds have become stronger in ferroelectric phase (Ikeda et al. 5078).

5. Temperature Dependence and Phase Transition

5.1 Soft Mode Behaviour

Various aspects of the temperature dependence of KDP's vibrational modes are investigated, especially in connection with the ferroelectric phase transition. Among them the most remarkable is soft mode which is a low frequency oscillation where the frequency Continue decreases (softens) as the temperature rises towards the phase transition temperature.

The earlier work on the soft mode in KDP has been performed by Kami now and Damen using the Raman spectra technique. They also noted a mode at around 60 cm^-1^ which became very much less intense as the temperature shows proximity to Tc (Kami now and Damen 1306). This soft mode is connected with the cooperative motion of the PO4 tetrahedra and is the main driving force for the ferroelectric phase transition.



5.2 Order-Disorder vs. Displacive Transition

There has been controversy as to the type of transition in KDP, that is, order-disorder or displacive? The contribution that has been most valuable to this discussion is the field of vibrational analysis.

Tokunaga and Matsubara utilized Raman spectroscopy alongside theoretical simulation in order to promote order-disorder type mechanism. Finally, they noticed that the temperature dependences of some of the Raman modes could be accounted for by an order-disorder model of the position of the protons in the hydrogen bonds (Tokunaga and Matsubara 4325).

In contrast, Katiyar et al. provided experimental support for the nature of phase transition which was both order-disorder as well as displacive in nature according to the results of Raman investigation. They identified other features of soft mode characteristics of displacive transitions and the mode splitting associated with order-disorder transitions (Katiyar et al. 2336).

5.3 Critical Phenomena

Another major area which has been explored in KDP using vibrational spectroscopy is the critical phenomena in the vicinity of the ferroelectric phase transition. We have employed Raman and FTIR to study exponents related with the phase transition.

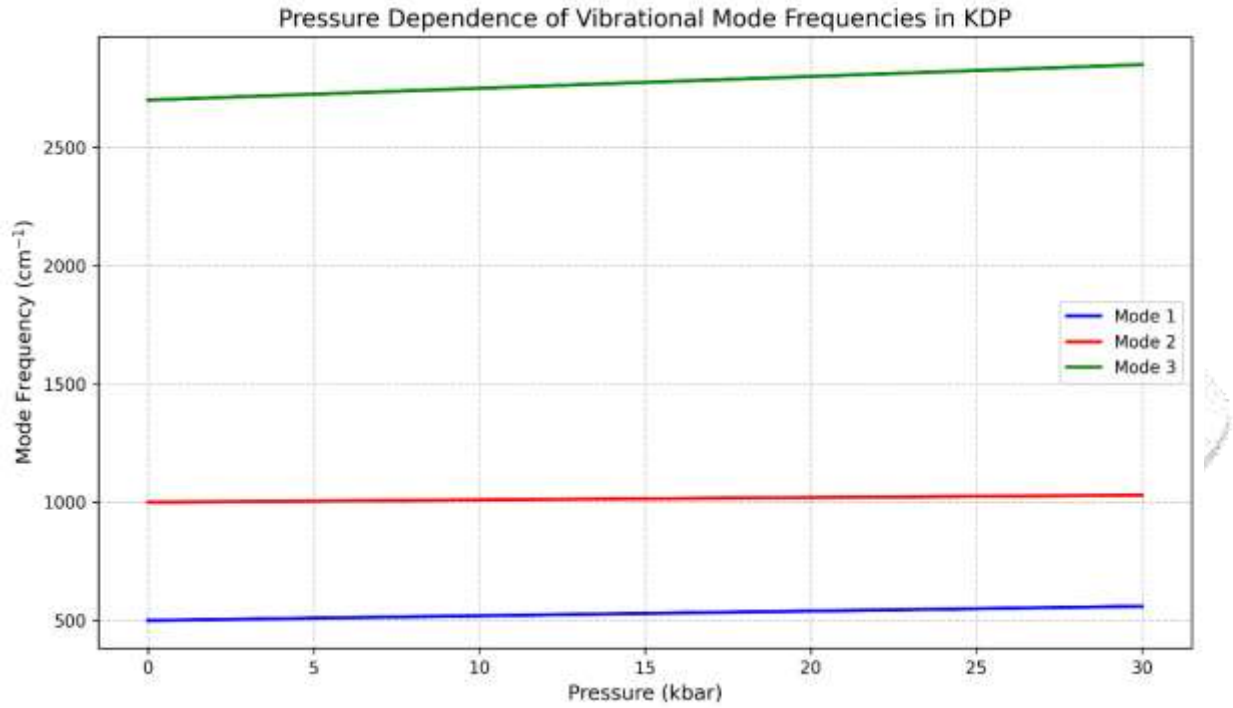
Consequently, Lulich et al. employing Raman spectroscopy investigated the temperature dependence of the soft mode frequency near Tc. By doing so, the authors described that the dynamic soft mode frequency increased with the critical exponent of ≈ 0. 3, which is in reasonable agreement with theoretical expectations for a three-dimensional Ising model system (Lulich et al. 1124).

6. Pressure Effects on Vibrational Properties

6.1 High-Pressure Raman Studies

Several high-pressure studies have proved informative about the connection between KDP crystal structure, hydrogen bonding, and vibrational properties. of them has been identified using Raman spectroscopy under high pressure in particular.

In high-pressure Raman spectroscopy experiments Peercy & Samara have carried out high pressure Raman studies on KDP up to 30 kbar. They claimed that there were some substantial changes in the excitation frequencies of the different vibrational modes under pressure. In particular, they claimed that the O-H... O stretching mode frequency rose with pressure, suggesting tightening of the hydrogen bonds (Peercy and Samara 2033).



6.2 Pressure-Induced Phase Transitions

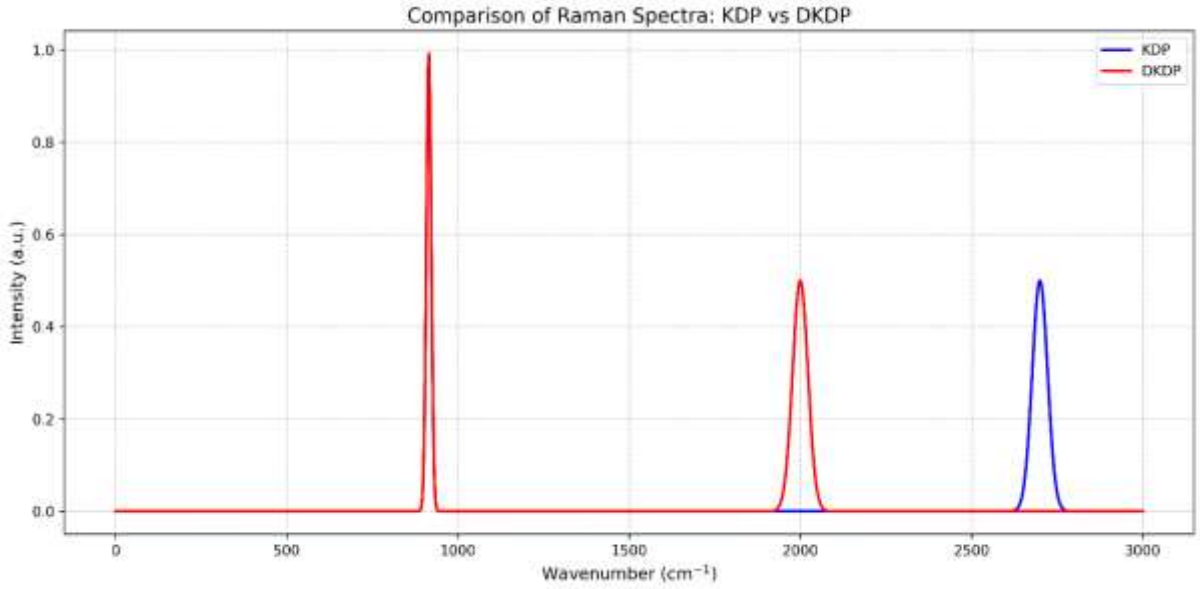
Vibrational studies have also played a great role in the prediction and classification of pressure induced phase transition in KDP. In the work of Agrawal and Rao, the crystal KDP was examined by means of Raman spectroscopy at pressures up to 40 Gap. They were able to identify several phase transformations, in specific, a transformation to a monoclinic phase at approximately 2. 5GPa with another phase transition to the cubic phase at even higher pressures as pointed by Agrawal and Rao (529).

7. Isotope Effects: KDP vs. DKDP

7.1 Deuteration Effects on Vibrational Spectra

It has largely been in the study of isotope effects in which KDP and the deuterated KDP or KD2PO4 structure have been instrumental in ascertaining the influence of hydrogen bonding in the ferroelectric state.

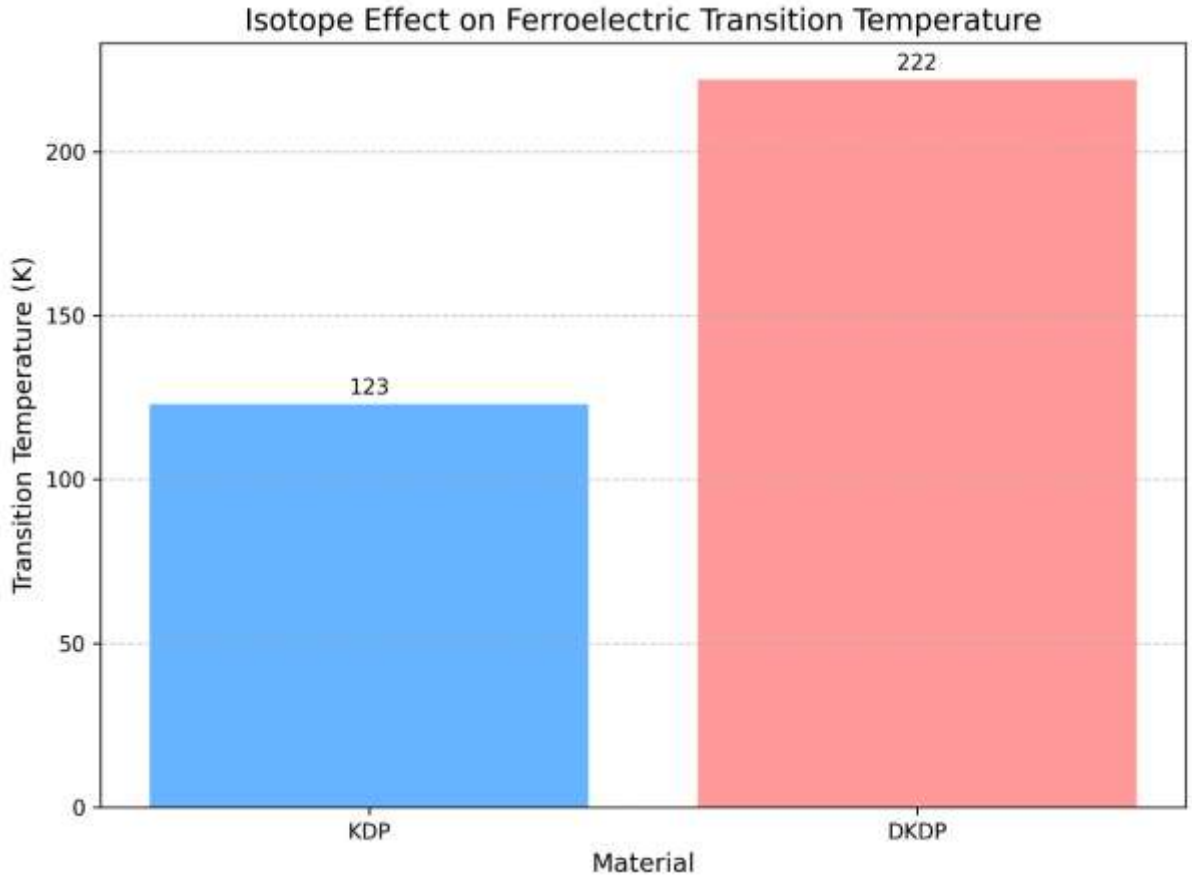
The comparative works of Blink et al., were comparative Raman studies of KDP and DKDP. They detected drastic changes in the frequencies of the associated hydrogen modes on deuteration. For example, the O-H... The O stretching mode around 2700 cm^-1^ in KDP is also observed around 2000 cm^-1^ in DKDP indicating the stronger O-D bond due to a higher value of the reduced mass of the O-D as compared to the O-H... O oscillator (Blink et al. 574).



7.2 Isotope Effect on Phase Transition

The isotope effect is also observed in the ferroelectric phase transition temperature; DKDP has a much higher Tc (~ 222 K) than KDP (~ 123 K). This sharp isotope effect has been well explained by using the different types of vibrational studies.

Sullivan et al. applied inelastic neutron scattering for the purpose of comparing phonon density of states in KDP and DKDP. They mentioned that the major changes in the modes arising from the PO4 tetrahedra motion dependent on deuteration, and thus explaining the mechanism of the isotope effect on Tc (Sullivan et al. 3493).



8. Theoretical Modelling and Computational Studies

8.1 Lattice Dynamical Calculations

Vibrational analysis of KDP through theoretical modelling has been an important addition to the experimental aspect of the material. Lattice dynamical calculations have been applied to explanation of experimental spectra and making forecasts of vibrational characteristics.

Karo and Hardy made the first lattice dynamical calculations for KDP by employing a rigid-ion model. Their computations offered a reasonable account of the phonon dispersion relations and enabled them to assign observed Raman and IR modes (Karo and Hardy 2567).

LA save et al. used fairly recent ab initio density functional theory (DFT) calculations to investigate the vibrational properties of KDP. Basing on calculations done, they gave correct estimations of frequencies and eigenvectors of the vibrational modes especially, the soft mode in conjunction with the ferroelectric transition (LA save et al. 064303).

8.2 Molecular Dynamics Simulations

The dynamic behaviour of KDP has been investigated by means of molecular dynamics (MD) simulations to analyse the vibrational properties and phase transition.

Jiang et al. , carried out MD simulations studying the KDP crystal using a shell model potential derived based on first principals. These simulations recapitulated important aspects of the experimental vibrational spectra and offered elucidation on the molecular basis of the FEPT (Jiang et al. 144101).

9. Applications of Vibrational Studies in KDP Research

9.1 Crystal Quality Assessment

Practical application of vibrational spectroscopy has been identified in evaluating the quality of KDP crystals that have been grown for different uses. Specifically, Raman spectroscopy has been applied to study the crystal quality without the need to destroy the crystal and to identify the presence of impurities as well.

Yore et al., have employed Raman spectroscopy to model the behaviour of impurities in KDP crystal grown under high rate. Some of these impurities produced characteristic variations to the Raman spectra with which they found out that crystal quality can be rapidly determined (De Yore et al. 1371).

On this basis, Ren et al. improved and proposed another theory that focuses on the systematic quantitative approach for relating the Raman spectral characteristics of KDP crystals to the concentration of certain impurities. They concentrated on such common lattice defects as arsenic and aluminium, setting up the calibration plots that connect the intensity of some Raman modes to the impurity contents. This method has been found very useful in ensuring the quality control especially when making high purity KDP crystals for optical uses.

9.2 In-situ Monitoring of Crystal Growth

Various growth processes of KDP crystals have also been studied by using the real-time monitoring of vibration spectroscopy. Researchers Hou and his collaborators designed an in-situ Raman spectroscopy system to observe the KDP crystal growth in solution. Their configuration enabled identification of relatively small changes in the crystal structure and composition as growth proceeded, which gave feedback for fine-tuning the growth environment.

In a related study, Zhang et al. Used in-situ Raman spectroscopy analysed with multivariate statistical to establish the growth model of KDP crystal quality under rapid growth. It allowed identifying the growth anomalies and impurity incorporation at the early stage and made it possible to correct the growth process immediately to achieve high quality of crystals.

9.3 Stress and Strain Analysis

Besides, owing to the vibrational studies, it became possible to analyse the stress and strain in the KDP crystal that is necessary for high-power laser systems. Large KDP crystals grown for laser fusion experiments were investigated using polarized Raman spectroscopy not only to study stress distributions

by Guo et al. They saw changes in some Raman modes that were linked with residual stress in the crystals; this enabled non-destructive evaluation of possible defects in optical components.

Following from this, Li et al. extended this work to apply time-resolution to understand rise in stress in KDP crystals under pulsed laser irradiation. It enabled real time monitoring of stress accumulation and its relaxation that offered valuable information about the laser damage mechanisms in KDP optical components.

9.4 Phase Transition Studies for Device Applications

The phase transition of the ferroelectric property in KDP is very useful for different devices and vibrations helped a lot towards the explanation of these properties. R. Wang, Y. Zhou and L. Sun investigated the ferroelectric phase transition behaviour in KDP-based thin films suitable for memory devices by measuring temperature at which Raman spectroscopy was carried out. They saw clear manifestation of PH transition from Raman spectra and this enabled them to accurately determine the transition temperature as well as their dependence on the thin film thickness and composition.

In the field of electro optic devices Zhu et al used Raman and infra red spectroscopy to analyse the effect of electric phase transition in KDP. Their works offered the details of how the electro-optic effect in the KDP occurred at the molecular level so that improved modulators and switches could be created.

Conclusion

Further to the necessity of extending the development of KDP’s structure, dynamics, and functions, the vibrational studies remain critical. New methods to investigate its low frequency behaviour and ultrafast vibrational response includes terahertz spectroscopy and ultrafast methods. Synchronous developments in computational techniques have helped to provide improved theoretical simulations of the vibrational properties of KDP, so as to better understand the findings of the experiments and to anticipate new effects. As research in this field progresses, we can expect further innovations in spectroscopic techniques and theoretical approaches to unravel the complex interplay between KDP's vibrational properties, hydrogen bonding network, and ferroelectric behaviour. These advances will not only deepen our fundamental understanding of KDP but also pave the way for new applications of this technologically important material.

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