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Monocrystal growth, X-ray diffraction, photoluminescence, thermal and dielectric studies of cadmium thiourea acetate complex doped with L- cystine

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ABSTRACT

Single crystal of L-cystine (LC) doped cadmium thiourea acetate (CTA) material has been grown by slow solution evaporation technique. The crystalline phase and structural parameters of LC doped CTA crystal has been evaluated using the powder X-ray diffraction technique. The color centered emission in grown crystal has been examined in the visible region of interest using the photoluminescence study. The thermal stability and the melting point of LC doped CTA crystal has been investigated using the simultaneous thermogravimetric and differential thermal analysis (TG/DTA) technique employed in the temperature range of 50–500 °C. The dielectric properties of pure and LC doped CTA crystal has been comparatively investigated at different temperatures by means of dielectric measurement study.

1. Introduction

The ever increasing demand of organometallic single crystals for optoelectronics, photonics, laser frequency conversion, optical switching and data storage devices has encouraged the approach of many researchers to focus on the development of semiorganic nonlinear optical thiourea metal complex (TMC) crystals [1,2]. A large number of crystals from TMC family have been under extensive study which include bis thiourea cadmium chloride, zinc thiourea sulphate, potassium thiourea iodide, bis thiourea zinc acetate, zinc thiourea chloride, copper thiourea chloride and cadmium thiourea acetate (CTA) [3,4]. In few recent studies the researchers have explored that the doping of selected quantity of external additive/impurity plays crucial role in modifying the characteristic properties of host crystal in constructive manner [5,6]. On the other hand, to achieve improved quality of the crystal the amino acids are observed to be the most effective dopant in case of TMC crystal and more particularly the CTA crystal. The appreciable enhancement in structural, optical, dielectric, NLO and mechanical properties of CTA crystal has been achieved by doping glycine and L-alanine [7] . In similar manner, very recently our group has reported the significant impact of L-cystine (LC) on UV–vis, SHG efficiency, third order nonlinear optical, laser damage

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Fig. 1. LC–CTA single crystal.

threshold and surface properties of CTA crystal. The LC doped CTA crystal was found to be promising NLO material with the laser damage threshold value of 7.58 GW/cm^2 [8]. However, the photoluminescence, thermal and dielectric properties of LC doped CTA crystal were not studied. Therefore, in present investigation we report the extended work on LC doped CTA (LC–CTA) crystal by attempting the good quality single crystal growth of LC–CTA material followed by powder X-ray diffraction, photoluminescence, thermal and dielectric characterization study.

2. Experimental procedure

The CTA crystal complex has been synthesized by dissolving 1:2 mole concentrations of cadmium acetate and thiourea in double distilled de-ionized water. The CTA complex was repeatedly recrystallized to minimize the impurities and enhance the purity of complex. In order to dope LC in CTA crystal the precisely measured 2 mole of LC was gradually added to the supersaturated solution of CTA. The LC added CTA solution was allowed to stir for six hours and later the solution was filtered in a rinsed beaker and kept for slow solution evaporation in a constant temperature bath at 38 ($\pm$0.01) $^\circ$C. To achieve improved crystalline quality the LC doped CTA crystal material was successively recrystallized for four times and the grown good quality LC doped CTA (LC–CTA) single crystal harvested within 2 weeks is shown in Fig. 1.

3. Results and discussion

3.1. Powder X-ray diffraction (PXRD) study

The PXRD pattern of LC-CTA crystal has been recorded using the Rigaku Miniflex (II) powder X-ray diffractometer with the scan rate of 0.02°/sec in the 2θ range of 10–70°. The PXRD pattern of the LC–CTA crystal shown in Fig. 2a reveals sharp diffraction peaks which were indexed using the powderX software (the 2θ error was 0.01). The grown LC-CTA crystal is confirmed to be oriented with orthorhombic crystal structure and the determined cell parameters are a = 7.541 Å, b = 11.818 Å, c = 15.893 Å with cell volume V = 1416.37 (Å) ^{3}. The evaluated cell parameters of LC–CTA crystal are in close agreement with our earlier reported work [8]. It is also evident that the LC–CTA crystal express sharp diffraction peaks which indicates that the crystal possesses lesser grain boundaries and excellent crystalline nature [9,10].

3.2. Photoluminescence study

The electronic impurities and transitions governed by the recombination of different energy states associated with material can be effectively probed by examining the photoluminescence nature of the material in visible region [11]. In present analysis the grown crystal has been characterized by the photoluminescence study using the HIOKI-3540 FL spectrophotometer. The LC–CTA crystal material has been photo-excited with the energy wavelength of 330 nm and the emission spectrum has been recorded in the range of 400–580 nm. The PL spectrum shown in Fig. 2b reveals that the LC–CTA crystal exhibits single color emission centered at 464 nm corresponding to blue color and the energy of 2.67 nm. The expressed single emission peak evidences the improved electronic impurity of LC–CTA crystal. The lower intensity in the higher wave-

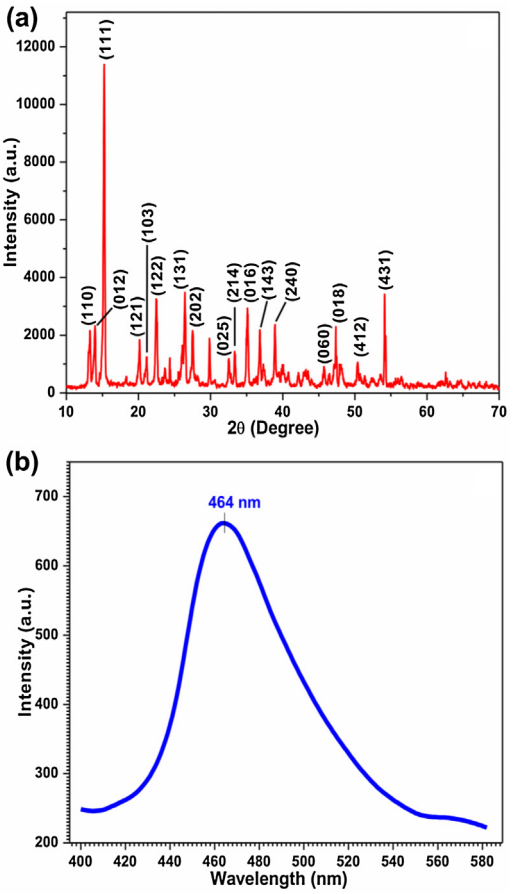

Fig. 2. (a) PXRD pattern of LC–CTA crystal (b) PL emission spectrum of LC–CTA crystal.

length region might have been occurred due to the less rotation of carboxyl group around the C–C bond accompanied within crystal [12].

3.3. Thermal analysis

The LC–CTA crystal has been characterized by simultaneous thermogravimetric and differential thermal analysis (TG/DTA) in the temperature range of 50 to 500 °C using the SQT-600 thermal analyzer. The TG/DTA thermogram of LC–CTA crystal was recorded in the homogeneous nitrogen atmosphere by increasing the temperature by 20 °C min^{-1} as shown in Fig. 3a. The TGA curve reveals that the grown crystal material shows no weight loss up to 174 °C on the contrary the sharp exothermic peak at 170 °C in DTA curve resembles to the melting point of LC–CTA crystal. The sharpness of the peak confirms the good crystalline nature of material [13], which is observed in DTA curve of LC–CTA crystal material. Further increase in temperature above 174 °C causes rapid decomposition of compound in steps. The significant weight loss of compound might have been attributed by the rapid decomposition of volatile and unstable constituents associated with the LC–CTA crystal compound. The exothermic peaks attributed at 207 °C and 263 °C in DTA are also in corroboration with the step wise decomposition of LC–CTA crystal material as observed in TGA curve. As laser driven device applications demand materials with high temperature, the LC–CTA crystal might be subjected to frequency conversion device applications up to 174 °C.

3.4. Dielectric studies

The dielectric parameters of pure and LC-CTA crystal has been measured in the range of 35 to 100 °C using the HIOKI 3532 LCR tester. Before analysis the pure and LC–CTA crystal samples of thickness 2 mm were smoothly polished to prepare flat surface and were gently applied by the silver paste to measure accurate data. The temperature dependent dielectric response of pure and LC–CTA crystal is shown in Fig. 3b. In bulk crystals the dielectric constant is attributed by the ionic, electronic, dipolar and space charge polarization activity which are highly influenced by external electric field as well as temperature [14]. At lower temperatures the dielectric constant is attributed by all foresaid polarization mechanism however, as the temperature of the material is increased the dielectric constant is majorly contributed by active space charge polarization

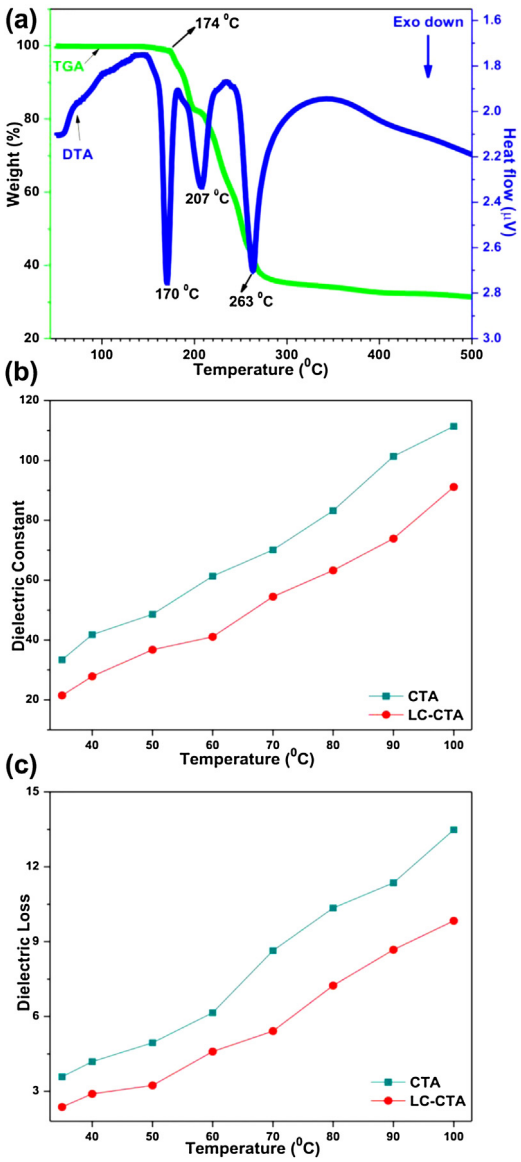

Fig. 3. (a) TG/DTA thermogram of LC–CTA crystal (b) Dielectric constant (c) Dielectric loss.

itself [15]. In millers study the lower dielectric constant favors enhancement in second harmonic generation (SHG) efficiency of material [16] which is in agreement with observed enhancement in SHG efficiency of LC–CTA crystal [8]. Amongst the studied crystals the LC–CTA crystal exhibits lower dielectric constant and the materials with lower dielectric constant consume less power which is vital factor for designing broad band electro-optic modulators and field detectors [17]. The dielectric loss attributed by grown crystals is plotted in Fig. 3c. The analysis of dielectric loss gives an understanding of loss of energy associated with intrinsic and extrinsic defects present in bulk crystal [18]. The LC–CTA crystal possesses lower dielectric loss as compared to CTA indicating the occurrence of relatively less electrically active defects [19]. It is notable that the dielectric constant and dielectric loss of LC–CTA crystal is lower as compared to CTA which designates LC–CTA crystal as a potential candidate for designing photonics, THz wave generators and optoelectronics devices [20,21].

4. Conclusion

The good quality LC–CTA single crystal has been successfully grown by slow solution evaporation technique at a temperature of 38 °C. In PXRD analysis, the grown crystal was revealed to have orthorhombic structure and the sharp diffraction peaks confirmed good crystalline nature of LC–CTA crystal. The photoluminescence study revealed that the LC–CTA crystal exhibits blue colored emission with peak maxima centered at 464 nm in visible spectrum. In TG/DTA analysis the melting

point of LC–CTA crystal is found to be 170 °C and the thermal stability is up to 174 °C. The doping of LC facilitated significantly lower dielectric constant and dielectric loss to CTA crystal throughout the temperature range of 35–100 °C. All above studies infer that the LC–CTA crystal possesses good crystalline quality, promising luminescence nature, high thermal stability and lower dielectric constant which make it appealing candidate for designing optoelectronics and NLO device applications.

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References

[1] Mohd Anis, S.S. Hussaini, M.D. Shirsat, Optik 127 (2016) 9734–9737.
[2] Mohd Anis, S.S. Hussaini, M.D. Shirsat, G.G. Muley, Mater. Res. Innov. 20 (2016) 312–316.
[3] Mohd Anis, S.S. Hussaini, A. Hakeem, M.D. Shirsat, G.G. Muley, Optik 127 (2016) 2137–2142.
[4] G. Pabitha, R. Dhanasekaran, Opt. Laser Technol. 50 (2013) 150–154.
[5] S.S. Kirupavathy, S.S. Mary, P. Mythili, R. Gopalakrishnan, J. Cryst. Growth 310 (2008) 2555–2562.
[6] Mohd Shkir, V. Ganesh, N. Vijayan, B. Riscob, Anoop Kumar, Devendra Kumar Rana, Mohd Shoeb Khan, Mohd Hasmuddin, M.A. Wahab, R. Ramesh Babu, G. Bhagavannarayana, Spectrochem. Acta A 103 (2013) 199–204.
[7] V. Ganesh, T. Bhaskar Rao, K. Kishan Rao, G. Bhagavannarayana, Mohd Shkir, Mater. Chem. Phys. 137 (2012) 276–281.
[8] S.M. Azhar, Mohd Anis, S.S. Hussaini, S. Kalainathan, M.D. Shirsat, G. Rabbani, Opt. Laser Technol. 87 (2017) 11–16.
[9] Mohd Anis, G.G. Muley, M.D. Shirsat, S.S. Hussaini, Cryst. Res. Technol. 50 (2015) 372–378.
[10] M.S. Pandian, K. Boopathi, P. Ramasamy, G. Bhagavannarayana, Mater. Res. Bull. 47 (2012) 826–835.
[11] H.Gfroerer Timothy, Photoluminescence in analysis of surfaces and interfaces, in: Encyclopedia of Analytical Chemistry, Chichester, John Wiley & Sons Ltd., 2000, pp. 9209–9231.
[12] N.N. Shejwal, Mohd Anis, S.S. Hussaini, M.D. Shirsat, Optik 127 (2016) 6525–6531.
[13] S. Anbu Chudar Azhagan, S. Ganesan, Optik 124 (2013) 6456–6460.
[14] S.M. Azhar, Mohd Anis, S.S. Hussaini, M.D. Shirsat, G. Rabbani, Optik 127 (2016) 4932–4936.
[15] R.N. Shaikh, Mohd Anis, G. Rabbani, M.D. Shirsat, S.S. Hussaini, Optoelectron. Adv. Mater. Rapid Commun. 10 (2016) 526–531.
[16] R.C. Miller, Appl. Phys. Lett. 5 (1964) 17–19.
[17] Mohd Anis, G.G. Muley, Phys. Scr. 91 (2016) 85801–85808.
[18] Min-hua Jiang, Qi Fang, Adv. Mater. 11 (1999) 1147–1151.
[19] N.N. Shejwal, Mohd Anis, S.S. Hussaini, M.D. Shirsat, Int. J. Mod. Phys. B 30 (2016) 1650159–1650170.
[20] Mojca Jazbinsek, Lukas Mutter, Peter Gunter, Int. J. Sel. Top. Quantum. Electron. 14 (2008) 1298–1311.
[21] Mohd Anis, S.S. Hussaini, M.D. Shirsat, G.G. Muley, Mater. Sci. Poland (2016), http://dx.doi.org/10.1515/msp- 2016-0070.