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GROWTH AND CHARACTERIZATION OF PURE AND METAL DOPED BIS THIOUREA ZINC ACETATE (BTZA) SINGLE CRYSTALS

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ABSTRACT

Undoped and Nickel Nitrate (Ni^{2+}) and Zinc Nitrate (Zn^{2+}) doped Bis Thiourea Zinc Acetate (BTZA) single crystals were grown by cost effective Slow Evaporation Solution Growth. The grown crystals were subjected to various characterization techniques. The structure of the crystals was confirmed by single crystal x-ray diffraction. Powder x-ray diffraction analysis confirms the absence of multiple phases in the crystal and it suggests that the crystalline nature of the samples remain unaltered even after the addition of the dopants. The spectral properties were assessed by FTIR spectral analysis. The amount of dopant incorporated in the parent crystal was revealed by the inductively coupled plasma (ICP-OES) studies. Optical characters were analyzed by UV-Vis spectral studies. Mechanical properties of the doped and undoped crystals were evaluated by Vicker's Micro hardness study. SHG studies confirm that $Ni^{2+}$and Zn^{2+}doped BTZA crystal is a potential candidate for NLO applications.

KEYWORDS

Single Crystal XRD, FTIR, UV, Hardness, SHG and NLO.

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INTRODUCTION

The nonlinear optical properties of the organic molecular crystals have received a great deal of interest for the past two decades due to their extensive application in the fields like laser technology, telecommunication, optical information processing and storage[1,2]. The nonlinear response of the crystal is due to the application of strong sources of electric field which gives rise to the second and higher order nonlinear properties like second harmonic generation, d-c rectification, frequency mixing, sum generation and self focusing[3]. One can explore all these nonlinear effects from the asymmetric systems by attributing them into high intense optical beam. The performance of the organic NLO materials in the optical region placed a great demand on these materials owing to which, several attempts have been made by the scientists to identify the good quality nonlinear organic crystals. The search for new frequency conversion materials in recent years has concentrated on semi-organic complexes in which many optically active organic amino acids are mixed with the inorganic salts in order to enhance their physical and chemical properties. The semi-organic materials have the potential for combining the high optical nonlinearity and flexibility of organics with temporal, thermal stability and excellent transmittance of inorganic[4-8].

In search of new frequency conversion materials, recent interest focused in semi-organic materials due to their large nonlinearity, high resistance, too large induced damage, low angular sensitivity and good mechanical hardness[9-11]. Thiourea is an interesting inorganic matrix modifier due to its large dipole moment[12] and has the ability to form extensive network hydrogen bonds. Thiourea which is centro symmetric yields excellent non centro symmetric materials when it is incorporated into the respective inorganic salt[13]. Thiourea in combination with metal complexes forms semi-organic compound gives a low cutoff wavelength and it is applicable for high frequency conversion. Some of the potential Thiourea complexes are Zinc Thiourea Chloride (ZTC)[14], Zinc Thiourea Sulphate (ZTS)[15], and Bis Thiourea Cadmium Chloride (BTCC)[16], Copper Thiourea Chloride [CTC]. Bis Thiourea Cadmium Acetate (BTCA) is an efficient semi organic NLO compound[13] whose SHG efficiency is superior to KDP.

A three dimensional X-ray analysis of BTZA has been carried out by Luigi Cavalcaetal[17] and growth and characterization of pure BTZA have already been reported by V. Kannan *et al*, M. Lydia Caroline *et al*, and by D. Jayalakshmi *et al*[18-20]. A metal doped semi organic single crystal such as Zn^{2+} doped cadmium Thiourea acetate have been reported by S. Selvakumar *et al*[21]. Li^{2+} doped thiourea zinc acetate have been reported by L. Ruby Nirmalaetal[22].

In continuation of the above works, a metal Nickel NitrateNi^{2+} and Zinc NitrateZn^{2+} doped BTZA crystal were grown. The characterization of pure BTZA single crystal and the Nickel Nitrate and Zinc Nitrate doped BTZA single crystal have been investigated. It has been observed that the additive has control on the crystallization, which is confirmed by comparing the results of pure and the doped single crystals.

METHOD

Synthesis and growth of undoped and Ni^{2+}, Zn^{2+}doped BTZA crystal

Thiourea and Zinc Acetate were mixed in the ratio of 2:1 in deionized water. The solution was stirred well continuously for 2 hours and the mixture is heated upto the temperature 50°C and not exceeding it to get the homogeneous mixture. Then the saturated solution was allowed to cool to room temperature and kept in a vibration free area with a tightly closed plastic cover. The successive crystallization process was carried out to improve the purity of the synthesized salt. Good quality single crystal of BTZA has been collected from the mother solution in a time span of 28 days a transparent good quality crystal has been harvested, which is shown in Figure No.1a.

The following reaction estimates the required quantity of Zinc Acetate and thiourea:

$$Zn\,(CH_3COO)_2 + (NH_2CS\,NH_2)_2 \rightarrow Zn\,(NH_2CSNH_2)_2\,(CH_3COO)_2$$

The growth of 1mole % of Ni^{2+} doped BTZA and 1 mole % of Zn^{2+}doped BTZA crystal has been carried out by slow evaporation technique. A good quality single crystal of Ni^{2+}doped BTZA with good transparency has been harvested in 35 days and 38 days Zn^{2+}doped BTZA which is shown in Figure No.1b and Figure No.1c.

RESULTS AND DISCUSSION

Characterization Techniques

X-ray Diffraction Analysis

The grown crystals are subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD 4 diffractometer with M_oK_α radiation (λ = 0.71073A°) to determine the unit cell parameters. The structure is solved by the direct method and refined by the full matrix least square technique using SHELXL programme. The unit cell parameter of pure BTZA crystal has already been reported[19]. On comparing the obtained cell parameter values with the reported literature, slight variations were observed in the cell values which may be due to the incorporation of the dopant. The obtained unit cell dimensions for Ni^{2+}, Zn^{2+} doped BTZA crystal has been compared with the pure BTZA crystal which is shown in Table No.1. Thus the variations in the cell parameters and the increase in cell volume show the incorporation of Ni^{2+}, Zn^{2+} into the pure BTZA crystal lattice.

Powder X-Ray diffraction analysis

JEOL JDX powder x-ray diffractometer was employed for tracing the powder XRD pattern. The obtained powder XRD pattern pure and Ni^{2+}, $Zn^{2+}$is shown in the (Figure No.2a-2c). The well-defined Bragg's peaks indicate that the Ni^{2+}, Zn^{2+} doped BTZA crystal is highly crystalline. The prominent peak at a specific 2θ angle suggests the crystalline of the sample. A set of prominent peaks were obtained from the powder XRD data. Powder XRD pattern suggests the single phase formation of Ni^{2+}, Zn^{2+}doped BTZA crystal.

Inductively Coupled Plasma optical emission spectrometry (ICP-OES) Studies

The amount of metal dopant incorporated in the parent crystal can be estimated using inductively coupled plasma optical emission spectrometry technique. 100 mg of fine powder of Ni^{2+}doped BTZA and Zn^{2+}doped BTZA crystal has been dissolved in 100 ml of distilled water and the solutions were subjected to ICP studies using Perkin Elmer Optima 5300 DV Spectrometer. It is observed that 0.25% of $Ni^{2+}$is present in the doped sample out of 1mole % by weight of the dopant and 0.37% $Zn^{2+}$is present in the doped sample out of 1mole % by weight of the dopant. The amount of dopant incorporated into the doped crystal is significant even though it is less than the concentration of the dopant in the corresponding solution.

Fourier Transform Infrared spectral analysis

The infrared spectroscopy is effectively used to identify the functional groups of the samples. The fine powder form of the grown crystals has been scanned between the wavelength range of 400 and 4000 cm^{-1} by a KBr pellet method in Perkin Elmer RXI FT-IR spectrometer in order to reveal the metal complex co-ordination. The recorded FT-IR spectra of undoped and Ni^{2+}, Zn^{2+} doped BTZA crystals are provided in Figure No.3 (a-c) respectively. The assignments confirm the presence of various functional groups in the material which are presented in Table No.2.

The observed spectra of these crystals are similar, except for a small shift in the peak positions and hence the crystals are expected to preserve nearly the same interactions among the groups and the ions. Most of the metals form complexes through sulfur In the case of BTZA, these are due to the vibration of thiourea and zinc-ion-coordinated tetrahedral bonds. The water twisted is occurred at 485cm^{-1}. There is a shift in lower frequency side from 777 cm^{-1} and 1403 cm^{-1} to 774 cm^{-1} and 1401 cm^{-1} for pure and doped one which shows the C=S, symmetric and asymmetric stretching respectively. The absorption band at 1586 cm^{-1} is due to NH_2 in group deformation. The symmetric NH_2 stretching is assigned to the band at 3386 cm^{-1}. Thus the shifts in frequency clearly established the presence of Ni^{2+}, Zn^{2+} in the lattice of BTZA which concludes that the crystal is free of water use per crystallization and doping of metal alters the bonding between zinc and thiourea.

UV-visible near infrared analysis

The UV-Vis spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves the promotion of the electron in s and p orbital's from the ground state to higher energy states. Transmission spectral analysis is important for any NLO material because a NLO material can be of practical use only if it has wide transparency window without any strong absorptions in the ultraviolet, visible and infrared regions. The optical characterization of pure and metal doped BTZA crystal was carried with the help of a LAMBDA35 UV Visible spectrophotometer. The transmission spectrum was traced within the range of 190 to 1100 nm. For achieving this, a sample of 2mm thick was used. Figure No.4 shows the transmission spectrum of pure and metal doped BTZA single crystal. The lower cut off falls around 290 nm for Ni^{2+}, Zn^{2+} doped BTZA crystals. Since the lower cut off value falls within 300 nm for all the crystals, metal doped BTZA crystals are efficient candidates in optoelectronic device applications. The percentages of transmission for pure BTZA doped $Ni^{2+}$and Zn^{2+} crystals are 50%, 63% and 72% respectively. Hence the transmission efficiencies of the crystals can be tuned expeditiously by varying the concentrations of the dopants.

Micro hardness study

The Mechanical properties of the grown crystals have been studied using LEITZ micro hardness tester, fitted with a Vicker's diamond pyramidal indenter. The grown crystals which were well polished have been placed on the platform of Vickers micro hardness tester. Loads of different magnitudes have been applied in a fixed interval of time. The indentation time of8 seconds was given for all the loads. Vickers micro hardness values have been calculated by using the formula H_v = 1.8544 x P/d^2 Kg/mm^2, where H_v is the Vickers micro hardness number, P is the applied load in Kg, d is the mean diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical fraction for the diamond pyramid. The trace of Vickers hardness number with load for pure BTZA and Ni^{2+}, Zn^{2+}doped BTZA crystals are shown in the Figure No.5. This shows that the hardness increased with the increase of load. Higher the hardness values, greater the stress required to form dislocation, thus confirming greater crystalline perfection.

Photoluminescence (PL) study

The PL spectrum of the pure BTZA and metal doped BTZA single crystals was recorded using Edinburgh luminescence spectrometer with the corresponding excitation wavelength of 325 nm and it is shown in Figure No.6. The analysis of PL emission spectrum of particular material provides the crucial information regarding the intrinsic/extrinsic impurities and recombination of electronic transitions associated with the material which is essential quality of a material to be utilized in photonics and biomedical applications[23-25]. The PL intensity is highly dependent on the crystalline and structural perfection of the grown crystals. A strong emission peak was observed in the yellow region with the peak at 571 nm which is due to the intrinsic optical behavior of BTZA crystal. Another peaks at 572 nm and 578 nm were observed in the spectrum is due to the presence of impurities present in the crystal. The strong broad PL emission in the yellow region confirms the suitability of metal doped BTZA crystals for optoelectronic and luminescence devices[26].

Nonlinear optical analysis

Kurtz and Perry powder technique[27] remains an extremely valuable tool for initial screening of materials for second harmonic generation (SHG). The grown crystals were subjected to the NLO study to measure the efficiency with respect to pure KDP single crystals. The SHG property of the grown crystals was tested by the Kurtz and Perry powder method. The fundamental beam of wavelength 1064 nm from a Q-switched Nd: YAG laser with a pulse energy 3 mJ/ pulse, pulse width 8 ns, and repetition rate 10 Hz was used. The salt was packed in a micro capillary of uniform bore and exposed to laser radiations. The output wavelength of 532 nm green colour emission was detected by a Photomultiplier tube. The SHG efficiencies of $Ni^{2+}$and Zn^{2+}doped BTZA crystals were determined to be 1.7 and 1.8 times that of KDP crystal respectively. Hence the results suggest that metal doped BTZA crystals are perfect candidates for nonlinear optical and optoelectronic device applications.

Table No.1: Single crystal data of pure and Ni^{2+}, Zn^{2+} doped BTZA crystals

S.No	Crystal parameters	BTZA (reported) [19]	Pure BTZA	LiCl doped BTZA [22]	Ni^{2+} doped BTZA	Zn^{2+} doped BTZA
1	a	7.1212A°	7.122A°	7.129 A˚	7.127 A˚	7.126 A˚
2	b	17.6654A°	17.680A°	17.708 A˚	17.704 A˚	17.705 A˚
3	c	11.1297A°	11.178A°	11.189 A˚	11.184 A˚	11.182 A˚
4	α	90°	90°	90°	90°	90°
5	β	103.16°	103.09°	103.19°	103.19°	103.19°
6	γ	90°	90°	90°	90°	90°
7	Volume	1365.5 A^3	1372 A^3	1375.4 A^3	1374.4 A^3	1373.4 A^3

Table No.2: FTIR Data comparison of pure and metal doped BTZA crystals

S.No	BTZA (cm^{-1}) (reported [19])	BTZA (cm^{-1})	BTZA+$LiCl_2$ (cm^{-1}) [22]	BTZA+Ni^{2+} (cm^{-1})	BTZA+Zn^{2+} (cm^{-1})	Tentative Assignment
1	487	482	486	485	485	S-C-N symmetric bending
2	777	777	772	776	774	C=S symmetric stretching
3	1135	1134	1128	1132	1130	C=S symmetric stretching
4	1403	1403	1401	1403	1402	C=S asymmetric stretching
5	1582	1583	1587	1582	1586	NH_2 bending
6	3375	3376	3388	3386	3386	NH_2 stretching vibrations

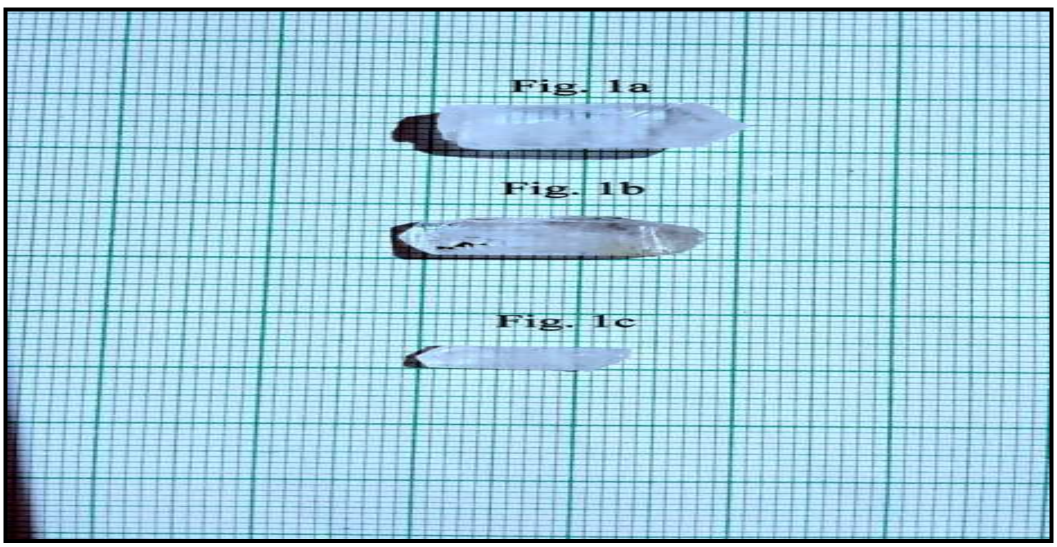

Figure No.1: A. As grown BTZA crystal, B. as grown Ni^{2+} doped BTZA crystals C. as grown Zn^{2+}doped BTZA crystals

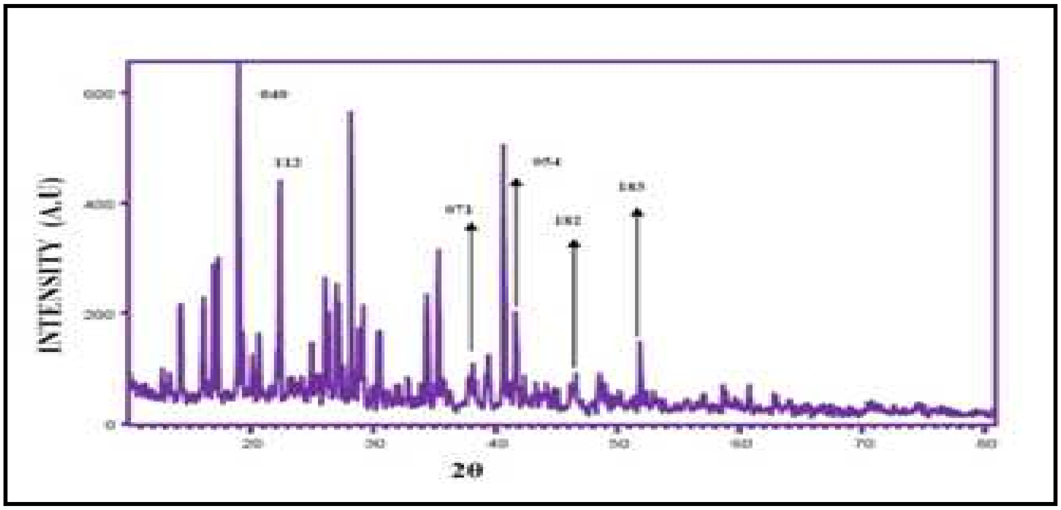

Figure No.2a: Powder XRD spectrum of BTZA crystals

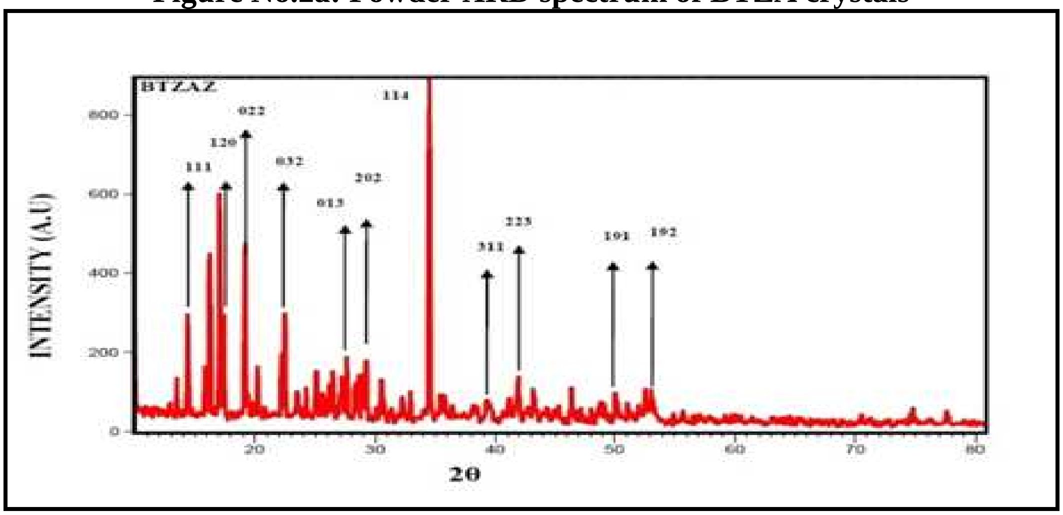

Figure No.2b: Powder XRD spectrum of Ni^{2+} doped BTZA crystals

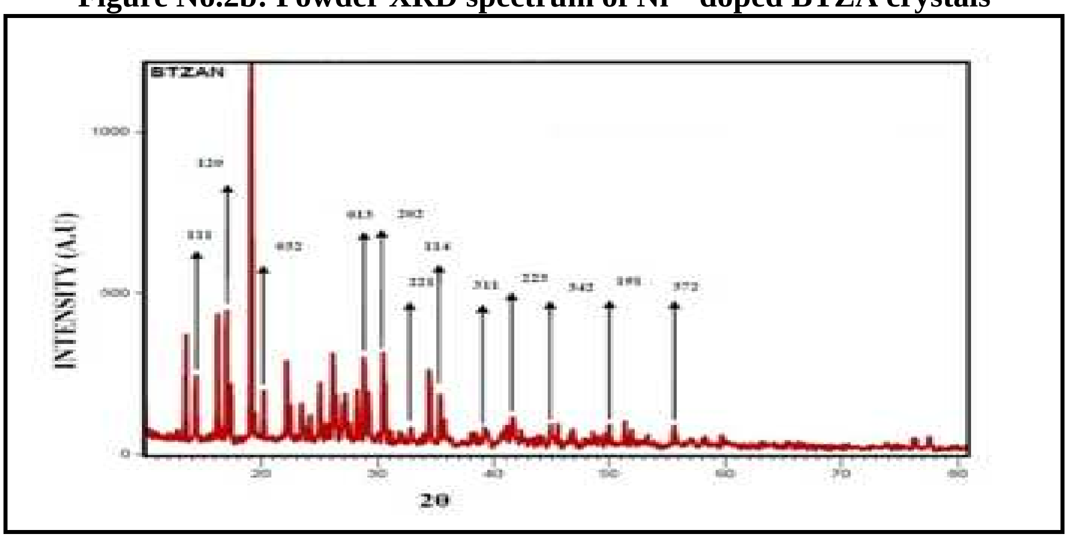

Figure No.2c: Powder XRD spectrum of Zn^{2+} doped BTZA crystals

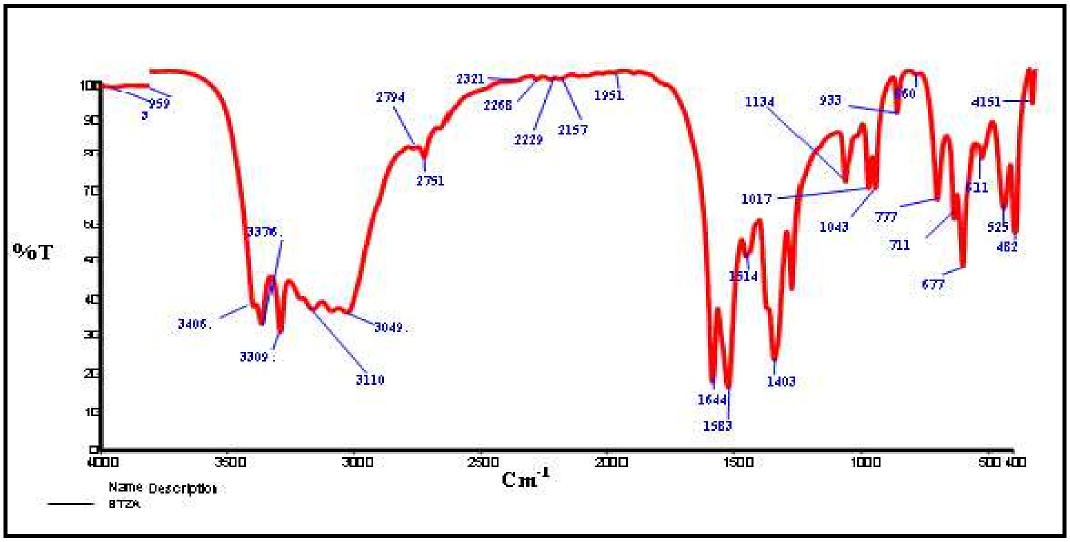

Figure No.3a: FTIR spectrum of BTZA crystals

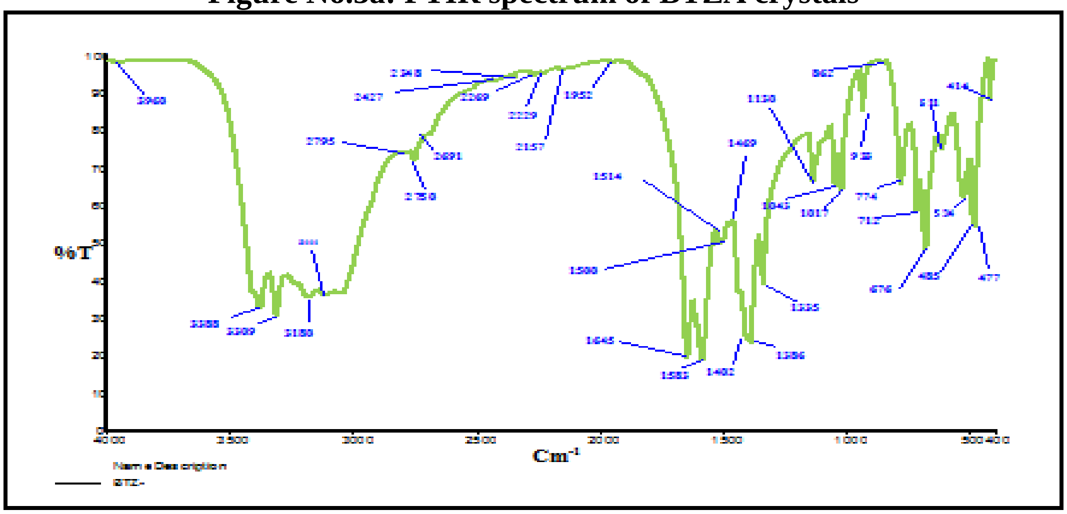

Figure No.3b: FTIR spectrum of Ni^{2+} doped BTZA crystals

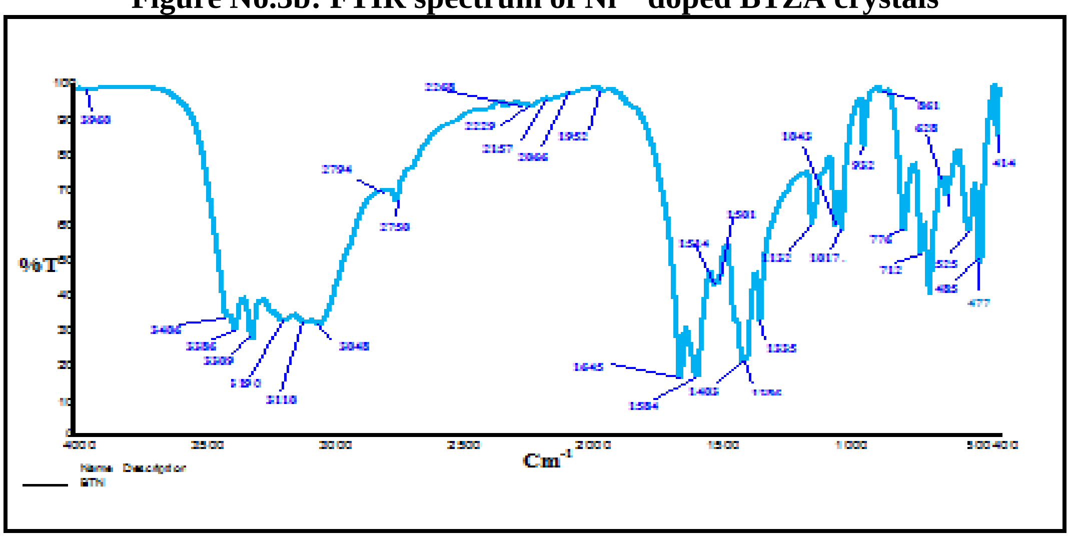

Figure No.3c: FTIR spectrum of Zn^{2+} doped BTZA crystals

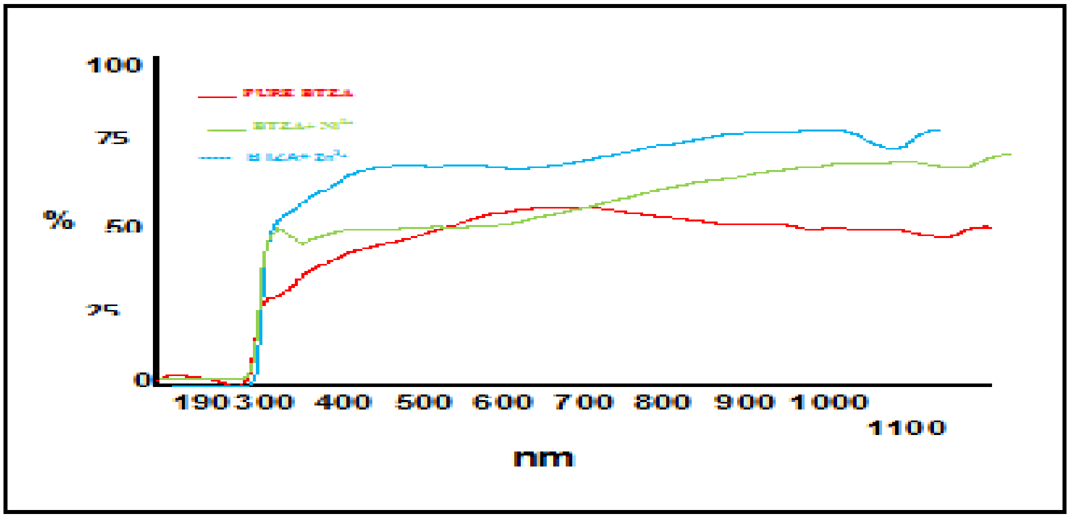

Figure No.4: UV-Vis spectrum Pure and Ni^{2+}, Zn^{2+} doped BTZA crystals

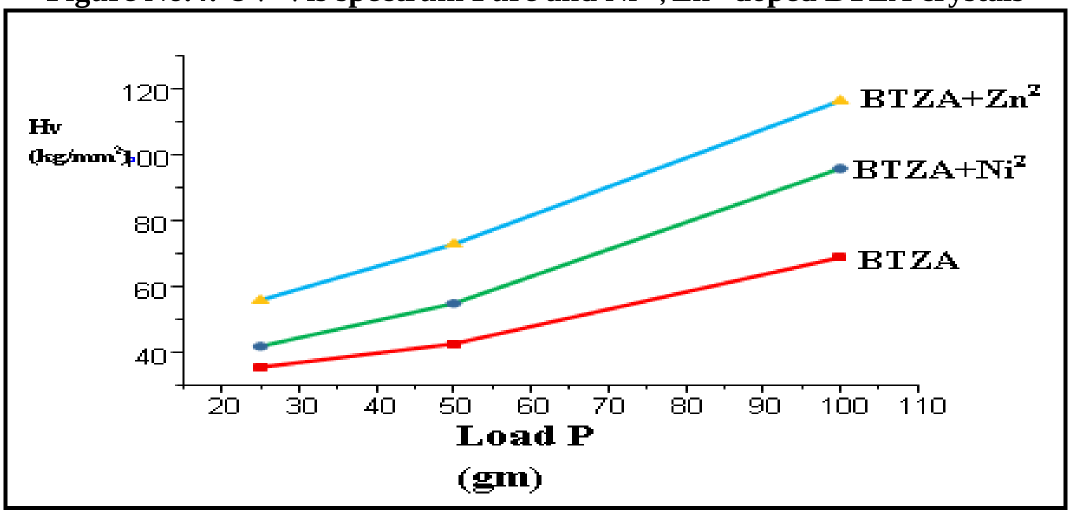

Figure No.5: Plot of Vickers hardness number with load for BTZA and Ni^{2+}, Zn^{2+} doped BTZA

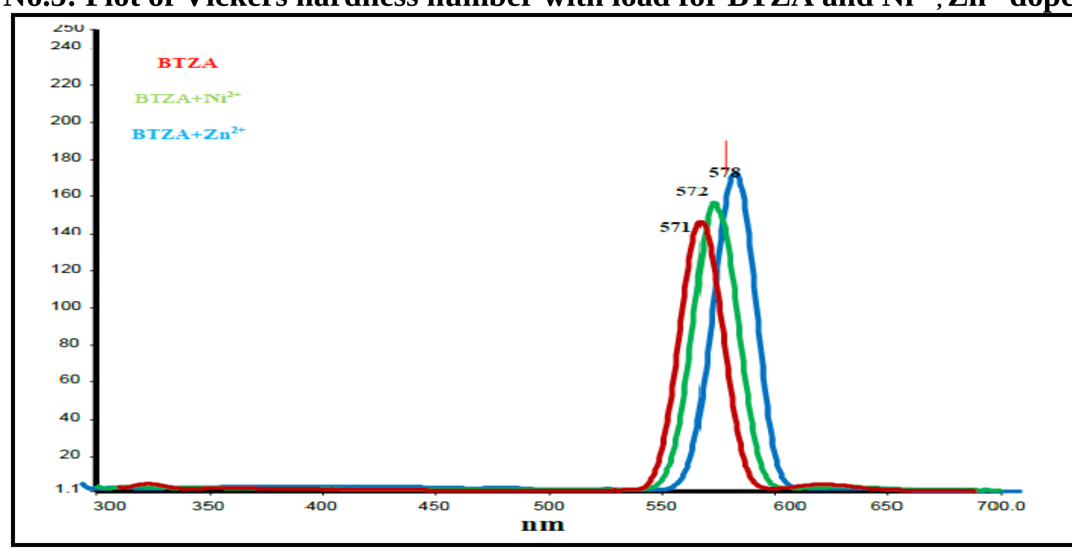

Figure No.6: PL spectrum of the pure and metal doped BTZA

CONCLUSION

Single crystals of Pure and Ni^{2+} doped BTZA, Zn^{2+} doped BTZA crystals have been grown from aqueous solution by slow evaporation technique using water as the solvent. The grown crystals were subjected to various studies. The observed features in the analysis of the different studies used are as follows. The single crystals of undoped and Ni^{2+} and Zn^{2+} doped BTZA have been grown by solution growth technique with transparent and well defined external appearance. The unit cell parameters of pure and Ni^{2+}, Zn^{2+} doped BTZA crystals were compared. They are in agreement with the literature values by using single crystal XRD results. ICP studies on the doped crystals show that the amount of dopant incorporated in the doped crystal is less than the concentration of the dopant in the corresponding solution. The functional groups of both the crystals have been obtained by FT-IR Spectral analysis. The transparency nature of the crystal in the Visible and Infrared regions confirms the NLO property of the crystal. The doped BTZA has a lower UV cutoff wavelength of 290 nm and has a transmittance of Ni^{2+}, Zn^{2+}63% and 72% respectively which is higher than that of the pure BTZA crystal. By Vickers micro hardness measurements the hardness of Ni^{2+}, Zn^{2+} doped BTZA crystal is higher than the hardness value of pure BTZA. The various studies revealed the incorporation of the impurity (Ni^{2+}, Zn^{2+}) into BTZA crystal lattice, and the investigations indicated that the impurity played an important role in the changes of the structural, spectral, optical, Photoluminescence and Mechanical properties of BTZA crystal.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest

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