Tb$^{3+}$ added sulfamic acid single crystals with optimal photoluminescence properties for opto-electric devices

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Abstract

Terbium doped Sulfamic Acid (Tb$^{3+}$:SA) single crystals were grown successfully by the slow evaporation solution (SEST) technique and the unidirectional method. The lattice parameters and the functional group were identified for the grown crystal by using single crystal X-ray diffraction and Fourier transform infra-red spectroscopy (FTIR), respectively. High resolution X-ray diffraction analysis (HRXRD) shows the crystalline perfection of the grown crystal. The optical transparency and band gap of the grown crystals were determined from UV-VIS spectroscopy. TG/DTA studies reveal that the grown crystals are thermally stable up to 190 °C. The frequency dependent dielectric properties were studied at different temperatures. Vickers micro hardness studies show that Tb$^{3+}$:SA belongs to the class of soft materials. Second harmonic generation efficiency of Tb$^{3+}$:SA is 3.7 times that of pure KDP. The photoluminescence emission and excitation studies of Tb$^{3+}$:SA single crystals indicated the green emission at 543 nm, which is due to a transition from the $^7F_5$ excited state to the $^7F_3$ ground state.

1. Introduction

The synthesis and fabrication of efficient luminescent nonlinear optical (NLO) materials have attracted worldwide tremendous interest in the field of opto-electric devices research. In this connection, bulk single crystals play a dominant role in many fields such as photonics, optical communication, optical image processing and optoelectronics [1]. Indeed, inorganic NLO crystals are more advantageous than the organic ones because of their thermal and mechanical stability and, thus, they are used in various laser systems for harmonic generation, optical switching, holographic data storage, optical computing, optical information processing, colour displays and medical diagnostics [2]. In fact, dopants play an important role in enhancing the properties of single crystals [1] and also with a significant effect on the growth rate and properties of the crystals [3]. The rare earth elements have been found for tremendous applications in the area of photonics, solid state lasers, phosphors for colour lamps and display devices, and optical fiber communication devices [4,5]. The rare earth elements have a partially filled inner (4$f^n$) shell shielded from its surroundings by the completely filled outer (5$s^2$ and 5$p^6$) orbitals. Due to the shielding of the intra 4f shell transitions result in very sharp optical emissions at wavelengths ranging from UV to IR [6]. The luminescence of the RE ions arises from the electron transition at the 4f shells of RE$^{3+}$ and depends strongly on the size, the shape, the degree of crystallization, the surface state, the composition, and the structure of the host materials [7]. Research has been done on various complexes of azomethine-zinc as blue light emitting luminescent materials [8]. Trivalent Terbium (Tb$^{3+}$) is one of the most investigated RE ion during the past decade [9] because of its narrow emission lines in the UV and visible spectral region at 584, 416 and 438 nm due to $^5D_3 \rightarrow ^7F_j$ ($j=6,5,4$) transitions and at 493, 543, 584, 620, 700 nm due to $^5D_4 \rightarrow ^7F_j$ ($j=6,5,4,3,2$), respectively [10]. Sulfamic acid (H$_2$NSO$_3$H) is a strong inorganic acid and the mono amide of sulphuric acid with the orthorhombic crystal system. It is highly stable and can be kept for years without any change.

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in properties. Research has been done on adding NaCl, KCl, [11], Gadolinium, [12], Lanthanum [13] and Cerium [14] and came to conclusions that the dopants increase the efficiency of the NLO property. In the present paper, we report on Tb\(^{3+}\) added sulfamic acid single crystals grown by SEST and unidirectional methods at low temperature. Owing to the trivalent Tb ions these crystals can afford optical devices in the regions of green as well as blue colour [15]. The grown crystals were characterized by XRD, HRXRD, FTIR, UV–VIS transmittance, TG/DTA, Vickers micro hardness, SHG and Photoluminescence (PL) studies. The strongest PL peak arising from the \(\delta D_{4g} \to \gamma F_{5} \) transition at 543 nm shows the characteristic green emission of the Tb\(^{3+}\) ions. It is inferred that the material has a potential for opto-electric device applications.

2. Experimental

2.1. Material synthesis

The Tb\(^{3+}:SA\) single crystals were synthesized from the solution of Terbium (III) oxide (\(\text{Tb}_2\text{O}_3\)) and Sulphamic acid (\(\text{H}_2\text{NSO}_3\text{H}\)) by using Merck Millipore 18 MΩ cm\(^{-1}\) resistance deionized water in the molar ratio 0.02: 0.98. Crystals of Tb doped SA was grown from the aqueous solution by the slow evaporation solution growth technique (SEST) and a well facet crystal was chosen for SR method. The (100) plane was selected in the present study to impose the orientation in the growing crystal. The synthesis was carried out using the reaction

\[
6\text{NH}_2\text{SO}_3\text{H} + \text{Tb}_2 \to \text{O}_3 2\text{Tb} (\text{NH}_2\text{SO}_3)_3 \to 3\text{H}_2\text{O}.
\]

2.2. Solubility measurement

The solubility of the material in the solvent plays a deciding role affecting the size of the crystal to be grown which depends on the amount of the material available in the solution. The solubility of crystals in the Merck Millipore 18 MΩ cm\(^{-1}\) resistance deionized water as a solvent has been determined at different temperatures 25, 30, 35, 40, 45, 50 °C. The solubility of Tb\(^{3+}:SA\) increases with the increase of temperature. The saturated doped SA solution was prepared at constant temperature with continuous stirring. The enhancement of dopant in crystalline materials is achieved under the applied stress [16]. Hence, the solubility of the doped sulphamic acid is higher than that of the pure sulphamic acid. The obtained solubility curve is shown in Fig. 1(a). To grow good quality seed crystals by the slow evaporation method the super saturated solution prepared at 35 °C was used.

2.3. Tb\(^{3+}:SA\) seed crystals grown by the slow evaporation solution technique

Sulfamic acid (\(\text{H}_2\text{NSO}_3\text{H}\)) and Terbium(III) oxide (\(\text{Tb}_2\text{O}_3\)) chemical reagents (analytical purity of 99.99%, Sigma–Aldrich Co., USA) were used in this experiment. Single crystals of Tb\(^{3+}:SA\) was grown from the aqueous solution by the conventional slow evaporation solution technique (SEST) using Millipore 18 MΩcm\(^{-1}\) resistance deionized water. The saturation solution of 0.02% of (\(\text{Tb}_2\text{O}_3\)) was dissolved in HCl and excess of HCl was evaporated by using double distilled water. 0.98% moles of SA was added to the solution and stirred continuously for 24 h. The saturated solution was filtered by what men filter paper and covered with a perforated lid. A Tb\(^{3+}:SA\) crystal of size 9 x 6 x 3 mm\(^3\) was grown in a period of 5 days, the picture of which is shown in Fig. 1(b).

2.4. Tb\(^{3+}:SA\) single crystal grown by unidirectional method

A well facet (1 0 0) direction seed crystal grown by the SEST method was chosen to grow Tb\(^{3+}:SA\) single crystal in the unidirectional method. The unidirectional method experimental setup [17] consists of temperature controllers, ring heaters, the ampoule, a thermometer and a water bath. The seed was kept at the bottom of the ampoule oriented in the chosen (1 0 0) direction. The saturated solution of Tb\(^{3+}:SA\) was poured into the ampoule without disturbing the seed and covered by a perforated sheet to control the evaporation. Different temperatures were maintained at top and bottom of the ampoule to create a temperature gradient that leads to concentration differences with the higher concentration at the bottom and a lower concentration at the top of the ampoule [18]. The temperatures of the top and the bottom portions were maintained at 38 °C and 33 °C, respectively. We found that the seed crystal started to grow after 3 days. A Tb\(^{3+}:SA\) single crystal of 90 mm length and 15 mm diameter obtained within 30 days of growth is shown in Fig. 1(c).

3. Results and discussion

3.1. Single crystal XRD

The crystal structure system and the lattice parameters of the as-grown Tb\(^{3+}:SA\) single crystal was identified by using the EnrafNonius CAD4 diffractometer with an incident MoK\(\alpha\) radiation. The crystal belongs to the orthorhombic system with the \(Pbca\) space group having a non-Centro symmetry. The derived lattice parameters are shown in Table 1. The incorporation of the RE ions in the host material induces changes in the lattice parameters due to the presence of the interstitial spaces and also the development of local compressive strain in the lattice [19]. The slight changes observed in the lattice parameters of the grown crystal confirmed that the structure was slightly disturbed due to the presence of Tb\(^{3+}\) ions in sulfamic acid crystal.

3.2. High resolution X-ray diffraction studies

HRXRD studies of Tb\(^{3+}:SA\) single crystals were carried out using a PAN Analytical X'Pert PRO MRD high-resolution X-ray diffraction (HRXRD) system with the CuK\(\alpha\) radiation. Fig. 2(a) and (b) shows the high-resolution diffraction curve (DC) recorded in symmetrical Bragg geometry [20] for the Tb\(^{3+}:SA\) crystal grown by the SEST and the SR method using the (100) diffracting planes. The sharp single peak of the DC curve confirms that the crystal is free from structural grain boundaries. The full width at half maximum (FWHM) of this peak is 10" arc which is proximate to that expected from the plane wave theory of dynamical X-ray diffraction [21,22]. Furthermore, the single diffraction curve with low FWHM reveals that the crystalline perfection is good. As seen in the Fig. 2(b), the DC contains a sharper single peak with FWHM of 9" arc which affirms that the crystalline perfection is better in the unidirectionally grown single crystals than in those Tb\(^{3+}:SA\) grown by the SEST.

3.3. FTIR spectral studies

The Fourier transform infrared (FTIR) spectra of the pure and Tb\(^{3+}\) added SA, recorded between 500 and 4000 cm\(^{-1}\) by using KBr pellet Elmer RXI FTIR spectrometer are shown in Fig. 3. To describe the effect of Tb\(^{3+}\) on the characteristic vibration frequencies of fundamental groups the FTIR is effectively used. The samples were prepared by pressed pellet technique. Due to the NH\(^{3+}\) mode of bonding the broad band is at 3000–3500 cm\(^{-1}\), the presence of the weak band around 2800 cm\(^{-1}\) due to the N–H stretching was
observed in both the pure and the doped SA crystal. In the pure SA crystal the bands observed at 1556 and 1448 cm\(^{-1}\) are due to the symmetric vibration of NH\(^3+\) and the asymmetric stretching of NH\(^3+\) mode, whereas these bands are slightly shifted to 1560 and 1440 cm\(^{-1}\), respectively, for the Tb\(^{3+}\):SA single crystals. The vibration band observed at 1034 cm\(^{-1}\) for the pure and at 1029 cm\(^{-1}\) for the Tb\(^{3+}\) doped SA are attributed to the SO\(^3-\) stretching. The rocking mode of vibration of NH\(^3+\) occurs nearly at 994 and 996 cm\(^{-1}\) for pure and Tb\(^{3+}\) doped SA, which confirms the zwitterionic nature of the sulphamic acid single crystal [23]. The shift of the N–S stretching vibration is also observed in the pure and doped samples at 680 to 700 cm\(^{-1}\). Shift occurs in the SO\(_3\) deformation from 557 to 600 cm\(^{-1}\) clearly confirms the presence of the dopant in the crystal. Vibrational assignment for the pure and the Tb\(^{3+}\) doped SA single crystal are shown in Table 2. All the observed IR bands are in good agreement with earlier reports [1]. The alteration in peak intensities and changes in peak positions in the doped SA confirms the incorporation of dopant into the SA single crystal.

| Crystal | Pure SA | Tb\(^{3+}\):SA (SR) |
|---------|---------|---------------------|
| Crystal system | Orthorhombic | Orthorhombic |
| \(a (\AA)\) | 8.0626 | 8.067 |
| \(b (\AA)\) | 8.0580 | 8.124 |
| \(c (\AA)\) | 9.2501 | 9.243 |
| volume \((\AA)^3\) | 606.9644 | 605.7 |
| \(\alpha = \beta = \gamma\) | 90° | 90° |
| Space group | Pbca | Pbca |

Fig. 1. (a) Solubility curve of pure SA and Tb\(^{3+}\):SA single crystal. (b) Tb\(^{3+}\):SA seed crystal grown by the SEST method. (c) Unidirectional growth of Tb\(^{3+}\):SA single crystal.
3.4. UV-VIS analysis

The optical transmission spectra of the grown samples were studied using Lab India analytical UV3092 spectrophotometer in the wavelength range between 200 and 900 nm. The transmission spectra has significant importance for any NLO material. From Fig. 4, the lower UV-cut off wavelength for the SR grown crystal is 255 nm which is in accordance with the reported value in Ref. [5] and for the SEST grown crystal it is 259 nm. Significant transparency of 93% and 95% are found for the SEST and the SR grown crystals.

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Table 2
Vibrational assignment for the pure and Tb$^{3+}$ doped SA single crystal.

| FTIR (Wavenumber cm$^{-1}$) | Vibrational Band assignments |
|-----------------------------|-----------------------------|
| **PURE SA** | Tb$^{3+}$:SA | **Tb$^{3+}$:SA** |
| 3169 | 3172 | NH$_3$ stretching |
| 2800 | 2801 | Sym. NH stretching |
| 1556 | 1560 | Sym. NH$^+$ stretching |
| 1448 | 1440 | Asym. NH$^+$ stretching |
| 1034 | 1029 | Sym. SO$_3$ stretching |
| 994 | 996 | Dege., NH$^+$ rocking |
| 680 | 700 | N–S stretching |
| 557 | 600 | SO$_3$ deformation |

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Fig. 4. (a) UV-VIS for SEST and SR grown Eu$^{3+}$:SA crystals. (b) Plot of $\alpha$ vs. photon energy.
Tb\(^{3+}\):SA single crystals, respectively and this reveals that they could be useful for various applications. Such excellent transparency confirms the colourless nature of the grown crystals. The transparency of the doped sulfamic acid crystals was found to decrease with the increasing doping concentration. The transmittance of the SR grown Tb\(^{3+}\):SA crystal is higher than that of the SEST grown Tb\(^{3+}\):SA and this improvement in the transmittance may be because of the reduced scattering from the crystal’s point and line defects [4]. It is observed that the transparency range is improved for the SR grown Tb\(^{3+}\):SA than the SEST grown SA. The grown crystals are found to possess a wide transparency region from 259 nm to the far IR region as it is shown in Fig. 4(a). There is no appreciable absorption of light in the entire visible range. The improved optical transparency range is very much desirable for this material to be used as an NLO material. The linear and nonlinear optical properties of the semi-organic crystals are due to photo induced effect [24].

3.5. Optical band gap

To determine optical energy gap for the grown Tb\(^{3+}\):SA crystals the absorption coefficients (\(\alpha\)) values were used. The measured transmittance (\(T\)) was used to calculate the optical absorption coefficient (\(\alpha\)) with the help of the relation:

\[ \alpha = - \frac{1}{t} \ln(T) \]

where \(t\) is the thickness and \(T\) is the transmittance of the grown crystals. The grown crystals of thickness 3 mm were used to determine the optical absorption co-efficient (\(\alpha\)) from the transmittance measurements. Fig. 4(b) shows the plot of \((\alpha h\nu)^2\) vs. \(h\nu\), where \(\alpha\) is the optical absorption coefficient and \(h\nu\) is the energy of the incident photons. The energy gap (\(E_g\)) is determined by extrapolating the straight line portion of the curve to \((\alpha h\nu)^2 = 0\) [25]. The direct band gap energy (\(E_g\)) of the Tb\(^{3+}\):SA crystals grown by SEST and SR methods are the found as 3.9 eV and 4.0 eV, respectively, which are in good accordance with the reported values. The value of the band gap of sulfamic acid was found to decrease with the increase in the impurity concentration [26].

3.6. Thermogravimetry (TG) and differential thermal analysis (DTA)

Thermogravimetry (TG) and differential thermal analysis (DTA) curves of the Tb\(^{3+}\) doped sulfamic acid single crystals were measured at a heating rate 10 °C/min between 25 and 800 °C in the nitrogen atmosphere using a Perkin Elmer Diamond analyzer. The thermogravimetric and differential thermal analysis (TG/DTA) spectrum recorded for the Tb\(^{3+}\) doped sulfamic acid single crystals grown by SR method is shown in Fig. 5. It is observed that there is no weight loss of the samples in temperatures up to 190 °C. There is an increase in weight in the temperature range from 190 °C to 242 °C; then is an abrupt loss in weight in the range from 242 °C to 440 °C. The total weight losses can be observed at 441 °C onwards. The nature of the weight loss indicated the decomposition point of the material. In DTA an endothermic peak is noticed at 189 °C which corresponds to the decomposition of the crystal. A systematic weight loss was observed when the temperature was further increased to above the melting point. It is noticed that the total decomposition of the crystals takes place at a temperature of 440 °C for the Tb\(^{3+}\):SA grown crystals. Hence, these compounds reveal good thermal stability up to 190 °C. We can, therefore, conclude that the grown crystals are suitable for applications up to 190 °C.

3.7. Surface morphology of the Tb\(^{3+}\):SA grown crystals

The influence of the dopants on the surface morphology of grown Tb\(^{3+}\):SA single crystals were studied by Scanning Electron Microscope (VEGA SEM, TESCAN) at 392× and 2390× magnification factor as depicted in Fig. 6(a) and (b), respectively. To discharge the
particles, the transparent growth plane of the grown crystal was coated with gold and scanned at two different temperatures. The morphology of the crystals shows agglomeration and no uniform size and shape. This non-uniformity in the size and shape is because of the non-uniform distribution of the temperature and of the mass flow in the combustion flame during the combustion process. However, smooth densely packed small tetragonal particles with few pores are observed in the SEM image at a higher (2390 x) magnification and particles are seen to share the edges with one another resulting large surface area.

3.8. Energy dispersive X-ray analysis (EDAX)

The existence of the Terbium ($\text{Tb}^{3+}$) ions in the crystalline lattice was confirmed by the EDAX analysis, a procedure for identifying the elemental composition of grown sample. Fig. 6(c) shows the EDAX spectrum of the $\text{Tb}^{3+}$:SA crystals recorded on a keV x delta class I micro analyzer attached to a JEOL (JSM-253, SEM), which suggests the small percentage of Terbium ($\text{Tb}^{3+}$) present in the EDAX spectra. In the EDAX spectra, the intense and broad peaks corresponding to the N, O, S elements and lower peaks indicating the Tb element are present which confirm the formation of the $\text{Tb}^{3+}$:SA composition. No other emission appeared apart those from Nitrogen (N), Oxygen (O), Sulphur (S) and Terbium ($\text{Tb}^{3+}$).

3.9. Micro hardness studies

The resistance of a material to the motion and displacement of dislocations, deformations or defects under an applied stress is measured by the hardness of the crystal. The ratio of the applied load to the projected area indentation gives the hardness. High purity and good quality crystals are known to have the minimum load to the projected area indentation. The Vicker’s micro hardness of the samples was measured using the Mitutoyo model MH 120 micro hardness tester. Vicker’s micro hardness indents formed on the SR grown crystals were measured using the Mitutoyo model MH 120 micro hardness tester. Vicker’s micro hardness indentation marks were made at room temperature by applying loads of 25, 50 and 100 g on the surface of the grown crystals. The diagonal lengths of the indentation ($d$) were measured in $\mu$m for various applied loads ($P$) in g. The Vickers hardness number ($H_v$) was calculated from the following relation:

$$H_v = \frac{1.8544P}{d^2} \text{Kg/mm}^2$$

where $P$ is the indentation load in kg and $d$ is the diagonal length of the impression in millimetre, 1.8544 is a proportional constant. The indentation marks were made at room temperature by applying loads of 25, 50 and 100 g on the surface of the grown crystals. Fig. 7(a) shows the variation of $P$ versus Vickers hardness number ($H_v$) for the pure $\text{Tb}^{3+}$:SA single crystals grown by the SEST and the SR method. From the plot, it is clearly to see that the Vickers micro hardness number of the grown crystals increases with the load applied up to $P = 46, 56, 60$ g. Above 46, 56, 60 g in the grown crystals cracks have been formed due to the release of internal stress and, hence, the hardness number decreased further with the increase in load satisfying the indentation size effect (ISE). The fact that the micro hardness of the $\text{Tb}^{3+}$:SA single crystals increases with the increasing load infers that the incorporation of the $\text{Tb}^{3+}$ ions enhances the hardness of SA. The increase in hardness will have a significant effect on fabrication and process, such as less wastage due to cracking/breaking while polishing. The plot of Vickers’s hardness ($H_v$) against load drawn for all crystals reveals that the variation of Vickers’s hardness with load is non-linear [5]. The relationship between load and the size of the indentation is given by well-known Meyer’s law $P = k_1d^n$, where $k_1$ is a constant and $n$ is the Meyer index or the work hardening exponent for a given material. The work hardening coefficient was calculated from the plot of log $P$ versus log $d$, and results are shown in Fig. 7(b), with fitting data before cracking. Least square fitting gives straight-line graphs, which are in good accordance with Meyer’s law. The value of $n$ is found from the slope of the graph. According to Haneman and Onitsch [28] $n$ should lie between 1 and 1.6 for hard materials and above 1.6 for softer materials. Thus $\text{Tb}^{3+}$:SA belongs to soft material group.

3.10. Dielectric studies

The measurement of the dielectric constant as a function of the frequency and the temperature is of immense interest in the field of NLO. Dielectric properties are useful to describe the electrical properties of the material media, because the dielectric properties of the grown crystals are correlated with electro-optic properties [29]. In the present study the dielectric constant and the dielectric loss of the $\text{Tb}^{3+}$:SA single crystals are discussed in term of a function of temperature and frequency using the Way nay Kerr Impedance Analyzer. The dielectric constant can be calculated using the relation:

$$\varepsilon_r = C_0d/\varepsilon_0A$$

where $d$ is the thickness and $A$ is area of the sample. A graph is plotted between dielectric constant ($\varepsilon_r$) versus the logarithm of the frequency for different temperatures 30°C, 60°C, 90°C and 120°C for the $\text{Tb}^{3+}$:SA single crystals. From Fig. 8 presenting the frequency dependence of the dielectric constant at various temperatures for the $\text{Tb}^{3+}$:SA (SEST) crystal and the SR crystal (see the inset), we can conclude that the dielectric constant is high at low frequencies due
to the space charge polarization, which depends on the purity and the perfection of the samples. The maximum values of the dielectric constant are 6.9, 6.8 and the minimum values are 1.4, 1.2, respectively, for SR and SEST grown Tb⁺³:SA single crystals. A graph is drawn between the dielectric loss and the logarithm of the frequency for different temperatures 30°C, 60°C, 90°C and 120°C. As seen in Fig. 9c and d, it is observed that the dielectric loss decreases as frequency increases. The low dielectric loss at high frequency of the grown crystals shows that these materials possess better optical quality with lesser defects [30].

3.11. NLO property

A prominent property of nonlinear optical crystals is the generation of higher harmonics. The second harmonic generation (SHG) efficiency test was performed using Kurtz Perry technique by illuminating the crystal with Q-switched Nd: YAG laser of wavelength 1064 nm, pulse width 10 ns and power ~2.5 mJ. The generation of the second harmonic was confirmed by the emission of green light. The second harmonic signals for undoped, SEST and SR grown Tb⁺³:SA were found at 30 mV, 34 mV, 36 mV which are about 3.0, 3.4 and 3.6 times, respectively, when compared with standard KDP, which is confirmed by green emission. Doping the impurities increases the SHG efficiency of the pure SA crystal, which is in good agreement with previously reported values [5]. The enhancement of the NLO efficiency is owing to the increase in the percentage of transparency of the doped SA single crystals. Hence, Tb⁺³ ion enhances the nonlinear optical property in the SR grown crystal compared with the pure and the doped SEST grown SA crystals.

3.12. Photoluminescence studies

The emission spectrum of the Tb⁺³:SA single crystal are depicted in Fig. 10(a). Under the excitation of the 263 nm light, the samples exhibit an excellent luminescence. It displays four emission peaks between 490 and 650 nm, which can be assigned to the 4f⁶→4f⁸ transition within the Tb 3⁺ 4f⁸ electron configuration [29]. The emission spectrum consists of 5D₄→7F₅ at 490 nm in the blue region and 5D₄ to 7F₂ at 543 nm in the green region, as well as 5D₄→7F₄ at 584 nm and 5D₄→7F₃ at 619 nm in the red region. The strongest peak at 543 nm should be assigned to the characteristic green emission arising from the 5D₄ to 7F₅ transition of Tb⁺³ ions. The excitation spectrum shown in the Fig. 10 (inset) recorded by the green emission at λ_em = 543 nm contain peak at 263 nm which is attributed to the 4f→5d (f-d) transition of Tb⁺³. The schematic Energy level diagram of Terbium doped sulphamic single crystal is shown in Fig. 11.

![Fig. 8. Frequency dependence of dielectric constant at various temperatures for Tb⁺³:SA (SEST) crystal and the SR crystal (see the inset).](image)

![Fig. 9. Frequency versus dielectric loss for Tb⁺³:SA (SEST) crystal and SR crystal (inset).](image)

![Fig. 10. Emission and excitation (inset) spectrum of Tb⁺³:SA (SR) single crystal.](image)

![Fig. 11. Energy levels of Tb⁺³ ion with main transitions.](image)
3.13. Decay curve of Tb$^{3+}$:SA single crystal

In the Tb$^{3+}$ doped SA single crystal the luminescence decay is very long because the $f$–$f$ transitions in Tb$^{3+}$ are spin and parity forbidden. The decay curve of the Tb$^{3+}$ doped SA single crystal with $\lambda_{ex} = 263$ nm and $\lambda_{em} = 543$ nm is shown in Fig. 12. The decay curve of Tb$^{3+}$ doped SA single crystal corresponds to $D_4$ level of Tb$^{3+}$ and is found to be single exponential with a lifetime value of 1.37 ms.

4. Conclusion

Bulk single crystals of Tb$^{3+}$ added sulfamic acid single crystals have been grown by SEST and unidirectional methods at low temperature. Single crystal X-ray diffraction studies confirm that the grown crystal belongs to an orthorhombic system. HRXRD analysis confirms better crystalline perfection of the SR grown crystal compared with those grown by SEST. Functional groups were identified by FTIR spectrum and the shift observed in the pure and the Tb doped crystals from 680 to 726 cm$^{-1}$ is attributed to the N–S stretching and that from 557 to 600 cm$^{-1}$ is attributed to the SO$_3$ deformation confirming the incorporation of the dopant. The optical transmission analysis indicates that Tb$^{3+}$:SA has a wide transparency with a lower cutoff wavelength at 259 nm. The band gap is determined to be 4.20 eV. The crystals have good thermal stability up to 190 °C. The presence of the terbium ions in the crystal lattice is confirmed using energy dispersive X-ray analysis (EDAX). The Vickers micro hardness test carried along the (100) plane confirmed that the crystal belongs to a soft materials group. Dielectric study showed that the higher dielectric constant and the lower value of the dielectric loss are due to less defects that are present in the Tb$^{3+}$:SA crystal grown by the SR method. The Tb$^{3+}$:SA crystals have SHG efficiency 3.6 times larger than that of the standard KDP crystal. In the photoluminescence studies, the strongest peak arising from the $^7F_5$ to $^5D_4$ transition at 543 nm shows the characteristic green emission of the Tb$^{3+}$ ions. The decay curve of the $D_4$ level of emission was observed with a long life time of 1377.11 μs. HRXRD, dielectric constant, dielectric loss, optical transmittance and mechanical strength studies shows that the SR method is a capable method to grow crystals of good crystalline perfection with high optical quality and good mechanical stability. Thus, the excellent luminescence emission makes Tb$^{3+}$:SA crystals, a potential candidate for detector applications.

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