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Physical properties of lauric acid crystals grown with KBr in aqueous solution

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Abstract. Lauric acid crystals were grown with potassium bromide (LAPB) in aqueous solution at room temperature by slow solvent evaporation technique. The monoclinic structure of grown single crystal was studied by single-crystal X-ray diffraction and powder X-ray diffraction analyses. The Fourier transform infrared spectrum incorporates signatures of functional groups. The optical absorbance study reveals the UV cut-off wavelength as 230 nm. The Kurtz powder technique ensures that LAPB crystal has 1.1 times greater second harmonic generation efficiency than that of KDP crystals. The thermogravimetric and differential thermal analyses ensure that the material has good thermal stability. A dielectric behaviour of the sample material is studied in the frequency range 10^1–10^6 Hz.

Keywords. Crystal growth; optical material; XRD; spectroscopy; SHG; thermal stability.

1. Introduction

New nonlinear optical material (NLO) investigation is a significant research field in optics after the materialization of laser [1,2]. Optical single crystals are widely attractive for their applications in electro-optic switches, frequency conversion, colour display, high-energy lasers for inertial confinement fusion research, etc. [3,4]. The characteristic limitation of pure organic and inorganic materials leads to an alternative emphasis for the semi-organic materials. The magnitude of nonlinear polarization is increased by adding an electron donating group or an electron withdrawing group into the π-electron conjugated framework [5] for sub-atomic outline.

Recently, we reported the NLO activity of lauric acid (LA) single crystal grown in ethanol solution [6]. When NLO materials are added with inorganic and organic materials, the properties of the host material have been enhanced [7]. Hence an attempt has been made to grow LA crystals with potassium bromide (LAPB) in aqueous solution by slow solvent evaporation technique and bulk single crystals were grown as desired for optoelectronic device fabrications. To the best of our knowledge there is no report on LA crystals grown from aqueous solution with good thermal stability. The grown LAPB crystals were investigated through structural, optical, thermal, second harmonic generation (SHG) and dielectric studies and are reported here.

2. Experimental

2.1 *Crystal growth*

The LAPB crystals were grown by taking 1:2 ratios of LA and potassium bromide in deionized water. The pure small LA pellets purchased were dissolved in large amount of deionized water by raising temperature gradually up to 40°C since LA dissolves hardly in water. The reactants were stirred well for about 4 h and filtered twice to get rid of lauric froth. After a typical period of 35–40 days, transparent colourless crystals of varying dimensions were harvested as shown in figure 1.

2.2 *Instrumental techniques*

Single-crystal X-ray diffraction (SCXRD) analysis was carried out using an Enraf Nonius CAD4-MV31 single-crystal X-ray diffractometer. The powder X-ray diffraction (XRD) pattern of the powdered sample was recorded using a PANlytical X'pert Pro powder X'celerator diffractometer. A Perkin-Elmer spectrometer at a resolution of 4 cm^{-1} was employed to record the Fourier transform infrared (FTIR) spectrum by the KBr pellet technique. A Varian, Carry 5000 UV–Vis–near IR (NIR) spectrophotometer in the range 190–1100 nm was used to record optical transmission spectrum. A Perkin-Elmer thermal analyser was used for thermogravimetric (TG) and differential thermal (DTA) analyses. The dielectric studies

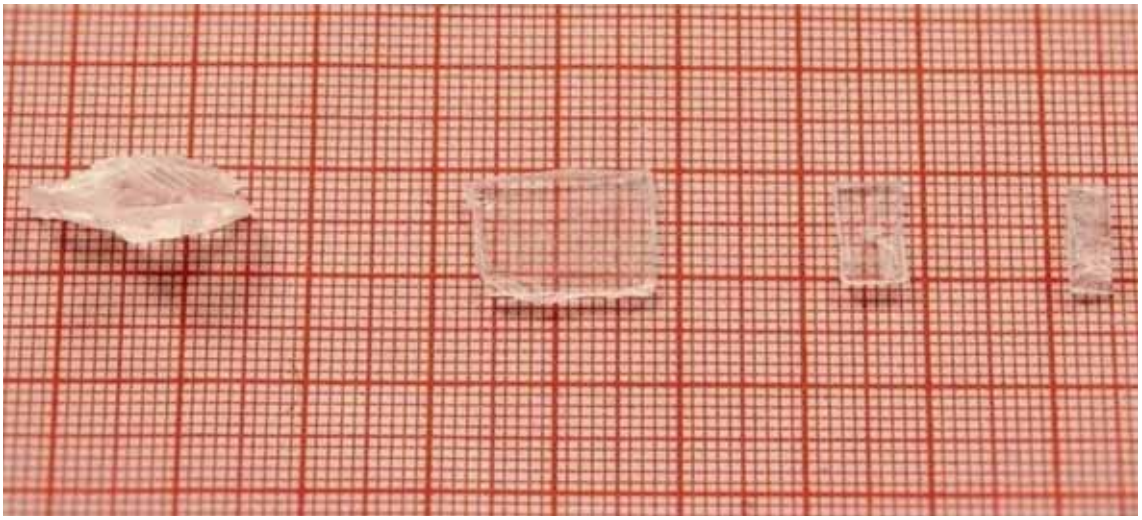

Figure 1. Photograph of LAPB crystals.

were carried out using an electrochemical work station. KBr content of the grown crystals was estimated by EDAX analysis.

3. Results and discussion

3.1 *XRD spectra*

The grown LAPB crystal was subjected to SCXRD study to estimate the lattice parameters. The unit cell dimensions obtained by SCXRD studies are $a = 5.109$ Å, $b = 11.996$ Å, $c = 5.469$ Å, $\beta = 111.70°$, $\alpha = \gamma = 90°$ and cell volume = 311.4 Å^3 with $P2_{1/m}$ space group. The reflection planes were identified through powder XRD technique. The LA crystal also crystallized in monoclinic structure with lattice parameters $a = 9.534$ Å, $b = 4.953$ Å, $c = 35.452$ Å, $\beta = 129.23°$, $\alpha = \gamma = 90°$ and cell volume = 1296 Å^3 [6] with $P2_{1/m}$ space group. The PXRD patterns of LAPB and LA crystals are depicted in figure 2a and b, respectively. Different prominent peaks of high intensity from those of LA were observed and indexed using TREOR software package. The purity and perfection of the grown LAPB crystal was witnessed by the sharp and well-defined Bragg peaks in the pattern. Comparing the line width of Bragg peak at 26° (2θ) of both LA and LAPB crystals, the line width of LAPB is reduced by 1° (2θ), which indicates improved crystalline quality of the present sample. The incorporation of K^+ and Br^- ions results in quite different XRD patterns of LAPB. In addition, there is variation in cell parameters and cell volume but the original monoclinic structure is retained. The perfect structure of grown compound may be due to KBr in the lattice of LA, which may decrease the nucleation centres in number.

3.2 *EDAX analysis*

From the EDAX spectrum (figure 3) the K and Br presence in LAPB crystal is clear. K with18.59 wt% and 11.01 at% and Br with 39.99 wt% and 11.59 at% has gone into the crystal. The atomic % and weight % of compound elements are presented in table 1.

3.3 *Optical spectral analysis*

The UV–Vis–NIR optical spectra of LAPB and LA crystals are shown in figure 4. The obvious absorbances around 300 and 800 nm were expected due to π–π^* and n–π^* transitions, respectively, in LAPB. LA shows stairs in the transmission spectrum between 260 and 800 nm. The delocalized π electron individually causes absorption in the UV region and NLO responses of sample material [8].

The lower cut-off wavelength of 230 nm enables LAPB's use in optoelectronics and the generation of SHG. The calculated optical band gap of LAPB is 5.4 eV, which is a characteristic dielectric material band gap value [9]. The NIR translucence permits industrial applications of the title compound [10]. The existence of KBr causes disorder in crystal lattice and this disorder leads to changes in lattice parameter and optical properties nonlinearly [11].

3.4 *FTIR analysis*

The FTIR spectrum of LAPB in figure 5 shows a complete shift in peaks from LA peaks, which may be due to physical interaction of COOH group of LA and alkaline moiety of KBr. The disturbed FTIR pattern may also be due to minor structural change as a result of KBr incorporation [12]. The peaks at 668.93 and 402.48 cm^{-1} are due to C–Br symmetric stretching and K–O stretching, respectively [13]. A medium strong peak at 2923.65 cm^{-1} and a broad strong peak at 3428.40 cm^{-1} were observed. The former is due to CH_2 function group and the latter is due to hydroxyl group stretching of LA. A very strong peak at 1620.52 cm^{-1} is observed due to the functional

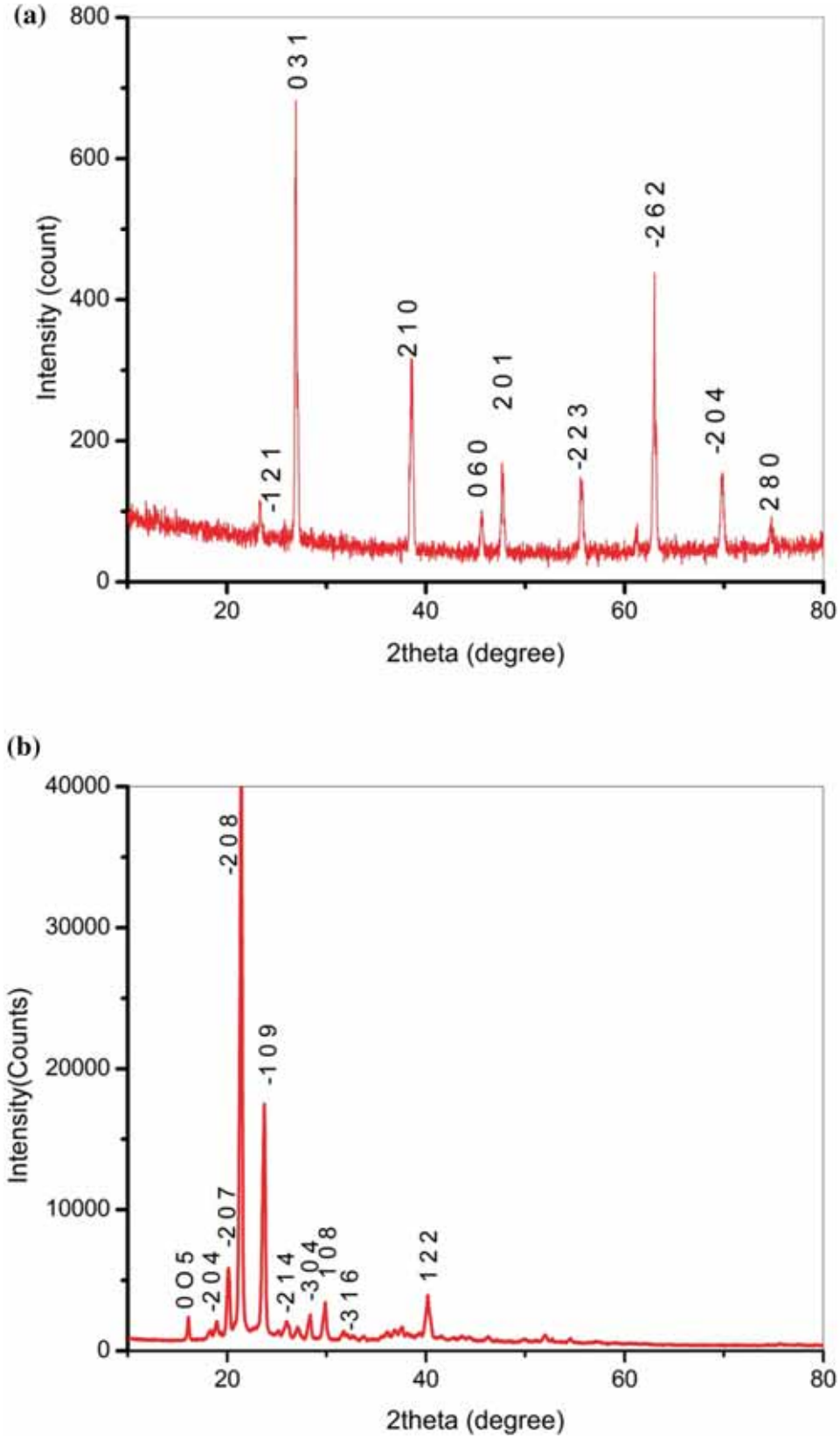

Figure 2. PXRD pattern of (**a**) LAPB and (**b**) LA crystals.

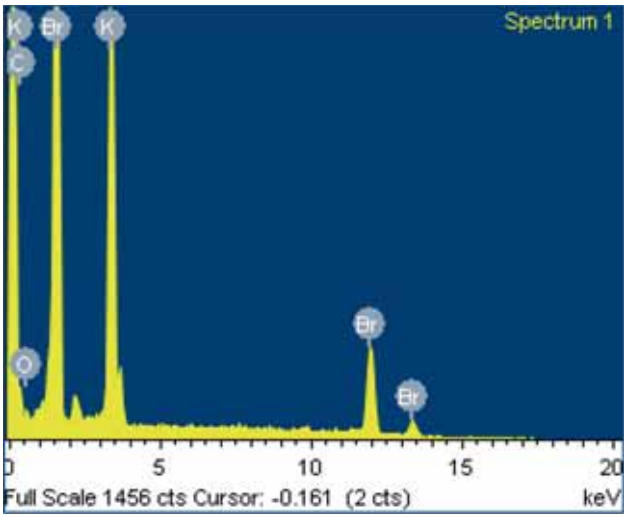

Figure 3. EDAX spectrum of LAPB crystal.

Table 1. Elements in LAPB crystal and their at% and wt%.

Element	Content	
	wt%	at%
C K	36.22	69.86
O K	5.20	7.54
K K	18.59	11.01
Br L	39.99	11.59

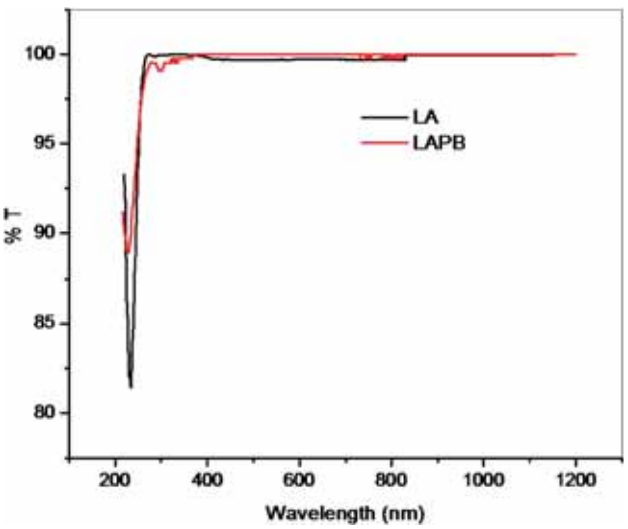

Figure 4. UV–Vis–NIR spectrum of LAPB and LA crystals.

carboxyl group of LA [14]. New peaks are seen with characteristic peaks of LA, which indicates that there is chemical interaction between LA and KBr.

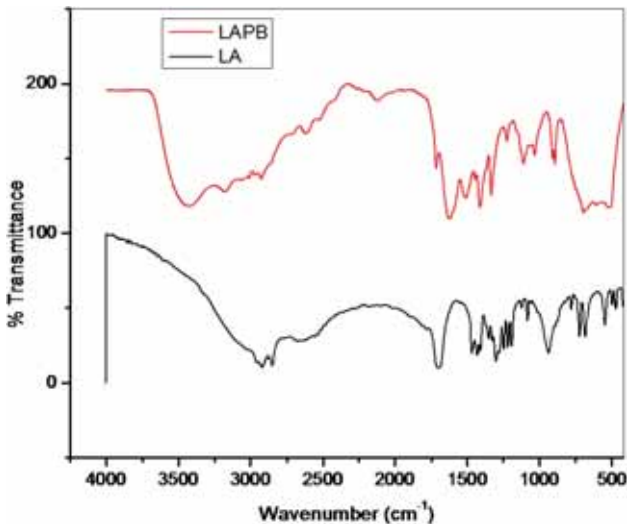

Figure 5. FTIR spectrum of LAPB and LA crystals.

3.5 *Thermal analysis*

The TG–DTA analysis (figure 6a) shows that thermal stability of the grown LAPB crystal is about 240°C. This is greater than thermal stability of LA (figure 6b) crystal. The change in lattice parameter, which changes binding energy, is responsible for melting. The metal–organic materials have the possibility of incorporating the thermal stability of inorganics [15]. Hence, the thermal stability of LAPB crystal is enhanced by KBr concentration. The sharp endothermic dip indicates good degree of crystallinity and purity of grown material. The crystallization of present sample is moisture free as required for laser applications [16]. The major weight loss observed between 240 and 730°C may be due to decomposition of volatile components of LAPB sample.

3.6 *SHG efficiency test*

Donor and acceptor molecules are held together in the compound material by Van der Walls bond and hence the hyperpolarizability (β) is enhanced [17]. In the present work, the SHG efficiency is observed to be 1.1 times more prominent than that of the KDP crystal.

3.7 *Dielectric studies*

The essential dielectric studies were performed to realize the lattice dynamics, polarization mechanism and transport phenomena in the grown LAPB crystal. Figures 7 and 8 show a normal dielectric behaviour of the sample. The presence of space charge, orientational, electronic and ionic polarization may increase the dielectric constant at lower frequencies and the gradual loss of significance of these polarizations

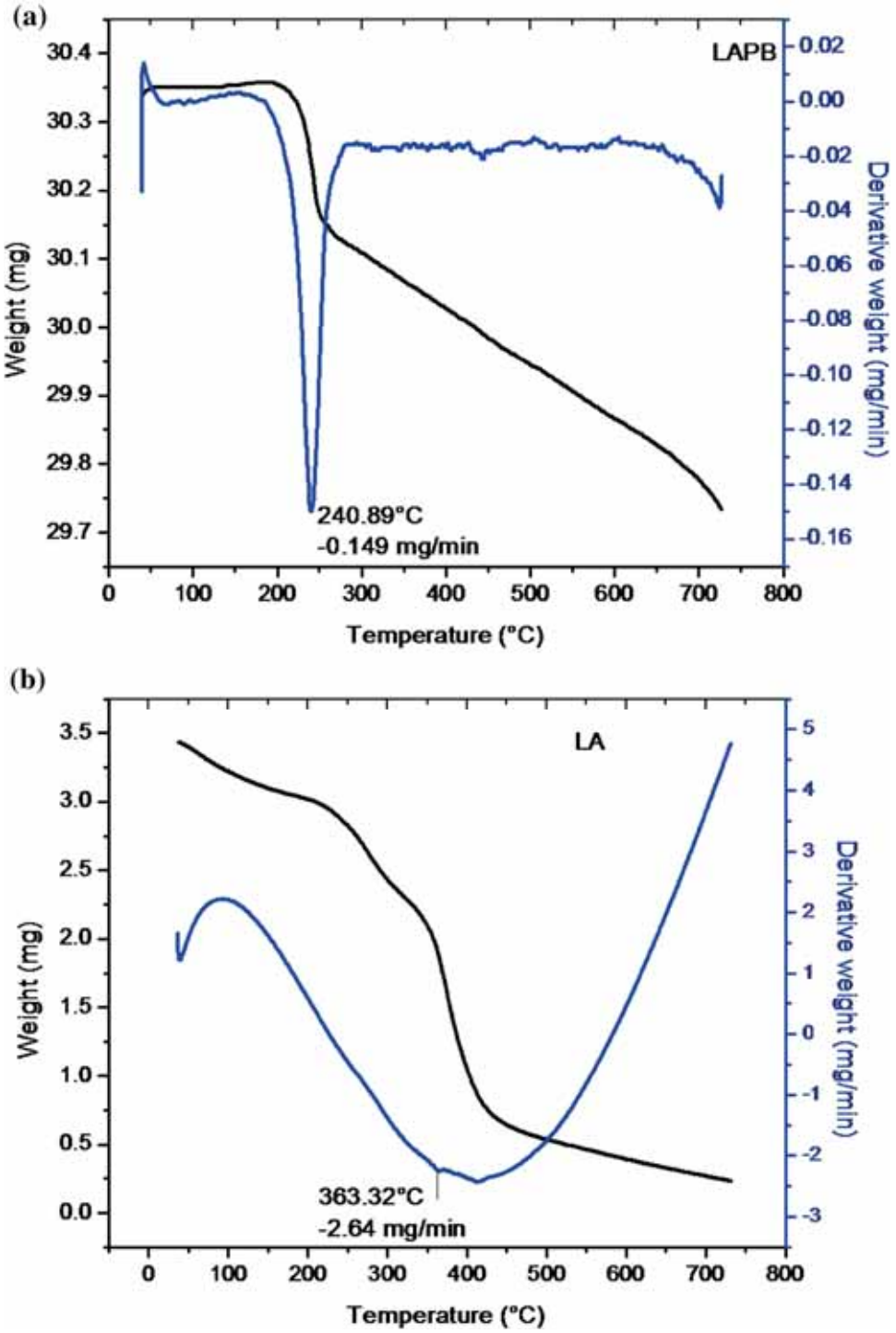

Figure 6. TG–DTA graph of (**a**) LAPB and (**b**) LA crystals.

and invariance of dipoles may decrease the dielectric constant value at higher frequencies [18]. The low value of dielectric loss in high frequency region suggests that the grown crystal has high optical excellence with lesser defects [19].

3.8 *Comparative analysis*

Table 2 presents comparative data of LA and LAPB crystals from similar studies. The lattice parameters, decomposition point and nonlinear properties of LA crystal grown with

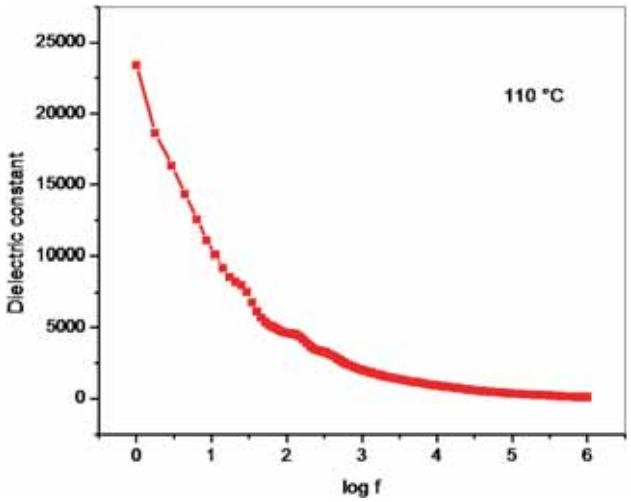

Figure 7. Variation of dielectric constant with log frequency.

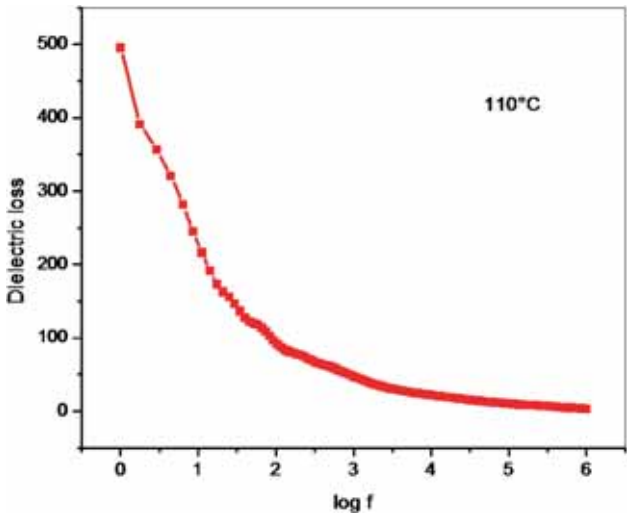

Figure 8. Variation of dielectric loss with log frequency.

potassium bromide in aqueous solution changed from those of LA crystals grown in ethanol solution. The enhancement of NLO properties of LAPB crystal may be due to the presence of KBr in the crystal lattice.

4. Conclusion

Optically transparent single crystals of LA were grown with potassium bromide in aqueous solution by slow solvent evaporation technique at room temperature successfully. The unit cell parameters were evaluated by SCXRD and powder XRD techniques. The FTIR analysis revealed functional groups and new elements present in the crystal lattice. The prerequisite NLO property of LAPB was studied through SHG efficiency and wide optical transparency in optical transmission spectrum. The enhanced SHG efficiency, optical properties and

Table 2. Comparative data on crystals of LAPB and LA.

Properties	LA crystal grown in ethanol solution [6]	LAPB crystal grown in aqueous solution (present work)
Lattice parameters	$a = 9.534$ Å, $b = 4.953$ Å, $c = 35.452$ Å, $\beta = 129.23°$, $\alpha = \gamma = 90°$	$a = 5.109$ Å, $b = 11.996$ Å, $c = 5.469$ Å, $\beta = 111.70°$, $\alpha = \gamma = 90°$
Cell volume (Å^3)	1296	311.4
Symmetry	Monoclinic	Monoclinic
Space group	$P2_{1/m}$	$P2_{1/m}$
Decomposition point (°C)	45	240
Relative SHG efficiency (reference: KDP sample)	0.87	1.1

thermal stability make the LAPB crystal a potential candidate for opto-electronic device application. The dielectric studies confirm that the grown material has lesser defects with higher optical excellence.

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