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Synthesis, growth, vibrational, optical and thermal studies of potassium diboro oxalate single crystals

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ABSTRACT

Single crystals of novel semiorganic material, potassium diboro-oxalate (PDO) have been grown from aqueous solution by slow evaporation technique. The lattice parameters for the grown crystals were determined by the single crystal X-ray diffraction analysis and the crystallinity of the grown crystal was confirmed by powder X-ray diffraction analysis. The presence of functional groups was estimated qualitatively by using Fourier transform infrared (FTIR) analysis. The optical absorption spectrum shows that the UV cut-off wavelength for the grown crystal is at 240 nm and the band gap was calculated. The thermal stability of the grown crystal was studied by using TG/DTA analysis. The second harmonic generation and the phase-matchable tests were performed by Kurtz powder technique. The crystal perfection was analyzed by SEM photographs.

1. Introduction

In recent years, semiorganic crystals find considerable interest among researchers due to their high damage threshold, wide transparency range, less deliquescence, excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties [1–4]. In the past few decades, borate family crystals have attracted much attention because of their excellent properties for ultraviolet (UV) nonlinear optics (NLO) [5–8]. They are widely used in the fabrication of optical devices based on frequency conversion, optical parametric oscillation as well as in electro-optic modulation devices which are applied in full color laser displays, high resolution laser printing, color projection, high density optical data storage, under water communications, stereo lithography, etc. The extensive search for new types of borate crystals has led to the discovery of many excellent materials such as CsB_3O_5 (CBO) [9], $CsLiB_6O_{10}$ (CLBO) [10], $Sr_2B_2Be_2O_7$ (SBBO) [11], $K_2Al_2B_2O_7$ (KABO) [12], etc.

2. Experimental details

2.1. Solubility test

In the solution growth technique, the size of a crystal depends on the amount of the material available in the solution, which in turn is decided by the solubility of the material in that solvent. Knowledge of solubility also helps in selecting the crystal growth method. Hence, the solubility of the raw material is as explained below.

The starting material was the commercially available potassium carbonate, boric acid, oxalic acid (Ran boxy, AR grade). The purity of the salts has been improved by recrystallizing in water for several times. A volume of 100 ml of water was taken in an air tight container and recrystallized salt was added. The experiment was carried out in a constant temperature bath with temperature accuracy ±0.01 °C. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The experiment was carried out for temperature ranges as 35, 40, 45, 50 and 55 °C. The solubility increases linearly with increase of temperature in the growth region. A graph of temperature versus concentration is shown in Fig. 1.

2.2. Crystal growth

Potassium diboro oxalate single crystal was grown by the solution method with a slow solvent evaporation technique. In

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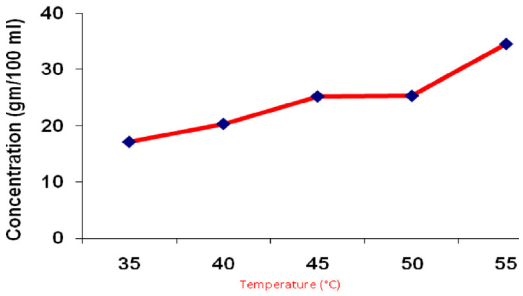

Fig. 1. Solubility curve of potassium diboro oxalate.

accordance with the solubility data, saturated solution of the synthesized salts of PDO was prepared and it was constantly stirred for about 2 h using a magnetic stirrer. The saturated solution was filtered using WHATMAN filter papers to remove insoluble impurities. Then the filtered solution was kept in borosil beakers covered with porous papers and kept in a dust-free atmosphere. The crystals were harvested after a period of about 25 days and it is depicted in Fig. 2.

2.3. Characterization

The single crystal X-ray diffraction studies of the grown crystal was carried out using ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoKα (λ = 0.717 Å) radiation and the cell parameters are calculated using SHELXL program. The powder XRD was carried out using RICH SEIFERT diffractometer with CuKα (λ = 1.5417) radiation. The Fourier Transform Infra-red (FT-IR) spectrum was recorded in the range of 4000–400 cm^{-1} using PERKIN ELMER RX1 spectrometer. The UV–vis-NIR spectrum was recorded in the range of 190–1100 nm using PERKIN ELMER LAMDA 35 spectrophotometer. The SHG efficiency of the crystal was evaluated by the Kurtz and Perry powder technique using a Q-switched, mode locked Nd:YAG laser. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using SDT Q600 V20.5 Build15 thermal analyzer in the range of temperature from 0 to 1000 °C at a heating rate of 20 °C/min in nitrogen atmosphere.

3. Results and discussion

3.1. Single crystal and powder XRD studies

The synthesized materials were subjected to powder X-ray diffraction (PXRD) studies to confirm the crystallinity of the material. The PXRD pattern of the grown crystal is shown in Fig. 3. From this figure, it is confirmed the crystalline nature of the grown crystals. The well-defined Bragg's peak at specific 2θ angles shows high crystallinity of potassium diboro oxalate. The observed *d* values and the corresponding theta values are tabulated in Table 1.

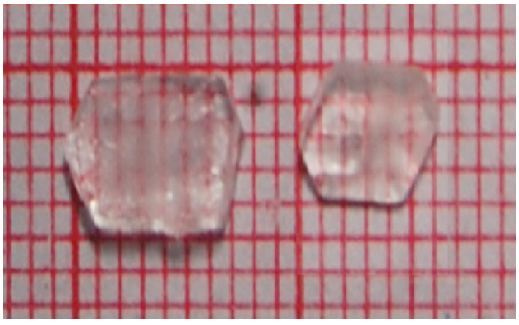

Fig. 2. As grown potassium diboro oxalate single crystal.

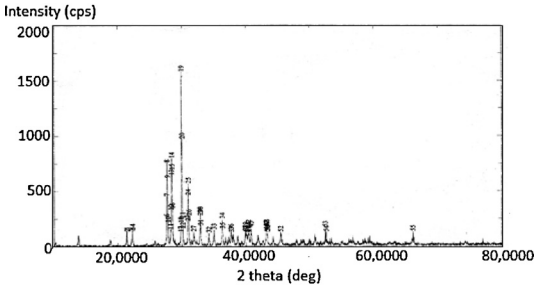

Fig. 3. Powder XRD pattern of potassium diboro oxalate.

Table 1
Powder X-ray diffraction data for potassium diboro oxalate.

2θ	*d* value	*I*/*I*o
22.300	3.9833 12	22
27.600	3.2292 29	36
27.660	3.2224	48
27.720	3.2155	40
28.280	3.1531	21
28.320	3.1488	41
28.380	3.1422	51
28.420	3.1379	44
28.480	3.1314	22
29.900	2.9859	100
29.980	2.9781	62
30.920	2.8896	30
30.960	2.8860	36
32.820	2.7266	18
32.840	2.7250	19

From the single crystal XRD measurement, it is observed that the grown crystal belongs to monoclinic system. The cell parameters are: $a = 10.265$ Å, $b = 17.754$ Å, $c = 11.257$ Å, $\alpha = \gamma = 90°$, $\beta = 111.40°$ and the volume is1910 $Å^3$.

3.2. FT-IR spectral analysis

Infrared spectroscopy is effectively used to identify the functional groups and determine the molecular structure of the synthesized compounds. The FT-IR spectrum of ADO is shown in Fig. 4. The characteristic vibrational frequencies are assigned and compared with the L-citrulline oxalate monohydrate (LCO) and potassium pentaborate (KB_5) single crystal [13,14].

The asymmetric and ring stretching vibration of B-O ions are identified at 1223 and 801 cm^{-1} respectively. Further, the carboxylate stretching vibration frequencies are identified at 1715 cm^{-1}. The other frequencies of the grown crystals are identified and compared with similar compounds (Table 2).

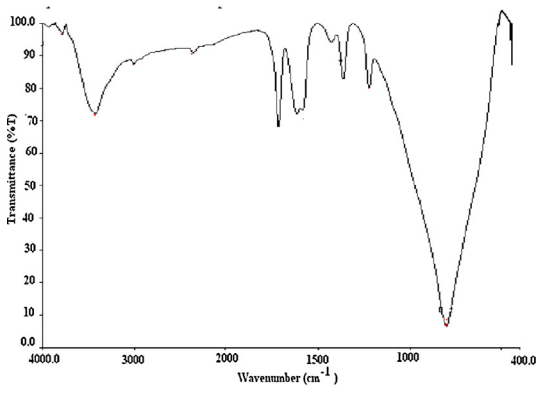

Fig. 4. FT-IR spectrum of potassium diboro oxalate.