Spectral, Mechanical, Thermal and SHG Studies of Urea Sodium Fluoride Crystals Grown By Slow Evaporation Technique

J.Jude Brillin[1] and P.Selvarajan[2]

[1]Research Scholar, Reg.No. 7429, Physics Department, Manonmaniam Sundaranar University, Abishekapatti-627012, Tirunelveli, Tamilnadu, India.

[2]Associate Professor of Physics, Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India.

(Affiliated to Manonmaniam Sundaranar University, Abishekapatti-627012, Tirunelveli, Tamilnadu, India)

Abstract

Solution method with slow evaporation technique was adopted to grow the single crystals of urea sodium fluoride (USF) at room temperature (30 °C). The grown crystal of USF is observed to be transparent and colourless. Single crystal XRD studies were carried out to find the lattice parameters of the sample. SHG studies were carried out by Kurtz-Perry method using a Nd:YAG laser. The mechanical parameters were determined for the grown crystal of USF by Vickers hardness method at different applied loads. TG/DTA studies for the grown crystal of USF were performed to find thermal stability. Photoluminescence and EDAX studies were carried out to characterize the grown crystals of USF and the results are analyzed.

Key words: NLO; single crystal; solution growth; XRD; SHG; microhardness; TG/DTA; photoluminescence; EDAX

1. Introduction

Usually, nonlinear optical (NLO) materials can be classified into organic, inorganic and semiorganic NLO materials. An organic NLO material and an inorganic NLO material are mixed in a particular proportion to form a semiorganic NLO material. The advantages of both organic and inorganic materials are taken into account for forming the semiorganic NLO materials and the single crystals of semiorganic materials are grown by methods like solution and melt methods. Semiorganic NLO crystals are the technologically important crystals and they are useful in the scientific fields like optical telecommunication, optical computing, photonics etc [1-3]. In this work, a semiorganic crystal viz. urea sodium fluoride (USF) was grown by solution method with slow evaporation technique and grown crystals were studied by various characterization methods. Here urea is an organic NLO material and sodium fluoride is an inorganic material and these are combined to form a semiorganic NLO crystal. In urea, the oxygen atom has more electronegativity compared to the nitrogen atom and it causes a decrease in the electron density around the nitrogen atoms. The charge transfer among the C, H and N atoms will lead to create H^+ ions become weaker and O^- become stronger and this is responsible for forming many complexes of NLO materials [4,5]. From the literature survey, it is observed that varieties of NLO crystals have been grown by combining urea and other compounds [6-10]. The aim of this paper is to report the results obtained from various studies like XRD studies, FTIR studies, hardness studies, EDAX studies of the grown urea sodium fluoride crystals.

2. Crystal growth

AR grade chemicals like urea and sodium fluoride were purchased commercially from Merck India. The reactants were taken in 1:1 molar ratio and they are dissolved in double distilled water to prepare the saturated solution. The solution was stirred for about 1 hour using a hot plate magnetic stirrer at a temperature of 45 ^{o}C. The solution was heated for taking place chemical reaction between urea and sodium fluoride. The reaction takes place in the accordance with the chemical reaction NH2CONH2 + NaF → NH_2CONH_2.NaF. Then the solution was filtered well using a Whatman filter paper. The filtered solution was taken in a growth vessel and it was covered using a perforated sheet. Due to slow evaporation, the following steps are taking place during the crystal growth [11].

i) Conversion of the saturated solution into supersaturated solution
ii) Formation of crystal nuclei in the supersaturated solution
iii) Growth of small crystal nuclei into big-sized single crystals.

Re-crystallization was carried out twice to grow the good quality crystals of urea sodium fluoride. After a growth period of about 35 days, white coloured and transparent urea sodium fluoride (USF) crystals are harvested. A single crystal of USF is shown in the figure 1.

Fig. 1. A grown single crystal of urea sodium fluoride

3. Resutls and discussion

3.1 FTIR studies

Fourier Transform Infrared spectroscopy (FTIR) is used to find the functional groups of the samples and in this technique, the samples like solid samples and liquid samples can be used. FTIR technique is an advanced computerized method and this technique has high resolution and high accuracy. FTIR spectrum of the grown crystal of USF is recorded using an FTIR spectrometer in the wave number range 400-4000 cm^{-1}. Here a small piece of the grown crystal was mixed with large amount of potassium bromide and it was pelletized using a hydraulic press. When infrared radiation interacts with the pelletized sample, absorption of infrared radiation will take place and the molecules are excited. When molecules return from the excited state to the ground state the absorbed energy is released in the form of peaks/bands in the FTIR spectrum. The recorded FTIR spectrum of USF crystal is presented in the figure 2. The broad infrared absorption band in the 3550-3250 cm^{-1} is corresponding to NH and OH stretching vibrations. The presence of OH is due to hydrogen bonding in the crystal. The peaks at 1672 and 1623 cm^{-1} are due to C=O stretching and NH asymmetric deformation respectively. The peaks in the wave number range 2900-2010 cm^{-1} are corresponding to CH stretching.

The peak appearing at 787 cm^{-1} is due to C–O–H stretching of USF crystal. The peaks at 575 and 557 cm^{-1} are arising due to torsional oscillations of NH and metal-O bond. The peak at 1045 cm^{-1} is corresponding to vibration of N-C-N mode. The peak at 1460 cm^{-1} is due to symmetric NH deformation. The assignments are given in accordance with the data in the literature [12,13]

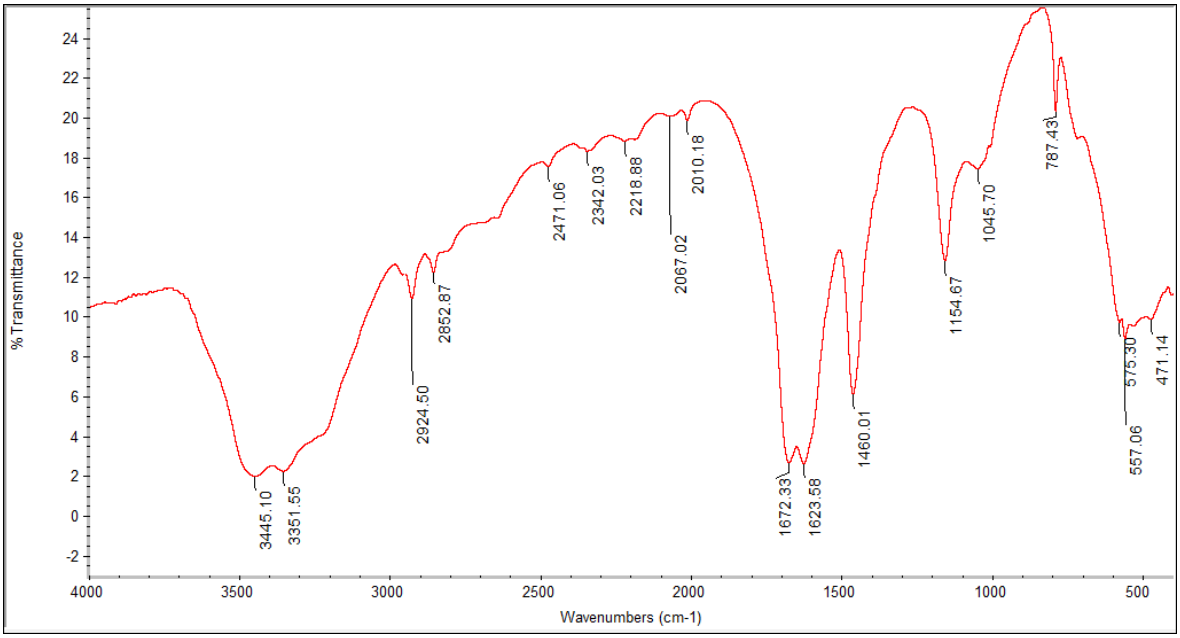

Fig.2. FTIR spectrum of urea sodium fluoride crystal

3.2 EDAX studies

Energy Dispersive analysis by X-Rays (EDAX) or Energy dispersive spectroscopy (EDS) is a spectroscopic technique used to find the different elements present in the sample. In this technique, the detector detects X-rays emitted from the sample during bombardment by an electron beam. The data generated by EDS analysis consist of spectrum showing peaks corresponding to the elements making up the true composition of the sample being analyzed. The minimum detection limits vary from approximately 0.1 to a few atom percent, depending on the element and the sample matrix. Using this technique, the light elements like hydrogen or lithium cannot be detected. Here EDS studies were carried out using the EDAX detector (Oxford Instruments, INCA Penta FETx3) at Karunya University, Coimbatore. The recorded EDS spectrum of USF crystal is shown in the figure 3. From the spectrum, the elements like Na, F, C, O and N have been identified and hence the formation of urea sodium fluoride is confirmed.

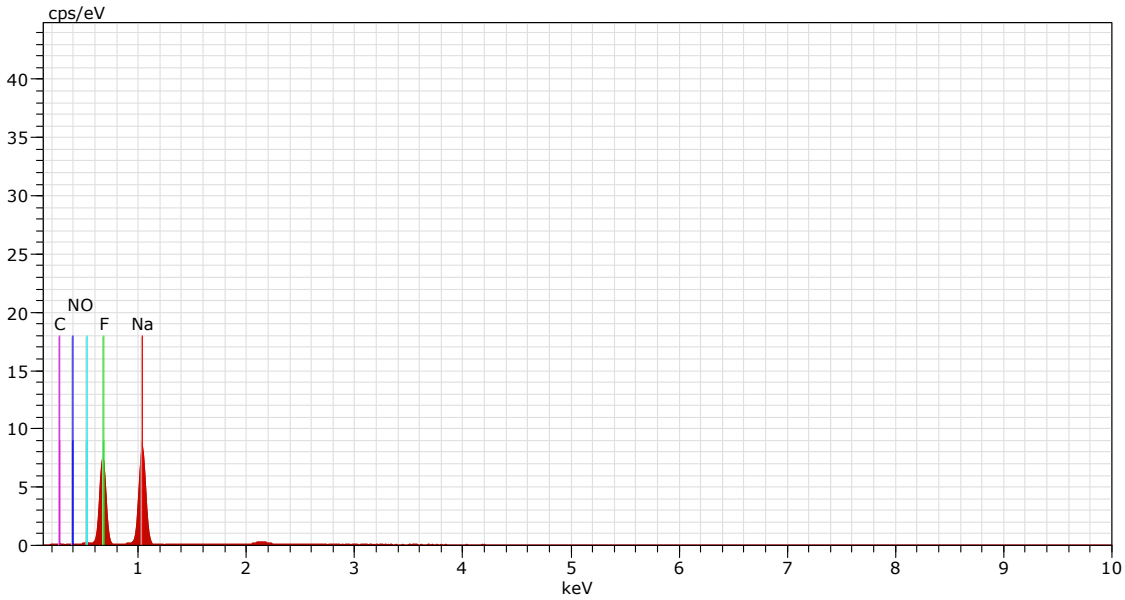

Fig.3. EDS spectrum of urea sodium fluoride crystal

3.3 X-ray diffraction studies

X-ray diffraction (XRD) technique is the basic method to find the lattice parameters of the grown crystals and the principle of this method is the Bragg's law. If Bragg's law is satisfied, the crystal diffracts the X-rays and these diffracted X-rays give the positions of atoms, bond angle, bond length and lattice constants. There are two methods of X-ray diffraction viz., single crystal X-ray diffraction and powder X-ray diffraction. Since the grown crystal here is a single crystal, single crystal XRD method was adopted find the crystal parameters and crystal structure. In this work, the grown crystal of urea sodium fluoride is subjected to single crystal X-ray diffraction analysis using ENRAF-NONIUS CAD-4 automatic X-ray diffractometer to determine the unit cell parameters of urea sodium fluoride crystal. The obtained lattice parameters for urea sodium fluoride crystal are a = b = 5.724 (4) Å, c = 4.913 (3) Å and $\alpha = \beta = \gamma = 90^{o}$. Hence, the crystal structure of urea sodium fluoride crystal is found to be tetragonal structure.

3.4 Photoluminescence studies

Photoluminescence (PL) is light emission from any sample when light falls on the sample. When UV light falls on a sample, the electrons are excited from lower energy level to higher energy level and the electrons are photoexcited. Due to relaxation process, visible or UV light are emitted from the sample. Usually, the time period between absorption and emission will be milliseconds or microseconds. The electronic structure of the crystalline samples could be understood by PL spectroscopy. The PL spectrum of urea sodium fluoride crystal is shown in the figure 4 and it was recorded using a a Perkin-Elmer fluorescence spectrometer (Model: LS45) in the wavelength range 250-500 nm. The sample was excited at 220 nm. The results show that there are five prominent peaks in the spectrum and they are at 280 nm, 340 nm, 365 nm, 420 nm and 470 nm. Thus, when the sample is excited with high energetic radiation of wavelength of 220 nm, comparatively low energetic UV and violet-blue radiation are emitted from urea sodium fluoride crystal.

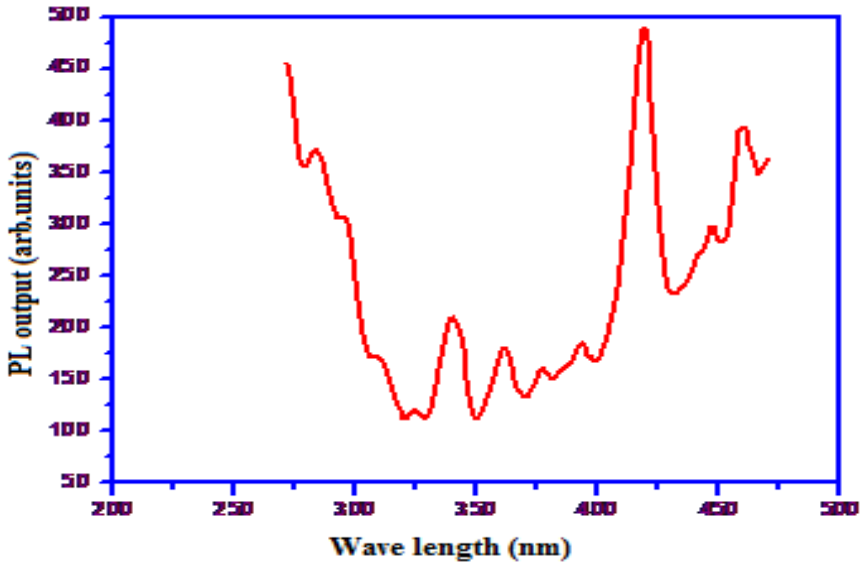

Fig.4. PL spectrum of urea sodium fluoride crystal

3.5 TG/DTA studies

Thermogravimetric/differential thermal analysis (TG/DTA) are useful to find melting point, decomposition point, endothermic reaction, exothermic reaction and other thermal properties of the samples. Here TG/DTA thermal curves are recorded simultaneously using a thermal analyzer in the temperature range 40-600 °C. In TG, there will be a change of weight of the sample and in DTA, difference between the temperature of sample and temperature of the reference or heat energy difference is measured when the temperature of the sample is increased. The weight loss occurs due to decomposition, reduction or oxidation taking place in the sample. DTA thermal curve shows endothermic and exothermic peaks. There will be no mass loss in the sample when phase changes like melting, crystallization or glass transitions taking place [14, 15]. The recorded TG/DTA thermal curves of the urea sodium fluoride crystal are presented in the figure 5. The results indicate that there is almost no weight low upto 190 °C and there is heavy weight loss about 35% at 250 °C. Between 250-400 °C, about 20% weight loss is noticed in the TG curve. Beyond 400 °C, there is almost no weight loss in the sample. The DTA curve shows an endothermic peak at 250 °C and it corresponds to the decomposition point of the sample. Below 250 °C in the DTA curve, there are many peaks and these peaks may be presence of impurities in the sample. The broad exothermic peak between 300 and 400 °C is due to emission of gaseous particle from the sample. The two endothermic peaks at 400 °C and 470 °C may be due to impurities present in the sample.

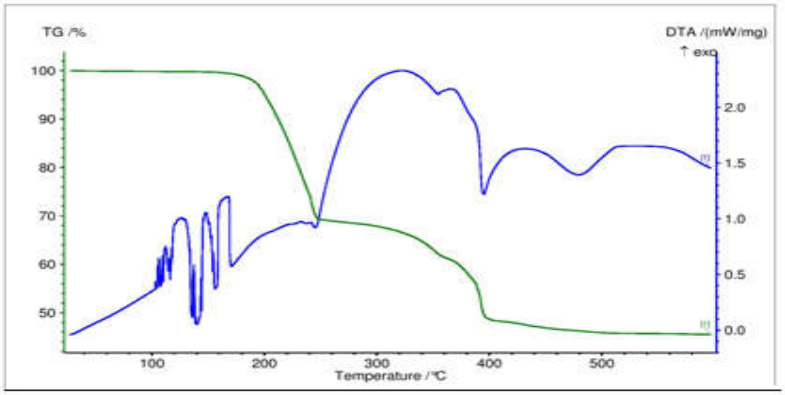

Fig.5. TG/DTA thermal curves for sodium fluoride crystal

3.6 Microhardness studies

Using microhardness studies, the mechanical strength of the samples have been established. The mechanical parameters like hardness, stiffness constant and yield strength of the samples have been evaluatd. Microhardness studies were carried out using a Vickers microhardness tester and a diamond pyramidal indenter. When the load is applied on the indenter, an indentation or impression is formed on the crystalline sample and using a powerful microscope, the average diagonal length of indentation (d) is measured [16]. The variation of average indentation length with the applied load for urea sodium fluoride crystal is presented in the Fig.6. It is observed that the average indentation length increases with the applied load. The Vickers hardness number (H_v) is determined using the formula $H_v = (1.8544\ P)/\ d^2$ where P is the applied load. Here the obtained values of d is in micrometers and the applied load is in grams. The calculated values of H_v are put in the form of a plot and it is shown in the figure 7. From the results, it is observed that the hardness number increases with increase of the applied load and hence this sample shows reverse indentation size effect. The depth of indentation in urea sodium fluoride crystal is found using the relation h = d /7.006 where d is average indentation length. The plot of depth of indentation versus applied load for the sample is shown in the figure 8. The results indicate that the depth of indentation in the sample is very low and hence sample has more hardness and mechanical strength.

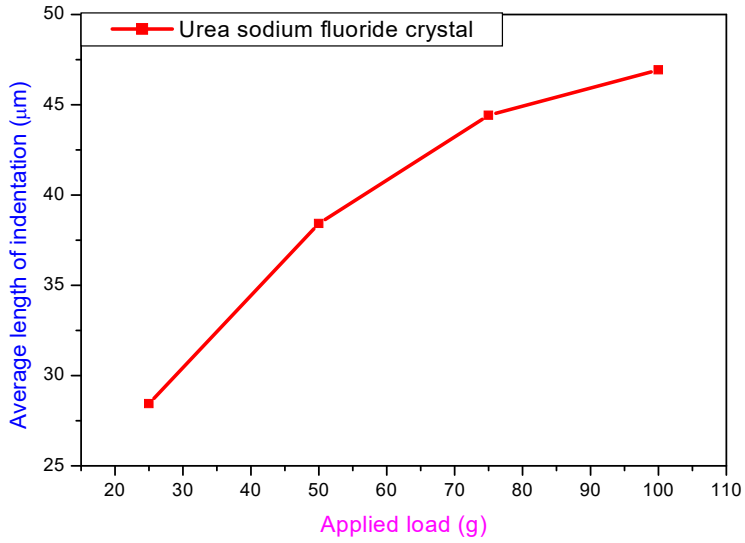

Fig.6. Variation of average length of indentation with applied load for urea sodium fluoride crystal

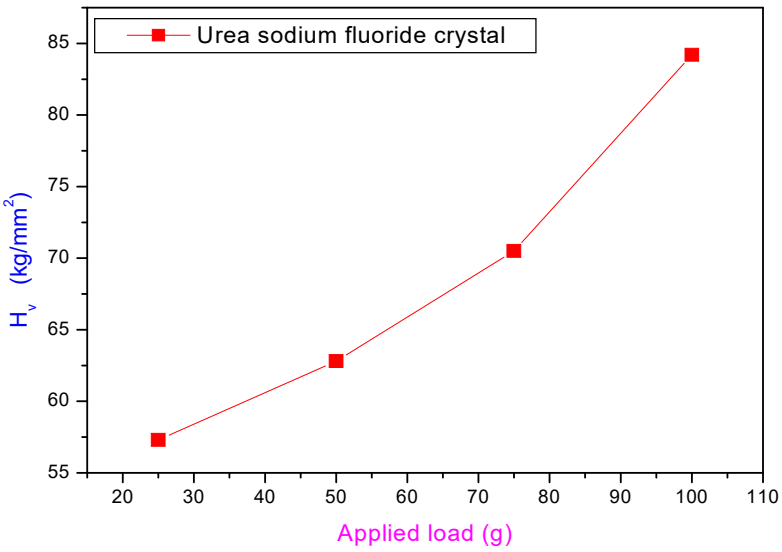

Fig.7: Plot of microhardness number versus applied load for urea sodium fluoride crystal

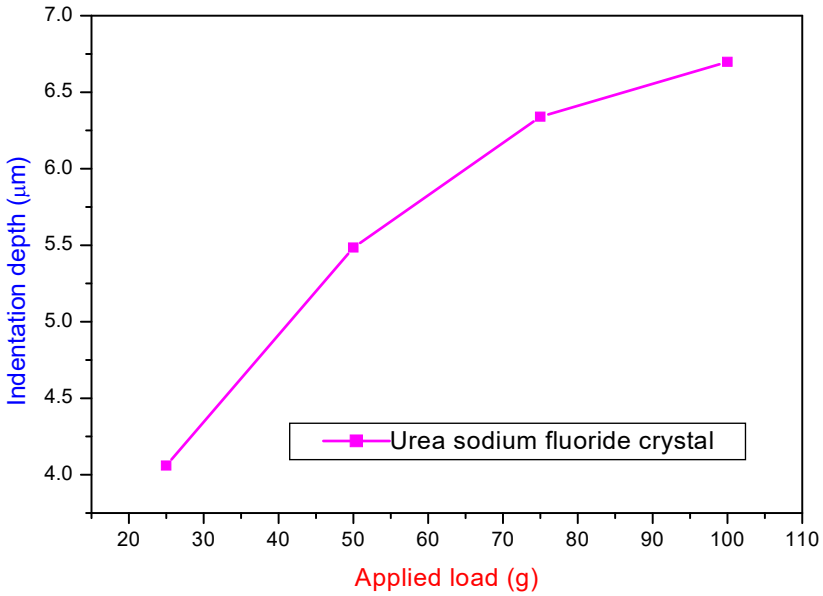

Fig.8: Plot of depth of penetration versus applied load for urea sodium fluoride crystal

3.7 SHG measurement

Usually, second harmonic generation (SHG) occurs in a non-centrosymmetric crystal having no centre of inversion or no centre of symmetry. In a non-centrosymmetric crystal, the second order susceptibility is not equal to zero and this creates second order NLO phenomena like SHG, SFG, DFG etc. In SHG, the frequency of incident laser light is doubled and this is due to three-wave mixing in the NLO crystal. The relative value of SHG efficiency of urea sodium fluoride crystal was measured using a Nd:YAG laser of wavelength 1064 nm by Kurtz-Perry powder technique. Here this laser is pulsed laser with pulse duration of 8 nanoseconds. The SHG was confirmed by the emission of green radiation from the sample.

The wavelength of the green laser radiation is 532 nm and hence the wavelength is reduced to half of the wavelength of incident laser light and the frequency of laser is doubled. Here, potassium dihydrogen phosphate (KDP) was used as the reference sample. It is to be mentioned here that the particle size of the both urea sodium fluoride and KDP samples was kept approximately 200 μm. The obtained values in connection with SHG measurement are given in the table 1. It is observed that the relative SHG efficiency of urea sodium fluoride crystal is 1.73 times that of the reference KDP sample. The result indicates that the grown urea sodium fluoride crystal is the better candidate for NLO applications.

Table 1. Data in connection with SHG measurement for urea sodium fluoride crystal

Sample name	Input energy (joule/pulse)	Output energy (milli joule/pulse)	Relative SHG efficiency
Urea sodium fluoride	0.70	15.41	1.73
KDP (Reference sample)	0.70	8.91	1

4. Conclusions

The reactants like urea and sodium fluoride were used to prepare the single crystals of USF. Single crystal XRD study indicates that the crystal structure of the sample crystal of USF is tetragonal structure. The relative SHG efficiency of urea sodium fluoride crystal is found to be 1.73 times that of the reference KDP sample. From TG/DTA studies, it is observed that USF crystal is thermally stable upto 190 °C. The mechanical parameters such as hardness, average length of indentation and depth of penetration of USF crystal were determined. The elements present in the grown USF crystal is identified by EDAX studies. The functional groups of USF crystal were found by FTIR studies. Photoluminescence studies reveal that there are many emission peaks in UV-visible region when USF crystal is excited with UV light of 220 nm.

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