Synthesis, Growth And Characterization Of Ammonium Dihydrogen Phosphate Doped With Potash Alum For Nonlinear Optical Applications

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Abstract- *Growth of crystals demands theoretical knowledge of thermodynamics, kinetics, and transport processes. Crystal growth, a fundamental process in material science involves the controlled formation of crystalline solids from a supersaturated state, encompassing nucleation and subsequent growth of the crystal lattice. In practice, some general aspects have to be considered, including choice of raw materials, conditions, methods, and characterization. The laboratory techniques of crystal growth are discussed. Economical aspects dominate the developments in the future, that is, growing of larger crystals at higher quality to raise yields and device performance. This paper will explore the aspects of crystal growth, including the different characterization techniques of Nonlinear optical materials Ammonium Dihydrogen Phosphate doped with Potash Alum.*

Keywords- Crystal growth, Slow evaporation, Nonlinear optical material, Powder XRD

I. INTRODUCTION

Nonlinear optical materials exhibit unique properties where their interaction with light depends on the light's intensity, leading to effects like frequency doubling and optical modulation. Single crystals are crucial for these applications because their ordered structure allows for efficient and predictable nonlinear optical behaviour. The Ammonium Dihydrogen Phosphate Potash Alum (ADPPA) is an excellent piezo-electric crystal utilized for variety of nonlinear optical applications. It has retained good transparency in a wide region of optical spectrum, resistance to damage by laser radiation and relatively high nonlinear optical efficiency. The crystal of nonlinear optical material Ammonium Dihydrogen Phosphate Potash Alum (ADPPA) was grown from slow evaporation method at room temperature. Different techniques such Powder X-Ray Diffraction (PXRD), Fourier Transformer infrared spectroscopy (FTIR), UV-Visible spectroscopy and Fluorescence measurement have been used to investigate the grown material and the obtained results are discussed.

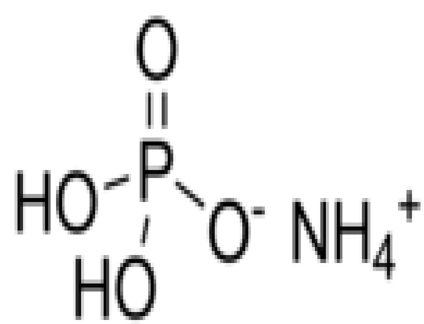
II. MATERIALS

Ammonium dihydrogen phosphate (ADP

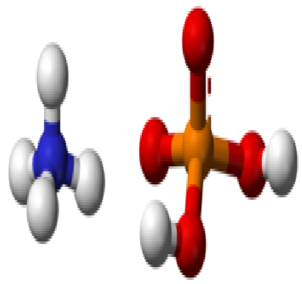
Ammonium dihydrogen phosphate (ADP), also known as monoammonium phosphate (MAP), is a chemical compound with the formula $(NH_4)(H_2PO_4)$ used as a fertilizer, in dry chemical fire extinguishers, and in optics and electronics. Ammonium dihydrogen phosphate (ADP) is a crystal material and is a member of large family of compounds which possess a chemical formula: MH_2XO_4. Ammonium dihydrogen phosphate is soluble in water and crystallizes from it as the anhydrous salt in the tetragonal system, as elongated prisms or needles.

Chemical Properties and Structures

- **Formula:** $(NH_4)\ H_2PO_4$
- **Nature:** It's the ammonium salt of phosphoric acid.
- **Melting Point:** 190°C
- **Boiling Point:** 87.4°C
- **Density:** 1.8 g/cm³ (20 °C)
- **pH:** Around 4.2 (in a 2.3% solution)
- **Solubility:** Highly soluble in water



Chemical structure



Molecular Structure of ADP

- **Molecular Weight:** 115.03 g/mol.

Uses:

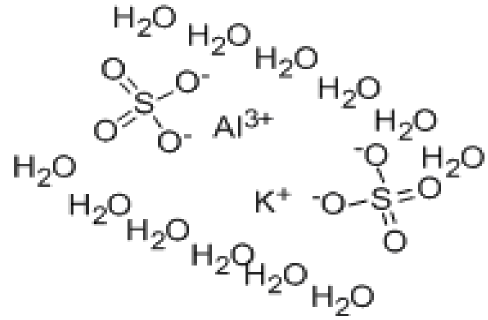
- **Fertilizer:** A major ingredient in agricultural fertilizers, providing both nitrogen and phosphorus to plants.
- **Optics and Electronics:** Has significant uses in these fields, including as a nonlinear optical material.
- **Battery Applications:** Can be used as a precursor to fabricate cathode materials for Li-ion batteries and as an electrolyte additive to enhance ionic conductivity.
- **Flame Retardant:** Can be used to fabricate flame-retardant polymer composites.
- **HPLC Buffer:** Used as a buffer salt in HPLC applications.
- **Biochemical Sensor:** Used in the development of a self-powered biochemical sensor for agricultural applications.
- **Fire Extinguisher:** Used in dry chemical fire extinguishers.

Potash Alum (PA)

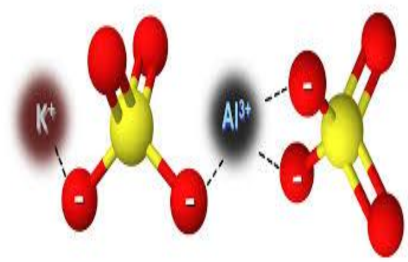
Potash alum is a chemical compound widely used as the potassium sulphate dodecahydrate. It is double salt that is used commonly in medicine and the water treatment process. Potash alum is also known as potassium alum or potassium aluminium sulphate.

Chemical Properties and Structure

- **Formula:** $(KAl_2(SO_4)_3 12H_2O)$
- **Nature:** It's the ammonium salt of phosphoric acid.
- **Melting Point:** 92.5°C
- **Boiling Point:** 200Molecular °C
- **Density:** 1.76 g/cm³
- **Molecular Weight:** 474.39 g/mol



Chemical structure



Molecular structure of Potash Alum

Uses of Potash Alum

- **Fire Retardant:** The use of potassium alum for textiles, wood and paperless flame resistance is a fire-retardant.
- **Tanning:** For leather tanning, potassium alum is used to extract moisture from the hide and avoid rotting. Alum is not covered and can be washed out, as compared to tannic acid.
- **Iron and Steel Dissolving:** This aluminium solution has the property that steels are dissolved without affecting aluminium or base metals. For machined castings of steel parts of machinery, alum solutions can be used.
- **Gourmet Food:** Potassium alum may be an acidic component in baking powder to provide a second leavening step at high temperatures.
- **Used for Dyeing:** Alum was used to form a permanent link between natural textile fibres like wool and dye, as mordant.
- **Pigmentation of the Lake:** Aluminium hydroxide from alum acts as a base for most lake pigments.
- **Blocking Chemicals:** Potassium alum was used for purifying turbid liquids. The drinking water and industrial water systems, effluent treatment, and post-storm lake procedures continue to be commonly used for the treatment of pollutants in precipitation. Water is applied to the domestic waste waters roughly 30 to 40 ppm of alum, but more commonly to the industrial waste water to clump negative particles into the flocs and float them up to the liquid bottom, or more conveniently filter them out

of liquid before further filtration and disinfection of the water.

III. EXPERIMENTAL PROCEDURE

Synthesis The ammonium dihydrogen phosphate potash alum (ADPPA) crystal was synthesised by mixing the component in distilled water in the ratio of 1:1 has a coordinating capacity from a variety of semi organic complexes. The mixture of the reactants had to be stirred well to void the co- precipitation of multiple phases. The solution was stirred of about 2 hours. The photograph of the material synthesis using a magnetic stirrer is shown in Fig.1. The chemical equation of the grown crystal is obtained as follows:

$$3(NH_4)H_2PO_4 + KAl_2(SO_4)_3 12H_2O \rightarrow Al_2(NH_4)_3H_2KPO_4(SO_4)_3$$

Fig.1 Material Synthesis

Crystal Growth

A clean saturated solution of ammonium dihydrogen phosphate potash alum (ADPPA) was filtered through Whatman filter paper into the clean dry beakers, to remove the suspended A clean saturated solution of ammonium dihydrogen phosphate potash alum (ADPPA) was filtered through Whatman filter paper into the clean dry beakers, to remove the suspended impurities. The filtrated was kept side undisturbed in a room for the growth of crystal ADPPA by slow evaporation solution growth method at ambient temperature. Good optical quality crystal was obtained in 14 days. The as grown crystals of ADPPA is shown in Fig.2.

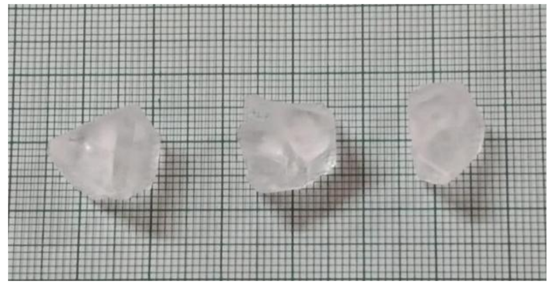


Fig. 2 Photograph of as grown Crystal of ADPPA

IV. RESULT AND DISCUSSION

Powder X-Ray Diffraction (PXRD)

Powder X-ray diffraction (PXRD) is a technique that uses X-rays to analyse the structure of crystalline materials, providing information about their phase, composition, and crystallinity. The phase identification that determines the types of crystalline phases present in the material. Crystallinity assesses the degree of order in the Material. PXRD estimating the size of the crystalline domains and determining the dimensions of the unit cell, helps to analyse the orientation of crystallites and also assessing stress within the material.

The grown crystals of ADPPA were characterized by powder XRD. The sample ADPPA was scanned in the range of 10-80 at a scan rate of 28 min. The powder diffraction pattern of ADPPA is shown in Fig. 3. The well-defined Bragg's peak reveals the crystalline nature of the grown sample. Crystalline size (D) was calculated using Scherrer's formula from the full width at half maximum (FWHM).

$$D = K\lambda / \beta\cos\theta$$

Where,

K→ The shape factor or Scherrer Constant (0.9)
λ → X-ray wavelength nm (1.54060Å)
β → The broadening of diffraction line measured at half of its maximum intensity.

The crystalline size was found to be 1.785 nm as given in the Table 1.

Table 1: Crystalline size of ADPPA

θ (deg)	d spacing (Å)	FWHM (β)	Crystal size nm
18.10778	2.48048	0.1181	1.60
18.88995	2.38126	0.0787	1.76
12.22165	3.64174	0.0787	1.87
19.25745	2.33750	0.0787	1.91
		Mean	1.784

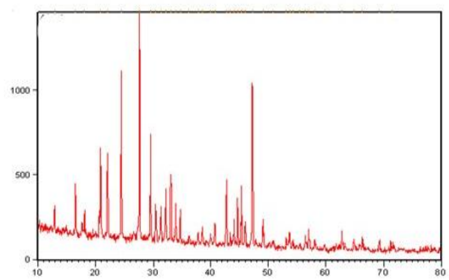


Fig.3 Powder XRD pattern of ADPPA

FTIR Spectral analysis

A Perkin Elmer-Fourier transformation spectroscopy was used to record the FTIR spectrum of ADPPA in the range 400-4000 cm^{-1}. The x-axis or horizontal axis represents the infrared spectrum, which plots the intensity of infrared spectra. The peaks, which are also called absorbance bands, correspond with the various vibrations of the sample's atoms when it's exposed to the infrared region of the electromagnetic spectrum. The y-axis or vertical axis represents the amount of infrared light transmitted or absorbed by the sample material being analysed.

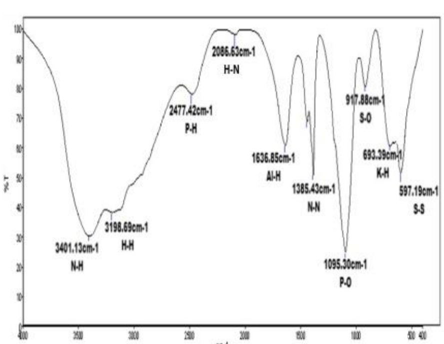


Fig. 4 FTIR spectrum of ADPPA

AFTIR spectrum of ADPPA material recorded is shown in Fig.4. Functional groups were analysed from FTIR Spectrum taking into account the molecular structure of the ADPA. The broad peak at 3401.13 cm^{-1} corresponds to stretching vibration of N-H molecule. The band at 3198.69 cm^{-1} is attributed to bending vibration in the compound. The band at 2477.42 cm^{-1} is attributed to P-H stretching vibration in the compound. A peak at 2086.63 cm^{-1} confirms the presence of H-N group in the final compound. The band at 1636.85 cm^{-1} corresponds to bending vibration. The band at 1385.43 cm^{-1} represents the ammonium bending. The bands at 1095.30 cm^{-1}, 917.88 cm^{-1} and 693.39 cm^{-1} confirms the P-O-H stretching vibration in the final compound. A peak at 597.19 cm^{-1} confirms the presence of S-S bond assignment and PO_4 vibration assignment of ADPPA. The vibration band assignment of ADPPA crystal is given in Table 2.

Table 2: Vibration band assignment of ADPPA

Wavelength (cm^{-1})	Bond Assignments	Vibration Assignments
597.19	S-S	Stretching
693.39	K-H	Stretching
917.88	P-O-H	Stretching
1095.30	P-O	Stretching
1385.43	N-N	Bending
1636.85	Al-H	Bending
2086.63	H-N	Stretching
2477.42	P-H	Stretching
3189.69	O-H	Bending
3401.13	N-H	Bending

UV-Visible Spectroscopy

UV-Visible spectroscopy characterizes materials by analysing their interaction with ultraviolet and visible light, revealing information about their electronic structure, composition, and concentration. It measures the absorbance or transmittance of light across a specific wavelength range 200-800 nm, to identify and quantify substances.

A good optical quality crystal of Ammonium dihydrogen phosphate potash alum (ADPPA) was harvested from aqueous solution by using slow evaporation solution growth technique (SEST) at ambient condition. Its optical properties were scrutinized by UV–visible spectroscopy. A crystal ADPPA of thickness 1 cm was taken for the study.

UV Absorption

UV-Visible spectroscopy is a technique that utilizes the interaction between light and matter to analyse chemical compounds. It measures the absorption of ultraviolet (UV) and visible light by a sample, providing information about its composition and structure. The UV-Visible absorption spectrum of ADPPA is shown in Fig.5.

UV Transmission

UV Transmittance refers to the amount of light that is passed completely through the sample and strikes the detector. The transmittance spectrum of ADPPA is shown in Fig.6. The transmittance study shows that the upper cut off wavelength of ADPPA is observed at 640.3nm. The percentage of transmittance is 93%.

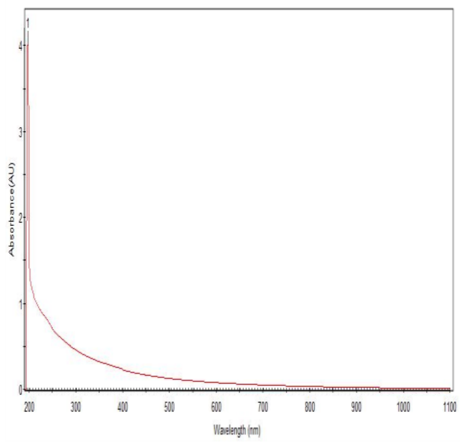


Fig. 5 UV - Absorption spectrum of ADPPA

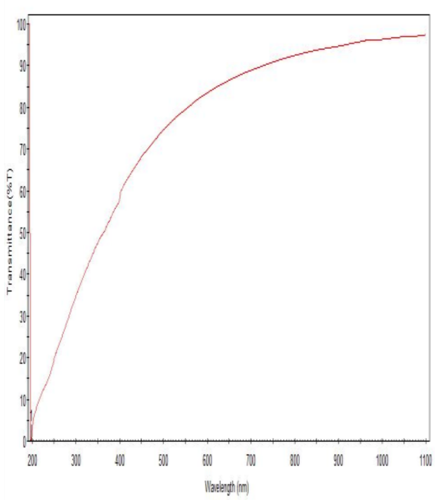


Fig. 6 UV - Transmission spectrum of ADPPA

UV - Transmission spectrum can be used to determine the band gap energy of materials by analysing the absorption of light, specifically by identifying the wavelength where absorption begins and using that to calculate the corresponding energy, which represents the band gap. Band Gap

Energy, $E = hC / \lambda$

Where,

h→Planck's constant (6.626×10^{-34} Joule sec)
C →Velocity of Light (3×10^{8} meter/sec)
λ→ Wavelength (640.03 nm)
The determined band gap energy of ADPPA is 3.11 eV.

Fluorescence Spectroscopy

Fluorescence generally found in compounds with low energy $\pi \rightarrow \pi^*$ transition level. A highly conjugate double bond structure exhibits fluorescence. The fluorescence spectrum of ADPA crystal was recorded in the range 300-900 nm and is shown in Fig. 7. The sharp intense peak obtained at 611.814 nm in the emission spectrum confirms the emission of red radiation of light. The optical band gap of ADPPA Crystal is calculated as 3.24 eV.

V. CONCLUSION

The organic material Ammonium Dihydrogen Phosphate Potash Alum (ADPPA) was synthesized and grown from slow evaporation method at room temperature using distilled water as solvent. The various characterization techniques have been employed to confirm the grown crystal such as Powder X-ray Diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), UV-Visible spectroscopy and fluorescence studies.

From Powder X-Ray Diffraction Analysis, the crystalline size (D) was calculated using Scherrer's formula from the Full Width at Half Maximum (FWHM) and the size was found to be 1.785 nm.

A Perkin Elmer-Fourier Transform Infrared spectrometer was used to record the FTIR spectrum of ADPPA in the range 400-4000 cm^{-1}. The functional groups of the compound ADPPA were analysed from FTIR Spectrum taking into account the molecular structure of the ADPPA. The bond assignments and vibration frequency assignments were reported.

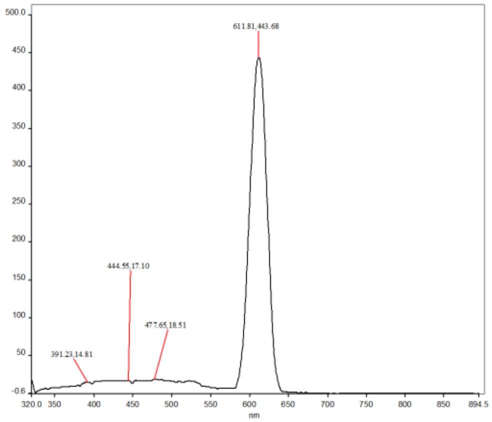


Fig. 7 Fluorescence Spectrum of ADPPA

The UV-absorption and UV-transmission spectrum of ADPPA were recorded in the range 200-1100 nm. The percentage of transmittance was 93%. The optical band gap of ADPPA was calculated as 3.11 eV.

The fluorescence spectrum of ADPPA crystal was recorded in the range 300-900 nm. The sharp intense peak obtained at 611.814 nm in the emission spectrum confirms the emission of red radiation of light. The optical band gap of ADPPA was calculated as 3.24 eV.

ADPPA crystals may be subjected to various studies for future scope. Ammonium Dihydrogen Phosphate Potash Alum (ADPPA) crystals, known for their unique nonlinear optical, piezoelectric, antiferroelectric properties, could focus on enhancing their performance in electro-optic modulators, harmonic generators, and parametric generators, as well as exploring new applications in fields like quantum technology and advanced materials.

REFERENCES

[1] Lefaucheux, F, Roberts, M C & Manghi, E, "A Comparison Between Gel Grown and Solution Grown Crystals - Case of ADP and KDP" J. Cryst. Growth, Vol.56, No.1, (1982), pp 141-150.

[2] Brouwer, G, Rosmalen, G M V & Bennama, P, "The Growth of Single Crystals of Rb_2PtCl_6 and Similar Alkali Precious Metal Chlorides and of $BaSO_4$ in an Ion-exchanged Sodium-free Silica Gel", J. Cryst. Growth, Vol. 23, No. 3, (1974), pp 228-232.

[3] Garcia Ruiz, J M & Amoros, J L, "Morphological Aspects of Some Symmetrical Crystal Aggregates Grown by Silica Gel technique"', J. Cryst. Growth, Vol.55, No.2, (1981), pp379-383.

[4] Boulin, D & Ellis, W C, "Gel-growth of Silver Acetate Crystals", J. Cryst. Growth, Vol.6, No.3, (1970), pp 290-292.

[5] Ramet X. Sun, X, Xu, Z. Gao, Y. Fu, S. Wahg, H. Zong, Y. Li, J. Cryst. Growth, 217, (2000), pp 404.

[6] Armington, A F & O'Connor, J J, "Gel Growth of Cuprous Halide Crystals", J. Cryst. Growth, Vol.3, No.4, (1968), pp 367-371.

[7] Arthi M, & Jothi L, "Effect of Adipic Acid on the Growth And Characterization of Potassium Dihydrogen Phosphate", IJSART, Vol.7, No.4, (2021), pp 36-40.

[8] Bo Wang .Chang – Shui Fang. Sheng – Iai Wang, Xun Sun, Quing-tian Gu, Yi-ping Li, Xin-guang Xu, Jianqin Zhang, Bing Liu, with potassium carbonate as additives. J. Cryst. Growth, 310, (2008), pp 5341-5346.

[9] Zaitseva, N Carman, L & Smolsky, I, J. Cryst. Growth, 241, (2002), pp363.

[10] Gits, S, F, Cheux, Le Au & Robert, M C, "Effect of Stirring on Crystalline Quality of Solution Grown Crystals – Case of Potash Alum", J. Cryst. Growth, Vol.44, No.3, (1978), pp 345-355.