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Growth, spectroscopic, optical, mechanical and thermal studies of β – alanine cadmium chloride crystal, a semi-organic nonlinear optical material

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The title compound, β – alanine cadmium chloride (BACC), a new semiorganic nonlinear optical (NLO) crystal is grown by slow evaporation technique. The Powder X – Ray Diffractogram of the crystal has been recorded and the various planes of reflection are identified. The qualitative analysis on the crystal has been carried out using Fourier Transform Infrared (FTIR) and Fourier Transform Raman spectral measurements. Also, the presence of hydrogen and carbon in the grown crystal was confirmed by proton and carbon NMR spectral analyses. The percentage of cadmium in the crystal was determined by Atomic Absorption Spectroscopy (AAS). Optical behaviour such as UV – visible – NIR absorption spectrum and Second Harmonic Generation (SHG) for the crystal were investigated. The mechanical strength of the grown crystals was found by using Vickers microhardness tester. The thermal stability of the crystal was analyzed with the aid of Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

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Keywords: Growth from solution, NLO materials, X-ray diffraction, Mechanical studies, Thermal studies

1. Introduction

Nonlinear optical materials play a pivotal role in the evolution of nonlinear optics and its impact in technology. Many researchers have identified the nonlinear optics (NLO) have created a new frontier for applied physics. This technology requires nonlinear optical materials, i.e. the material which alter the frequency of laser light, material which have an index of refraction that varies with light intensity or with applied electrical field. NLO materials have recently attracted much attention because of their potential application in emerging optoelectronics technology [1-2]. Devices which have been conceived utilizing NLO materials include parametric amplifiers, oscillators, second harmonic generator, and modulator. Such devices provide, second harmonic generation, phase conjugate navigation and laser beam combing which employs optical phase conjugation, as well as laser beam spatial (and spectral) mode clean up, wavelength agile rejection filtering, laser radar, image correlation and enhancement, communication, optical data storage and optical computing [3].

Many optically active amino acids show high efficient optical second harmonic generation and are promising candidates for laser and optical communication technology [4-5]. Crystals capable of generating second harmonics must have a unit cell with no centre of inversion and this requirement is met by the crystals of pure amino acids since these molecules themselves are dissymmetric. NLO properties of organo metallic materials are currently under intense investigation, triggered by potential application in optoelectronics because of the inherent advantages of both organic and inorganic materials [6]. Presently, inorganic and organic materials are being replaced by semi-organics. They share the properties of both organic and inorganic materials. The approach of combining the high nonlinear optical coefficient of the organic molecules with the excellent physical properties of the inorganic has been found to be overwhelmingly successful in the recent past. In particular, optically active amino acids display specific features of interest such as molecular chirality, wide transparency range in the visible and UV spectral region and zwitter ionic nature of the molecule, which favours crystal hardness [7-12]. Further to that, amino acids possess both donor-acceptor molecules having large hyperpolarizabilites, which results in the discovery of L-alanine, L-asparagine and organic-inorganic compounds like L-arginine phosphate (LAP), L-histidine tetrafluoroborate (LHFB) [13].

Subha Nandhini et al [14] have investigated the crystal structure of the β – alanine cadmium chloride. They have reported that in the title compound, β – alanine residues exists in the zwitter ionic nature and the cadmium atoms are coordinated with four chlorine atoms and two oxygen atoms forming a distorted octahedral environment. These octahedral are linked through chlorine – chlorine edges and are bridged by carboxyl groups of β – alanine residues. In the present work, the title compound has been synthesized by slow evaporation method and the grown crystals were characterized by powder XRD, FTIR and FTRaman spectra, FT NMR studies, AAS, UV – Visible – NIR spectrum, Second Harmonic Generation (SHG), Vickers microhardness and the thermal analyses such as TGA, DTA and DSC and the results are presented.

2. Experimental

2.1 Synthesis and growth

β – Alanine and cadmium chloride monohydrate procured from LOBA (AR grade, 99% purity) were used for the growth of the crystals. A mixture of triple distilled water and acetone taken in the ratio 1:1 was used as solvent. The calculated amounts of β – alanine and cadmium chloride monohydrate were dissolved in the solvent according to the stoichiometric ratio (1:1).

$$(C_3H_7NO_2) + (CdCl_2.\ H_2O) \rightarrow [CdCl_2\ (C_3H_7NO_2)] + H_2O$$

The solution was stirred well using a magnetic stirrer and filtered using micro filter paper (10 μm) and transferred to beaker. The beaker was optimally closed using a perforated thin polyethylene sheet and was kept in a constant temperature bath equipped with EUROTHERM temperature controller of accuracy ± 0.01 K. The temperature was maintained at 35°C and solutions were allowed to evaporate. Transparent crystals of size $6 \times 4 \times 3$ mm^3 were grown in a period of one month. The grown crystals of β – alanine cadmium chloride (BACC) are shown in Fig. 1.

2.2 Characterization

The grown crystal was characterized by X- ray powder diffraction analysis, FTIR and FTRaman Spectral Analysis, NMR Studies, Atomic Absorption Spectroscopy (AAS), UV – Visible – NIR absorption Studies, NLO studies, Vickers microhardness test and Thermal Analyses.

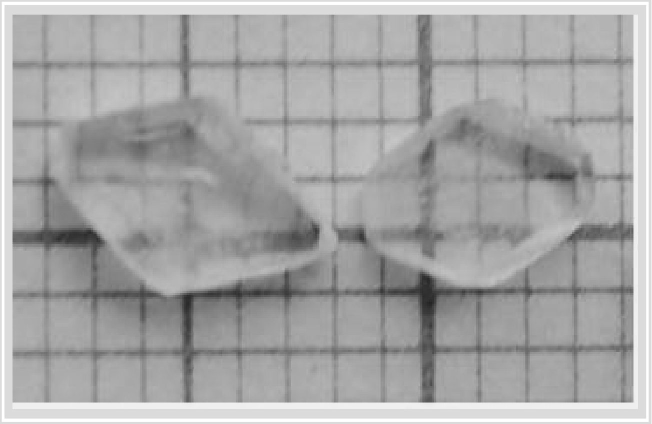


Fig. 1. Photograph of the as grown crystals of BACC.

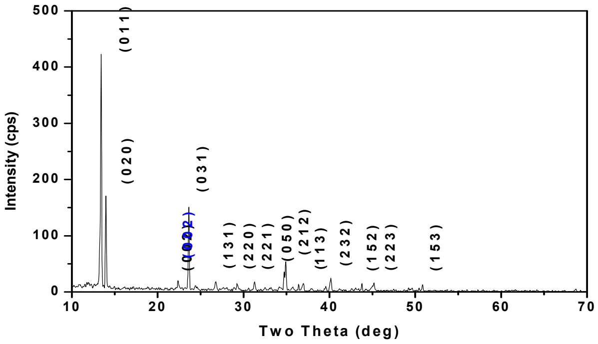


Fig. 2. Indexed powder XRD pattern for BACC.

3. Results and discussion

3.1 X- ray powder diffraction analysis

The powdered sample of β – Alanine Cadmium Chloride (BACC) single crystal was subjected to powder X- ray diffraction studies with a high resolution GUINER X-ray diffractometer (SEIFERT, Germany). Finely ground powder of the crystals were subjected to intense X-rays of wavelength λ = 1.5406 Å with a scan speed of 0.04° per second. The sample was scanned over the range of (2θ) 10º - 70º. The XRD powder pattern has been indexed using UNIT CELL and CELLREF programs and the lattice parameters are evaluated as: a = 6.9664 Å, b = 12.9222 Å, c = 7.9546 Å, $\alpha = \beta = \gamma = 90°$ and V = 716.0781 Å^3. The obtained lattice parameters from the powder XRD analysis are in good agreement with the literature reported [14]. The crystal (BACC) crystallizes under orthorhombic system and space group $Pna2_1$. The indexed powder XRD pattern is shown in Fig. 2. The morphology of the grown crystal has been identified by BRUKER AXS KAPPA APEX (II) single crystal X-ray diffractometer with Mo K_α (λ= 0.710693 Å) radiation. The prominent faces (011), (100), $(00\bar{1})$, (001), $(\bar{1}00)$, $(2\bar{1}2)$ and $(\bar{2}1\bar{2})$ planes are indicated in the Fig. 3.

3.2 FTIR and FTRaman spectral analysis

To understand the chemical bonding and molecular structure of the compound, FTIR and FTRaman spectra have been recorded. The FTIR spectrum was recorded using PERKIN ELMER SPECTRUM I spectrophotometer in the range 4000 – 400 cm^{-1} following KBr pellet technique. The FTRaman spectrum has been recorded using NICOLET NXR 9650 FTRaman Spectrometer equipped with Nd: YAG laser, in the range 3700 – 100 cm^{-1}. The spectra were measured with a scanning speed of 1cm^{-1} per second and the frequencies for all sharp bands were expected to be accurate to ± 1 cm^{-1}. The FTIR and FTRaman spectra are presented in the Fig. 4. (a) and 4.(b) respectively.

The overall character of the vibrational spectra is in accordance with the results of the crystal structure of the title compound. Assignments of the bands in the vibrational spectra of BACC were based on the results of a previous study on interpretation of the vibrational spectra of β – alanine and its complexes [15-20]. In the title compound, the β – alanine residues exists in the zwitter ionic form. This is also confirmed by spectral measurements. The coordination between the cadmium chloride and β – alanine take place via chlorine atom and carboxyl oxygen atom. Rosado et al [16] have assigned the NH_3^+ stretching vibrations in the region 3350 – 3200 cm^{-1} for β – alanine crystal in zwitter ionic form. In consonance with this, very strong band observed at 3206 cm^{-1} in the FTIR spectrum is due to NH_3^+ stretching vibration. The corresponding vibration in FTRaman appeared at 3210 cm^{-1} and 3022 cm^{-1} with weak intensity. The NH_3^+ deformation appeared at 1553 cm^{-1} in the FTIR spectrum and 1556 cm^{-1} and 1592 cm^{-1} in the FTRaman spectrum. The medium intensity band observed at 1117 cm^{-1} and strong band at 1245 cm^{-1} in FTIR spectrum could be assigned to NH_3^+ rocking vibrations. The same vibrations appear in the FTRaman spectrum at 1111 cm^{-1} and 1244 cm^{-1}. The torsional vibration of NH_3^+ appears in the FTIR spectrum at 507 cm^{-1} and 514 cm^{-1} in FTRaman spectrum. Several methylene vibrations are observed in the FTRaman spectrum: asymmetric stretching (2983 cm^{-1}), symmetric stretching (2913 cm^{-1}), scissoring (1451 cm^{-1}), deformation (1407 cm^{-1}), wagging (1378 cm^{-1} and 1328 cm^{-1}), twisting (1300 cm^{-1}) and rocking (1178 cm^{-1}). The coordination of the carboxyl group with cadmium chloride is reflected in the spectrum of the complex through a significant decrease in the asymmetric frequency of COO^- stretching (1553 cm^{-1}) and increase (1420 cm^{-1}) in the frequency of the symmetric vibrational mode in comparison to the corresponding band of the free ligand [15]. The bands observed at around 604 cm^{-1} and 707 cm^{-1} are attributed to COO^- rocking and deformation respectively. The metal - chlorine and metal - oxygen vibrations usually appear in the low frequency region [21]. The bands in the FTRaman spectrum at 164 cm^{-1} and 239 cm^{-1} are due to Cd - Cl and Cd - O stretching vibrations.

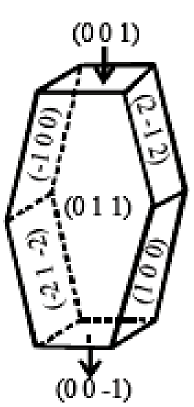
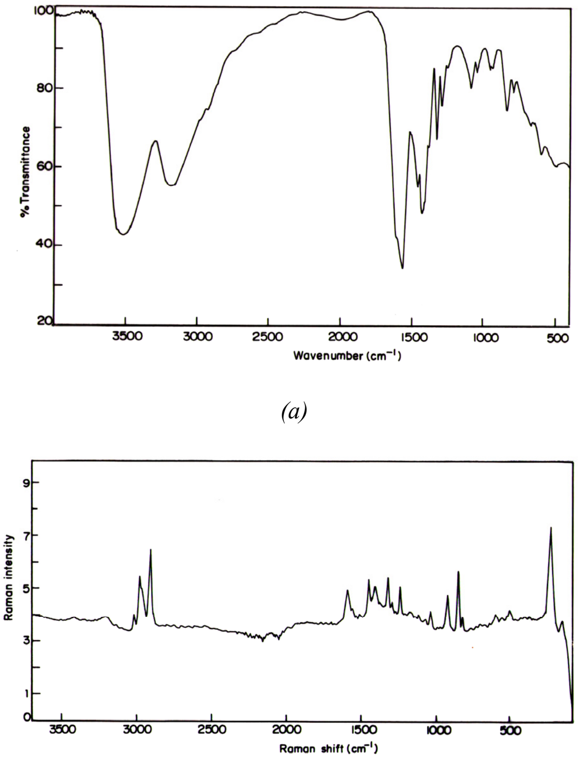


Fig.3.Morphology of the BACC.



(a)

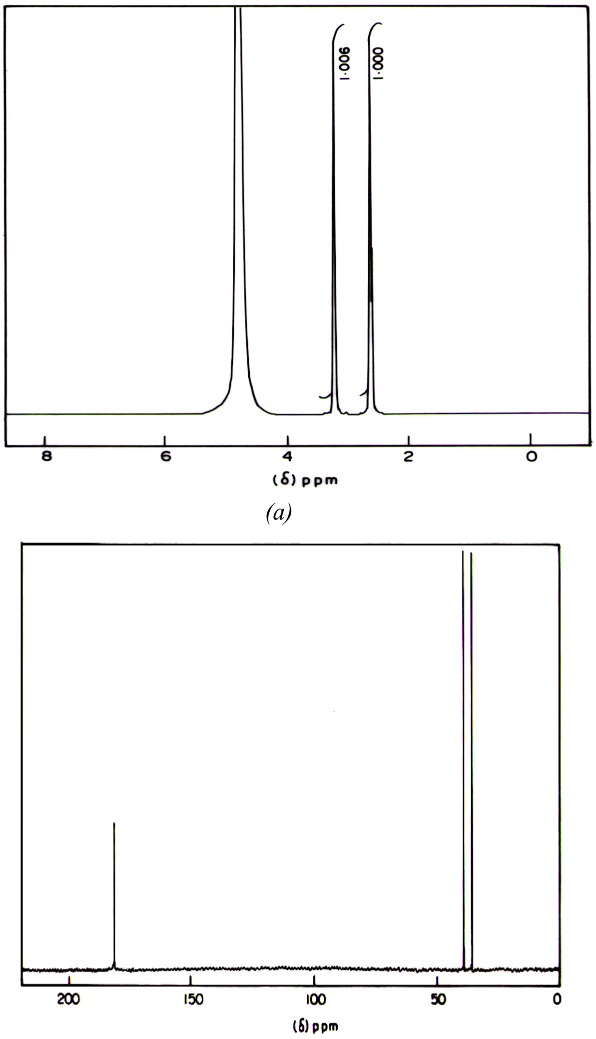
(b)

Fig. 4. (a) FTIR Spectrum of BACC; (b) FT Raman Spectrum of BACC.

3.3 NMR Studies

PMR and C^{13} NMR Spectral Analyses are the two important modern analytical techniques used for the study of the structure of organic compounds. In the present investigation, the ^1H NMR and C^{13} NMR spectra of the grown crystal have been recorded with a JEOL-GSX 400 NMR Spectrometer operating at 500 MHz with D_2O as solvent. The spectra are presented in Fig. 5.(a) and 5.(b) respectively.

In the adduct formed between 3-amino propionic acid and cadmium chloride, there are two pairs of methylene protons. In this compound, one methylene carbon is directly bonded to carboxyl group and the other to the amino group. The amino group gets protonated to give ammonium group (NH_3^+) of its zwitter ionic form. This appears as a three proton singlet downfield at 4.8 ppm. There are two triplets at 3.229, 3.213 and 3.200 ppm and 2.633, 2.616 and 2.603 ppm. The downfield signal is due to the hydrogen atoms of the methylene directly bonded to the NH_3^+ group. This is explained by the electron attracting power of the ammonium group. The high field signal is for the proton of the methylene attached to the carboxyl group. The signals for the two methylene protons are infact two sets of triplets, which can be explained by the splitting due to the two adjacent methylene protons. In C^{13} NMR spectrum, signals at 39.334 and 35.782 ppm indicate the two methylene carbon atoms. The carbon atom of the carboxyl group appears at 181.455 ppm. The carboxyl carbon is known to be much deshielded so as to give signals in this range181.455 ppm of BACC. This is similar to the results observed by Godzisz et al [19].



(a)

(b)

Fig. 5 (a) PMR and (b) C^{13} NMR spectra of BACC crystal.

3.4 Atomic absorption spectroscopy (AAS)

The presence of metal in the grown (BACC) crystal was confirmed by atomic absorption spectroscopy (AAS). The AAS studies were carried out by using GBS AVANTA Spectrophotometer. The calculated and experimentally determined amounts of cadmium in the crystal are 41.4%and 41.3% respectively which are very close to each other.

3.5 UV – Visible – NIR absorption studies

Optical transmittance is an important parameter for NLO crystals. If there is any absorption in a NLO material, it will lead to loss of conversion efficiency of SHG near the fundamental or the second harmonic of an Nd: YAG laser. The UV – Visible – NIR absorption spectrum for the title compound has been recorded using a Varian Cary 5E UV – Vis – NIR spectrophotometer in the range 200 – 2500 nm covering the entire UV, Visible and NIR regions. The spectrum is shown in Fig. 6. From the spectrum, it is seen that there is no significant absorption in the range 200 – 800 nm and this indicate that the crystal is having good transmittance in the region. This behaviour of the crystal finds it suitable for optoelectronics applications.

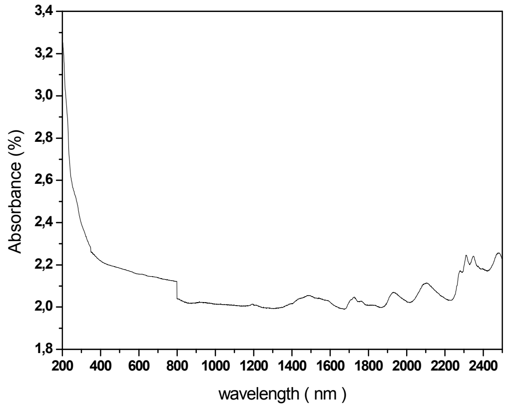


Fig. 6. UV –Visible -NIR absorption spectrum of BACC.

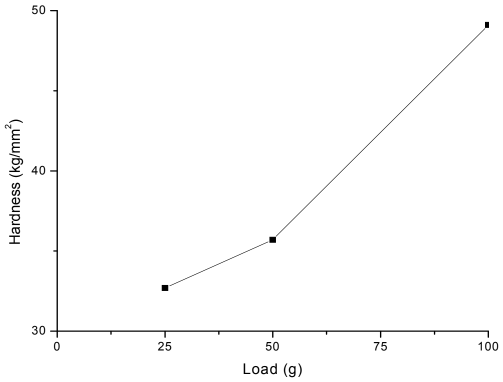


Fig. 7. Plot of hardness (Vs.) load for BACC.

3.6 NLO studies

Kurtz and Perry powder method [22] was employed to check the SHG efficiency of BACC crystal. The crystalline sample was powdered to uniform particle size around 150 µm packed in a micro capillary of uniform bore and was exposed to Q – switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 5.8 mJ/pulse. The output from the sample was allowed through a monochromator to collect the intensity of 532 nm component and to eliminate the fundamental. The generation of second harmonic was focused by a lens and detected by the photomultiplier tube. The generation of the second harmonic was confirmed by the emission of green light (532 nm). A sample of Potassium dihydrogen phosphate (KDP), also powdered to the same particle size as the experimental sample, was used as reference material in the SHG measurement. The SHG conversion efficiency of the title compound is found to be 0.55 times that of standard potassium dihydrogen phosphate (KDP) crystal.

3.7. Vickers microhardness test

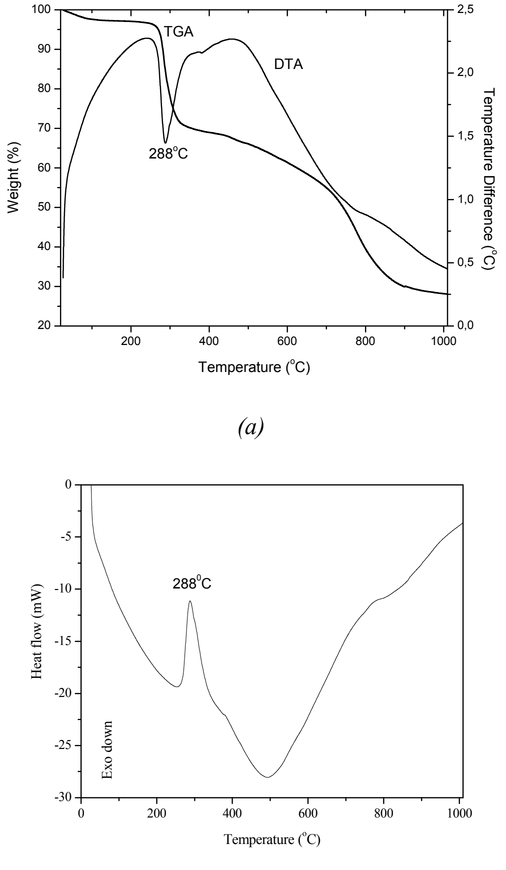
The good quality crystals, which are required for device fabrication, must have good optical performance and good mechanical behaviour. The microhardness studies were carried out on the grown crystals (BACC) using Vickers microhardness tester attached with an optical microscope (SHIMADZU hardness tester). Load of 25, 50 and 100 g were used for microhardness studies. The loads were applied on the plane (011). The Vickers microhardness number was determined using

$$H_v = \frac{1.8544P}{d^2} \quad (\text{kg/mm}^2)$$

where P is the applied load in kg and d is the average diagonal length of impression in mm. The hardness versus load is presented in Fig. 7. The hardness of the BACC increases with increase of load. The cracks are formed in the crystal beyond 100 g which is moderately harder when compared to the other crystals like L – arginine bromide and L – prolinium picrate.

3.8 Thermal analyses

The thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry of the BACC crystal were recorded using the instrument SDI Q600 V8.3 Build 101. The TGA – DTA and DSC were carried out in nitrogen atmosphere at a heating rate of 20° C /min from 30° C to 1000° C. Alumina is used as a reference material and the initial mass of 2.3130 mg of a BACC crystal was subjected to analysis. From the TGA-DTA traces shown in Fig. 8, it is found that the crystal is thermally stable up to 241° C. There is a strong endotherm at 288° C, which indicates the melting point of the crystal. This is also confirmed by endotherm at 288° C in DSC (Fig. 8).The melting point of the crystal was also determined experimentally, which is in consistent with the results of thermograms. There are two stages of decomposition; the first stage of decomposition starts from 264° C and extends up to 697° C. The major weight loss of 40.5% occurs in the first stage of decomposition. The gaseous substances like NH_3, CO_2 may be liberated. The second stage of decomposition, occurring between 697° C and 904° C may correspond to evolution of CO_2, CH_4, Cl and mass loss in this range is 25.24%. The end residue is around 28.10%, which may correspond to a part of CdCl.



(a)

(b)

Fig. 8. (a) and (b) TGA-DTA and DSC traces for BACC Crystal.

4. Conclusions

A potential semiorganic NLO material from the metal complex of amino acids was grown successfully using slow evaporation technique at 35°C and characterized by powder XRD to confirm the formation of the material. Vibrational spectral analysis confirms the presence of all the functional groups of the sample. The coordination between cadmium chloride and amino acid is also confirmed by the FTRaman spectrum.The presence of the organic compound alanine in BACC has been analyzed by FTNMR. The percentage of cadmium in the grown crystal is determined by using AAS. The UV – Visible – NIR absorption spectrum establishes that the crystal acts as a good transmittance window and allows for frequency conversion down to UV region. Kurtz and Perry powder experiment confirm the SHG using Nd: YAG laser and conversion efficiency is 0.55 times that of the standard KDP crystal. Vickers hardness values measured on (011) plane gives its mechanical strength. From the thermal studies, it is concluded that the crystal is stable up to 241°C and its melting point is 288°C. The thermal study has established its suitability to withstand the high temperature encountered in laser experiments.

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