Vibrational Analyses of PO_4^{3-} and NH_4^+ in NH_4-KH_2PO_4 (AKDP) Crystals by using FTIR Spectroscopy

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Abstract

Crystals of Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP) with two different impurity molar ratios of (1:15) and (1:20) Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (ADP) were grown by slow evaporation method at room temperature from aqueous saturated solutions. The as-grown crystals were characterized by Fourier Transform Infrared (FTIR) spectroscopy to analyze the vibrational characteristics and mode assignments of PO_4^{3-} (phosphate) and NH_4^+ (ammonium) in each of the crystal. FTIR transmission spectra of the crystals were observed by FTIR-8400 SHIMADZU spectrophotometer using Potassium Bromide, KBr pellet method.

Keywords: AKDP15, AKDP20, FTIR, vibrational characteristics and mode assignments

Introduction

Since the discovery of second harmonic generation (SHG) of ruby laser radiation in a quartz crystal by using Franken in 1961, the search for new crystals with good frequency conversion properties continues even today. The very first material to be used and exploited for their non linear optical (NLO) and electro-optic (EO) properties was Potassium Dihydrogen Phosphate, KH_2PO_4 (abbreviated as KDP). With the aim of improving the SHG efficiency of KDP, researchers have attempted to modify KDP crystals by doping different types of impurities. There are only few reports available on the effect of ammonium (NH_4) salts on the NLO efficiency of KDP crystals (Kittel, 1999).

Crystal of Potassium Dihydrogen Phosphate, KH_2PO_4, belongs to the scalenohedral (twelve-sided polyhedron) class of tetragonal crystal system and has created considerable interest among several researchers. A research programme on the growth, structural, optical and thermal characterizations of pure and impurities added KDP and ADP crystals are on hand in our laboratory. As a part of the programme, in the present work, structural analysis of the (1:15) and (1:20) molar ratios of ADP doped KDP crystals (abbreviated as AKDP15 and AKDP20) were grown by slow evaporation method and characterized by Fourier Transform Infrared (FTIR) spectroscopic method (Smith, 1996).

Materials and Method

Growth of AKDP15 and AKDP20 Single Crystals

Crystals can be grown in multiple ways and in multiple environments. Sometimes, changing the ways that crystals are grown and the environments that they are grown in will have an effect on the crystal structure, mass, color or other attributes of the crystals. If the substance chosen is soluble in water, specimens are usually best prepared by crystallization from the appropriate solvent. Inorganic salts are usually soluble enough in water (Tanaka & Tatsuzaki, 1984).

In the present study, crystals of AKDP15 and AKDP20 were grown by slow evaporation method from the aqueous saturated solutions of (1:15) and (1:20) molar ratios of

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Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (ADP) and Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP). Distilled-water was used as the solvent to grow and synthesize the crystal. Crystal growth conditions were as follows:

(1) starting materials of $NH_4H_2PO_4$ and KH_2PO_4 salt powders were weighed with molar ratios

(2) stirring and slow-increased the temperature up to 35^oC

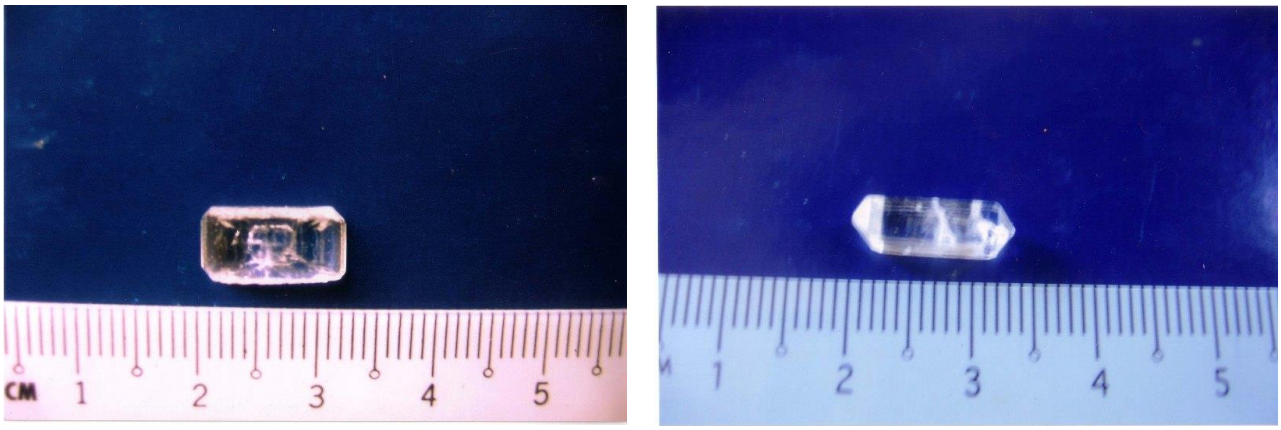
(3) saturated solution was filtered into the beaker and placed at room temperature for one week

(4) seed crystal withdrawn and selected to grow an enough size crystal

(5) duration of growth two months and

(6) slow evaporation method.

At room temperature, the crystals are colourless. Photographs showing the as-grown AKDP15 and AKDP20 are shown in figures (1a and 1b).



(a) (b)

Figure (1) Photographs showing the as-grown crystals of (a) AKDP15 and (b) AKDP20.

FTIR Spectroscopic Measurement

The most popular way of obtaining infrared spectra is to pass the infrared beam directly through the sample, known as the transmission technique. The advantage of this technique is the transmission spectra haveing signal-to-noise ratio. Infrared spectroscopy is a versatile analytical technique. It is relatively easy to obtain spectra from solids, liquids and gases. Transmission method is the oldest and most basic infrared method. The method is based upon the absorption of infrared radiation at specific wavelengths as if passed through a sample. It is possible to analyze samples in liquid, solid or gas form by using this approach (Stuart & Ando, 1996).

Potassium Bromide (KBr) pellets are used to obtain the infrared spectra of solids, and are particularly well suited to powder samples. KBr is an inert, infrared transparent material, and acts as a support and a diluent for the sample. The most commonly used alkali halide is potassium bromide (KBr), which is completely transparent in the middle IR region ($400cm^{-1}$ – $4000cm^{-1}$).

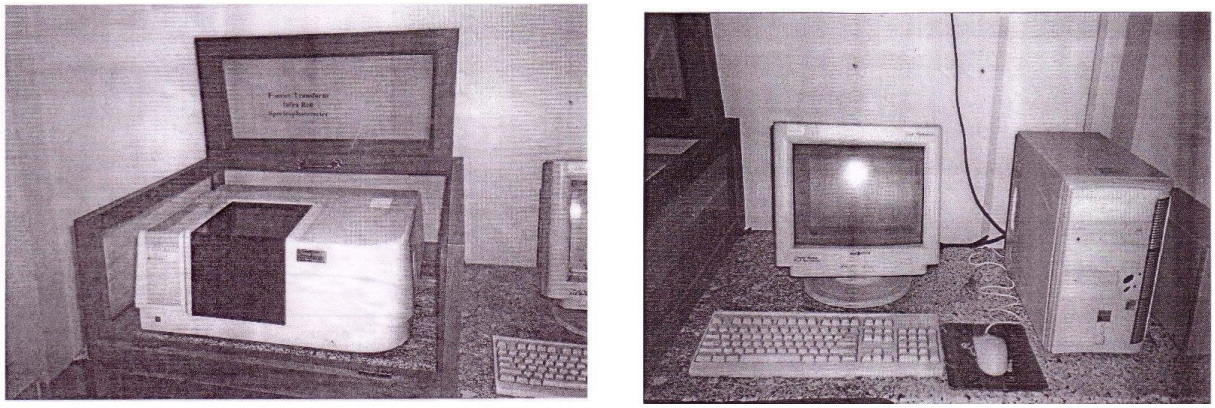
In the present work, FTIR transmission spectra of AKDP15 and AKDP20 crystals are recorded on FTIR-8400 SHIMADZU Spectrophotometer at room temperature. This experiment was performed at the Medical Research Laboratory, Department of Medical Research (Lower Myanmar). Photographs of the FTIR-8400 (SHIMADZU) spectrophotometer and its PC-control system are shown in figures (2a and 2b). The experimental conditions were as follows:

Measurement mode : %T

Wavenumber range : 400 cm^{-1} – 4000 cm^{-1}

Number of scan : 60 s

Method : KBr pellet.



(a) (b)

Figure (2) Photographs of (a) FTIR-8400 (SHIMADZU) Spectrophotometer and (b) its PC control system.

Results and Discussion

FTIR Spectroscopic Study

FTIR transmission spectra of AKDP15 and AKDP20 crystals with KBr pellet method are shown in Fig 3(a) and (b). The observed wavenumbers (absorption lines or frequencies) and corresponding vibrational modes assignments of the molecules in the crystals are tabulated in Table (1) and Table (2).

According to vibrational analysis, the phosphate (PO_4^{3-}) and ammonium (NH_4^+) molecules in free-state obeys tetrahedral-pyramidal type T_d-symmetry (Gaulitz & Vo-Dinh, 2003). In ideal case, a free tetrahedral T_d ion has four types of fundamental modes of vibrations; namely, ν_1-mode (symmetric-stretching), ν_2-mode (bending), ν_3-mode (dipole) and ν_4-mode (polarization). In general, most of the cases, PO_4^{3-} molecule may be distorted from an ideal T_d symmetry due to their crystalline environments, (i.e., K^+ and NH_4^+).

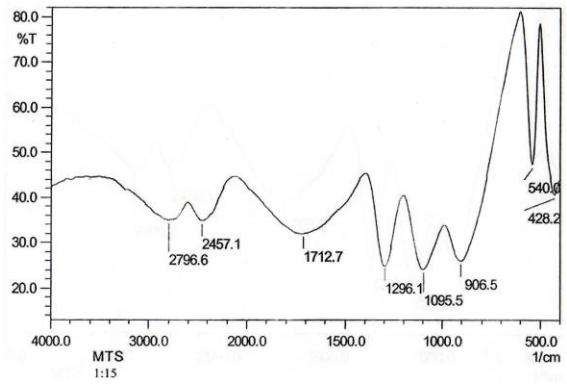


Figure (3a) FTIR transmission spectrum of AKDP15 crystal.

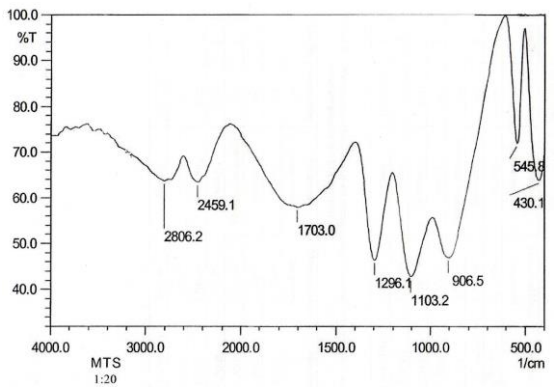


Figure (3b) FTIR transmission spectrum of AKDP20 crystal.

Table (1) Wavenumbers (Frequencies) and corresponding vibrational characterizations and mode assignments of AKDP15 crystal.

Line No.	Wavenumber (cm^{-1})	Vibrational Characteristics	Vibrational Mode Assignment	Molecule
1	428	Bending	$\nu_2(PO_4^{3-})$	(PO_4^{3-})
2	540	Polarization	$\nu_4(PO_4^{3-})$	(PO_4^{3-})
3	907	Symmetric-stretching	$\nu_1(PO_4^{3-})$	(PO_4^{3-})
4	1096	Dipole	$\nu_3(PO_4^{3-})$	(PO_4^{3-})
5	1296	Polarization	$\nu_4(NH_4^{+})$	(NH_4^{+})
6	1713	Bending	$\nu_2(NH_4^{+})$	(NH_4^{+})
7	2457, 2797	Bending	$\nu_2(CO_2)$	CO_2 (due to KBr)

Table (2) Wavenumbers (Frequencies) and corresponding vibrational characterizations and mode assignments of AKDP20 crystal.

Line No.	Wavenumber (cm^{-1})	Vibrational Characteristics	Vibrational Mode Assignment	Molecule
1	430	Bending	$\nu_2(PO_4^{3-})$	(PO_4^{3-})
2	546	Polarization	$\nu_4(PO_4^{3-})$	(PO_4^{3-})
3	907	Symmetric-stretching	$\nu_1(PO_4^{3-})$	(PO_4^{3-})
4	1103	Dipole	$\nu_3(PO_4^{3-})$	(PO_4^{3-})
5	1296	Polarization	$\nu_4(NH_4^{+})$	(NH_4^{+})
6	1703	Bending	$\nu_2(NH_4^{+})$	(NH_4^{+})
7	2459, 2806	Bending	$\nu_2(CO_2)$	CO_2 (due to KBr)

As shown in each of the FTIR spectrum, eight absorption lines were observed in the wavenumber range of $400cm^{-1}$ – $4000cm^{-1}$ region. These lines were represented by the vibrational characteristics of three types of molecules (PO_4^{3-}, NH_4^{+} and CO_2). Four fundamental modes of PO_4^{3-} and only two fundamental modes of NH_4^{+} molecules were found and assigned by molecular vibrations of T_d-symmetry type molecules. Two fundamental modes (ν_1 and ν_3) of NH_4^{+} were not found in each of the spectrum because these lines normally appeared in the wavenumber range of 3100 cm^{-1} – 3200 cm^{-1} region. In the collected

FTIR spectra, these lines overlapped under the shoulder in the wavenumber range of 3000 cm^{-1} – 4000 cm^{-1} region.

Furthermore, wavenumbers of ν_3-mode (dipole) and ν_4-mode (polarization) of PO_4^{3-} in AKDP15 and AKDP20 are found to shift. It can be considered as the PO_4^{3-} molecule distortion due the crystalline environments of K^+ and NH_4^+. The absorption lines at 2457 cm^{-1} and 2797 cm^{-1} in AKDP15 and 2459 cm^{-1} and 2806 cm^{-1} in AKDP20 were represented by the ν_2-mode (bending) of CO_2 due to KBr pallet method. These lines often appear in FTIR transmission spectrum of KBr pellet method. However, the observed FTIR spectra are the same in spectral line patterns.

Conclusion

Crystals of (1:15) and (1:20) molar ratios of Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (ADP) and Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP) (AKDP15 and AKDP20) were grown and characterized by FTIR spectroscopy. FTIR spectra of the crystals were collected by (SHIMADZU) FTIR-8400 spectrometer between the wavenumber range of 400 cm^{-1} and 4000 cm^{-1} region. From the observed FTIR spectra, four fundamental modes of PO_4^{3-} and two fundamental modes of NH_4^+ were found and precisely assigned by vibrational theory in which wavenumbers of ν_3-mode (dipole) and ν_4-mode (polarization) of PO_4^{3-} were found to shift due to the crystalline environments of K^+ and NH_4^+. Thus, AKDP15 and AKDP20 crystals can be non-linear optical system and IR (infrared) detector because collected absorption lines are precisely assigned by molecular vibrational theory and standard data library.

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