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S.I. : CURRENT STATE-OF-THE-ART IN LASER ABLATION

Investigation on structural, elemental, thermal, mechanical, linear, and nonlinear optical nature of potassium pentaborate tetrahydrate inorganic single crystals

S. Chidambaram[1] · A. David Kalaimani Raj[2] · R. Manimekalai[1]

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Abstract
Potassium pentaborate tetrahydrate (PPBTH) is an inorganic nonlinear optical single crystal. It was grown by slow evaporation solution growth method at room temperature and physical properties there are studied. The lattice parameters of grown crystal were determined using single-crystal and powder X-ray diffraction analysis. The functional group of various vibrational modes was assigned using FTIR spectrum. The optical transmittance, optical band gap, optical constants, and extinction coefficient were determined by recording UV–Vis–NIR spectrum. The fluorescence study confirmed the green emission of PPBTH. Vickers hardness test estimates the mechanical properties for various loads. This material exhibited the soft material category. The magnetic properties of PPBTH were studied by vibrating sample magnetometer. Thermal behaviours of the grown crystals have been investigated using TGA/DTA analysis. The nonlinear optical studies confirm the second harmonic generation signal of the grown sample.

Keywords Crystal growth · Single-crystal XRD · Optical studies · SHG analysis · Magnetic property

1 Introduction

Growing crystals of desired size and shape are still considered as an art. Every day, new crystals are being grown and new devices are coming out using these crystals. In recent years, the synthesis of nonlinear optical (NLO) materials has been extensively investigated than other materials due to their potential application as versatile tools and devices in the fields of photonics and optoelectronics. Even though organic NLO crystals possess high non-centrosymmetric behaviour and large nonlinear susceptibilities, they have low optical, thermal, and mechanical properties [1, 2]. Inorganic crystals are ionic bonded crystals, which are highly and chemically inactive. Inorganic crystals with high melting point and mechanical stability are required in a variety of applications like piezoelectricity, ferroelectricity, and electro-optics. Inorganic materials are also used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The well-known, most important inorganic crystals are potassium dihydrogen phosphate (KDP), caesium lithium borate (CLB), potassium titanyl phosphate (KTP), and potassium pentaborate (KB_5) [3–8]. The same title crystals have been grown by various authors [9, 10]. We have chosen the different chemical route to grow the same title crystal. In addition to this, several borate crystals have been reported [11, 12].

In this work, we have selected ammonium pentaborate and potassium sulphate as parent materials. The crystals were grown from aqueous solution by the slow solvent evaporation technique at room temperature (29 °C). When potassium sulphate is added to ammonium pentaborate, it yields potassium pentaborate tetrahydrate $2(KB_5\ O_8)0.4H_2O$ single crystals and the ammonium sulphate $(NH_4)_2\ SO_4$ is evaporated. Further, it is confirmed and cross-checked that the grown crystal is $2(KB_5O_8)0.4H_2O$ using elemental analysis. The grown crystals have high crystalline nature, and it belongs to orthorhombic crystal system. In the present study, we found that the grown crystal possesses all the functional groups of potassium pentaborate tetrahydrate [10, 13]. The optical study reveals that the grown crystals have sufficient

✉ R. Manimekalai
maniabi64@gmail.com

[1] Department of Physics, A.V.V.M. Sri Pushpam College (Autonomous), Poondi, Tamil Nadu 613 503, India

[2] Department of Physics, BDUMC, Aranthangi, Tamil Nadu 614 616, India

transmittance and with an optical band gap of 4.5 eV. It follows direct optical transition and emits green fluorescence. SHG measurement has shown that the grown crystal exhibits its NLO properties. The potassium pentaborate tetrahydrate (PPBTH) got excellent outcome of thermal and mechanical properties. The grown crystals belong to soft materials categories [13, 14]. Magnetic properties of the grown crystal have been studied. In this research work, the grown PPBTH single crystal's characterization analysis such as lattice parameters, FTIR, structural properties, UV–visible, mechanical, thermal, elemental, SHG and VSM studies and their results are reported.

2 Experimental procedure

The PPBTH single crystal was synthesized from analar grade ammonium pentaborate ($B_{10}H_8N_2O_{16}.8H_2O$) and potassium sulphate (K_2SO_4) in stoichiometric molar ratio of 1:1 [15]. The solution was stirred continuously for 3 h to obtain the saturated solution. It was filtered well to remove suspended impurities and allowed to settle down in a clean environment maintained at 39 °C with the help of constant temperature bath with the accuracy of ± 0.01 °C [16]. After 14 days, colourless and transparent crystals were harvested with a dimension of 5 × 4x3 mm^3 as shown in Fig. 1. The chemical reaction is as follows:

$$B_{10}H_8N_2O_{16}.8H_2O + K_2SO_4 \rightarrow 2\left(KB_5O_8\right).4H_2O + \left(NH_4\right)_2SO_4 \uparrow$$

3 Results and discussion

3.1 Single-crystal and powder X-ray diffraction studies

The single-crystal X-ray diffraction analysis of PPBTH was carried out using an ENRAFNONIUS CAD4 automatic X-ray diffractometer with MOKα (λ = 0.717 Å) radiation. It confirms that crystal belongs to orthorhombic system and the unit cell parameters are $a = 11.06$ Å, $b = 11.17$ Å, $c = 9.054$ Å and $\alpha = \beta = \gamma = 90°$, volume $V = 119.14$Å^3. They crystallize with non-centrosymmetric space group, Aba2. The determined values are well matched with the reported values [17].

Powder X-ray diffraction studies of PPBTH crystals were carried out by using X'Pert-Pro diffractometer with CuKα radiation (λ = 1.540600 Å) as shown in Fig. 2. The sample is scanned from range 10° to 80° at a rate of 2°/ min. The hkl values of the obtained peaks are indexed. The sharp and well-defined peaks confirm the good crystalline nature of PPBTH [18].

3.2 EDAX analysis

The energy-dispersive X-ray analysis (EDAX) is carried out using Geon 5610LV Model, and it is the useful tool for the elemental analysis. The presence of various components of the grown crystal is analysed. From this analysis, coordination of the element of title compound is proved precisely. The EDAX spectrum of PPBTH crystal is illustrated in Fig. 3. Table 1 shows the weight percentage of the elements present in the sample [19].

3.3 Fourier Transform infrared (FTIR) analysis

The FTIR spectrum (Fig. 4) of potassium pentaborate tetrahydrate was recorded using PerkinElmer RX1 spectrometer in the range 4000–400 cm^{-1}. In this FTIR spectrum, almost all functional groups in a molecule absorb characteristically a definite range of frequency [16]. The peak appearing at 3442 cm^{-1} is attributed to the presence of water molecule in the grown sample. The band at 3379 cm^{-1} is due to asymmetric stretching vibration of H–O–H. The wavenumbers at 2668 cm^{-1} and 2486 cm^{-1}

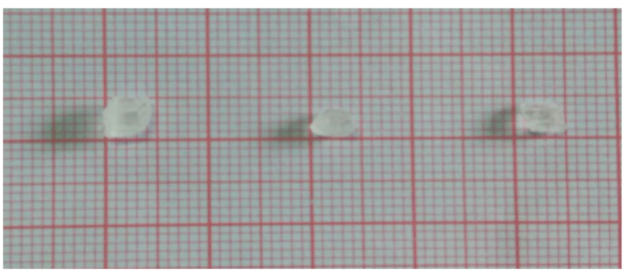

Fig. 1 Photograph of potassium pentaborate tetrahydrate crystal

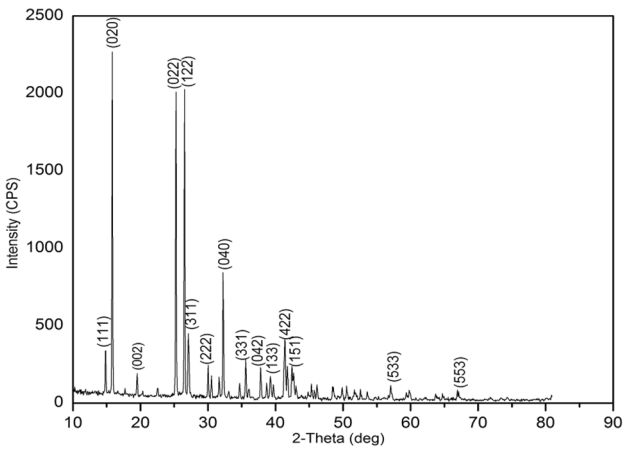

Fig. 2 Powder XRD pattern of PPBTH crystal

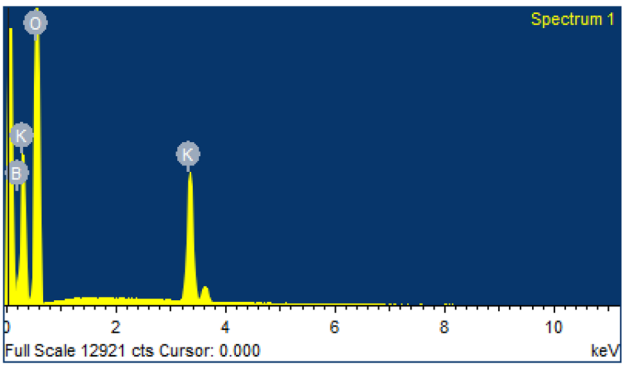

Fig. 3 EDAX pattern of PPBTH crystal

Table 1 Elemental composition of PPBTH crystal

Element	BK	OK	KK	Totals
Weight %	21.16	71.26	7.58	100.00
Atomic %	29.64	67.43	2.93	100.00

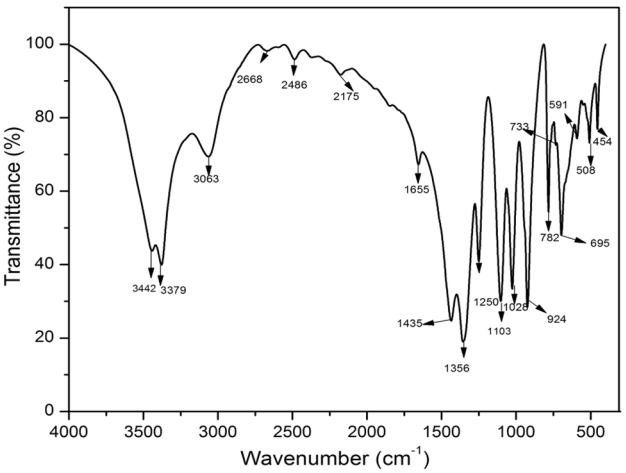

Fig. 4 FTIR spectrum of PPBTH crystal

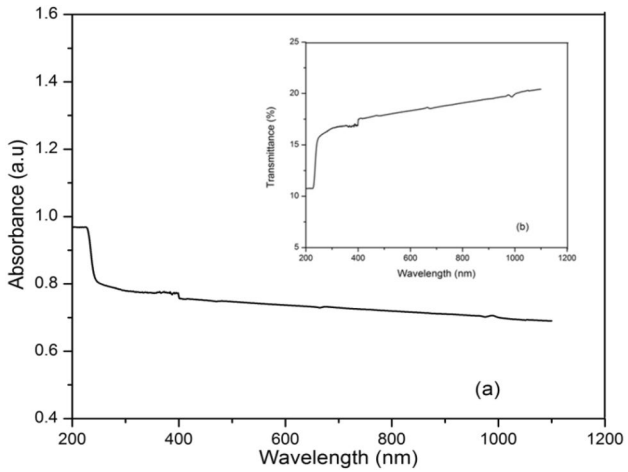

Fig. 5 (a) Absorbance curve of PPBTH, (b) optical transmittance of PPBTH

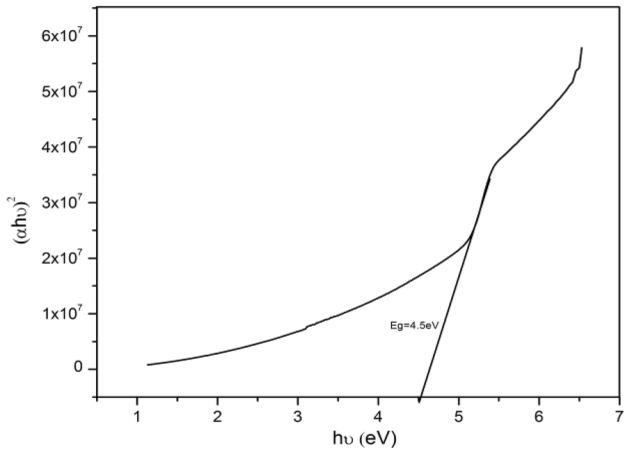

Fig. 6 Optical band gap of PPBTH crystal

are due to overtones and combination bands of hydroxyl group. The peak at 1655 cm^{-1} was attributed to bending vibration mode of H–O–H. The absorption peaks at 1435 cm^{-1}, 1356 cm^{-1}, and 1250 cm^{-1} are due to the asymmetric stretching mode of vibration. The symmetric and the asymmetric stretching frequencies at 1103 cm^{-1} and 1028 cm^{-1} are attributed to B–O group. The sharp peak at 924 cm^{-1} represents symmetric stretching of B–O in BO_3. The bands at 695 cm^{-1} and 454 cm^{-1} are representing an out-of-plane bending and ring bending mode of B–O–B, respectively. The sharp peak 508 cm^{-1} is assigned to K–O stretching vibration [9, 10].

3.4 UV–Vis spectral studies

In general, the crystals which are mainly used in optical applications, the determination of optical transmission range, the transparency cut-off, and band gap energy are important. The optical and absorption transmittance spectrum (Fig. 5a & 5b) of PPBTH crystal was recorded in the range of 190–1100 nm using Bruker UV–Vis–NIR spectrophotometer. The potassium pentaborate tetrahydrate single crystal has a good transmittance, and the lower-cut-off wavelength is nearly 230 nm. The absorption in the visible region clearly indicates that PPBTH crystals can be used as optical devices in optoelectronic instruments [20]. The optical band gap of PPBTH crystal was evaluated by plotting $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) using the formula $\alpha h\upsilon = A(h\upsilon\text{-Eg})^{1/2}$. From Tauc's plot, the large optical band gap of 4.5 eV is obtained in Fig. 6. The extinction coefficient

is nothing but the rate of loss of electromagnetic radiation through scattering and absorption of the crystal. $K = \frac{\alpha\lambda}{4\pi}$, where K is the extinction coefficient. From Fig. 7, the extinction coefficient increases with the increase in energy. The studies confirm that the grown PPBTH is well suited for optoelectronic applications.

3.5 Photoluminescence

The photoluminescence spectrum was carried out for PPBTH crystal using Cary Eclipse Photoluminescence Spectrometer (Fig. 8). The fluorescence spectrum was recorded in the range of 300 to 800 nm with an excitation wavelength 280 nm. The observed peak at 530.95 nm indicates the green emission of the title compound. The sharp peak indicates the crystalline nature and second harmonic conversion property of the grown crystal. Hence, the PPBTH is well suited for optoelectronic applications, and also nonlinear optical property of the as-grown sample is cross-checked through Kurtz–Perry SHG analysis [21]

3.6 Nonlinear optical study

The nonlinear optical behaviour of PPBTH crystal was confirmed by Kurtz and Perry powder technique. The Nd:YAG laser (QUANTUM RAY model LAB-170-10) emitting a fundamental wavelength (λ) of 1064 nm, with input energy 0.70 J, 6 ns pulse width, and a repetition rate of 10 Hz was allowed to fall on the powdered sample. The output energy was detected by a photomultiplier tube. The SHG in the crystalline sample was confirmed by the emission of green radiation at λ = 532 nm for the sample. The emitted output energy of potassium pentaborate tetrahydrate crystal powder was 4.34 mJ against 8.94 mJ for the reference KDP crystal. It is clear that the SHG conversion efficiency of PPBTH is

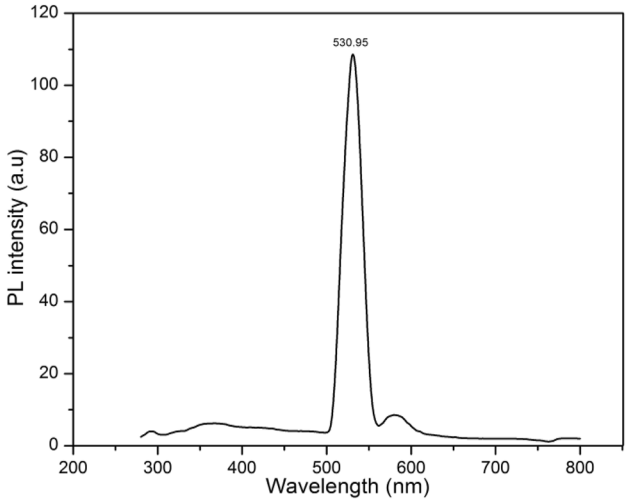

Fig. 8 Photoluminescence spectrum of grown crystal

0.48 times that of KDP. This confirms the nonlinear optical behaviour of PPBTH crystals [22].

3.7 Thermal studies

The TGA/DTA analysis of powdered crystals of potassium pentaborate tetrahydrate was carried out in nitrogen atmosphere from the temperature range of 28 to 1200 °C at a heating rate of 10 °C min^{-1} using a TGA/DTA300 thermal analyser as shown in Fig. 9. Initially, 4.482 mg weight of the sample was taken for the investigation. The TGA curve shows that the sample is thermally stable up to 144 °C. After that, the crystal has sustained decomposition. Finally, at 1100 °C (60.06%) the residue with 2.0 mg of weight was retained. The weight loss was due to the liberation of water molecules and potassium from the host

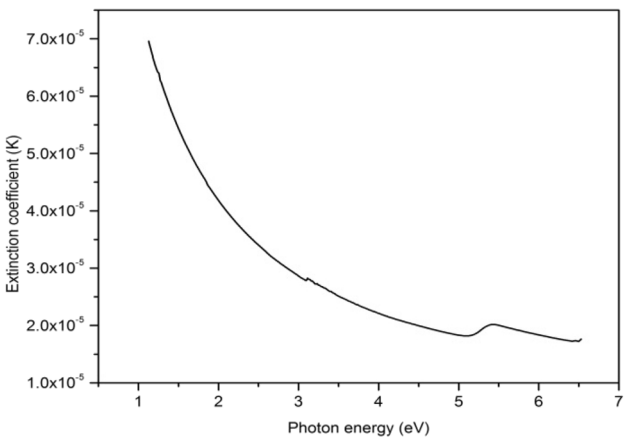

Fig. 7 Photon energy (eV) versus extinction coefficient (K)

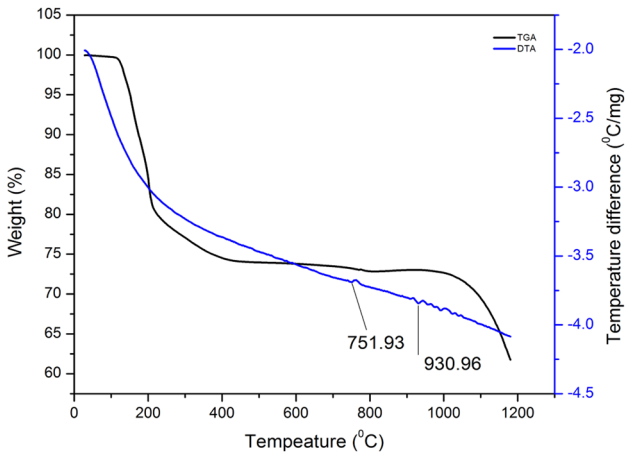

Fig. 9 TGA/DTA of PPBTH crystal

material [23]. The small endothermic peaks observed in DTA curve at 751 and 930 °C represent the decomposition of the grown material. This portrait establishes the fact that the material can be utilized for NLO applications.

3.8 Microhardness studies

The microhardness studies were carried out to determine the mechanical strength of the grown PPBTH single crystal using with 2aHMV-2 microhardness tester. The indentation marks were made on the surface of PPBTH single crystal at room temperature by varying the load of 25, 50, and 100 g. The diagonal lengths were measured, and Vicker's hardness number Hv was calculated by the relation:

$$\mathrm{Hv} = 1.8544P/d^2\left(\mathrm{Kg/mm^2}\right)$$

where P is the applied load and d is the average diagonal length. From the graph, it can be seen that there is a linear variation of load with the hardness number in Fig. 10. So, the grown crystal is having good mechanical properties. It is suggested that the grown crystal can be used for device fabrication below the optimum load of 100 g. The work hardening coefficient 'n' was found to be 4.2, as shown in Fig. 11, which is greater than 2. The value of n comes out to be 1–1.6 for hard materials and more than 1.6 for soft materials [24]. Thus, it is clear that the grown PPBTH crystal belongs to soft material category. The stiffness constant (C_{11}) is determined using

$$C_{11} = (H_V)^{7/4}.$$

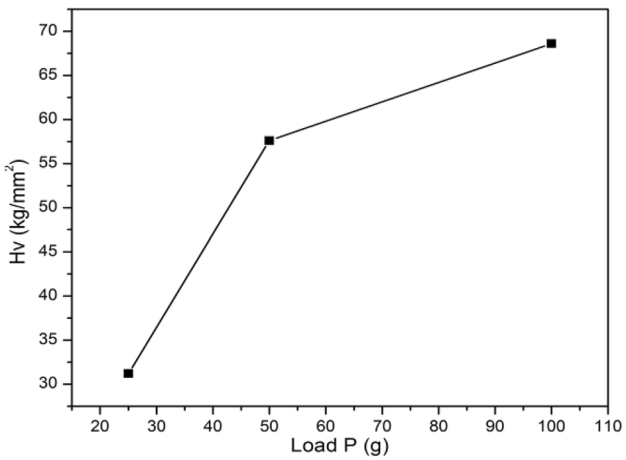

Fig. 10 Variation of Vicker's hardness number with load

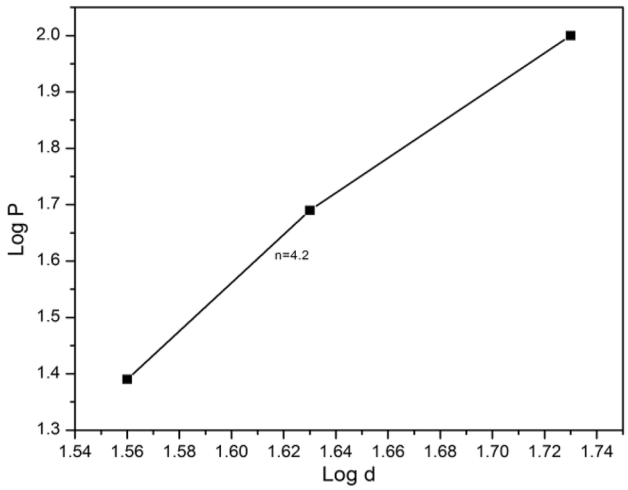

Fig. 11 Plot of Log d vs Log P for PPBTH crystal

The stiffness constant increases with the increase in applied load as shown in Fig. 12 (plot of the load P vs C_{11}).

3.9 Vibration sample magnetometer

The magnetic properties of variety of materials have been investigated so far using vibrating sample magnetometer. The PPBTH crystalline sample of 20 mg as a powder was placed in a glass ampoule fixed in VSM (CR155 quantum design), and the applied field ranges from 0 to 3 T. The magnetization (M) is measured with respect to the applied magnetic field (B) at room temperature. The graph was plotted between magnetic field and magnetic moment as shown in Fig. 13. From the plot, it is seen that the grown PPBTH single crystal has a diamagnetic nature [25].

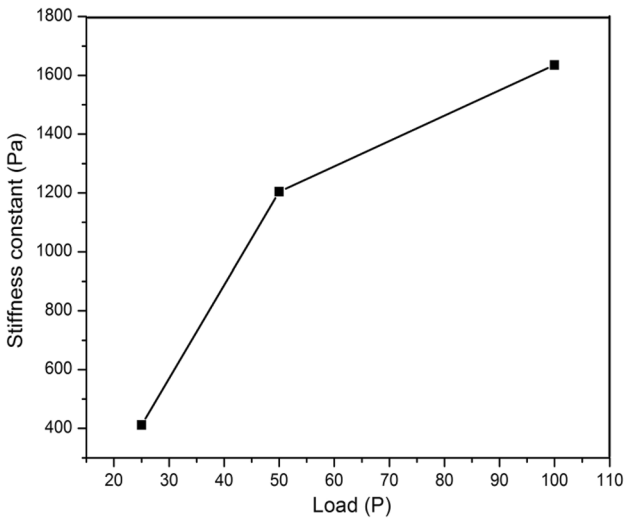

Fig. 12 Variation of stiffness constant with load for PPBTH crystal

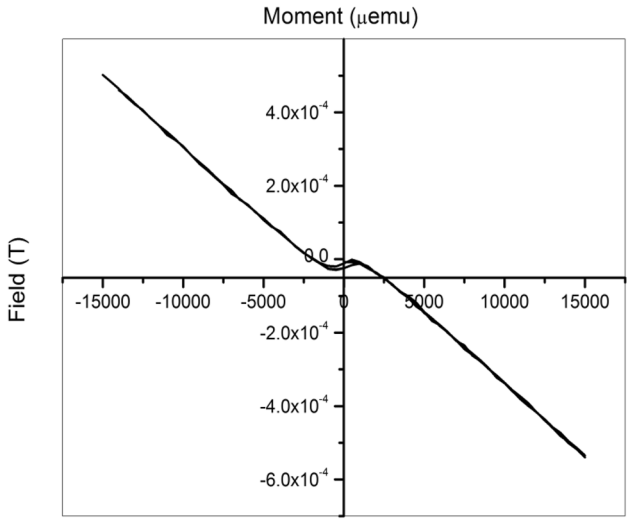

Fig. 13 VSM plot of grown PPBTH crystal

4 Conclusion

Good optical quality potassium pentaborate tetrahydrate single crystal was grown by slow evaporation solution growth method. The crystals were subjected to various characterizations. Single-crystal X-ray diffraction study revealed that PPBTH crystal belongs to orthorhombic system with lattice parameters $a = 11.06$ Å, $b = 11.17$ Å, and $c = 9.054$ Å. The crystalline nature and purity of grown crystal is confirmed by power XRD technique. The photoluminescence spectrum indicated the green emission of PPBTH. The SHG efficiency of the crystal exhibited that it can be used in NLO applications. The functional groups present in the grown PPBTH crystal were confirmed by FTIR analysis. The UV–Vis–NIR spectral studies show that it has a wide transparency range in the entire visible range. The presence of constituent molecules of the grown inorganic compound is confirmed by elemental analysis. Thermo-gravimetric and differential thermal analyses showed that the sample is thermally stable up to 144 °C. The grown crystal possesses high thermal stability. Mechanical behaviour of the grown crystal has been studied by the Vicker's microhardness test, and the work hardening coefficient is found to be 4.2. The VSM studies established that PPBTH crystal exhibits diamagnetic nature.

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