Structural, Thermal, Mechanical, Dielectric And Optical Properties Of Magnesium Sulphate Doped In Potassium Borooxalate: A New Nonlinear Optical Material

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Abstract: Nonlinear optical (NLO) materials are useful in many industrial applications. A new semiorganic nonlinear optical Magnesium sulphate doped Potassium Borooxalate single crystals have been grown by Slow Evaporation technique at ambient temperature. The title compound has been subjected to single-crystal X-ray diffraction analysis to identify the unit cell parameters. Fourier Transform Infrared spectroscopic analysis was carried out on the grown sample to ascertain the fundamental functional groups. Optical absorption studies illustrate low absorption in the entire UV and Visible region. The crystal was subjected to DSC analysis to find its thermal stability. The dielectric response of the crystal with varying frequencies was studied. The mechanical property of the grown crystals had been analysed by Vickers's microhardness method. The NLO property of the grown crystal has been confirmed by the Kurtz powder Second Harmonic Generation (SHG) test.
Keywords: Slow evaporation technique, X-ray diffraction, NLO property, Vickers's microhardness.

1. INTRODUCTION

Nonlinear optics (NLO) is at the vanguard of current research, because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging techniques in areas such as telecommunications, signal processing and optical interconnections [1,2]. The NLO phenomena occur when the optical properties of molecules change in the presence of strong external electric fields, i.e., high-energy laser beams. Most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible for damage during processing even though they have large nlo efficiency. Also it is difficult to grow larger size optical-quality crystals of these materials for device applications. Purely inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity because of the lack of extended -electron delocalization [3,4]. Hence it may be useful to prepare semiorganic crystals which combine the positive aspects of organic and inorganic materials, resulting in useful nonlinear optical properties.

The basic requirements for a NLO crystal to be successfully utilized in frequency conversion are a lack of center of symmetry for the molecular charge transfer, significant change in dipole moment upon excitation from the electronic ground state to some excited states , small to moderate excitation energies of the corresponding excited states , Hammett constants of the substituents ,nonzero NLO coefficient, transparency at all wavelengths involved, efficient transfer of energy between the optical waves propagating through the crystal, and

good physical (low vapour pressure, high thermostability) and optical (high damage threshold, large birefringence, low dispersion) properties [5,6].

According to the Philips-Van Vechten-Levine-Xue bond theory [7], constituent chemical bonds of the single crystal determine its NLO responses. Semiorganic materials structurally involve one or more kinds of hydrogen bonds, which have been identified as one of the NLO functional bonds. Semiorganic materials possess several attractive properties such as high damage threshold, wide transparency range, less deliquescence and high non-linear coefficient, which make them suitable for frequency doubling [[8,9].

The extensive search for new types of borate crystals has led to the discovery of many excellent materials such as Lithium bis-L malato borate [10], Rubidinium bis-DL-malato borate [11], Potassium boromalate [12], Potassium borosuccinate [13]. In this sequence, a new semiorganic borate family crystal doped with inorganic salt namely, Magnesium sulphate doped in Potassium borooxalate has been developed.

In the present investigation, we report the bulk growth, crystalline perfection, optical, thermal, dielectric, mechanical, and second harmonic generation (SHG) properties of Magnesium sulphate doped Potassium Borooxalate (KBO) single crystals.

2. CRYSTAL GROWTH

Merck GR grade Magnesium sulphate, Potassium hydroxide, Boric acid and Oxalic acid along with de-ionized water were used for the synthesis and growth. Potassium Borooxalate (KBO) was synthesized by equimolar incorporation of Potassium hydroxide, Boric acid and Oxalic acid. The component salt was well dissolved in de-ionized water. To synthesize $MgSO_4$ doped KBO, 1 mole % of $MgSO_4$ $7H_2O$ was added to the aqueous solution of KBO. Single crystals of $MgSO_4$ doped KBO were grown by solution growth employing slow evaporation technique at room temperature (31°C).For the formation of KBO solution, the amount of solute i.e. (KBO salts) required to prepare the supersaturated solution is given by the formula,

$$m = \frac{M x X x V}{1000} \quad \text{(in gram units)},$$

Where M is the molecular weight of the solute,
X is the supersaturated concentration in molar units (1M in the present work) and V is the required volume of the solution [14].

The supersaturated solution was stirred well for 28 hours at room temperature using a temperature controlled magnetic stirrer to yield a homogenous

mixture of solution. Then the solution was filtered using a whattmann filter paper and was transferred in a beaker covered with airtight thick filter paper so that the rate of evaporation can be minimised. Optically transparent crystals were formed due to spontaneous nucleation. Among them defect free crystals were selected as seeds in order to grow bulk crystals. The synthesized salt was purified by successive recrystallization process. After a period of 32 days single crystals of $MgSO_4$ doped KBO having dimensions 5x3x2 mm^3 were obtained by isothermal solvent evaporation method at room temperature. The photograph of the as grown crystal is as shown in Fig. 1.

Fig. 1

3. CHARACTERIZATION

Single crystal X-ray diffraction analysis was carried out using Enraf Nonius CAD-4 Circle Diffractometer with CuK (=1.5418 Å) radiation. The FT-IR spectra of MgSO4 doped KBO crystals were recorded in the range 400–4000 cm$^-$1 employing a Perkin–Elmer spectrometer by KBr pellet method in order to confirm the presence of functional groups in the crystal lattice. Transmission spectra of the crystals were recorded using a Shimadzu UV-Visible Spectrophotometer. Differential scanning calorimetry (DSC) was carried out at a scanning rate of 10 K/min in nitrogen atmosphere, by Perkin Elmer, DSC-4 equipment. The Vickers's microhardness measurement was carried out on the grown crystals to assess the mechanical properties by employing Shimadzu HMV-2000 microhardness tester for different loads. The dielectric constant of the title crystal was measured at low frequency using the LCZ meter (Model-Chen Hua 1061). Vickers's micro-hardness studies were carried out on the grown crystals using Leitz Wetzler hardness tester fitted with a diamond pyramid indenter, to investigate the mechanical property. To confirm the nonlinear property, Kurtz powder SHG test was performed on MgSO4 doped KBO crystals.

4.RESULTS AND DISCUSSION

4.1 Single crystal XRD analysis

The grown crystals were subjected to single crystal x-ray diffraction analysis using an ENRAF NONIUS CAD-4 single crystal X-ray diffractometer with CuK radiation (=1.5418 Å) to determine the lattice parameters. The calculated lattice parameters are a = 3.74 Å , b = 9.50 Å , c = 17.77 Å , = = = 90°. The volume of the unit cell , V = 632 Å . The crystal belongs to the Orthorhombic system with a noncentrosymmetric space group $P2_12_12_1$.

4.2 FTIR Analysis

In order to analyze the presence of functional groups qualitatively in the grown crystal, the FTIR spectrum was recorded between 400 and 4000 cm^{-1}

using IFS BRUKER 66v spectrometer by KBr pellet technique and the resultant spectrum is shown in Fig.2. The broad band at 3299 cm^{-1} is due to O-H stretching. The Carbonyl stretching C=O is found to be near 1729 cm^{-1} .The peak at 1421 cm^{-1} indicates the presence of C-O-H bending. The B-O asymmetric stretching vibrations appear at 1119 cm^{-1} . A sharp band observed at 829 cm^{-1} has been assigned to the B-O symmetric stretching vibrations. A peak at 706 cm^{-1} is assigned to C-H bond in the wagging vibration. The COO⁻ plane deformation has been found to be near 659 cm^{-1}.A peak at 462 cm^{-1} has been attributed to COO⁻ rocking vibration [15,16]. All the assignments confirm the incorporation of the constituent ions in the title compound and are tabulated in Table 1.
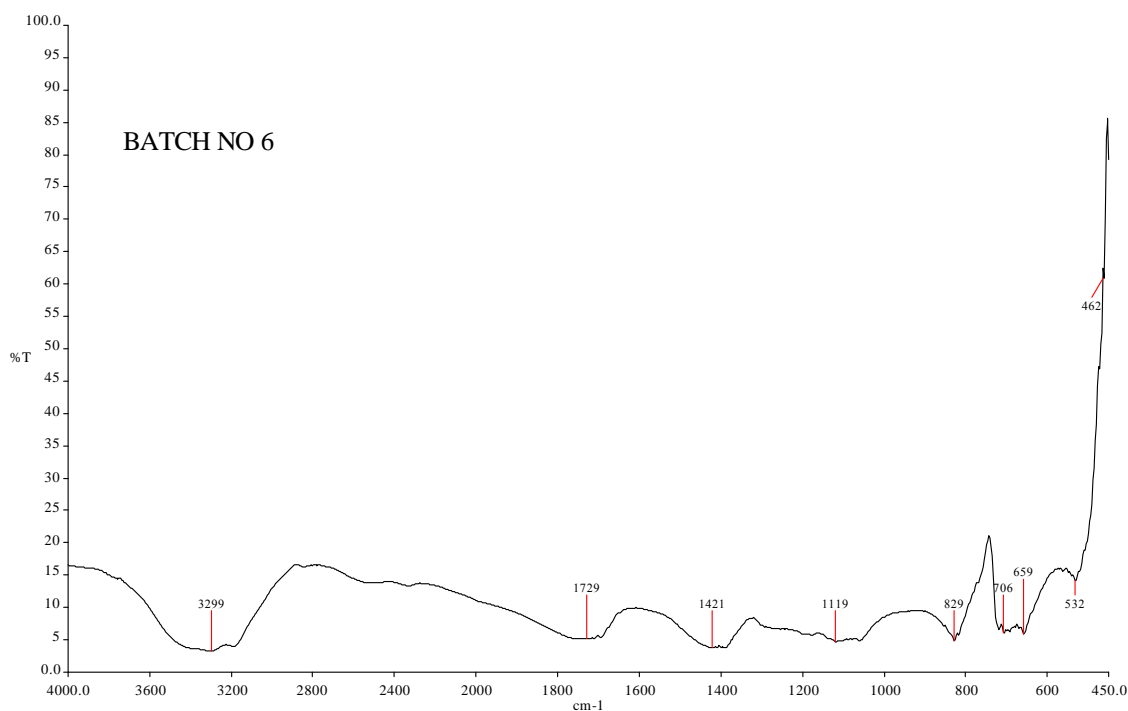

Fig. 2

Table 1: Fundamental frequency of vibrations in MgSO4 doped KBO crystals.

Frequency in wavenumber cm^{-1}	Assignment of functional groups
3299	OH Stretching
1729	C=O Stretching
1421	C-O-H bending
1119	B-O asymmetric stretching
829	B-O symmetric stretching
706	C-H wagging
659	COO⁻ plane deformation
532	K-O stretching vibration
462	COO⁻ rocking

4.3 UV-VIS-NIR spectral analysis

The absorption spectrum of $MgSO_4$ doped KBO was recorded in the wavelength range between 190 and 1100 nm, using Lamda 35 UV-VIS spectrophotometer (Fig.3) and its optical transmission spectrum was recorded in the range 200-2000 nm using VARIAN CARY 5E spectrophotometer (Fig. 4). The spectrum gives information about the structure of the molecule because the absorption of UV and Visible light involves promotion of the electron in the   and   orbital from the ground state to higher states [17]. The crystal has excellent transmission in the entire visible region. The lower cut off wavelength is 240 nm.   Single crystals are mainly used in optical applications and hence optical transmittance window and the transparency lower cut off (200-400 nm) is very important for the realization of SHG output in this range using lasers. This transparent nature in the visible region is a desirous property for the material used for NLO applications. The forbidden gap energy gap (E_g) of MgSO4 doped KBO was estimated form the relation $E_g = 1.243 \times 10^3 / _{max}$ and is found to be 5.17 eV,which is typical of dielectric materials [18]. The absence of absorption bands in the visible region and the wide band gap of the grown crystal attest to the suitability of the grown crystal for photonic and optical applications [19]. The larger energy band gap shows that the defect concentration in the grown crystals is very low.
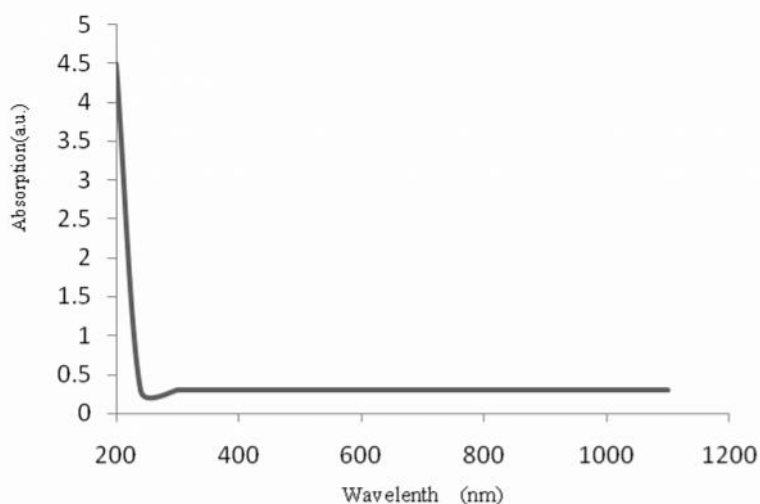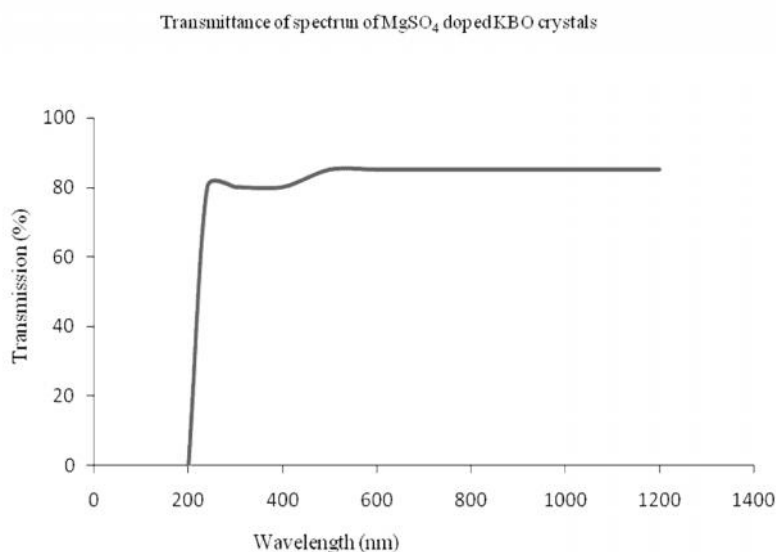

Fig. 3 Absorption spectrum of $MgSO_4$ doped KBO

Fig. 4 Transmission spectrum of $MgSO_4$ doped KBO

4.4 Dielectric studies

The as grown crystal is subjected to dielectric studies using HIOKI 3532 – 50 LCR HITESTER. The selected samples were cut using a diamond saw and polished using paraffin oil. Silver paint was applied on the both faces to make a capacitor with the crystal as a dielectric material. The dielectric constant is calculated using the relation.

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

where C is the capacitance, d is the thickness, A is the area and ε_0 is the absolute permittivity of the free space (8.85×10^{-12} F/m). The variation of dielectric constant (ε') and dielectric loss were studied as a function of frequency for room temperature. It is clear from Fig. 5 and Fig. 6 that both dielectric constant and dielectric loss of title material decrease gradually with increasing frequency. The decrease of dielectric constant with increasing frequency is a normal dielectric behaviour and can be explained on the basis of polarization mechanism. There are four primary mechanisms of polarization that exists in materials, i.e., electronic, ionic or atomic, dipolar or orientational and space charge or interfacial polarization. At low frequencies, all the mechanisms of polarization contribute to the dielectric constant and with the increase in frequency, the contributions from different polarizations start decreasing [20]. For example, at very high frequencies (10^{15} Hz), only electronic polarization contributes to the dielectric constant, while ionic polarization takes place at IR frequencies (10^{13} Hz). The high rise of dielectric constant at lower frequencies may be attributed to space charge polarization and also due to crystal lattice defects [21]. The characteristic of low dielectric loss at high frequency for a given sample as evidence from Fig. 6 suggests that the sample possesses good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical applications [22].
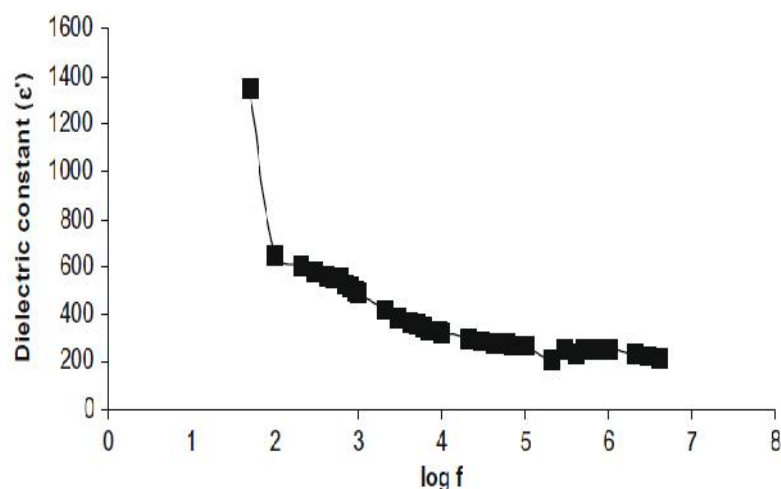

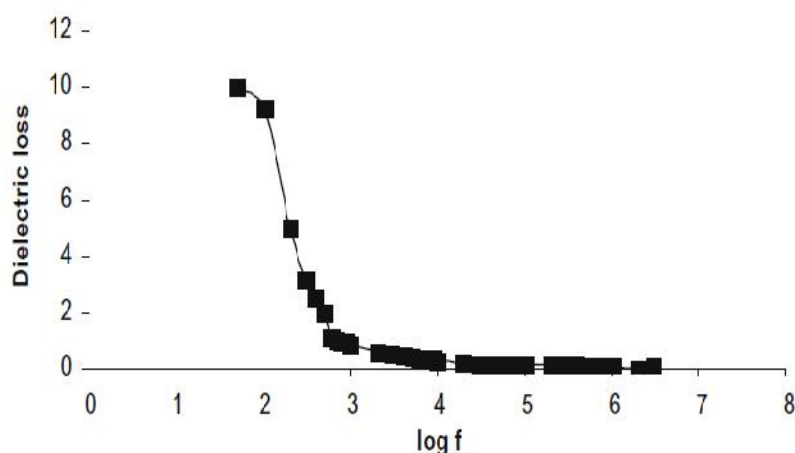Fig. 5 Variation of dielectric constant vs. log f for MgSO$_4$ doped KBO

Fig. 6 Variation of dielectric loss vs. log f for MgSO$_4$ doped KBO

4.5 Microhardness study

The microhardness testing is the simplest characterization technique that can be best employed to study the mechanical properties of material, such as fracture behaviour, yield strength, brittleness index and temperature of cracking [23]. The hardness of the material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing [24-26]. According to Ariouli et al [27], during an indentation process, the external work applied by the indenter is converted to a strain energy component which is proportional to the volume of the resultant impression and the surface energy component is proportional to the area of the resultant impression. Microhardness is a general microprobe technique to assess the bond strength, apart from being a measure of bulk strength [28-30]. The selected smooth surfaces of the crystal were subjected to indentation tests. For each load several trials of indentations were carried out. The Vickers's microhardness H_v of the crystal was evaluated using the relation $H_v=1.8544\ (P/d^2)$ kg/mm^2 [31], where P is the indenter load in kg and d is the mean diagonal length of the impression in mm. Optically clear and defect free crystal plate taken perpendicular to the growth direction was subjected to indentation tests at room temperature. The diagonal length of the indentation (d) in µ-m for various applied load (P) in g was measured for a constant indentation period of 15 s. Fig. 7 shows that the Vickers's hardness number linearly increases by increasing the applied load. Due to the application of mechanical stress by the indenter, dislocations are generated locally in the region of indentation. The Mayer's index number was calculated from the Mayer's law [32], which relates the load and indentation diagonal length $P = kd^n$

Log P = logk + n logd

Where k is the material constant and n is the Mayer's index (or work-hardening coefficient). The above relation indicates that H_v should increase with load P if n>2 and decrease with load P when n<2. We have determined n from slope of the plot that is shown in Fig. 8. The value of n for $MgSO_4$ doped KBO was found to be 2.5. Low value of work hardening coefficient n illustrates fewer defects [33] in the as grown crystal. According to Onitsch [34], n should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. By Mayer's law,

the value of Mayer's index (n) estimated to be 2.5, which indicates that $MgSO_4$ doped KBO crystal belongs to soft material category. Meyer number is a measure of the Indentation Size Effect (ISE).For the normal ISE behaviour, the exponent is n<2. When n > 2, there is the Reverse Indentation Size Effect (RISE) behaviour [35].
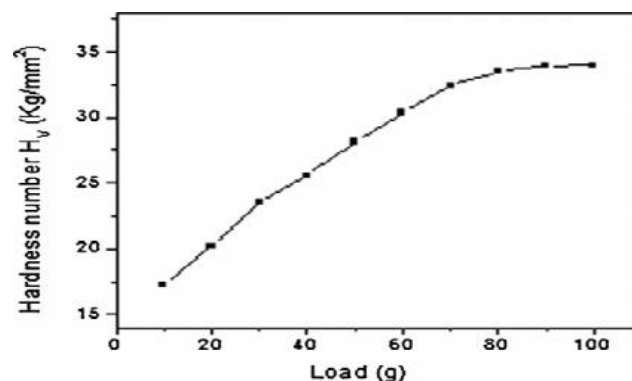

Fig. 7 Hardness of MgSO$_4$ doped KBO

4.6 Differential scanning calorimetry

Differential scanning calorimetry of the crystal was carried out in the temperature range 30–300°C in nitrogen atmosphere at a heating rate of 10°C/min. A small amount of $MgSO_4$ doped KBO sample weighing 15.090 mg was placed in aluminium pan. The pan was encapsulated with a dome lid, which was crimped in position. In order to obtain a sharp peak and resolution, very fine particles were used to maximize the contact surface between the sample and pan. The normal lid crimping procedure made a tight seal over the pan. A thermogram was obtained by using the Perkin Elmer, DSC-4 equipment. The DSC curves can be used to calculate enthalpies of transitions. This is done by integrating the peak corresponding to a given transition. It can be shown that the enthalpy of transition can be expressed using the following equation: H = KA; where   H is the enthalpy of transition, K is the calorimetric constant, and A is the area under the curve [36]. The measured enthalpy value was equal to 332 J/g for1 mole % $MgSO_4$ doped KBO crystal. The DSC thermogram in Fig.8 shows a sharp exothermic peak at 110.5 C, signifying the melting point of the crystal. Further, the sharpness of the peak indicates good degree of crystalline perfection of the sample.
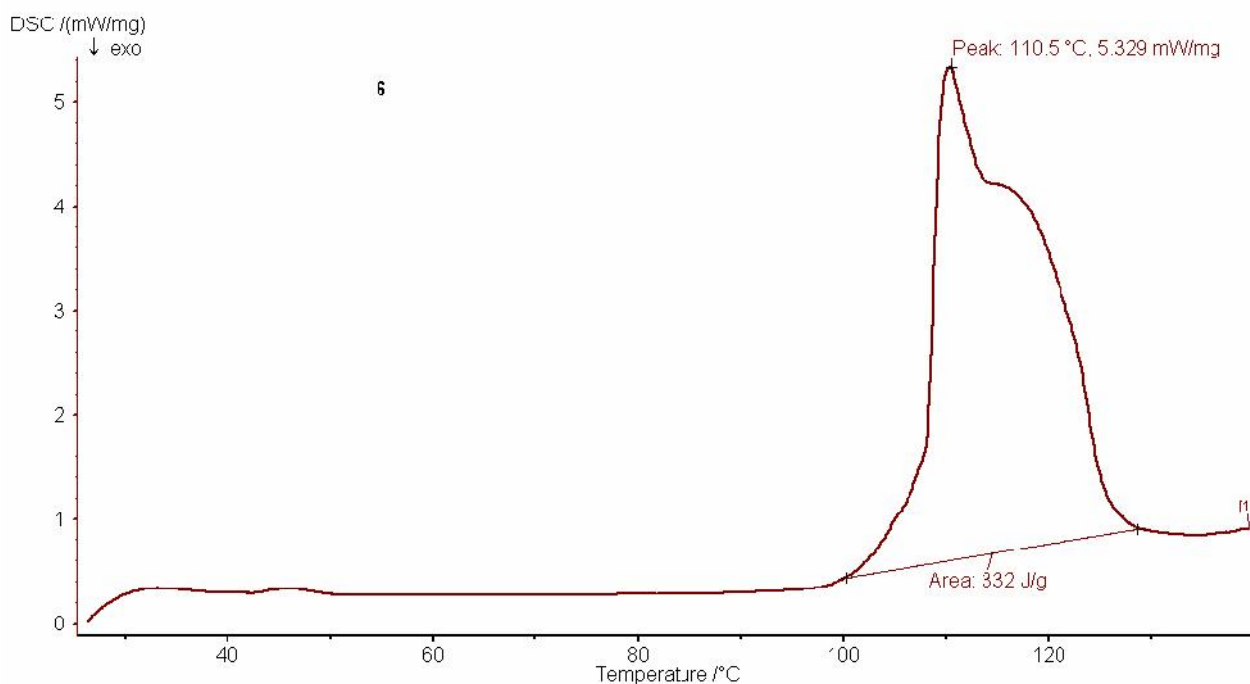
Fig. 8 DSC thermogram of MgSO₄ doped KBO

4.7 Nonlinear optical studies

The second harmonic generation behaviour of the grown crystal was detemined by Kurtz powder technique [37,38]. The sample was grounded into the fine powder and tightly packed in a micro capillary tube. The crystal was illuminated using Spectra-Physics Quanta-Ray DHS-2, Nd:YAG laser using the first harmonics output of 1064 nm with a pulse width of 8 ns and energy 7 mJ/ pulse. The emission of green radiation confirmed the second harmonic efficiency of the grown crystal.

CONCLUSIONS

Good quality and transparent single crystals of MgSO₄ doped KBO crystal have been grown successfully in double distilled water by slow evaporation method. Single crystal X-ray diffraction analysis confirms the crystal system and lattice parameters. The functional groups present in the title compound were confirmed by FT-IR analysis. Optical transmission studies showed that MgSO₄ doped KBO crystal was optically transparent. The dielectric constant and dielectric loss were measured as a function of frequency at 300 K. The microhardness studies reveal that the hardness of crystal is moderately good. The powder Kurtz method was used to confirm the second harmonic generation in the grown crystal. The crystal possesses a relatively large specific heat. All these properties show that the titled material may be a promising candidate for the fabrication of NLO devices.

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