

Structure and Crystal Growth of Urea Doped P- Block Element

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Abstract

Transparent single crystals of lead acetate-doped urea, an organic nonlinear optical (NLO) material, were successfully grown using the slow evaporation solution growth technique at room temperature. Triply distilled water was employed as the solvent to ensure high purity and controlled crystal formation. The incorporation of lead acetate as a dopant significantly influenced the growth behavior and physicochemical properties of the resulting crystals. The grown crystals exhibited good transparency, indicating their potential suitability for optical and photonic applications. A detailed investigation was conducted to assess the structural characteristics of the doped crystals.. Single-crystal X-ray diffraction analysis confirmed the crystalline nature and revealed that the lead acetate-doped urea crystal belongs to the tetragonal crystal system. The lattice parameters were determined as $a = 7.500 \text{ \AA}$, $b = 7.500 \text{ \AA}$, and $c = 7.549 \text{ \AA}$, with a unit cell volume of $867 \text{ \AA}^3$. The interaxial angles were found to be $\alpha = \beta = \gamma = 90^\circ$, consistent with the tetragonal symmetry. Comparison with pure urea crystals showed slight variations in the lattice parameters, suggesting successful incorporation of lead acetate impurities into the crystal lattice. Detailed refinement and data collection studies further supported the structural modification induced by the dopant. The presence of lead acetate is believed to alter intermolecular interactions within the crystal, resulting in subtle changes in the unit cell dimensions and overall crystal structure. These structural modifications may contribute to enhanced optical and nonlinear optical properties. The observed results demonstrate that lead acetate doping is an effective approach for tailoring the characteristics of urea crystals, making them promising candidates for applications in frequency conversion, optical modulation, and other advanced photonic devices.

Keywords: Transparent crystal, single crystal XRD, tetragonal, Urea, crystal structure

INTRODUCTION

Nonlinear optical (NLO) materials exhibiting second harmonic generation have attracted considerable attention over the past few decades because of their technological significance in areas such as optical communication, signal processing, and instrumentation [1, 2]. Urea, being an important NLO material, presents challenges in crystal growth and handling due to its highly hygroscopic nature.

Various derivatives of urea have been investigated for NLO applications, and some have shown promising potential in this field. Urea crystals have drawn interest from both theoretical and experimental researchers because of their nonlinear optical and piezoelectric properties [3–5]. Urea also finds application in photonics and has served as a reference material in the Diffusive Mixing of Organic Solution (DMOS) experiment conducted by NASA under microgravity conditions [6]. In addition, urea and its derivatives, such as thiourea and N,N-dimethyl urea, have been explored as dopants in KDP crystals. Several studies have

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Received Date: June 17, 2026

Accepted Date: June 30, 2026

Published Date: July 15, 2026

Citation: P. Girija. Structure and Crystal Growth of Urea Doped P- Block Element. International Journal of Crystalline Materials. 2026; 3(2): 8-13p.

reported on the second harmonic generation efficiency, laser-induced damage threshold, thermal behavior, pH-dependent morphology, optical properties, and growth kinetics of urea crystals. The influence of doping on the properties of urea has also been widely examined [7-9]. More recently, semiorganic TGDCC (tetra glycine dihydrated calcium chloride) single crystals have been synthesized, and the effect of urea on their structural and optical properties has been studied. Similarly, optical and thermal investigations have been carried out on pure and doped L-arginine phosphate crystals, urea oxalic acid crystals, and KDP crystals [10-12]. Characterization studies have also been reported for urea-induced ammonium nickel sulfate hexahydrate, comparative analyses of pure and urea-doped glycine phosphite crystals, and sulphamic acid single crystals. Furthermore, the growth and characterization of urea thiourea sodium sulphate crystals have also been investigated [13,14]. Bismuth fluoride introduced into the Urea crystals to alter the various properties, bismuth fluoride is the p-block element and if it is doped into the organic crystals like Urea, NLO properties of host material will be improved [15,16]. In this paper leadacetate doped urea crystal was grown by slow evaporation solution method for the first time and the results of single crystal XRD, its refinement structure, data collection of the grown crystals is reported [17,18].

MATERIALS AND METHODS

Crystal Growth

Lead acetate-doped urea crystals were successfully grown at room temperature by employing the slow evaporation solution growth technique. An equimolar mixture of lead acetate and urea in a 1:1 ratio was prepared using triply distilled water as the solvent. The required quantities of lead acetate and urea were dissolved in the solvent and transferred into a conical flask. The solution was continuously stirred for approximately 3 hours to ensure complete dissolution and homogeneous mixing of the constituents. During the stirring process, a colorless precipitate was formed, indicating the interaction between the two compounds.

The resulting mixture was then filtered to separate the precipitate from the clear solution. The filtrate was collected in a clean beaker and covered with a polythene sheet containing small holes to facilitate controlled evaporation of the solvent while preventing contamination from external impurities. The separated precipitate was retained for further observation. The beaker containing the filtrate was then kept undisturbed under ambient laboratory conditions for crystal growth.

Slow evaporation of the solvent led to gradual supersaturation of the solution. After approximately 15 days, small seed crystals began to appear in the growth medium. As the growth process continued, well-defined crystalline structures developed, and noticeable crystal growth was observed by the 18th day. Transparent bulk crystals were successfully obtained and harvested from the saturated solution. The crystals exhibited good clarity and transparency, indicating favorable growth conditions and high crystalline quality. The entire crystal growth process was completed within 25–30 days. The harvested bulk crystals, which remained clear and stable in the growth medium, were selected for further characterization studies. The morphology of the grown lead acetate-doped urea crystals is shown in Figure 1.

SINGLE CRYSTAL XRD ANALYSIS

Single-crystal X-ray diffraction (SCXRD) analysis was performed using a Bruker AXS (Kappa Apex II) X-ray diffractometer to determine the crystal structure and unit cell parameters of pure urea and lead acetate-doped urea crystals. The structural investigation confirmed the crystalline nature of the grown samples and provided detailed information regarding the incorporation of the dopant into the host lattice. The obtained unit cell parameters are depicted in Table 1, which compares the crystallographic data of pure urea and doped crystals.

The analysis revealed that the lead acetate-doped urea crystal crystallizes in the tetragonal crystal system with lattice parameters $a = 7.500 \text{ \AA}$, $b = 7.500 \text{ \AA}$, $c = 7.549 \text{ \AA}$, and a unit cell volume of $867 \text{ \AA}^3$.

The interaxial angles were found to be $\alpha = \beta = \gamma = 90^\circ$, confirming the tetragonal symmetry of the crystal. A slight increase in the cell parameter values compared to those of pure urea was observed. This variation can be attributed to the successful incorporation of lead (Pb) ions from lead acetate into the urea crystal matrix. The substitution or occupation of suitable lattice sites by the dopant ions causes local lattice distortion and expansion of the unit cell dimensions.

The observed changes in the crystallographic parameters indicate that lead acetate has been effectively incorporated into the host crystal without altering the fundamental crystal system. The crystals obtained were colorless, transparent, and showed good morphological quality, indicating that the presence of the dopant did not negatively influence crystal growth. These structural modifications induced by lead incorporation may influence the optical and nonlinear optical properties of the material, making lead acetate-doped urea crystals promising candidates for advanced optoelectronic and photonic applications. The detailed crystallographic parameters obtained from SCXRD provide strong evidence for successful crystal growth and dopant inclusion within the urea lattice.

Table 1. Cell parameters values of urea pure and urea doped lead acetate crystals.

Lattice Parameter Values	$a \text{ \AA}$	$b \text{ \AA}$	$c \text{ \AA}$	$v \text{ \AA}^3$	System/space group/Beta angle
Urea	5.589	5.589	4.695	146.65	Tetragonal/P42 ₁ m/ 90°
Urea doped lead acetate	7.500	7.500	7.549	867	Tetragonal/I/ 90°



Figure 1. Photograph of lead acetate doped urea crystals.

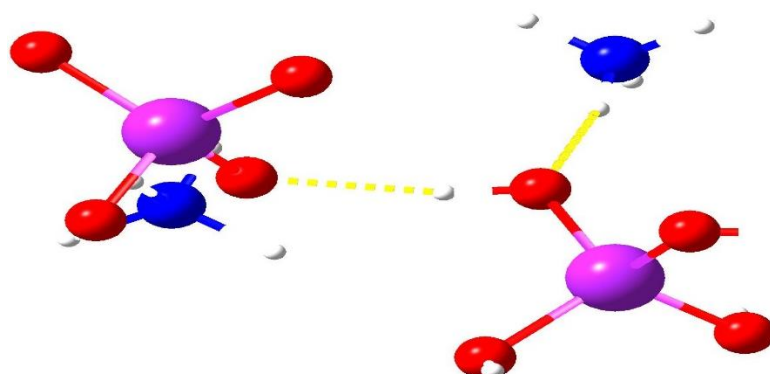


Figure 2. Structure refinement for lead acetate doped urea crystal

The structural analysis of urea doped lead acetate crystal was done by single crystal XRD analysis structure diagram of the crystal Diammonium tetraoxolead(II)tetrahydroxolead(II) complex is obtained, the ORTEP diagram and packing diagram are given in Figures 2-4. From Table 2 crystal data, the empirical formula $\text{H}_{12}\text{N}_2\text{O}_8\text{Pb}_2$ highly supports the presence of Pb(II) metal in the crystalline matrix. The structure is determined with a low value of [Final R indexes [$I \geq 2\sigma(I)$] R_1 factor (0.0233), $wR_2 = 0.0880$ using 529 Independent reflections $R_{\text{int}} = 0.0369$ $R_{\text{sigma}} = 0.0296$) and goodness of fit (F^2) = 0.805. It crystallizes in the tetragonal system with the noncentrosymmetric space group I.

Table 2. Crystal data of lead acetate doped urea crystal.

Empirical formula	$\text{H}_{12}\text{N}_2\text{O}_8\text{Pb}_2$
Formula weight	230.06
Temperature [K]	300(2)
Crystal system	tetragonal
Space group (number)	$I\bar{4}$ (82)
a [Å]	7.5000(7)
b [Å]	7.5000(7)
c [Å]	7.5493(7)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å ³]	424.65(9)
Z	2
ρ_{calc} [gcm ⁻³]	1.799
μ [mm ⁻¹]	0.531
$F(000)$	240
Crystal size [mm ³]	0.171×0.316×0.39
Crystal colour	colourless
Crystal shape	block
Radiation	Mo K_{α} ($\lambda=0.71073$ Å)
2θ range [°]	7.66 to 56.57 (0.75 Å)
Index ranges	$-7 \leq h \leq 10$
	$-6 \leq k \leq 9$
	$-10 \leq l \leq 10$
Reflections collected	1890
Independent reflections	529
	$R_{\text{int}} = 0.0369$
	$R_{\text{sigma}} = 0.0296$
Completeness to $\theta = 25.242^\circ$	99.0
Data / Restraints / Parameters	529 / 0 / 37
Goodness-of-fit on F^2	0.805
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0233$
	$wR_2 = 0.0805$
Final R indexes [all data]	$R_1 = 0.0243$
	$wR_2 = 0.0880$
Largest peak/hole [eÅ ⁻³]	0.30/−0.18
Extinction coefficient	0.56(6)
Flack X parameter	0.09(5)

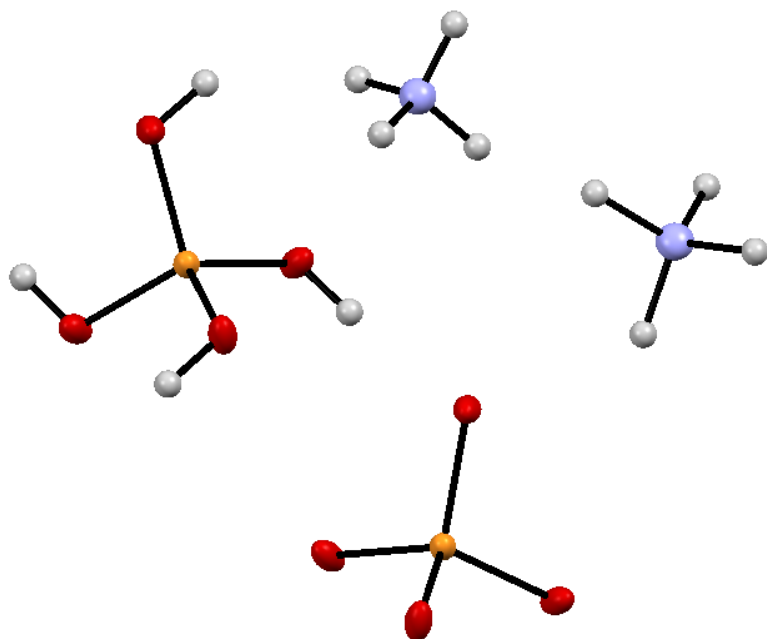


Figure 3. ORTEP diagram of lead acetate doped urea crystal.

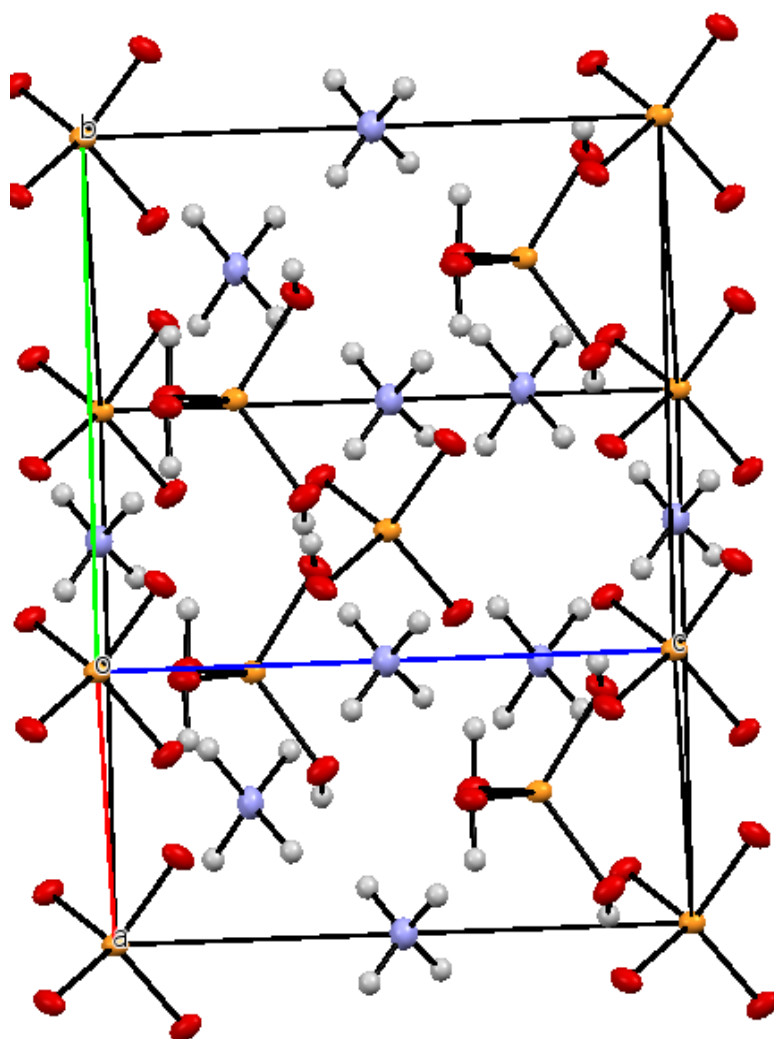


Figure 4. Packing diagram of lead acetate doped urea crystal.

Since the crystal system of Diammonium tetraoxolead(II)tetrahydroxolead(II) complex is tetragonal we can say that it is highly non-linear optical material. In the structure Diammonium tetraoxolead(II)tetrahydroxolead(II) complex Pb(II) is bonded tetrahedrally to four oxygen atoms and also in another tetrahedron Pb(II) is bonded to four hydroxyl group along with the presence of two ammonium. The bond length of Pb-O varies from 1.5365(16)-1.5407(16)Å, for N-H it ranges from 0.89(3)-1.07(4)Å, O-H bond length is 0.8200Å. The bond angle of H-N-H is 105.7°(16)-117°(4), Pb-O-H angle range is 109.5°, O-Pb-O varies from 108.60(7)-111.24°(14).

CONCLUSION

Colourless transparent crystals of lead acetate doped urea having reasonably good crystalline quality have been grown by solution evaporation solution growth technique taking triply distilled water as solvent at room temperature. The single crystal XRD analysis shows the difference in cell parameter values of urea doped lead acetate crystal than urea implying that the system and space group is different and its actual structure is refined and datas are collected showing empirical formula $H_{12}N_2O_8Pb_2$ of the so synthesised crystal with tetragonal system and I space group.

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