Growth and characterization of semiorganic nonlinear optical rubidium bis-DL-malato borate single crystals

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Abstract

A new semiorganic nonlinear optical rubidium bis-DL-malato borate (RBMB) has been synthesized and single crystals were grown by slow cooling technique from aqueous solution. The grown crystals have been characterized by X-ray diffraction (single crystal XRD) to confirm the formation of the crystalline phases. FT-IR and FT-Raman spectroscopic analyses confirm the presence of all the functional groups in the grown crystals. TG-DTA studies reveal that the material is stable up to 230 °C. The UV–vis transmission spectrum shows a lower cutoff wavelength of 230 nm. The emission of SHG using Nd:YAG laser is confirmed by a modified Kurtz and Perry powder setup.
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1. Introduction

Extensive investigations have been made on organic nonlinear optical (NLO) materials due to their high nonlinearity, variety of syntheses methods and better laser damage resistance. The microscopic origin of nonlinearity in these molecular NLO materials is due to the presence of delocalized π-electrons systems, connecting donor and acceptor groups, which enhance their asymmetric polarizability. In the actual applications, these crystals have certain inherent limitations such as, increased optical absorption and narrow transparency window, in addition to poor mechanical and thermal stability. To overcome these difficulties, a new strategy of synthesizing organic–inorganic hybrid compounds have been proposed, thus leading to a new class of materials namely, the semiorganics. In this class of materials, the organic ligand is ionically bonded to a suitable metal ion or an inorganic host, thereby imparting improved mechanical and thermal properties. Many efforts are being taken to develop and to study new nonlinear optical materials with specific properties such as large second harmonic generation, effective nonlinear coefficient, short UV cutoff

and moderate birefringence allowing phase matching angles. The development of nonlinear optical semiorganic materials leads to applications, such as frequency conversion by NLO crystals, light amplitude and phase modulation and phase conjugation due to their large nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness [1–3]. The contribution from the delocalized π-electrons of the organic ligand results in increased nonlinear optical and electro-optical behavior in the semiorganic materials. Prominent NLO materials like, L-arginine phosphate monohydrate (LAP), zinc Tris–thiourea sulphate (ZTS), bis-thiourea cadmium chloride (BTCC), L-histidine tetrafluoroborate (L-HFB), L-arginine hydro bromide (L-AHBr) [4], L-histidine tetrafluoroborate (LHFB) [5], L-arginine tetrafluoroborate (L-AFB) [6], L-alanine tetrafluoroborate (L-AlFB) [7], L-arginine fluoride (L-AHF) [8], L-arginine acetate [9] and L-alanine acetate [10] have been synthesized from this semiorganic approach.

In the present investigation, an attempt has been made to grow single crystals of a borate material by solution-growth technique at low temperatures. Further, this class of semiorganic borate materials, as a modification over the existing purely inorganic borates is expected to incorporate the advantages of the semiorganic class. Hence we have chosen a bis-DL-malato borate anion, which had a rich combination of the chiral α

dihydroxy functionality, DL-malic acid along with a tetra-coordinated boron atom and a prominent alkali cation, Rb to grow single crystals of rubidium bis-DL-malato borate (RBMB). Bulk crystals have been grown by slow cooling technique. The grown crystals were characterized for their structural, thermal, optical and mechanical properties.

2. Synthesis of RBMB and seed crystals preparation

Seed crystals of RBMB with stoichiometric composition was prepared by taking rubidium carbonate, boric acid and DL-malic acid in the ratio 0.5:1:2, respectively. The required amount of precursor materials for the synthesis of RBMB salt was calculated according to the reaction:

$$0.5Rb_2CO_3 + H_3BO_3 + 2C_4H_6O_5$$
$$\rightarrow C_8H_8BRbO_{10} + 0.5CO_2 + 3.5H_2O$$
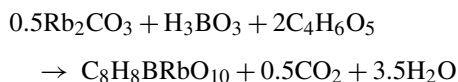
The calculated amounts of the boric acid and DL-malic acid were thoroughly dissolved in double distilled water using a temperature controlled magnetic stirrer. Then the calculated amount of rubidium carbonate was added slowly and stirred well using a magnetic stirrer for about 4 h for the completion of the reaction. After reaching the saturated level, it is evaporated to dryness to get the seeds of RBMB crystals. The saturation is obtained at 45 °C. The crystal quality was improved by repeated recrystallization process.

2.1. Solubility study

The solubility of RBMB was determined for four different temperatures 30, 35, 40 and 45 °C. The solubility was determined by dissolving the RBMB salt in deionized water in an airtight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analysed gravimetrically. The solubility curve of the RBMB is shown in Fig. 1.
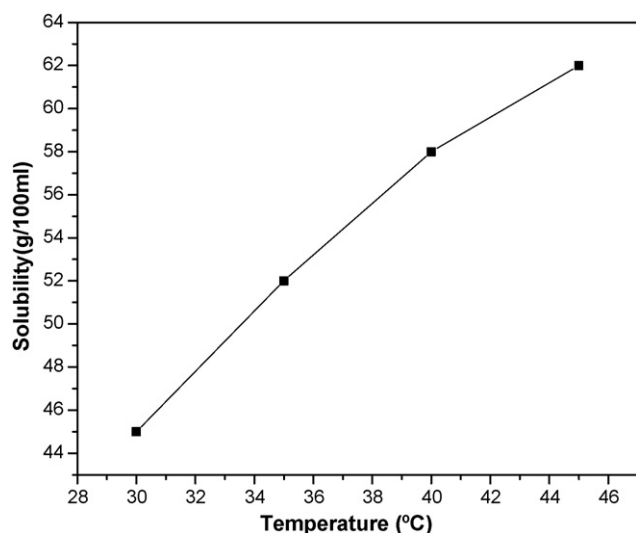

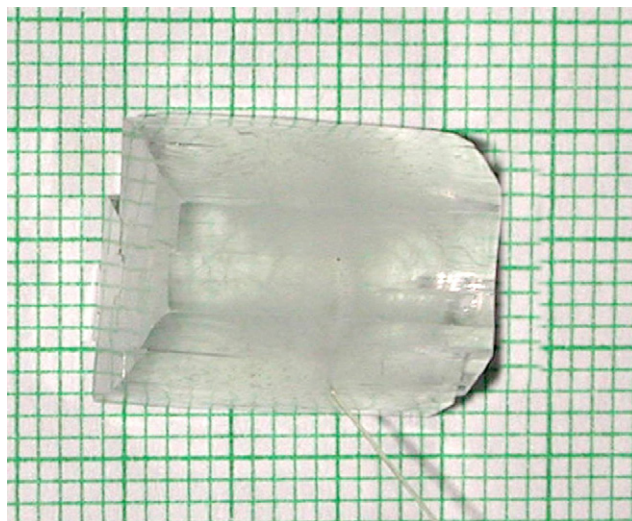Fig. 1. Solubility of RBMB in aqueous solution.

Fig. 2. RBMB single crystal grown by slow cooling method from aqueous solution.

3. Bulk growth of RBMB single crystal

Bulk growth of RBMB single crystal was carried out by low temperature solution-growth technique adopting slow cooling, in a constant temperature bath controlled to an accuracy of ±0.01 °C. An amount of 300 ml of the solution was saturated at 45 °C and then filtered to remove any insoluble impurities. Good quality of seed crystals obtained from slow evaporation was employed for the growth. The solution was maintained at 45 °C for 2 days before seeding. The temperature reduction was at the rate of 0.03–0.2 °C per day as growth progressed. The period of growth ranged from 30 to 35 days. An optical quality crystal of RBMB with dimensions 16 mm × 13 mm × 4 mm was grown as shown in Fig. 2.

4. Characterization studies

Single crystal X-ray diffraction analysis was carried out using an ENRAF-NONIUS-FR-590, CAD4, automatic X-ray diffractometer with Mo Kα radiation of wavelength, $\lambda = 0.717$ Å to confirm the structure and to estimate the lattice parameter values. Powder X-ray diffraction analysis was also carried out using a Rich Seifert diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation to verify the correctness of lattice parameter values. To confirm the nonlinear optical property, Kurtz powder SHG test was performed on the grown crystals. The FT-IR spectra of RBMB crystals were recorded in the range 400–4000 cm^{-1} employing a Perkin-Elmer spectrometer by KBr pellet method in order to study the metal complex coordination and to confirm the presence of functional groups. Linear optical properties of the crystals were studied using a Shimadzu UV–vis spectrophotometer. The Vickers's hardness measurement was carried out on the grown crystals to assess the mechanical property. TGA and DTA analyses are of immense importance as far as fabrication technology were concerned, as they provide thermal stability of the material for fabrication where a considerable amount of heat is generated during the cutting process. Thermal analysis
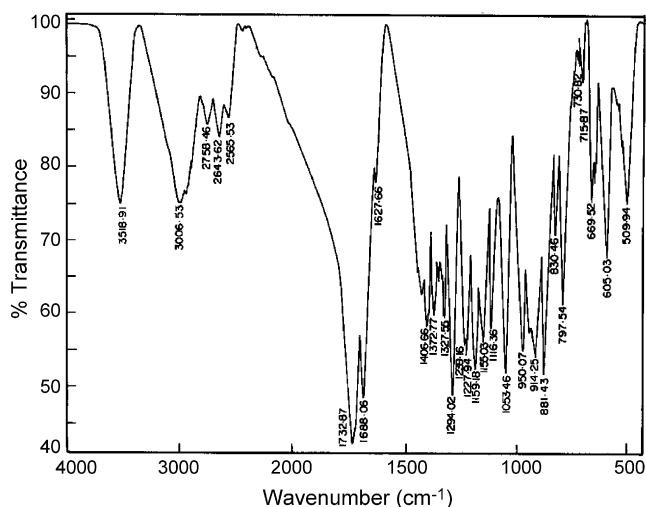
Fig. 3. FT-IR spectrum of RBMB crystals.

was performed on the RBMB crystal in the temperature range RT-850 °C.

4.1. Single crystal X-ray diffraction analysis

For the single crystal X-ray diffraction analysis, small crystal of dimension 0.3 mm × 0.3 mm × 0.3 mm was mounted on a four-circle goniometer for measurement of the unit cell parameter. The cell dimensions are measured to be $a = 5.3927$ Å, $b = 11.4938$ Å, $c = 21.1508$ Å, $\alpha = \beta = \gamma = 90°$, volume = 1310.9725 Å. The studies confirm the orthorhombic structure of the grown crystals.

4.2. FT-IR and FT-Raman spectral analysis

The FT-IR spectrum of the RBMB compound has been obtained in the range of 400–4000 cm^{-1}, by KBr pellet technique as shown in Fig. 3. The FT-Raman spectrum obtained by FT-Raman Bruker IFS66 is also shown in Fig. 4. Comparison of both the spectra shows that the higher wave number region shows the characteristic peak and provides interesting information
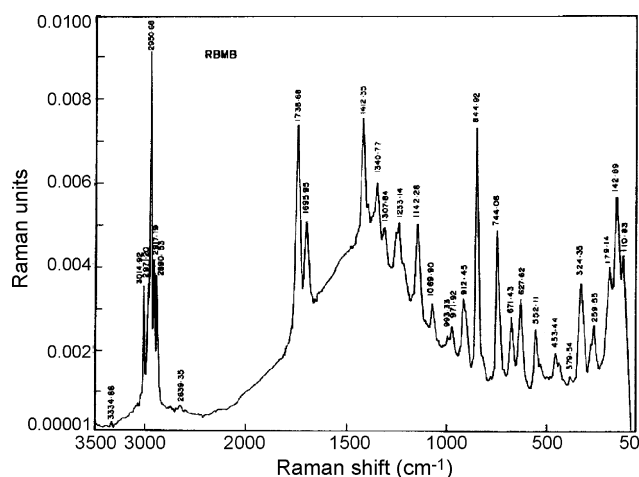

Fig. 4. FT-Raman spectrum of RBMB crystals.

Table 1
Comparison of characteristics absorption of FT-IR and FT-Raman spectral analyses

Wave number (cm^{-1})		Assignments
FT-IR	FT-Raman	
3818.91	3334.66	O—H stretching
3006.53	3014.92	C—H stretching
1732.87	1738.68	C=O stretching
1327.55	1340.77	CH$_2$ wagging
1116.36	1142.28	C—H in plane bending
914.25	912.45	Asymmetric stretching of BOO$_4$ tetrahedra
830.46	844.92	C—H out of plane bending
669.52	671.43	C=O in-plane bending
550	552.11	Symmetric stretching of BO$_4$ tetrahedra
	453.44	C=O out of plane bending

about the bonding of the functional group present in the crystal. The carboxylic OH–groups (CO–OH) gives rise to stretching vibrations around 3518.9 cm^{-1} in the form of a very broad O–H absorption in FT-IR which is obtained at 3334.66 cm^{-1} in FT-Raman. The weaker C–H stretching bonds at 2758, 2643 and 2565 cm^{-1} are seen superimposed upon the broad O–H bond in FT-IR, which is seen at 3014.92 cm^{-1} in FT-Raman. The normal dimeric carboxylic C=O stretching is observed at 1732.87 cm^{-1} in FT-IR which is obtained at 1738.68 cm^{-1} in FT-Raman. C–H in plane bending and C–H out of plane bending modes occur at 1116.36 and 830.46 cm^{-1}, respectively, in FT-IR, which is obtained at 1142.28 and 844.92 cm^{-1} in FT-Raman. The wave number of the symmetric stretching vibrations and the asymmetric stretching vibrations of the BO$_4$ tetrahedra are around 550 and 914.25 cm^{-1}, respectively, in FT-IR and was obtained at 552.11 and 912.45 cm^{-1} in FT-Raman. The compound vibrations occur at 605.03 and 914.25 cm^{-1} in the FT-IR spectrum thereby confirming the presence of the BO$_4$ tetrahedra in the molecular structure. Other characteristic absorptions are given in the comparison Table 1.

4.3. Optical transmission and NLO property studies

Optical transmission spectrum was recorded using a 2 mm thick c-cut crystal plate. The recorded transmission spectrum is shown in Fig. 5. From the spectrum, it is evident that RBMB crystal has UV cutoff 230 nm, which is sufficient for SHG laser radiation of 1064 nm or other application in the blue region. Kurtz powder SHG test confirmed the nonlinear property of crystal. In this technique, the sample was packed as a polycrystalline powder into a cell sandwiched between two glass slides and exposed to a Q-switched Nd:YAG laser emitting 1064 nm, 10 ns laser pulses with spot radius of 1 mm to assess the SHG intensity. The powder SHG conversion efficiency is two times greater than the KDP crystal. It is very clear that this crystal has potential and prospects for frequency conversion applications.

4.4. Thermal studies

The TG-DTA spectra for RBMB were recorded for the range of temperature from 28 to 1000 °C with a simultaneous thermal
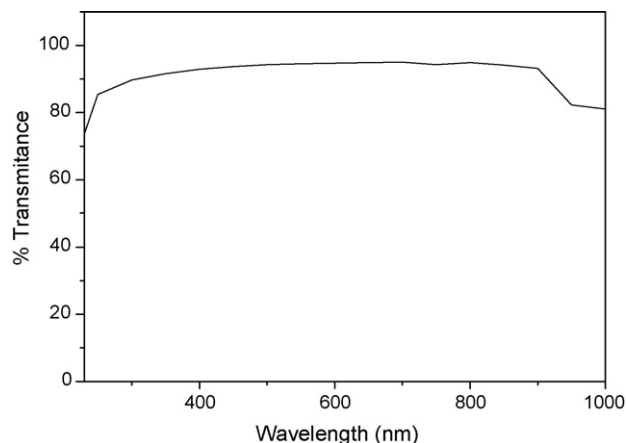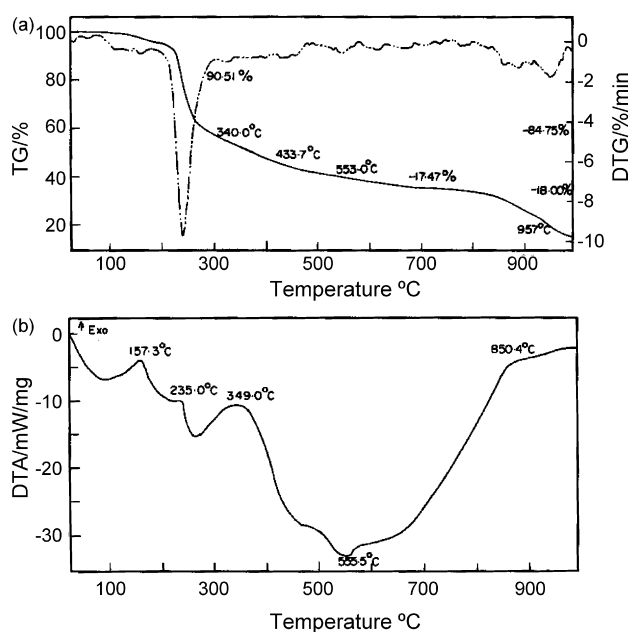
Fig. 5. UV–vis-NIR spectrum RBMB crystals.

Fig. 6. (a) TG/DTG analysis of RBMB crystals. (b) DTA analysis of RBMB crystals.

analyzer, STA-409. A ceramic (Al_2O_3) crucible was used for heating and the analysis was performed in nitrogen atmosphere at a heating rate of $20\,°C\,min^{-1}$. The initial mass of the material subjected to analysis was 9.950 mg. The final mass of the residue after the analysis was 18.61% of the initial mass. The results of the thermal analyses are represented by the curves in Fig. 6. From the TGA curve it is obvious, that the material is very stable and there is no phase transition up to 230 °C and then it undergoes a weight loss. Between 157.5 and 235.0 °C

there is loss of weight, which may be assigned to the removal of weakly absorbed water. Between 235 and 349 °C, there is a conspicuous loss in weight due to the probable removal of $C_4H_4O_5$. Further, between 349 and 555.5 °C there is a significant loss of weight indicating the possible evolution of CO. The DTA curve of RBMB is consistent with the above deductions. The sharp endothermic peak observed at 157.5 °C corresponding to the decomposition of the material and another prominent exothermic peak at 555.5 °C could be attributed to the expulsion of CO. Thus the result suggests that the material is thermally stable in the working temperature range 30–230 °C.

5. Conclusions

A potential semiorganic material for second order NLO applications, Rubidium bis-DL-malato borate (RBMB) was synthesized; single crystals were grown, and characterized by X-ray diffraction (single crystal XRD) to confirm the formation of the crystalline phase. FT-IR and FT-Raman spectroscopic analyses confirm the presence of all the functional groups in the crystal lattice. The absorptions due to BO_4 tetrahedra have been identified. TG-DTA studies reveal that the material starts melting at 230 °C thereby indicating the thermal stability of the material to withstand the high temperatures encountered in laser experiments. The UV–vis spectrum establishes the good transmittance window and the lower cutoff is found to be as low as 230 nm, allowing for frequency conversion down to UV-region. The emission of SHG using Nd:YAG laser is confirmed by a modified Kurtz and Perry powder method.

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