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Crystal growth and ferroelectric properties of thiourea picrate single crystal

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Ferroelectric hysteresis (P-E) loop study strongly confirmed that Thiourea Picrate (TUP) crystal is a new lead free, prolific ferroelectric material and good switching behavior of the polarization. Curie phase transition at 70^{O}C was observed in the dielectric analysis and AC conductivity study followed the power law with frequency depended. The elemental composition and surface morphology of the TUP crystal were investigated by EDX and SEM analysis. The thermal behavior of the TUP crystal was analyzed using TG/DTA, and found that the melting point of the prepared crystal was 155 ℃. The photoluminescence study shows TUP has a Blue Emission Property.

Keywords: Curie point, Conductivity, Ferroelectrics, Phase transitions, Single Crystal.

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Introduction

Symmetry concerns demand that ferroelectric materials also possess piezoelectric and pyroelectric properties. Piezoelectricity is the process by which a material produces surface charge in response to an external stress. Pyroelectricity is the term for a change in a substance's spontaneous polarisation in reaction to a change in temperature. Medical and military equipment including piezoelectric sensors, transducers, and actuators could use high performance piezoelectric materials. [1,2]. The mechanism of phase transition in mixed lead based ferroelectric materials was reported by Mathe et al. [3] and Patankar et al. [4]. Lead oxide based ferroelectric materials such as lead magnesium niobate possess excellent piezoelectric properties [5-9]. The lead oxide based ferroelectric materials are toxic and hazardous to the environment; it has created a greater demand for the development of environmentally friendly without lead ferroelectric samples. Hence many researchers are finding an environmental friendly with good alternative lead free ferroelectric material such as ferroelectric ceramics with the perovskite structure and single crystals. Rahimkutty et al. [10] has reported $SrC_4H_4O_6$ is a most important ferroelectric with electronic applications. Our research group also published an investigation regarding growth and properties of novel ferroelectric and NLO single crystal N,N-dimethylurea picrate [11]. In this line, I introduce another new ferroelectric material like thiourea picrate single crystal (TUP), which exhibit ferroelectric property. The grown crystals were characterized by various studies like Ferroelectric hysteresis (P-E) loop, dielectric, EDX and SEM, TG/DTA and photoluminescence were discussed and reported.

I. Experimental Details

1.1. Growth of TUP Crystal

The TUP single crystal was grown through the slow evaporation method at normal room temperature using a solution growth technique. A mixture of R grade Thiourea and Picric acid, dissolved in N, N-dimethylformamide at a molar ratio of 1:1, formed the saturated solution, prepared with recrystallized TUP salt and N,N-dimethylformamide solvent based on solubility data at room temperature. After 45-50 days, stable, non-hygroscopic, yellow crystals of various sizes were

successfully harvested. Figure 1 depicts photographs of the grown crystals.

Fig. 1. Image of TUP single crystal.

1.2 Characterization

The photoluminescence emission spectrum of the TUP single crystal was captured at room temperature using a Perkin Elmer luminescence spectrophotometer (model LS 45). Dielectric measurements of the TUP crystal were conducted using an LCR meter (Agilent 4284A). To ensure uniform surface thickness, the selected TUP sample was polished with paraffin oil and fine-grade alumina powder. A silver plate was affixed to the opposite face to create a capacitor with the crystal serving as the dielectric medium. Melting point and phase transition analysis of the TUP crystal were performed via TG/DTA analysis using a Perkin-Elmer thermal analyzer, with TUP as the sample and alumina as the reference. The EDAX spectrum of the TUP sample was obtained using a computer-controlled scanning electron microscope (JEOL Model JED – 2300), while the SEM image was captured using a JEOL microscope (Model JSM - 6390LV) with 8 nm resolution and SEI mode. Hysteresis P-E loop measurement of the TUP crystal was conducted using a fully computer-interfaced P–E loop tracer based on a modified Sawyer-Tower circuit.

II. Results and Discussion

2.1. Energy Dispersive X-ray (EDX) studies

The elemental composition of the TUP single crystal was analyzed via energy dispersive study, with the EDX spectrum depicting a curve correlating binding energy and emitted photoelectron intensity. The peak heights or areas in the spectrum indicate the quantity of respective elements present in the specimen, as illustrated in Figure 2. It was confirmed from the spectrum that elements including C, N, O, and S were detected in the sample.

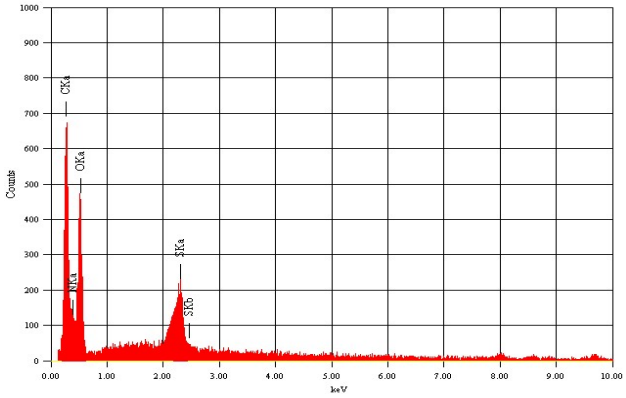

Fig. 2. EDX spectrum of TUP crystal.

Table 1.

Chemical Composition of TUP

Element	KeV	Mass%	Atom%	K
C	0.277	68.33	75.65	1
N	0.392	7.21	6.84	055
O	0.525	17.69	14.7	0.3805
S	2.307	6.77	2.81	0.3582
Total		100	100	

2.2 Scanning Electron Microscopic (SEM) analysis

SEM image is explain of the surface morphology, shape and size of the particles that relate between distributions of elemental composition on the surface. The grown TUP crystal with smooth surface and well defined planes, and was selected for the SEM analysis, and no polishing was done. The SEM micrographs (5 µm, 10 µm and 50 µm scale) are shown in Figures 3(a), (b) and (c). The micrographs of TUP were well dispersed and different magnifications were coalescing. It explains that the crystals have some oval and lenticular shape microcrystals on the surface. It also explains that some visible inclusions on the surface and they may be due to temperature oscillation during the crystal growth.

2.3 Photoluminescence study

The manner of photo excitation, the electron generally has excess strength which it loses earlier than coming to rest at the lowest strength in the conduction band. At this factor the electron ultimately falls back off to the valence

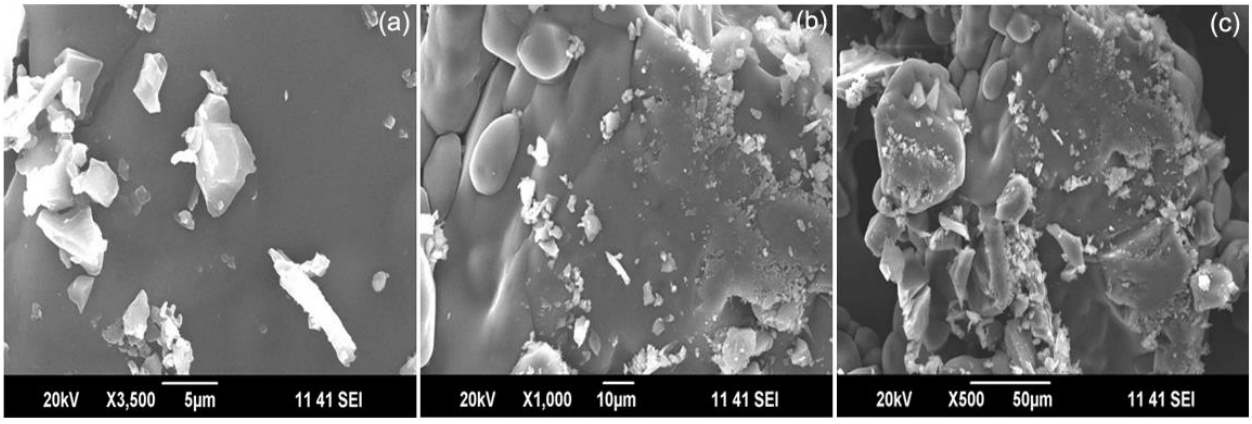

Fig. 3. (a). SEM image of TUP crystal (5 µm), (b). TUP crystal (10 µm), (c). TUP crystal (50 µm).

band. As it falls down, the power it loses is transformed again into a luminescent photon that's emitted from the materials. The method of photon excitation observed by means of photon emission is called photoluminescence. The Photoluminescence spectrum was used to study the near band edge excitation state and structural quality in materials. In this work, Photoluminescence emission spectrum of TUP single crystal (excited below and above the cut off wavelength 490 nm) is displayed in Figure 4. Two broad emission bands at 307 nm, 444 nm and three sharp emission peaks of wavelength 389 nm, 517 nm and 789 nm are observed from the emission spectrum. Typically, peaks observed in the UV region can arise from the relaxation of excited molecular states, while those in the visible region often relate to lattice processes. The primary peaks centered around 389 nm indicate that the TUP crystal was excited at this wavelength. This suggests a blue shift, attributed to radiative recombination between donors and acceptors from the amino group to the carboxyl group [12]. Additionally, the presence of peaks at 517 nm and 789 nm in the visible region strongly indicates the potential utility of this material in various devices.

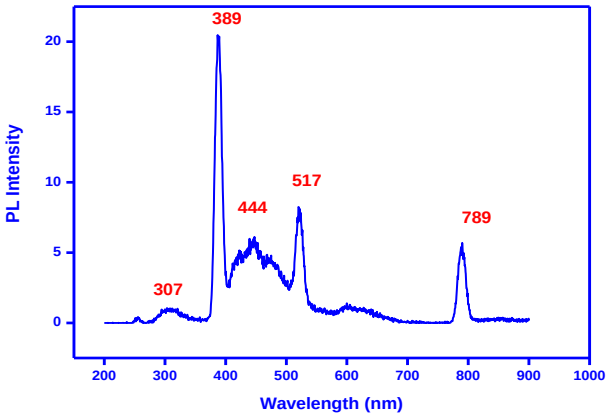

Fig. 4. Photoluminescence spectrum of TUP crystal.

2.4 TG/DTA Analysis

The thermal properties of the TUP single crystal were examined using TG and DTA in a temperature range of 40°C to 750°C with a heating rate of 10°C per minute under N_2 atmosphere. A 9.51 mg powder form crystal was placed in an aluminum crucible for analysis, yielding the TG/DTA profile depicted in Figure 5. The TG curve revealed no weight loss up to 224°C, indicating the absence of physically adsorbed water. An intense endothermic peak at 155°C in the DTA indicated the material's melting point, reflecting its high crystallinity and purity [13]. Two-stage decomposition of the TUP compound was observed from the TG curve, with the first stage occurring between 224°C and 277°C, resulting in a 68% weight loss. The second stage, between 277°C and 477°C, led to a gradual weight loss of about 22% due to the release of volatile substances, potentially sulfur oxide. The residue at the end accounted for approximately 10% by weight, likely attributed to residual carbon. Notably, no phase transition occurred before reaching the melting point.

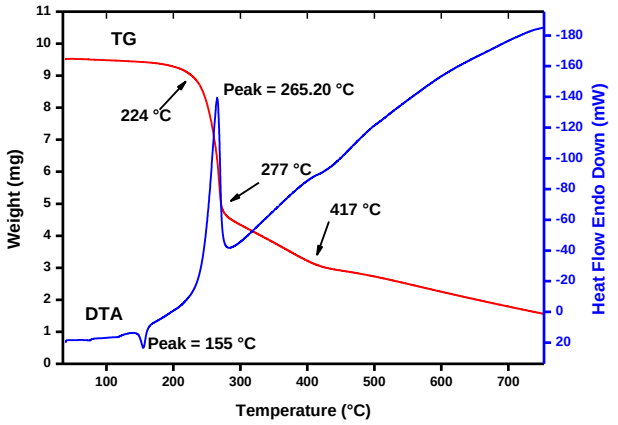

Fig. 5. TGA/DTA spectrum of TUP crystal.

2.5 Dielectric study

The variations of dielectric constant and dielectric loss (tan δ) of the TUP crystal as a function of temperature at different frequencies are shown in Figures 6 and 7 respectively. It can be easily noticed that a smooth increase of the dielectric constant with temperature reached a maximum at 70 ℃ and then decreased with increasing temperature, indicating suspected ferroelectric to paraelectric first order phase transition [14]. It can also be observed that the transition temperature T_c is the same for all the frequencies and can indicate that the TUP crystal shows a normal ferroelectric behavior.

In this case, the temperature dependence of the dielectric constant and dielectric loss (tan δ) reveals the pyroelectric behavior of the crystals. Initially, at low frequencies, the dielectric constant increases with temperature due to space charge polarization. However, after reaching the Curie temperature (Tc), the decrease in dielectric constant with rising temperature suggests compensation between ion dipole interactions and thermal energy, resulting in polarization relaxation and dielectric dispersion. Beyond 50 kHz, variations are minimal. In the lower frequency range, the higher dielectric constant is attributed to charge carriers that can migrate under applied fields, leading to the development of a space charge region and a significant increase in dielectric constant [15, 16]. It's important to minimize dielectric loss (tan δ) for practical purposes [17].

2.6 AC conductivity study

Variation of the AC conductivity with log frequency at different temperatures is provided in Figure 8. Various frequency dependent responses can be explained using power law

$$\sigma_{ac} \propto \omega^{s}$$

Where s is the index, $0 \leq s \leq 1$ [18]. Index s can be calculated by measuring the slope of the plot between log σ_{ac} and log of frequency. Conductivity (Figure 8) shows strong frequency dependence. If the index s value is greater than 1 the AC conductivity is independent of the frequency and it does not follow the power law and if it is less than 1 it is dependent on the frequency. In this work, the slopes of the plots show that the values of s vary from 0.96 - 0.74. It reveals that the AC conductivity is dependent on the frequency, and it follows the power law.

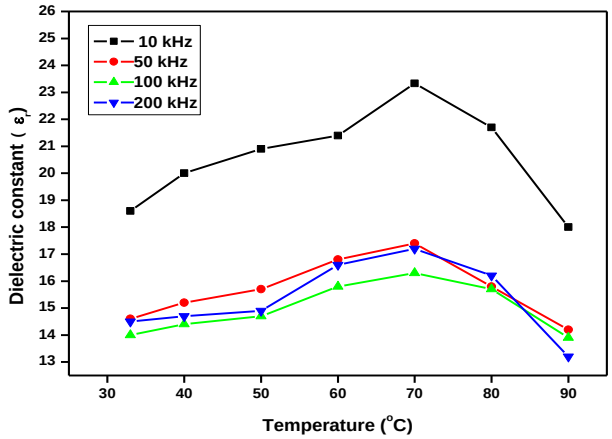

Fig. 6. Variation of dielectric constant with temperature for TUP crystal.

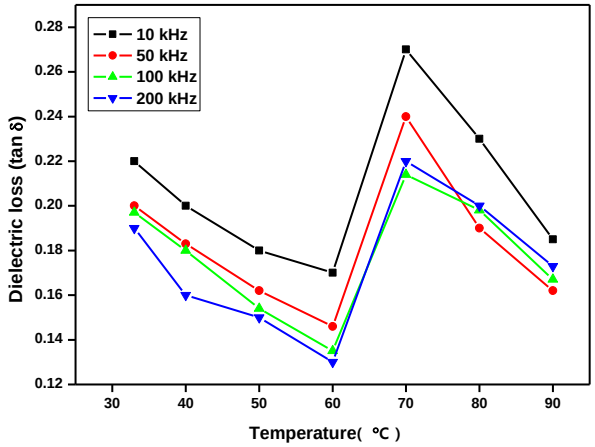

Fig. 7. Variation of dielectric loss with temperature for TUP crystal.

2.7 Ferroelectric hysteresis loop study

The prominent characteristic of ferroelectric materials is the alteration of spontaneous polarization induced by an external electric field. Consequently, the ferroelectric hysteresis loop typically serves as definitive proof of the ferroelectric state within the crystal. Caspari and Merz theorized that the hysteresis arises from the existence of parallel and antiparallel domains, which undergo switching at different field strengths. This hysteretic behavior, correlating polarization with electric field, finds utility in nonvolatile memory applications.

Figure 9 depicts the hysteresis (P-E) loop of electrical polarization versus electric field for the TUP crystal at room temperature. Ferroelectric behavior was confirmed by poling the selected single crystal with a 15 kV/cm field at 40°C for 10 minutes, while the sample was immersed in insulating oil during measurements. The hysteresis loop was traced using a fully computer-interfaced P-E loop tracer based on a modified Sawyer Tower circuit. The plot revealed a good and slightly asymmetric hysteresis loop, attributed to the appearance of internal biasing voltage with temperature [19]. This bias arose from domain relaxation in random directions, influencing coercivity variation with different polarities of the applied field. The values of saturated spontaneous polarization (Ps), remnant polarization (Pr), and coercive field (Ec) were determined as 3.3 μC/cm2, 1.9 μC/cm2, and 34 kV/cm, respectively, indicating the promising ferroelectric properties of the TUP crystal.

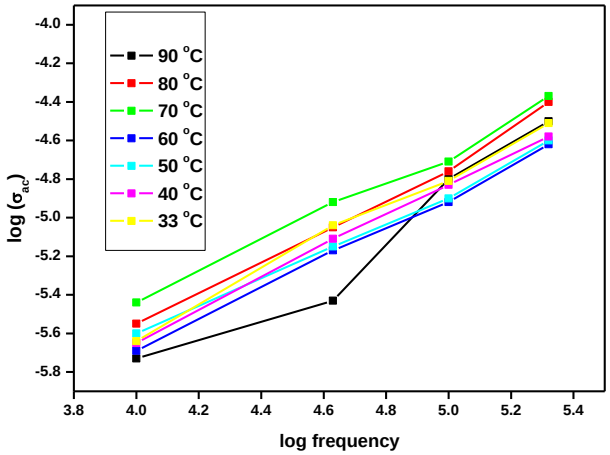

Fig. 8. Variation of Ac conductivity with log frequency for TUP crystal.

The squareness parameter of the loop was determined by using the empirical relation between remnant polarization (P_r), saturation polarization (P_s) and polarization at fields above coercive field ($P_{1.1Ec}$)

$$Rsq=PrPs+P_{1.1\,Ec}\ Pr \qquad (1)$$

Using this relation, the squareness parameter for the TUP sample was found to be 2.1. For an ideal hysteresis loop, the squareness parameter is equal to 2. It indicates good switching behavior of the polarization.

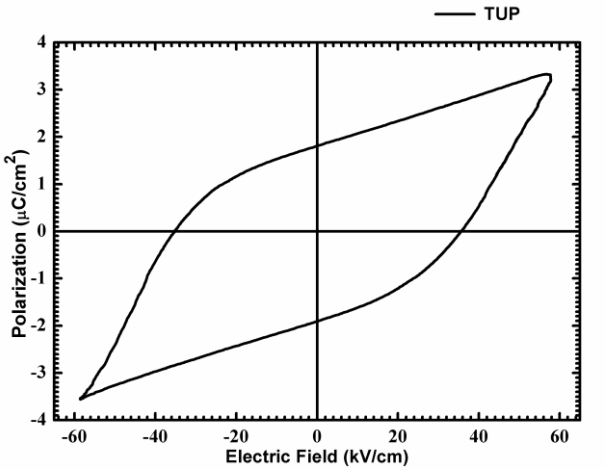

Fig. 9. Hysteresis (P-E) Loop for TUP crystal.

Conclusion

Good quality of ferroelectric and nonlinear optical thiourea picrate crystals were grown in N,N-dimethylformamide solution by slow evaporation method. The EDX spectrum find out the elemental composition of TUP single crystal. The photoluminescence spectrum revealed that the grown TUP has a blue emission property. The surface properties were investigated by SEM analysis. Dielectric study revealed

that ferroelectric first order phase transition occurs at 70 ℃ and the AC conductivity is dependent on the frequency and it follows the power law. Ferroelectric hysteresis loop study confirmed that the TUP crystal is an excellent ferroelectric material and remnant polarization (P_r) and saturation polarization (P_s) coercive field (E_c) and the squareness parameter (R_{sq}) are determined.

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Вирощування та фероелектричні властивості монокристалу пікрату тіосечовини

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Дослідження петлі фероелектричного гістерезису (P-E) чітко підтвердило, що кристал Thiourea Picrate (TUP) є новим безсвинцевим, продуктивним фероелектриком із добрим перемиканням поляризації. В діелектричному аналізі та при дослідженні провідності змінного струму за степеневим законом із частотою спостерігався фазовий перехід Кюрі при 70°C. Елементний склад і морфологія поверхні кристала TUP були досліджені за допомогою EDX і SEM аналізу. Теплова поведінка кристала TUP проаналізована за допомогою TG/DTA. Виявлено, що температура плавлення підготовленого кристала становила 155°C. Дослідження фотолюмінесценції показує, що TUP має властивості синього випромінювання.

Ключові слова: точка Кюрі, провідність, фероелектрики, фазові переходи, монокристал.