Growth, linear–non-linear optical, fluorescence, thermal and electrical studies of glycine-doped bis-thiourea cadmium formate crystal for electro-optic device applications

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In the present investigation, glycine has been doped in bis-thiourea cadmium formate (BTCF) and single crystal was grown by slow solution evaporation technique. The incorporation of glycine in BTCF crystal was confirmed by Fourier transform infrared (FTIR) analysis. The UV-visible transmittance spectrum of pure and doped BTCF crystals was recorded to comparatively analyse the optical transparency, optical bandgap and other optical constants. The third-order non-linear behaviour of grown crystals has been investigated at 632.8 nm using *Z*-scan technique, and vital third-order non-linear optical (NLO) constants were calculated. The second harmonic generation (SHG) efficiency of doped BTCF crystal is found to be 2.15 times that of KDP material. The fluorescence studies of doped BTCF crystal confirmed the red colour emission in the visible region. The thermal stability of grown crystals was determined by means of thermogravimetric analysis (TGA). The dielectric measurement studies were performed at room temperature. The surface morphology of doped BTCF crystal was analysed by scanning electron microscopy (SEM) technique.

Keywords: Crystal growth, Dielectric studies, Optical studies, SEM analysis, Thermal studies

Introduction

In the current era, researchers have shown great interest in non-linear optical (NLO) metal complexes of thiourea because of their wide applications in the field of optical data storage, optical switching devices, second harmonic generation (SHG), photonics, optoelectronics, laser alignment and ultrafast telecommunication systems. The coordination of thiourea with metal ion mainly offers fast electrical response, high mechanical strength, excellent SHG coefficient, large transparency and higher thermal stability. A variety of metal complexes of thiourea have been already reported in literature.[1,2] Bis-thiourea cadmium formate (BTCF) is one exceptional NLO material that foreshow higher SHG efficiency than KDP, good optical transparency, lower cutoff wavelength, lower dielectric response, high hardness (109.7 kg mm^{-3} along <021> plane) and the thermal stability is up to 190°C.[3–5] It is noticed that doping of amino acids can offer large enhancement in characteristic properties of thiourea metal complexes, particularly glycine. Glycine is the simplest amino acid that can enhance the charge delocalisation through donor–acceptor group; in addition, glycine has successfully promoted the linear optical and NLO properties of thiourea metal complexes like bis thiourea zinc chloride, zinc thiourea sulphate, bis thiourea cadmium chloride and bis thiourea cadmium acetate crystals.[6–9] In the current developments of doped thiourea metal complex crystals, no literature is available on doping of any amino acid in BTCF crystal. The present manuscript successfully investigates the impact of glycine on linear-nonlinear optical, thermal and dielectric properties of BTCF crystal to explore its usability for designing various NLO devices.

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Experimental procedure

The pure BTCF salt was successively synthesised by dissolving the Merck make cadmium oxide, formic acid and thiourea in deionised water in 2: 2: 1 molar ratio. The BTCF salt was repeatedly recrystallised using slow solution evaporation technique for achieving the high purity of salt. The supersaturated solution of repeatedly recrystallized

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BTCF salt was prepared at room temperature, and 4 mol.-% of glycine was gradually added to it. This solution was allowed to agitate for 6 h at constant speed to achieve the homogeneity. The glycine-doped BTCF (BTCFG) solution was filtered using No. 1 Whatman filter paper in rinsed beakers and kept for evaporation at 38°C in a constant temperature bath of accuracy ± 0.01°C. The as-grown BTCFG crystal is shown in Fig. 1.

Results and discussion

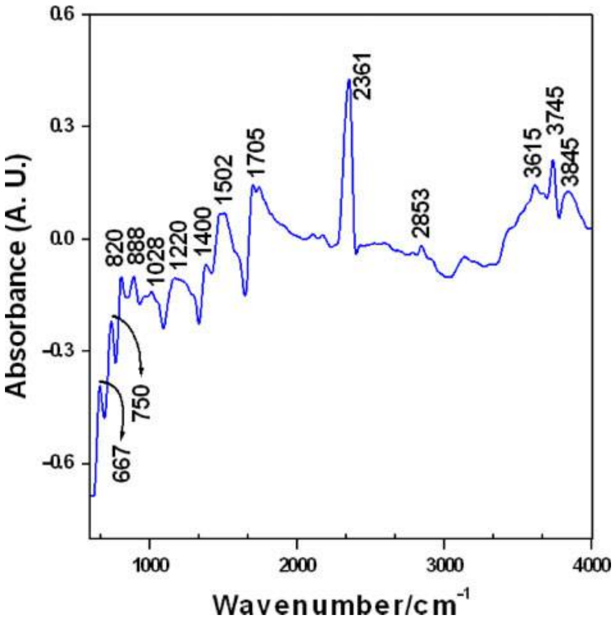
Fourier transform infrared (FTIR) analysis

The incorporation of glycine in BTCF complex has been qualitatively analysed by recording the Fourier transform infrared (FTIR) spectrum of BTCFG crystal in the range of 600–4000 cm^{-1}, shown in Fig. 2. The absorption peaks at 667 and 1400 cm^{-1} corresponds to the characteristic C═S bond stretching vibrations of metal coordinated thiourea molecule. The N–H wagging mode of vibration is attributed at 750 cm^{-1}. The NH_2 twisting of ammine group associated with glycine is evident at 820 cm^{-1}. The N—O bond stretching vibration is contributed at 888 cm^{-1}. The C—N—C stretching vibration is cited at 1028 cm^{-1}. The absorption peak at wave number 1220 cm^{-1} corresponds to the C—O bond stretching vibration. The absorption peak at 1500 cm^{-1} corresponds to the NH_3+ deformation in glycine. The C=O stretching of carboxyl group is evident at 1705 cm^{-1}. The absorption peak at 2853 cm^{-1} corresponds to the C—H bond stretching vibration. The peaks between 3600 and 4000 cm^{-1} corresponds to the O—H bond stretching vibrations associated with glycine.[10] The above spectral analysis confirms the presence of dopant glycine in BTCF crystal.

Linear optical studies

The optical transparency of pure and doped BTCF crystals (2 mm thickness) was tested within 200–900 nm range using the Shimadzu UV-2450 spectrophotometer. The recorded transmittance spectrum shown in Fig. 3*a* reveals that the doped BTCF crystal acquired higher optical transparency and remarkably lower transmittance cutoff edge than pure BTCF crystal. The crystalline defects largely affect the optical properties such as light absorption,

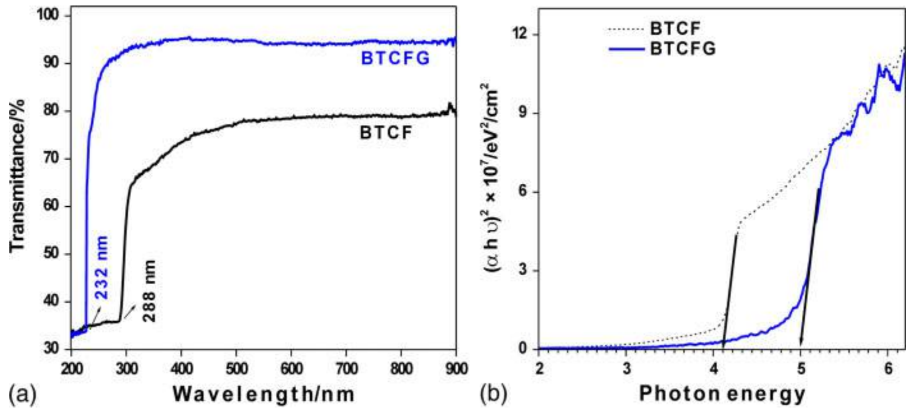
1 Photograph of glycine-doped bis-thiourea cadmium formate (BTCFG) crystal



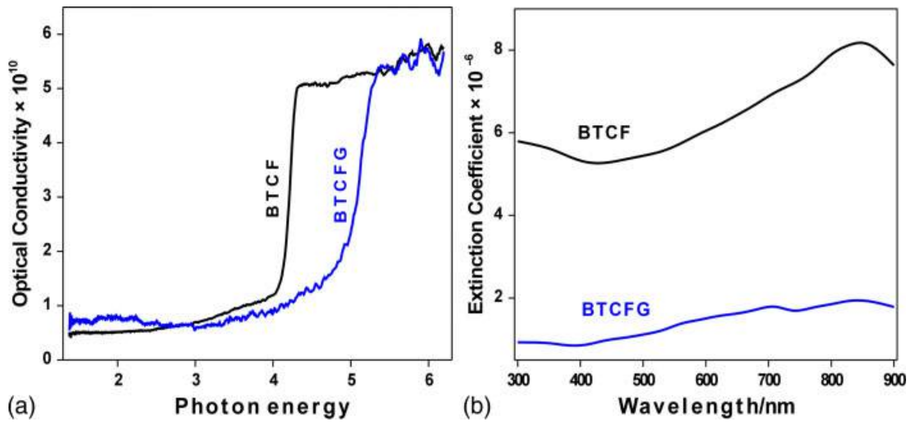
2 Fourier transform infrared (FTIR) spectrum of glycine-doped bis-thiourea cadmium formate (BTCFG) crystal

scattering, and refractive index, and for practical devices, crystals free from light scattering and absorbing defects are required.[11,12] It has been already reported that as density of defect increases, the possibility for the occurrence of the scattering centres also increases and this is responsible for the optical loss into the crystals.[13,14] The higher optical transmission in BTCFG crystals may be because of lesser defects and absence of solvent inclusions, which in turn reduced scattering in BTCFG crystals and increases the output intensity. The shift in cutoff wavelength of doped BTCF crystal to lower values is because of *n* to π* transition favoured by excess nitro group of glycine. The high and wide transparency window of doped BTCF crystal is of extreme advantage for NLO applications such as efficient transmission of second and third harmonic frequencies of Nd:YAG laser.[15] It is of vital importance to study the dependence of absorption coefficient (α) on photon energy (hν), which eventually helps to calculate the optical bandgap of material using equation $(\alpha h\nu)^2 = A(h\nu - E_g)$, where E_g is the optical bandgap of the material. The Tauc's extrapolation plot shown in Fig. 3*b* confirms the large enhancement in bandgap of BTCF crystal because of the presence of dopant glycine. The higher bandgap indicates the strong candidature of doped BTCF crystal for optoelectronics applications.[16] The evaluation of optical constants facilitates to tailor the device suitability of grown crystals for integrated optical applications for which, the optical conductivity (σ_{op}), extinction coefficient (*K*), refractive index (*n*) and reflectance (*R*) of the grown crystals were evaluated using the theoretical formulae given in literature.[17,18]

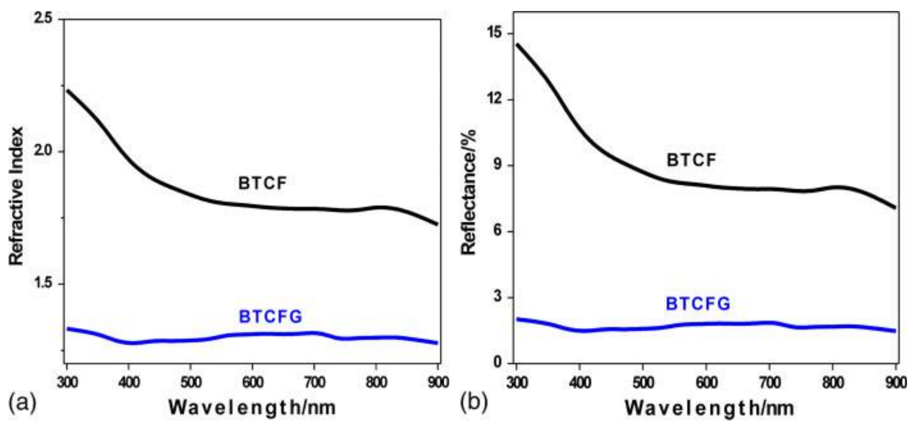
The increasing nature of optical conductivity and lower extinction coefficient of doped BTCF crystal shown in Fig. 4*a* and *b* indicates the minimum loss of electromagnetic energy while propagation. Also, high optical conductivity and lower extinction coefficient of doped BTCF crystal suggest its prominence for fast information processing and optical computing devices.[16,19] The plot of refractive index and reflectance as a function of wavelength is shown in Fig. 5*a* and *b*,



3 ***a*** **UV-visible transmittance spectrum and** ***b*** **Tauc's plot**



4 Plot of ***a*** **optical conductivity and** ***b*** **extinction coefficient as a function of wavelength**



5 Plot of ***a*** **refractive index and** ***b*** **reflectance as a function of wavelength**

respectively. The precise measurement of refractive index benefits to assess the merit of optical components such as filters, resonators and reflectors of laser systems and also the lower refractive index of doped BTCF crystal is an appealing parameter for photonics applications.[20] The high transparency, lower refractive index and lower reflectance of doped BTCF crystal make it a promising antireflectant essential for external coating of solar thermal devices.[16,19] The lienar optical constants of crystals necessary for designing the optical devices are discussed in Table 1. The encouraging optical qualities of doped BTCF crystal substantiate its utility for lasers and NLO device applications.

NLO studies

The second-order NLO behaviour of grown crystals was investigated by Kurtz–Perry powder technique using the Q-switched Nd:YAG laser (1064 nm) delivering the energy of 6.9 mJ/pulse with the repetition rate of 10 Hz. The grown crystals were finely powdered and tightly packed in the microcapillary tube of uniform bore. The prepared samples were focused by the polarised beam of Nd:YAG laser, and the emergence of bright green light at the output confirmed the efficient frequency doubling phenomenon by pure and doped BTCF material. The output signals of the sample were collected through the photomultiplier tube and displayed on the digital oscilloscope. In the present

Table 1 Linear optical parameters

Crystal	Cutoff	Transparency	Transparency range	E_g/eV	Calculated data at 532 nm		
					K	*R*	*n*
Pure BTCF	288 nm	74%	400–900 nm	4.11	5.5×10^{-6}	8.3%	1.81
Doped BTCF	232 nm	94%	310–900 nm	5	1.2×10^{-6}	1.6%	1.29

BTCF: bis-thiourea cadmium formate.

analysis, the SHG conversion efficiency of pure BTCF is found to be 1.98 times that of KDP, which is in close agreement with the available literature.[3] The SHG efficiency of doped BTCF is found to be 1.08 times that of BTCF and 2.15 times that of KDP material. Higher SHG efficiency of doped BTCF crystal is most desirable for fabrication of NLO devices.

The third-order NLO behaviour of grown crystals (1 mm thick) was investigated using the *Z*-scan technique developed by Sheik-Bahae *et al.*[21] The optical resolution of *Z*-scan set-up is detailed in Table 2. In this technique, the He–Ne laser functioning at 632.8 nm was tightly focused on the crystal surface through a convex lens to identify the close and open aperture transmittance profile of crystal along the *Z*-direction. As the closed aperture *Z*-scan analysis enables to determine the nature and magnitude of refraction non-linearity of the crystal, the sample crystal was gradually translated along the beam focused *Z*-direction. The transmitted signals of the crystal were recorded with respect to the sample position on *Z*-direction by closing the aperture of detector placed at a far field. The close aperture *Z*-scan curves of grown crystals is shown in Fig. 6*a*. The origin of sensitive refraction non-linearity is because of the spacial distribution of energy along the crystal surface caused by localised absorption of highly repetitive incident optical field.[22]

The peak to valley phase transition identifies the self-defocusing tendency of BTCF crystal assisted by negative refraction non-linearity. The materials with negative non-linear refraction are suitable for protection of night vision sensors.[23] The close aperture transmittance of doped BTCF crystal traces the valley to peak phase transition signifying the self-focusing tendency and occurrence of positive non-linear refraction phenomenon.[24] The difference between peak and valley transmission ($\Delta T_{\text{p-v}}$) in terms of phase shift is given as[21]

$$\Delta T_{\text{p-v}} = 0.406(1-S)^{0.25}|\Delta\phi| \tag{1}$$

where $S=[1-\exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The magnitude of non-linear refractive index (n_2) was calculated using the relation[21]

$$n_2 = \frac{\Delta\phi}{KI_0L_{\text{eff}}} \tag{2}$$

where $K=2\pi/\lambda$ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus ($Z=0$), $L_{\text{eff}}=[1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample depending on linear absorption coefficient (α) and *L* is the thickness of the sample. The higher magnitude of refraction non-linearity suggests the efficient Kerr-lens modelocking (KLM) ability of doped BTCF crystal, which essentially demanded for laser alignment and shorter pulse generation systems.[25] The open aperture *Z*-scan analysis helps to study the nature of non-linear absorption coefficient (β) of the crystal, which may be either saturable absorption (SA) or reverse saturable absorption (RSA). The open aperture *Z*-scan transmittance curves of grown crystals are shown in Fig. 6*b*. It reveals that the transmittance of BTCF crystal increases near the focus indicating the existence of SA effect and the fall in transmittance of doped BTCF crystal at the focus signify the prominence of RSA phenomenon. The origin of SA trend in pure BTCF crystal is because of dominance of linear absorption coefficient of material,[21] while the physical origin of RSA trace in doped BTCF crystal is favoured by prominent multiphoton absorption in the excited states.[22,26] The doped BTCF crystal with promising RSA effect falls to the regime of materials required for laser stabilisation systems, optical switching and optical limiting devices.[27–29] The β value of studied crystals was estimated according to the equation shown below[21]

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{\text{eff}}} \tag{3}$$

where ΔT is the one valley value at the open aperture *Z*-scan curve. The third-order non-linear susceptibility (χ^3) defines the cubic polarising ability of the material, which was determined using the following equations[21]

$$\text{Re}\chi^{(3)}(\text{esu}) = 10^{-4}(\varepsilon_0C^2n_0^2n_2)/\pi(\text{cm}^2\,\text{W}^{-1}) \tag{4}$$

$$\text{Im}\chi^{(3)}(\text{esu}) = 10^{-2}(\varepsilon_0C^2n_0^2\lambda\beta)/4\pi^2(\text{cm}\,\text{W}^{-1}) \tag{5}$$

$$\chi^3 = \sqrt{(\text{Re }\chi^3)^2 + (\text{Im }\chi^3)^2} \tag{6}$$

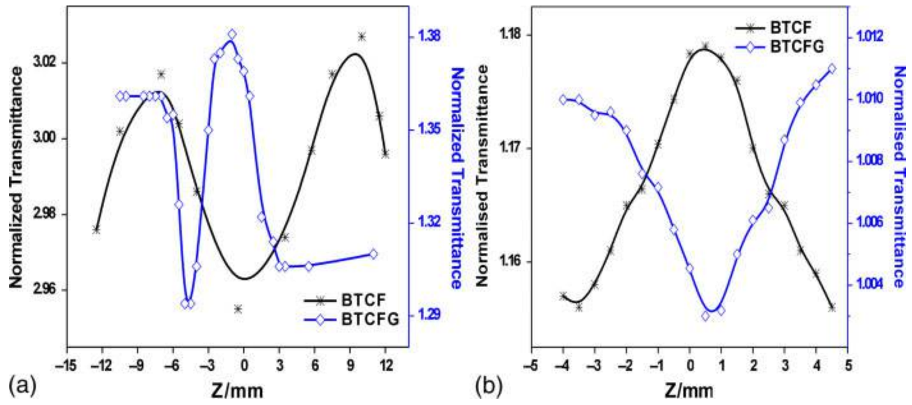
where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and *c* is the velocity of light in vacuum. The higher magnitude of χ^3 of doped BTCF crystal is found to be 2.05×10^{-7} esu, which is favoured because of extended π-electron delocalisation in the molecular orbits when the crystal is influenced by incident optical beam energy of laser.[28] The figure of merit of doped BTCF crystal was calculated using the relation, $\text{FOM}=\beta\lambda/n_2$. The dominant non-linear absorption over non-linear refraction confirmed the value of FOM to be 76.12. This recognises the suitability of doped BTCF crystal for optical power limiting devices.[29] The crucial NLO parameters are discussed in Table 3.

Table 2 Details of *Z*-scan set-up

Laser beam wavelength (λ)	632·8 nm
Lens focal length (*f*)	12 cm
Optical path distance (*Z*)	115 cm
Spot-size diameter in front of the aperture (ω_a)	1 cm
Aperture radius (r_a)	4 mm
Incident intensity at the focus (Z=0)	3·13 MW cm^{-2}

Fluorescence studies

The fluorescence studies provide the vital information about the quality, electronic states and influence of intrinsic impurities of the grown crystals.[30] The doped BTCF crystal



6 ***a*** **Close and** ***b*** **open aperture** ***Z*****-scan curves**

Table 3 Non-linear optical parameters

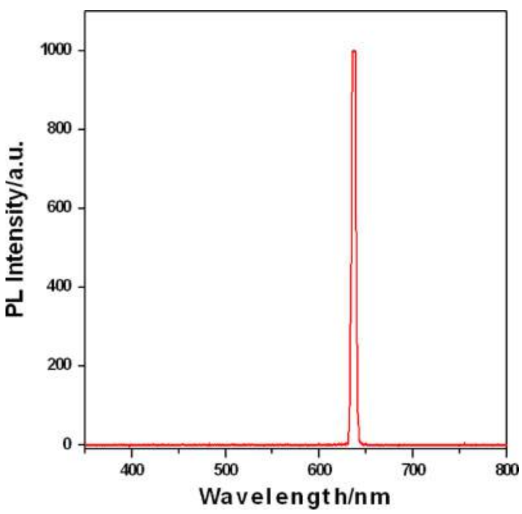
Crystal	n_2/cm^2 GW^{-1}	β/cm W^{-1}	χ^3/esu
Pure BTCF	-9.04×10^{-4}	3.08×10^{-9}	1.38×10^{-8}
Doped BTCF	7.77×10^{-4}	9.34×10^{-8}	2.05×10^{-7}

BTCF: bis-thiourea cadmium formate.

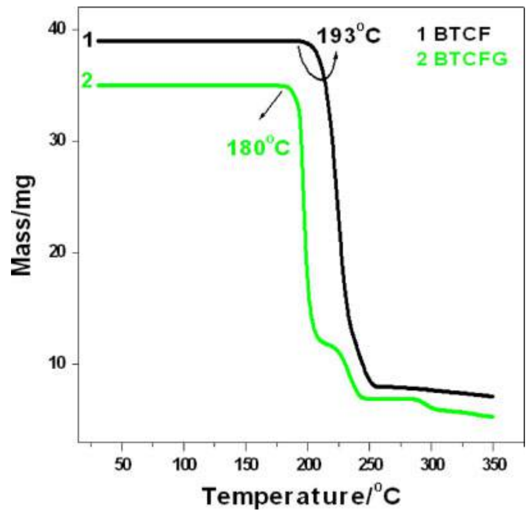
was photoexcited with the energy wavelength of 260 nm, and the fluorescence emission spectrum was recorded in the range of 350–800 nm as shown in Fig. 7. The single peak maxima at 640 nm demonstrating the full width half maximum (FWHM) of 7 nm indicates that the quality of doped BTCF crystal is exceptionally good. The BTCFG crystal with red coloured emission may be of huge advantage for low-pass optical filters.[31]

Thermogravimetric analysis

The designing of optical components of laser system requires materials with high thermal performance for which the grown crystals have been characterised by thermogravimetric analysis (TGA). The TGA curve of pure and doped BTCF crystal shown in Fig. 8 was recorded within the temperature range of 30–350°C. It reveals that both, pure and doped BTCF materials, do not show any phase change before decomposition temperatures, which is of vital importance for designing NLO devices.[3] The decomposition temperature of doped



7 Emission spectrum of doped bis-thiourea cadmium formate (BTCF) crystal

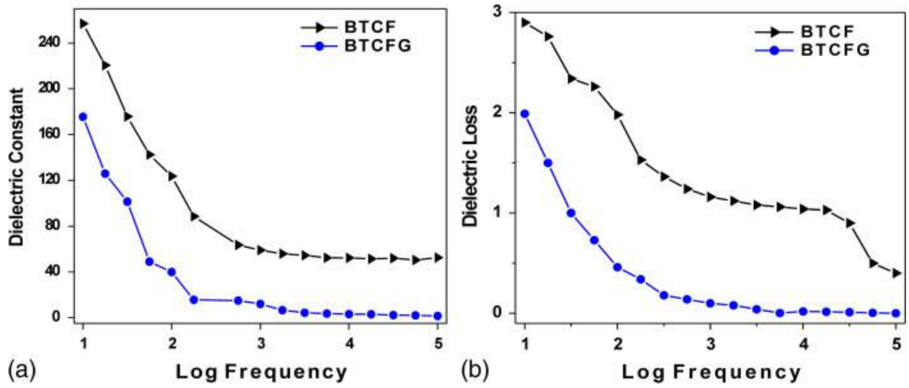


8 Thermogravimetric curve

BTCF material is 180°C indicating the unsteady nature of glycine at a higher temperature.[9]

Dielectric studies

The dielectric studies of the grown crystals were investigated using the Gwinstek 819-LCR multifrequency cubemetre. Before the analysis, the crystal samples were keenly coated with the silver paste to attain perfect electrical contact with the copper electrode. The frequency response of dielectric permittivity of grown crystals is shown in Fig. 9*a*. In accordance to Miller rule and the Phillips–Van Vechten–Levin–Xue bond theory, the lower values of dielectric permittivity at higher frequencies is a suitable parameter for the enhancement of SHG coefficient.[32] The dielectric permittivity of materials is because of the contribution of electronic, ionic, dipolar and space charge polarisations, which depend on frequencies.[33] The dielectric permittivity of grown crystals successively decreases with increasing frequency as polarisation mechanism becomes inactive at higher frequencies. The lower dielectric permittivity of doped BTCF crystal is remarkably lower, thus facilitating its usability for microelectronic and photonic devices.[34] The materials with lower dielectric permittivity consume less power, which is major asset for designing the broadband electro-optic modulators and field detectors.[35] The plot of dielectric loss as a function of frequency is shown in Fig. 9*b*. It reveals that doped BTCF crystal possesses relatively lower dielectric loss than BTCF



9 Frequency response of *a* dielectric constant and *b* dielectric loss

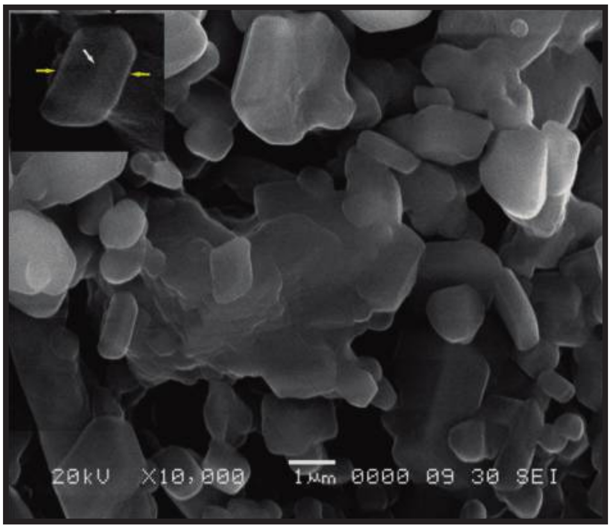
crystal. The lower dielectric loss indicates that the crystal is of good quality with minimum defects. The behaviour of dielectric losses in the low-frequency range depends on many factors, which can be controlled (temperature rate, defects, size of crystal).[36] Low value of dielectric loss indicates that BTCFG crystal contains very low defects, which is in tune with the optical transmittance results with higher transparency. Thus, lower dielectric parameters of doped BTCF crystal are beneficial for designing the electro-optic and NLO devices.[37]

SEM analysis

The SEM analysis is of principle importance to study the effect of growth habitat on the surface morphology of the crystal. The recorded SEM micrograph of doped BTCF crystal is shown in Fig. 10. The inset shown in Fig. 10 evidences the smoothly grown crystal faces with absence of pits and spots on it ensuring the perfect growth of crystal in isothermal atmosphere. The prominent face edge can be easily distinguishable, and the completely grown boundaries of the doped BTCF crystal are indicated in the inset of SEM micrograph.

Conclusion

Optically transparent BTCFG crystal was grown by slow solution evaporation technique. The FTIR analysis established the incorporation of glycine in BTCF crystal.



10 SEM micrograph of doped bis-thiourea cadmium formate (BTCF) crystal

The linear optical studies confirmed remarkable enhancement in optical transparency and bandgap of BTCF crystal because of addition of glycine. The doped BTCF crystal exhibits the single red fluorescence maxima at 640 nm indicating the good crystalline nature of crystal. The NLO studies confirmed the superior non-linear behaviour of doped BTCF crystal than pure BTCF crystal. The SHG efficiency of doped BTCF crystal is higher by 2.15 times that of KDP and 1.08 times that of BTCF crystal material. The *Z*-scan analysis determined the positive refraction non-linearity, effective RSA phenomenon and origin of higher cubic susceptibility in doped BTCF crystal vital for laser alignment systems and optical limiting devices. The thermal stability and improved dielectric properties of doped BTCF crystal are vital for microelectronic devices. The SEM analysis detected the smooth surface morphology of doped BTCF crystal. All the above studies evidence that the doped BTCF crystal possesses improved optical and electrical properties, for which it may be exploited for designing electro-optic engineering devices.

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