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Growth and Characterization of N,N'-Dimethylurea Admixtured Sulphamic acid Single Crystals

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The single crystals of N,N´-dimethylurea admixtured sulphamic acid (DMUASA) were grown by slow evaporation technique from an aqueous solution at room temperature. Good quality crystals of size 34 mm × 15 mm × 7 mm had been obtained within 30 days. To synthesise the N,N´-dimethylurea admixtured sulphamic acid salt, N,N´-dimethylurea and sulphamic acid were taken in 1:1 molar ratio. The solubility of N,N´-dimethylurea admixtured sulphamic acid salt in water had been carried out at various temperatures. The grown crystal was characterized by single crystal X-ray diffraction analysis to confirm the structure of sample. Powder X-ray diffraction studies confirm the crystalline nature of the grown crystals. Fourier transform infrared study was used to confirm the presence of various functional groups in the grown crystal. UV-visible-NIR transmittance spectrum was recorded to study the optical properties of the grown crystal. The existence of second harmonic generation signals was confirmed by performing Kurtz-Perry powder test and the output power generated by the crystal was comparable with that of potassium dihydrogen phosphate. Thermal properties of the crystal had been investigated using thermogravimetric analysis and differential thermal analysis. The mechanical strength of the crystal was estimated by Vickers hardness test.

Keywords: Second harmonic generation, Thermo gravimetric analysis, Differential thermal analysis, FTIR, DMUASA single crystal.

INTRODUCTION

The search for new nonlinear optical (NLO) materials have specific attention due to their effective usage in the field of electro-optic devices, data storage, optical signal processing, laser remote sensing, laser fusion reaction, medical diagnostic *etc*.,[1-4]. The generation of coherent blue light through second harmonic generation (SHG) from near infrared laser sources is an important technological problem that attracted the researchers in the last few decades. Although many inorganic and organic single crystals showing strong second harmonic generation effects are known for some years, there is a demand for newer and improved crystalline materials.

In the context of NLO, organic materials have advantages, such as high nonlinearity, fast response and synthesis flexibility but their practical applications are limited due to poor mechanical, thermal stabilities and inability to produce good crystals[5,6]. But inorganic materials have excellent mechanical and thermal stability when compared to organic materials[7]. In view of this, a new type of NLO materials have been designed by combining pure organic materials with high optical nonlinearity with the inorganic materials having favourable mechanical and thermal properties known as semi-organic materials. Semi-organic nonlinear optical materials are prominent one for device fabrication due to their high optical nonlinearity, high laser damage threshold and exceptional thermal and mechanical properties[8]. Nowadays many researchers focussed their attention on the growth and characterization of semi-organic crystals[9,10] due to their remarkable properties.

Sulphamic acid is a classical inorganic compound and an important industrial chemical[11]. It is highly stable and it can be kept for years without any change in its properties. It is a strong inorganic acid, while mixing it with water it exhibits zwitterionic form[12]. Sulphamic acid finds application in multistage flash evaporation, desalination plants for cleaning demisters, heat exchangers and cooling water system[13]. Many researchers have reported the effect of dopants on the growth and physical properties of sulphamic acid single crystals. Kannan *et al.*[14-16] reported the influence of rare earth elements like gadolinium, lanthanum and yttrium on the growth and characterization of sulphamic acid. The effect of metal ions (Mn^{2+}, Cu^{2+} and Ni^{2+}) on the growth and properties of pure sulphamic acid crystal has also been reported by Babu *et al.*[17]. *Hitherto* no attempt has been made to study the growth and of admixture characterization of organic materials with the inorganic sulphamic acid. In this view, an attempt has been made to synthesize and grow N-N´-dimethylurea admixtured sulphamic acid, a promising semi-organic material by slow evaporation method and characterized.

This work reports the synthesis, solubility and growth of the N,N´-dimethylurea admixtured sulphamic acid (DMUASA) where second harmonic generation efficiency has been estimated as 0.84 times that of potassium dihydrogen phosphate. The X-ray reveals that the grown crystal diffraction study belongs to the tetragonal system. The functional groups of the grown crystal observed from FTIR studies. A sharp endothermic peak observed around 420 °C in the thermal studies show that the good degree of crystallinity of the sample.

EXPERIMENTAL

Synthesis and growth of DMUASA single crystals: N,N'-dimethylurea admixtured sulphamic acid salt was synthesized from N,N'-dimethylurea (Merck GR grade) and sulphamic acid (Merck GR grade) in the molar ratio 1:1 by dissolving in deionized water. The recrystallization process was carried out to eliminate the impurities present in the salt. The recrystallized salt was used for preparing the saturated solution. The synthesized salt was dissolved in deionized water and stirred for about 3 h using hot plate magnetic stirrer. The saturated solution was filtered using Whatmann filter paper. After filtration the beaker containing the saturated solution was covered with perforated polyethylene sheet for controlled evaporation and kept at room temperature in undisturbed condition. The good quality DMUASA crystal was harvested with the dimension 34 mm × 15 mm × 7 mm in the period of 30 days. The as grown crystal is shown in Fig.1. The grown crystal is found to be highly transparent and colourless.

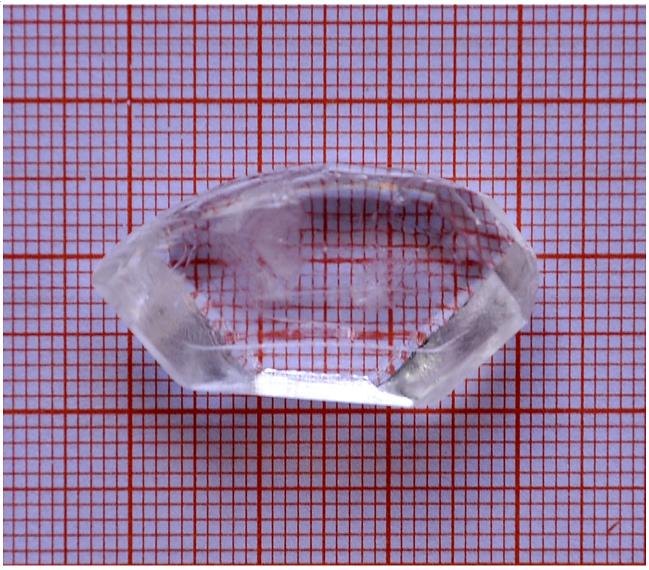


Fig. 1. As grown crystal of N,N'-dimethylurea admixtured sulphamic acid (DMUASA)

Solubility: The solubility test was carried out by gravimetric method[18] for the DMUASA salt in water at various temperatures. A constant volume of 100 mL of solution was used in the experiment. Solubility was performed using a hot-plate magnetic stirrer and a thermometer. Fig. 2 shows the solubility curve for DMUASA salt in water. From the graph, it was observed that the solubility of the synthesised sample increases with increase in temperature. The DMUASA possesses positive temperature coefficient of solubility in water which facilitates the growth of DMUASA crystal by slow evaporation technique.

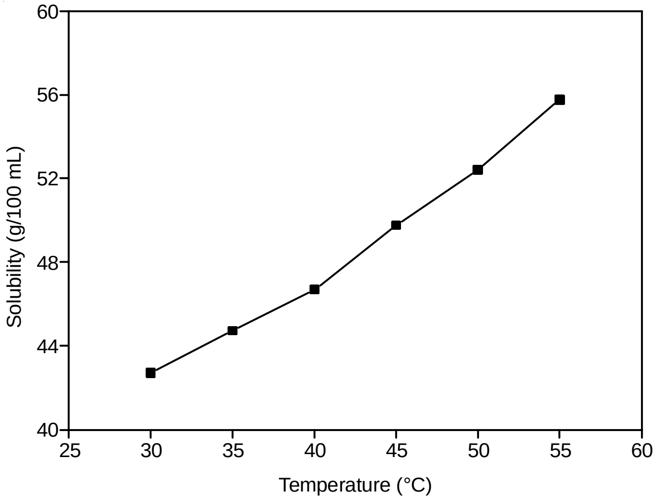


Fig. 2. Solubility curve for N,N'-dimethylurea admixtured sulphamic acid salt in water

RESULTS AND DISCUSSION

X-ray diffraction analysis: Single crystal X-ray diffraction study was carried out to identify the crystal structure of DMUASA crystal. The obtained unit cell parameters of DMUASA crystal are, a = 8.112 Å, b = 8.112 Å, c = 9.223 Å, $\alpha = \beta = \gamma = 90°$ and volume, v = 606.78(7) $Å^3$. The DMUASA crystal belongs to tetragonal crystal system, where as pure sulphamic acid belongs to orthorhombic system[19].

Powder XRD analysis was carried out to identify the reflection planes and the crystallinity of the grown sample using Bruker AXSD8 powder X-ray diffractomer. The well defined peaks at a particular 2θ values show the good crystalline nature of the grown crystals. The reflection planes were indexed using TREOR software packages following the procedure of Lipson and Steeple[20]. The indexed powder XRD pattern of grown crystal is shown in Fig. 3.

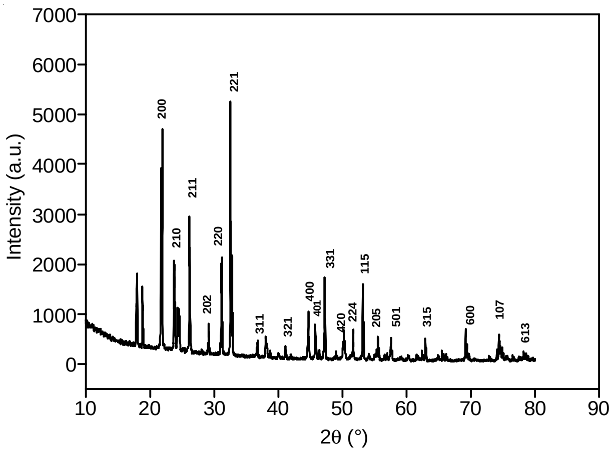
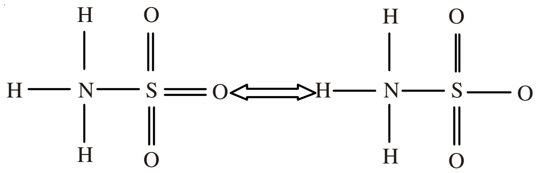


Fig. 3. Powder XRD pattern of N,N'-dimethylurea admixtured sulphamic acid crystalline sample

Fourier transform infrared (FTIR) analysis: The Fourier transform infrared spectrum of grown crystal was recorded in the region 4000-400 cm^{-1} using Perkin Elmer infrared spectrometer (Model: Shimadzu 80400S) with KBr Pellet containing DMUASA powder obtained from grown crystals. Fig. 4 shows the resulting spectrum in which the functional group present in the molecules can be identified.

Urea and its substituted derivatives have been extensively studied within the frame of organic crystal engineering due to their ability to form extended hydrogen bonded framework. In particular symmetrically substituted urea form α-network by donating two hydrogen bonds and chelating the carbonyl oxygen of the next molecule in the network[21]. N,N'-dimethylurea has only been found to coordinate as monodentate ligands through the oxygen atom. Upon coordination *via* oxygen the positively charged hydrogen atom present in the zwitterionic form of sulphamic acid stabilized the negative charge on the oxygen atom. The N-CO group now occurs in its polar resonance form and the double bond character of the C-N bond increases, while the double bond character of C-O decreases, resulting in an increase of the C-N stretching frequency with a simultaneous decrease in CO stretching frequency in DMUSA crystal. The adduct in the NH_3^+-SO_3^- tautomer of sulphamic acid (NH_2SO_2OH) whose crystal structure has been shown by both X-ray and neutron diffraction technique which comprise zwitterionic (NH_3^+-SO_3^-) form instead of amino sulphamic acid form. The different structural forms of sulphamic acid are shown below:



It exists as zwitterionic form as $NH_3^+SO_3^-$ in the solid state and as NH_3^+-SO_2-O^- in the aqueous solution. The infrared spectrum of sulphamic acid and its sulphamates were studied by Vuagnat and Wagner[22]. Infrared studies have been interpreted as a supporting evidence for this zwitterionic structure for the molecule in the solid state.

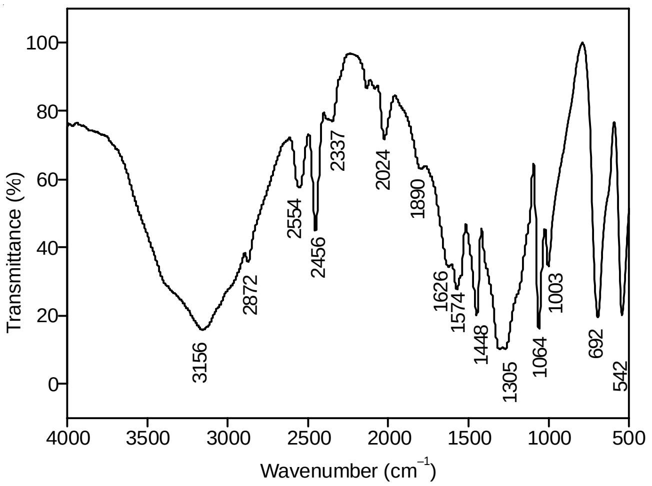


Fig. 4. FTIR spectrum of N,N'-dimethylurea admixtured sulphamic acid crystal

The FTIR spectral analysis of the zwitterionic form of sulphamic acid showed that the NH_3^+ group asymmetric and symmetric stretching vibrations occur at 3242 and 3119 cm^{-1}, respectively. The asymmetric deformation vibrations for this group were obtained at 1571 and 1547 cm^{-1}. The symmetric NH_3^+ group deformation was obtained at 1448 cm^{-1}, the asymmetric and symmetric stretching vibrations of SO_3^- group were shown at 1329 and 1273 cm^{-1}, respectively. The symmetric deformations for this group were found at 1059 and 1004 cm^{-1}. The N-S stretching frequency was appeared at 694 cm^{-1}.

But the FTIR spectral data for the crystal show that the NH_3^+ stretching vibration occurs at 3155 cm^{-1}. The asymmetric deformation vibrations of this group were obtained at 1625 and 1573 cm^{-1}. This is somewhat higher value compared to the stretching vibration due to NH_3^+ group in free sulphamic acid. The symmetric deformation of NH_3^+ group was obtained at 1448 cm^{-1}. The SO_3^- group of DMUASA has an asymmetric vibration at 1305 cm^{-1}. The N-S stretch was found at 692 cm^{-1}. The broadening of peaks in the case of DMUASA crystal suggested that an uniform binding of sulphamic acid on N,N'-dimethylurea. It is also suggested that the decrease in ν(C=O) stretching frequency in the DMUASA crystal indicates that the double bond character is reduced due to the interaction of CO group of N,N'-dimethylurea with the zwitterionic units of suphamic acid. It is also evidenced that the shift and decrease in the intensity of the stretching frequencies of DMUASA crystal and also suggested that there is some interionic interaction between N,N'-dimethylurea and suphamic acid (Table-1).

TABLE-1
FTIR SPECTRAL DATA FOR N,N´-DIMETHYLUREA ADMIXTURED SULPHAMIC ACID CRYSTAL

Wave number (cm^{-1})	Band assignment
3155	NH_3^+ symmetric vibration
2872	ν_{CH} or δasym (C-N) amide
1625	δ_{asym} & $\nu_{(N-H)}$ (asymmetric NH bending vibration)
1573	ν_{CO} or NH_3^+ asymmetric deformation
1448	νSO_{3-} (symmetric deformation)
1305	νNH_3^+ (symmetric stretching)
1064, 1003	ν_{sysm} SO_3^- (symmetric deformation)
692	N_{N-S} (N-S stretching vibration)

Vickers microhardness test: Microhardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behaviour, yield strength, brittleness index and temperature of cracking[23]. Microhardness analysis was carried out using Vickers microhardness tester. A well polished grown DMUASA crystal of thickness 2 mm was used for this analysis. The crystal was subjected to different loads varying from 25 to 100 g. Vickers microhardness number was calculated using the relation $H_v = 1.8544(P/d^2)$ kg/mm^2, where P is the load applied in gm and d is the diagonal length of the indentation impression in mm. Fig. 5 shows the relation between H_v and the load P for the as grown crystal. The relation between load and the size of indentation is given by Mayer's law,

$P = ad^n$. Here a and n are constants. The work hardening co-efficient (n) was calculated by plotting log (p) *versus* log (d). From the Fig. 6, the value of n was found to be 2.49423.

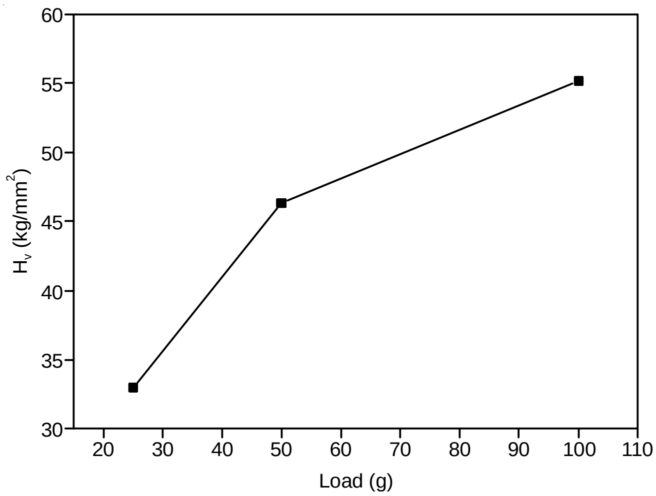


Fig. 5. Dependence of hardness with load of N,N'-dimethylurea admixtured sulphamic acid crystal

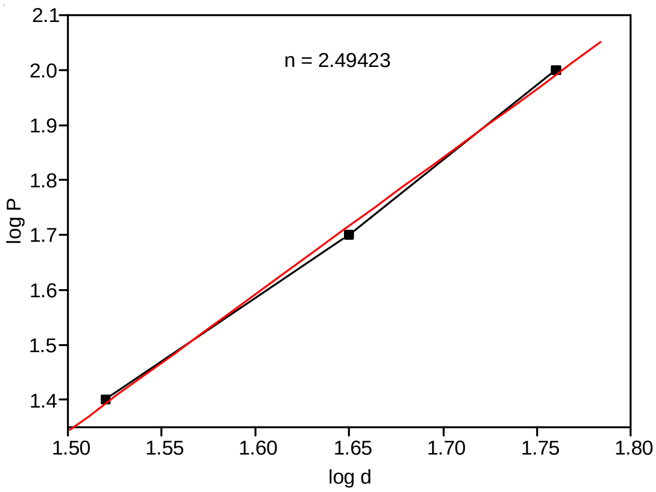


Fig. 6. Variation of log d with log P of N,N'-dimethylurea admixtured sulphamic acid crystal

According to Onitsch, the work hardening co-efficient lies between 1 and 1.6 for the hard materials, and it is greater than 1.6 for soft materials[24,25]. For the grown DMUASA crystal, the work hardening co-efficient is greater than 1.6, hence it is a soft material.

Optical transmission spectral analysis: The optical transmission range, transparency cut-off and absorbance band are the most important optical parameters for laser frequency conversion applications. To find the transmission range of DMUASA, UV-visible-NIR transmittance spectrum was recorded in the range 200-1200 nm using Perkin Elmer Lamda UV-visible-NIR spectrometer to reveal the optical properties of DMUASA single crystal. Fig. 7 shows the transmittance spectrum, in which the lower cut-off region is obtained at 231 nm. The maximum transmission of as grown crystal is 33 % and it shows no absorption of wavelength between 200 and 1200 nm, which clearly indicates that the grown crystal can be used as a window material in optical instruments. Hence it confirms that DMUASA is suitable for second harmonic generation device fabrication[26].

A strong absorption peak corresponding to the fundamental absorption appears at $\lambda = 231$ nm. The band gap energy of DMUASA crystal was calculated to be 5.4 eV using the formula

$$E_g = 1240/\lambda$$

As a consequence of wide band gap, the grown crystal has large transmission in the visible region.

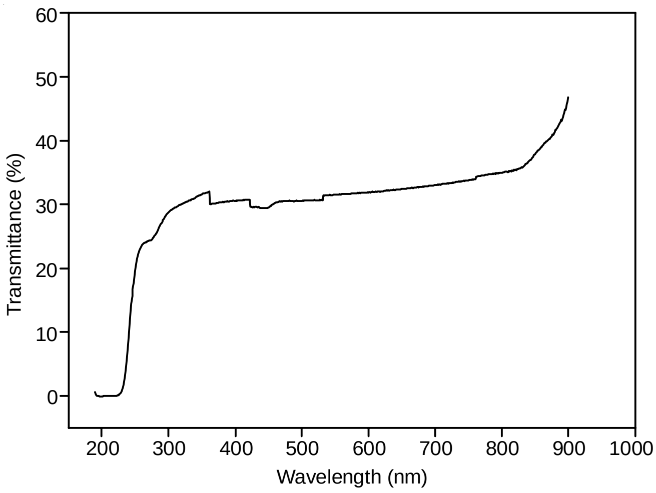


Fig. 7. Optical transmission spectrum of N,N'-dimethylurea admixtured sulphamic acid crystal

Thermal analysis: Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) provides the information regarding any weight change associated with a phase transition and the decomposition of the crystalline sample at different stages. The TG-DTA study was carried out using Perkin Elmer STA 6000 analyzer for the grown DMUASA crystal in nitrogen atmosphere at a heating rate of 10 °C/min from 40 to 700 °C. The initial mass of the material was taken to be 13.134 mg.

Fig. 8. shows the thermogram of DMUASA crystalline sample. From the thermo gravimetric analysis curve, it can be seen that the sample is very stable up to 219 °C. The thermogravimetric analysis shows that there is no mass reduction in 33-219 °C region. Thermogravimetric analysis curve of this crystal shows that the crystal is very stable in this temperature region.

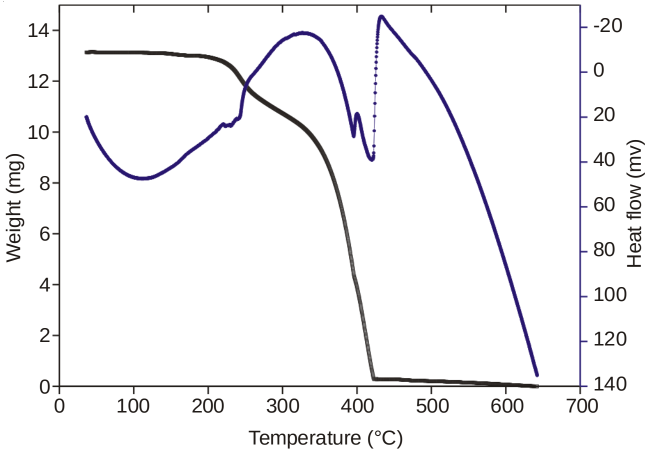


Fig. 8. TG-DTA curve of DMUASA crystalline sample

The first weight loss occurs between 219-350 °C, which may be due to the removal of nitrogen oxide (NO) and the weight loss extends up to 350 °C. The second stage weight loss of sulphur dioxide (SO_2)[13] in DMUASA crystal is from 350 to 420.41 °C. In the second stage of decomposition, it is observed that the weight loss is 70 %. The sharp endothermic peak at 420.41°C shows the good degree of crystallinity of the sample.

Nonlinear optical analysis: The famous Kurtz and Perry powder technique[27] was used to check the second harmonic generation from DMUASA sample. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample of DMUASA and the emission of green radiation of wavelength 532 nm confirms second harmonic generation. The second harmonic generation signal of 7.4 m J for DMUASA crystal was obtained for an input energy of 0.68 m J. But the standard potassium dihydrogen phosphate sample gave an second harmonic generation signal of 8.8 m J for the same input energy. Thus, it is observed that the second harmonic generation efficiency of the DMUASA sample is 0.84 times that of the standard potassium dihydrogen phosphate crystal. Thus, the grown DMUASA sample has good NLO property.

Conclusion

Good optical quality single crystals of DMUASA have been grown from slow evaporation technique. The DMUASA salt possess positive temperature coefficient of solubility. Tetragonal structure of grown crystal was confirmed by single crystal X-ray diffraction analysis. Various functional groups present in the grown crystal have been identified by FTIR spectroscopy. The optical transparency has been revealed by UV-visible-NIR study and thermal stability has been confirmed by TG-DTA thermal analysis. Microhardness test was carried out to measure the mechanical strength of DMUASA crystal. It is also observed that the second harmonic generation efficiency of the grown crystal was comparable with that of potassium dihydrogen phosphate. Due to broad transmission range and second harmonic generation behaviour of the DMUASA crystal, it can be used in technologies such as optical communication, optical computing and dynamic data storage.

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