

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 5, May 2017

Growth, Structural, Optical, Thermal, Mechanical and Non Linear Property of Ferrous Sulphate Doped Sulphamic Acid Single Crystal

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ABSTRACT: Single crystals of Ferrous Sulphate doped Sulphamic Acid have been grown by slow evaporation technique at room temperature. Structural characterization of grown crystal was carried out using single crystal and powder X Ray Diffraction studies. FTIR study was performed to identify the various functional groups present in the grown crystal. The cutoff wavelength of the grown crystal was found by UV-Vis-NIR spectral studies. Thermal stability of the grown crystal was analyzed from Thermogravimetric Analysis (TGA) and Differential Thermogravimetric Analysis (DTA). The mechanical strength and Second harmonic generation of the grown crystal was determined by Vicker's Microhardness Test and Kurtz powder technique respectively.

KEYWORDS: Slow evaporation method, XRD, FTIR, TGA, NLO.

I. INTRODUCTION

The search for new Nonlinear Optical materials and improving the properties of existing NLO material is a never ending process due to its wide application in the field of science and technology. In the developing field of optical communications and laser technology, the generation of second harmonics is very essential [1]. A Nonlinear Optical crystal should have high physical and optical properties, non zero NLO coefficient and transparency at required wavelengths to be used in frequency conversion. There should be good transfer of energy between the waves, when optical waves propagate through Nonlinear Optical crystal [2]. Semi organic materials have good chemical flexibility and excellent optical nonlinearity like organic materials and high thermal stability and good transmittance like inorganic materials [3]. Among the inorganic materials Sulphamate derivatives are most suitable for NLO property with its two planar rings configuration and good blue light transmittance [4].

Sulphamic acid is a highly stable inorganic acid with orthorhombic structure. It is soluble in water and exhibits zwitterionic form. Its molecular weight is 97.09 [1]. Large single crystals of SA can be grown at low temperatures [5]. Due to these characteristics IUPAC, British analytical methods committee and JIS (Japanese Industrial Standard) have accepted SA as a standard substance for titrimetric analysis [6]. The growth, structure, UV-Vis-NIR, Raman Studies, dielectric, neutron diffraction and etching of pure SA single crystal is already reported [1,5,7-10]. Here we report the growth and characterization of FeSO₄ doped SA Nonlinear optical crystal.

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II. RELATED WORK

Non Linear Optical materials have large nonlinearity and are satisfying all the technological requirements for applications such as wide transparency range, fast response and high damage threshold. Inorganic materials have short UV cutoff wavelength and high second order nonlinearity. Among the inorganic materials Sulphamic Acid is most used. The NLO property of all new materials is compared with Potassium Dihydrogen Phosphate (KDP). Pure SA crystals are grown by slow evaporation technique and its thermal and optical behaviours are studied [5]. In a related work, SA is doped with Ferric chloride and crystals are grown by slow evaporation technique. Its characterization confirms the incorporation of dopant into SA. Its NLO activity is 1.5 times that of KDP and its optical and thermal behaviours are good [11].

III. EXPERIMENTAL PROCEDURE

SA : FeSO₄ was synthesized using commercially available SA (Lobachemie AR grade) and FeSO₄ in the ratio 1:1 at room temperature by slow evaporation method. Both SA and FeSO₄ are dissolved in 20ml of double distilled water separately. To obtain homogeneous solution, the solutions are mixed together using magnetic stirrer. Then the solution was filtered using filter paper to get a clear solution. The filtered solution was taken in a beaker and closed tightly with perforated Aluminium foil to minimize evaporation. Good transparent single crystals were obtained in a month's time. The product was further recrystallized for getting pure single crystal. The photograph of the grown crystal is given in fig (1).



Fig (1) SA : FeSO₄ crystal grown by slow evaporation technique.

IV. CHARACTERIZATION TECHNIQUES

To determine the lattice parameter values, Single Crystal X-Ray Diffraction is carried out using BRUKER AXS KAPPA APEX II CCD with Shel xtl software. Powder X-Ray Diffraction analysis is done using BRUKER AXS D8 ADVANCE Diffractometer and the 2θ and d values are calculated using Diffrac Plus software. FTIR spectrum is recorded in the range 500cm⁻¹ to 4000cm⁻¹ using THERMO NICOLET AVATAR 370 to identify the incorporation of FeSO₄ in to pure SA. The Optical transmission spectrum is recorded using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200 nm to 800 nm. The Thermal behavior of the grown crystal is determined between 40 °C and 730 °C in nitrogen atmosphere at a heating rate of 10 °C/min using PERKIN ELMER

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DIAMOND Thermal analysis system. The microhardness measurement is done using Vicker's Hardness Tester. To measure SHG efficiency, Kurtz powder technique was performed on grown crystal.

V. RESULTS AND DISCUSSION

1. Single Crystal X-Ray Diffraction

Single Crystal X-Ray Diffraction is carried out using BRUKER AXS KAPPA APEX II CCD with Shel xtl software. Both Pure SA and SA: FeSO₄ crystallizes into orthorhombic structure. The lattice parameters are given in table (1). The variations in lattice parameters and cell volume of the grown crystal may be attributed to the incorporation of dopants into SA crystal lattice.

Table (1) shows the lattice parameters of pure & FeSO₄ doped SA. Both are having orthorhombic structures with different cell parameters and cell volume.

Parameter	Pure SA	SA:FeSO ₄
a Å ⁰	8.100	8.1092
b Å ⁰	8.049	8.0613
c Å ⁰	9.220	9.2417
V Å ⁰³	604.8	604.14

Table (1) Lattice parameters of pure & FeSO₄ doped SA.

2. Powder X-Ray Diffraction Analysis

Powder X-Ray Diffraction analysis of FeSO₄ doped SA is done using BRUKER AXS D8 ADVANCE Diffractometer and the 2θ and d values are calculated using Difrac Plus software. The samples are scanned in the range of 3 degrees to 80 degrees. All the observed reflections are indexed. Compared to pure SA, some extra peaks are obtained for SA : FeSO₄. The extra peaks (002), (121), (103), (323), (500), (405), (620), (444) and change in the intensity of peaks indicates the incorporation of the dopant into the crystal lattice of pure SA and thereby changing the bond length [5]. Definite Bragg peaks confirms the good crystalline nature of the grown crystal [12].

The PXRD of pure and grown crystal is shown in fig (2) and fig (3). Compared to pure SA, PXRD of grown crystal shows some extra peaks due to the incorporation of dopant into the crystal lattice.

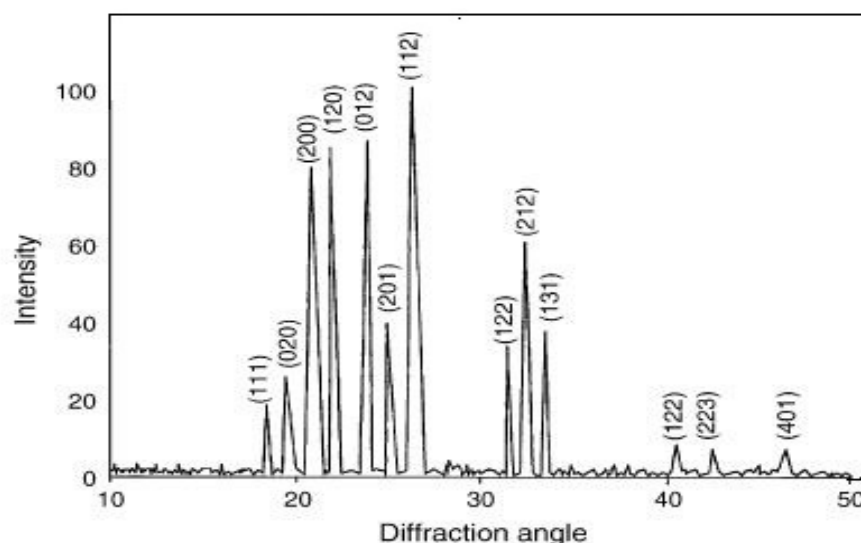


Fig (2) PXRD of pure SA crystal

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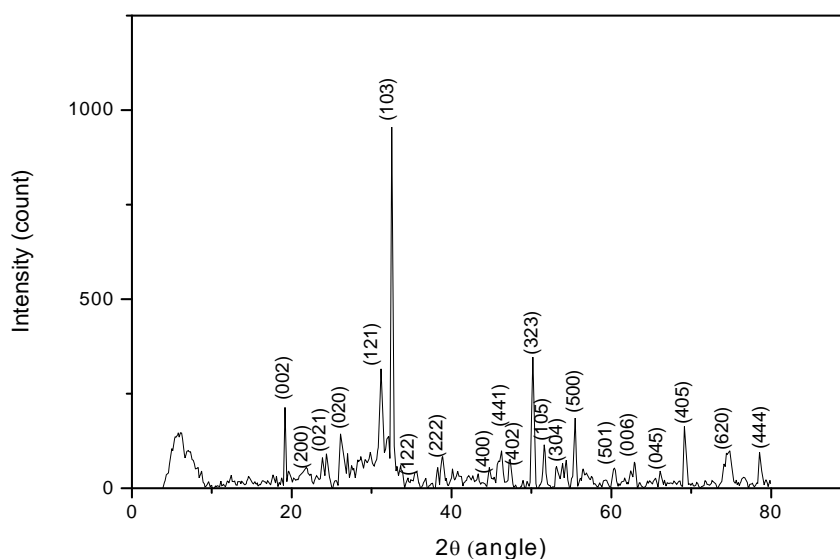


Fig (3) PXR of SA : FeSO₄ crystal.

3. Fourier Transform Infrared Spectroscopy

The functional groups present in the grown sample can be identified using FTIR spectroscopy [9]. Fourier Transform Infrared Absorption spectra of SA : FeSO₄ is recorded in the range 500 cm⁻¹ to 4000 cm⁻¹ using THERMO NICOLET AVATAR 370 and is given in fig (4). Doping of FeSO₄ into the lattice of pure SA shows some significant change in the absorption pattern. The presence of various functional groups in the grown sample makes the FTIR spectrum complex. The absorption band in the range 3000 cm⁻¹ to 4000 cm⁻¹ becomes narrow when compared to the absorption band of pure SA. This is due to the incorporation of the dopant in the grown crystal.

The various functional groups present in SA : FeSO₄ are assigned and recorded in the table (2). Vibrational band assignments for SA:FeSO₄ crystal shows variation in the absorption pattern compared to pure SA. FTIR of SA : FeSO₄ crystal shows variation in the absorption pattern due to the incorporation of dopant into sulphamic Acid. It is shown in fig (4).

Pure SA	SA : FeSO ₄	Assignment
3211	3151	Degen. NH ₃ ⁺ stretching
2871	2871	Sym. NH ₃ ⁺ stretching
1538	1542	Degen. NH ₃ ⁺ deformation
1455	1446	Sym. NH ₃ ⁺ deformation
1337	1268	Degen. SO ₃ ⁻ stretching
1069	1067	Degen. SO ₃ ⁻ deformation
1001	1005	S - O stretching
687	690	NH ₂ and N - H wagging

Table (2) Vibrational band assignments for SA:FeSO₄.

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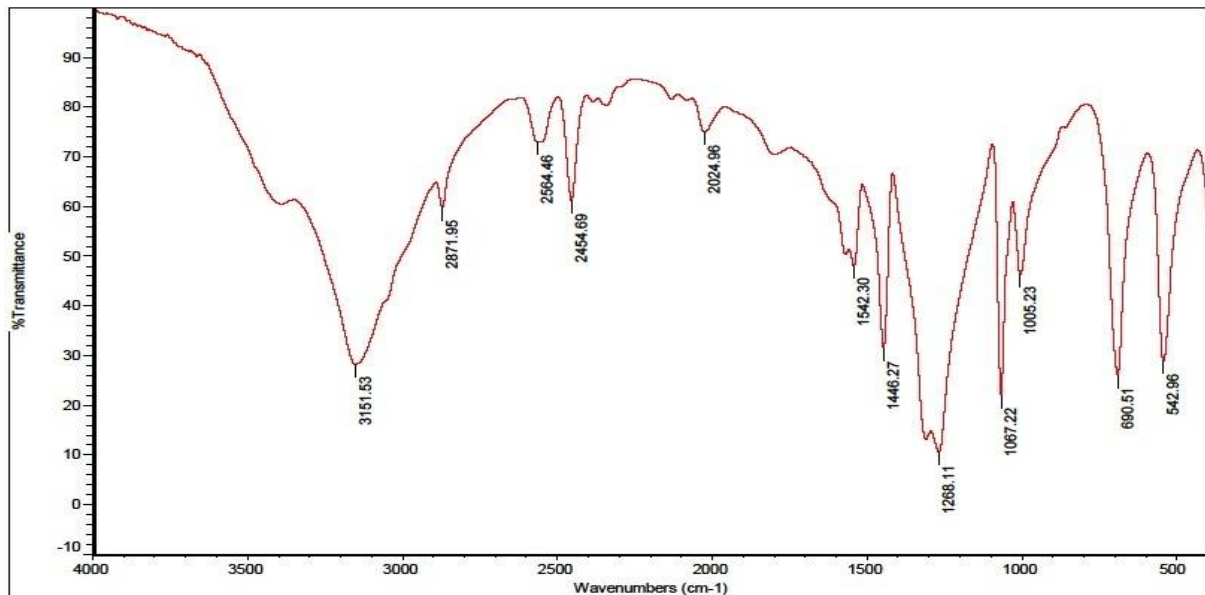


Fig (4) FTIR of SA : FeSO₄ crystal.

4. UV-Vis-NIR Studies

Optical transmission, absorption and transparency analysis of a crystal is very important which helps it to be used in optoelectronic field [9]. UV-Vis analysis of the grown crystal is carried out using VARIAN CARRY 300 SPECTROPHOTOMETER in the wavelength range of 200 nm to 800 nm. It is observed that the lower cutoff wavelength is 261 nm which is less than that of pure SA. This indicates that the dopant has improved the optical transparency of the grown crystal. There is no considerable absorption till 800 nm. So, it can be used for optoelectronic application in the visible region. The UV-Vis-NIR spectrum of grown crystal is given in fig (5) and fig (6).

In fig (5) UV-Vis-NIR of SA : FeSO₄ crystal shows the cutoff wavelength is 261 nm which is less than pure SA. Fig (6) shows good optical transparency of the grown crystal.

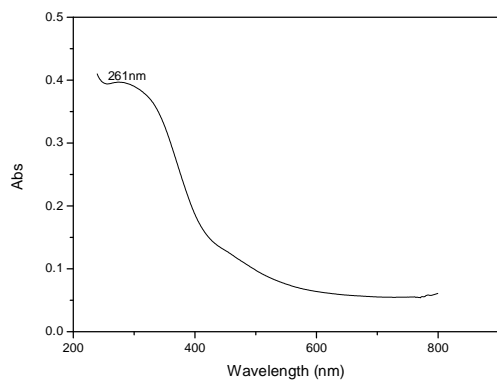


Fig (5) UV-Vis-NIR of SA : FeSO₄ crystal

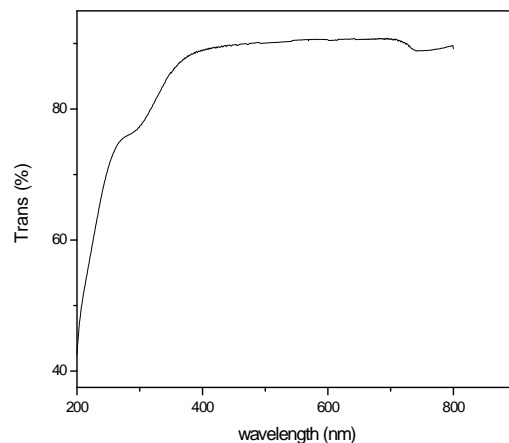


Fig (6) UV-Vis-NIR of SA : FeSO₄ crystal

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5. TGA/DTA Analysis

TGA/DTA analysis is carried out between 40 °C and 730 °C in nitrogen atmosphere at a heating rate of 10 °C/min using PERKIN ELMER DIAMOND Thermal analysis system. A crystal of weight 5.564 g is used for investigation. The grown crystal of SA : FeSO₄ undergoes single stage of decomposition in the vicinity of 225 °C. The sharpness of the peak indicates the high degree of crystallinity and purity of the grown crystal [3]. There is no weight loss till 225 °C, which confirms that the crystal is devoid of any physically absorbed water on it. So SA : FeSO₄ crystal can be used for Nonlinear Optical activity till 225 °C where as pure SA decomposes fully at 204 °C which corresponds to its melting point [5].

From TGA, it is observed that SA : FeSO₄ undergoes double stage of decomposition. The second stage of decomposition occurs at the vicinity of 414 °C with a weight loss of nearly 85.668% of initial mass.

In fig (7) TGA/DTA of SA : FeSO₄ crystal shows the two stages of decomposition. It confirms the nonlinearity until 225 °C.

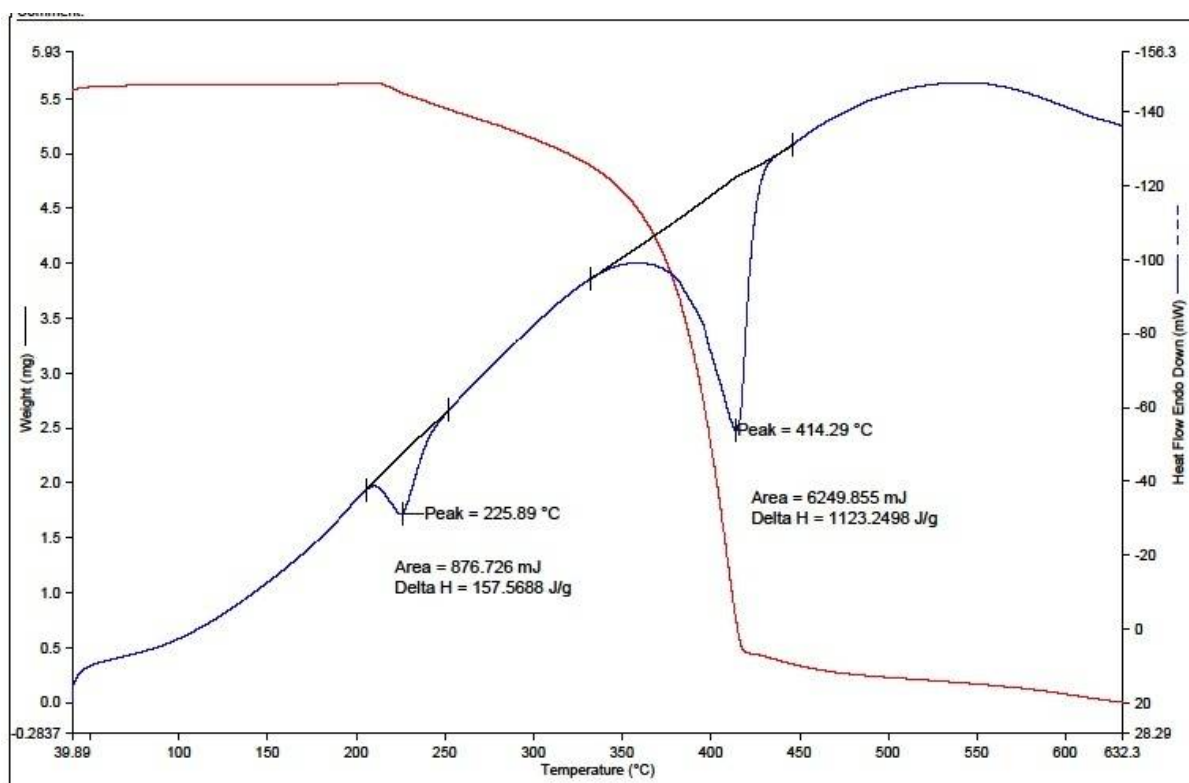


Fig (7) TGA/DTA of SA : FeSO₄ crystal.

6. Microhardness Study

The mechanical properties like Young's modulus and residual stress of crystals can be explained from Microhardness measurements [13]. The microhardness of SA : FeSO₄ crystal is measured using SHIMADZU MICROHARDNESS TESTER with a diamond intender. Loads of magnitude varying from 25 g to 100 g is applied for a fixed interval of time over a well polished grown crystal. There is an increase in hardness with load due to the work hardening of the surface layer. Beyond 100 g cracking occurs which is due to the release of internal stresses generated locally by

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indentation. The Vickers Microhardness Number H_v is calculated using the relation $H_v = 1.8544P/d^2$ kgmm^{-2} where P is the applied load in kg and d is the average diagonal length of the indentation in mm. A graph between Hardness number (n) and applied load (P) is shown in fig (8). According to Onitsch and Hannemann work hardening coefficient 'n' should lie between 1 and 1.6 for hard materials and above 1.6 for soft materials [14,15]. A graph is plotted with $\log P$ and $\log d$ and is shown in fig (9). From the slope of the graph the work hardening coefficient (n) is found to be 4.784 which shows the grown crystal is a soft material.

In fig (8) Plot of P Vs H_v of SA : FeSO_4 crystal shows the hardness increases with load until 0.1 kg and beyond this cracking occurs. From the slope of $\log P$ Vs $\log d$ in fig (9) confirms the crystal as a soft material.

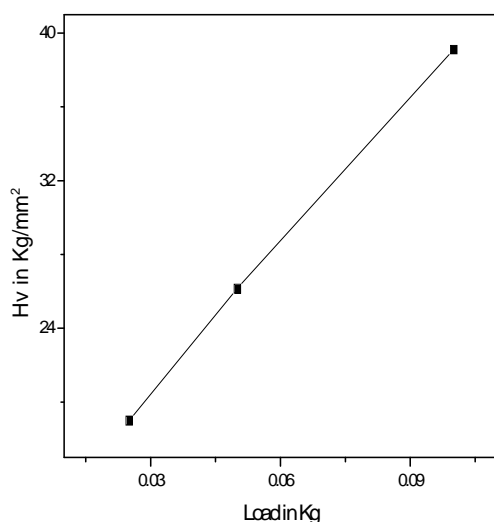


Fig (8) Plot of P Vs H_v of SA : FeSO_4 crystal

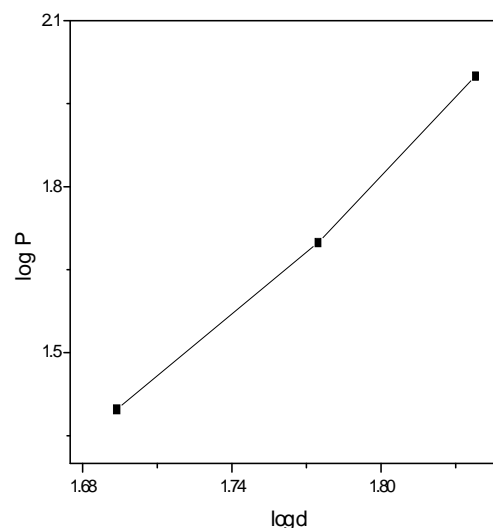


Fig (9) Plot of $\log P$ Vs $\log d$ of SA : FeSO_4 crystal

7. Nonlinear Optical study

Kurtz Perry technique is used to test the Second Harmonic Generation of grown crystals. A fundamental beam of 1064 nm from a Q-Switched Nd-YAG laser is made to fall on the powdered sample. Pulse energy is 300 mJ s^{-1} and pulse width is about 10 ns. The bright green emission from the grown crystal confirms second Harmonic Generation. The NLO efficiency of the grown crystal is compared with the standard KDP value and is found to be 0.509 times that of KDP crystal.

VI. CONCLUSION

Good optical quality single crystals of SA : FeSO_4 have been grown by slow evaporation method at room temperature. Single XRD data shows that the grown crystal belongs to orthorhombic structure. All functional groups in the grown crystals are confirmed by FTIR analysis. Good transmission range and cut off wavelength of 261 nm is detected by UV – Vis – NIR analysis. Thermal studies reveal that FeSO_4 has slightly improved the thermal stability of grown crystal. Microhardness studies show that the grown crystal is a soft material. NLO study confirms the Nonlinear Optical property of the grown crystal.

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