Growth and Characterization On Sodium Lead Bromide Crystals

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Abstract

Ternary alkali lead halide single crystals have been become important because of their potential applications in acousto-optic and opto-electronic devices. We have attempted, in the present study, to grow and characterize single crystals of sodium lead bromide .The crystals were grown, for the first time, by the solution method. The grown samples were subjected to single crystal XRD, AAS, EDAS, TGA/DTA, UV-Vis-NIR spectral and electrical (both AC and DC) measurements.

Keywords: crystal growth, alkali halides, electrical property etc.

1. Introduction

Ternary alkali lead halide single crystals have become important because of their potential applications in acousto-optic and opto-electronic devices .Lead bromide crystals hold much promise in applications for acouto-optic devices in signal processing and optical spectrum analyzing systems. Recently, it has been found that ternary alkali halide single crystals can be grown by the melt method and they become important due to their potential applications [1-9]. An important step towards practicality was made when the rare-earth-doped alkali-lead halide crystals MPb_2Hal_5 (M = Rb,K and Hal = Cl, Br) were identified as promising new low-phonon-energy host materials for mid-IR applications. Although it is known that pure and rare earth doped alkali lead halide single crystals are highly useful, there is no report available in the literature on sodium lead bromide single crystals. This prompted us to grow and characterize some sodium lead bromide single crystals. Hence, we have made and attempt in the present study, to grow by the solution method and characterize four sodium lead bromide single crystals, viz. $NaPb_2Br_5$, $NaPbBr_3$, Na_2PbBr_4 and Na_3PbBr_5.

2. CHARACTERIZATION

The single crystal X-ray diffraction studies of the crystals were carried out using ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoK_{α} (λ = 0.717 Å) radiation. The crystals were also characterized, as in the case of potassium lead bromide single crystals carrying out AAS, EDAS, TG/DTA, UV-Visible spectral, etc measurements. The frequency dependence of dielectric constant and dielectric loss factor of the samples were studied at different temperatures (ranging from 40-150°C) with five different frequencies, viz. 100Hz, 1kHz,10kHz,100kHz and 1MHz using an LCR meter (Agilent 4284A). The AC conductivities were also determined. The measurement of DC electrical conductivity was done using the conventional two-probe technique for different temperatures ranging from 40 to 150°C. As the crystals are needle shaped ones, the crystals were pelletized and used for the electrical measurements in a similar way followed by Mahadevan and his co-workers [10-14].

3. Results Obtained

3.1 Growth of sodium lead bromide single crystals

The preparation of sodium lead bromide was based on commercial starting materials of $PbBr_2$ and NaBr with 99.99% purity. The sodium lead bromide crystals were grown by dissolving lead bromide with sodium bromide in the molar ratios 1:.05, 1:1, 1:2 and 1:3 in distilled water. The solubility test gives a key to select the best solvent and temperature to grow good quality single crystals. Sodium lead bromide ($NaPb_2Br_5$/ $NaPbBr_3$/Na_2PbBr_4/Na_3PbBr_5) solution was prepared in distilled water and maintained at a particular temperature with continuous stirring. On reaching saturation the content of the solution was analyzed gravimetrically and set for free evaporation. Figure 1 shows the photograph of the grown crystal samples.

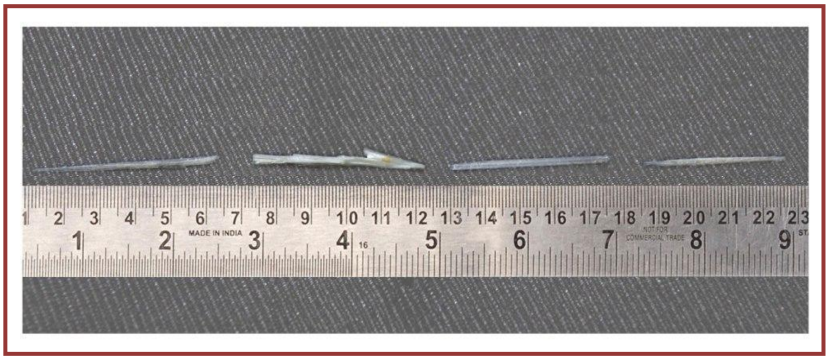

Figure 1: Photograph of the sample crystals grown [From left: $NaPb_2Br_5$, $NaPbBr_3$, Na_2PbBr_4 and Na_3PbBr_5]

3.2 Single Crystal X-ray Diffraction Analysis

The lattice parameters and cell volume of the grown crystals are presented in Table 1. All the four crystals belong to the class of orthorhombic crystal structure. The lattice parameters observed (see table 1) are comparable to that reported for $PbBr_2$ which are: a=8.0620(1), b=9.5393(13) and c=4.73480(6) Å, V=364.134 $Å^3$ [15]. This further shows that the $PbBr_2$ lattice is not significantly distorted due to Na^+ addition.

3.3 Atomic Absorption Spectra

AAS data could be used to check the metal atom contents in the mixed crystal. Atomic absorption spectroscopic (AAS) measurements were carried out using Perkin Elmer spectrophotometer to determine the metal atom contents (Na and Pb) of the mixed crystals grown. The AAS data obtained are given in Table 2.

3.4 Energy dispersive X-ray Absorption Spectra

EDAS was carried out using the recorder at the rate of 3638 CPS (FS=2564 CNT) in KVZ60 line at an angle of tilt 28. The EDAS spectra recorded are shown in Figure 2 which confirms the composition of the grown crystals. The dominant peaks correspond quite well to the

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energies of lead and bromine while small hemp at 1.04 keV corresponds to K line of sodium, giving a clue that lead is dominant over sodium in the crystals grown

Table 1: Single crystal XRD data for sodium lead bromide crystals grown in the present study

Crystallographic data	**$NaPb_2Br_5$**	**$NaPbBr_3$**	**Na_2PbBr_4**	**Na_3PbBr_5**
a (Å) b (Å) c (Å)	4.697 7.979 9.432	4.699 7.960 9.379	4.702 7.967 9.432	4.702 8.014 9.464
α^o β^o γ^o	90 90 90	90 90 90	90 90 90	90 90 90
Volume (Å^3)	353.5	350.9	353.4	356.6
Crystal Structure	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic

Table 2: **Atomic absorption spectral data**

Sample Code	**Atomic content (ppm)**	
	Pb	**Na**
$NaPb_2Br_5$	570374	96
$NaPbBr_3$	570326	108
Na_2PbBr_4	561037	120
Na_3PbBr_5	580317	162

The results obtained through X-ray diffraction, AAS and EDAS measurements indicate the absence of proper mixing of NaBr and $PbBr_2$ in all the four sodium lead bromide crystals grown. So, the grown crystals may be considered as Na^+ doped $PbBr_2$ single crystals.

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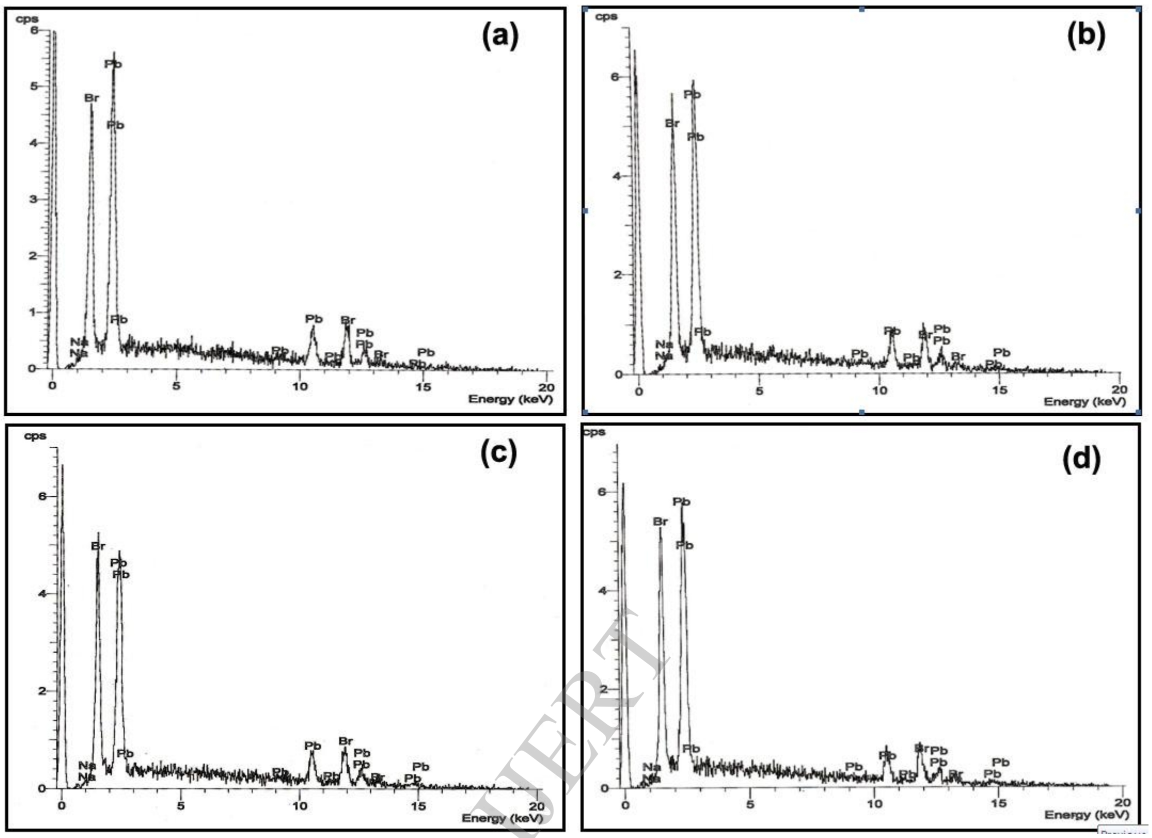

Figure 2: EDAS spectra for (a) Na Pb_2Br_5 (b) $NaPbBr_3$ (c) Na_2PbBr_4 and (d) Na_3PbBr_5

3.5 UV-Visible Absorption Spectra

The optical absorption spectral analysis is an important study for any optical material as it can be put into use only if it possesses the required cut-off wavelength as well as a low optical absorption. The UV-Visible spectra for the four grown sodium lead bromide crystals are shown in Figure 3. It can be seen from the Figure that the samples have optical absorption edges at 350nm, 363nm, 368nm and 370 nm respectively for $NaPb_2Br_5$, $NaPbBr_3$, Na_2PbBr_4 and Na_3PbBr_5. In the entire visible region, the absorbance is less than 1 unit. Like $PbBr_2$ crystal, the four sodium lead bromide crystals grown in the present study exhibit a large optical transparency. Moreover, the transmittance observed is significantly more than that observed for $PbBr_2$[15].Even though, they are not properly mixed sodium lead bromide crystals, all the four single crystals grown in the present study exhibit superior optical characteristics required for acousto-optical(AO) devices.

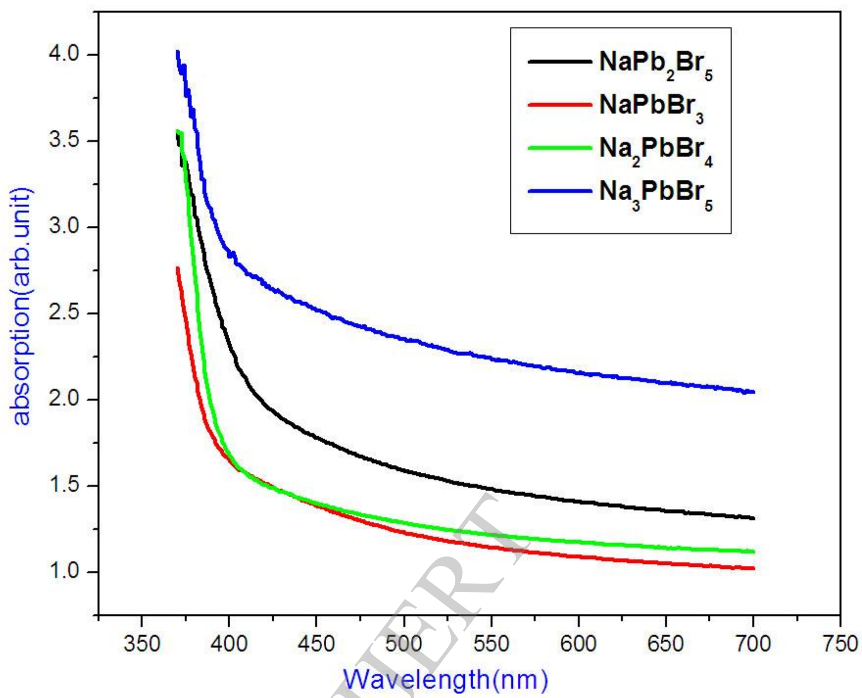

Figure 3: UV – Visible absorption spectra for sodium lead bromide crystals

3.6 Thermal Studies

In the present work, the thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of sodium lead bromide mixed crystals were carried out in the temperature range 30-900^{o}C. The TG/DTA of freshly crushed samples were carried out in nitrogen atmosphere, with a heating rate of 20^{o}C/ min. The TGA and DTA traces of the samples are shown in Figure 4.

The TGA trace illustrates that there is a sharp weight loss near 530 ^{o}C, which is attributed to the decomposition and volatilization of Sodium lead bromide mixed crystals. Below the onset of decomposition, no weight loss is observed and hence the crystal is completely free from physically adsorbed water or water of crystallization.

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The DTA trace (shown in Figure 4) indicates an intense sharp exotherm, at 370 ^oC , 371.81 ^oC ,654.26 ^oC and 370.84 ^oC for $NaPb_2Br_5$, $NaPbBr_3$, Na_2PbBr_4 and Na_3PbBr_5 respectively .This corresponds to the weight loss of the sample and it is interesting to note the absence of any exotherm / endotherm in the temperature below the temperature of 371 ºC. Hence, this study supports the results observed in TG analysis. The results obtained in the present study through thermal analysis also evidence the formation of NaBr added $PbBr_2$ crystals and not the proposed mixed crystals. So, the chemical formulae used to represent the grown sodium lead bromide crystals are not correct

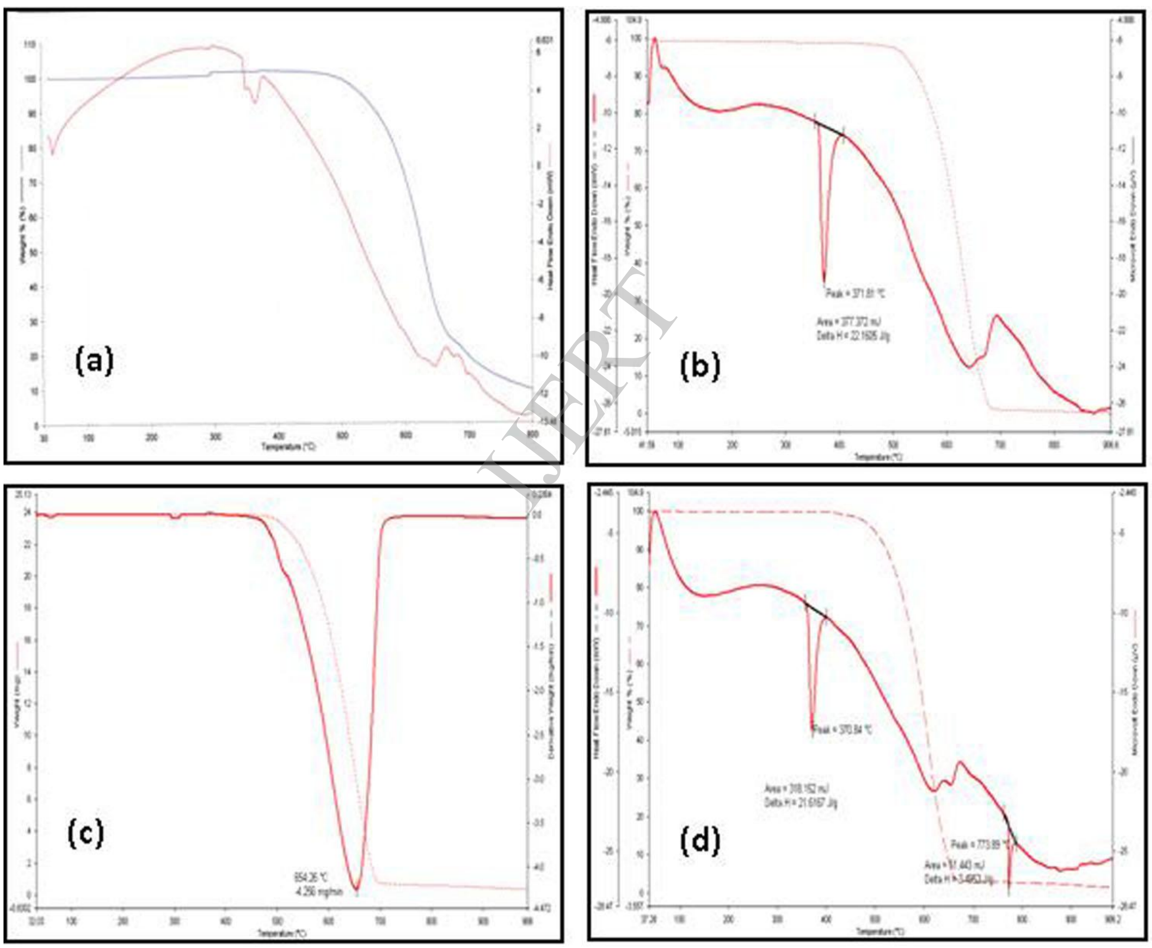

Figure 4: TG/DTA spectrum for (a) Na Pb_2Br_5 (b) $NaPbBr_3$ (c) Na_2PbBr_4 and (d) Na_3PbBr_5

3.8 Dielectric studies

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Figures 5 and 6 show the variation of dielectric constant and the dielectric loss factor of sodium lead bromide mixed crystals as a function of frequency at different temperatures (40-150^{o} C). The increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability which is explicitly interrelated with the corresponding temperature variation of compressibility [16]

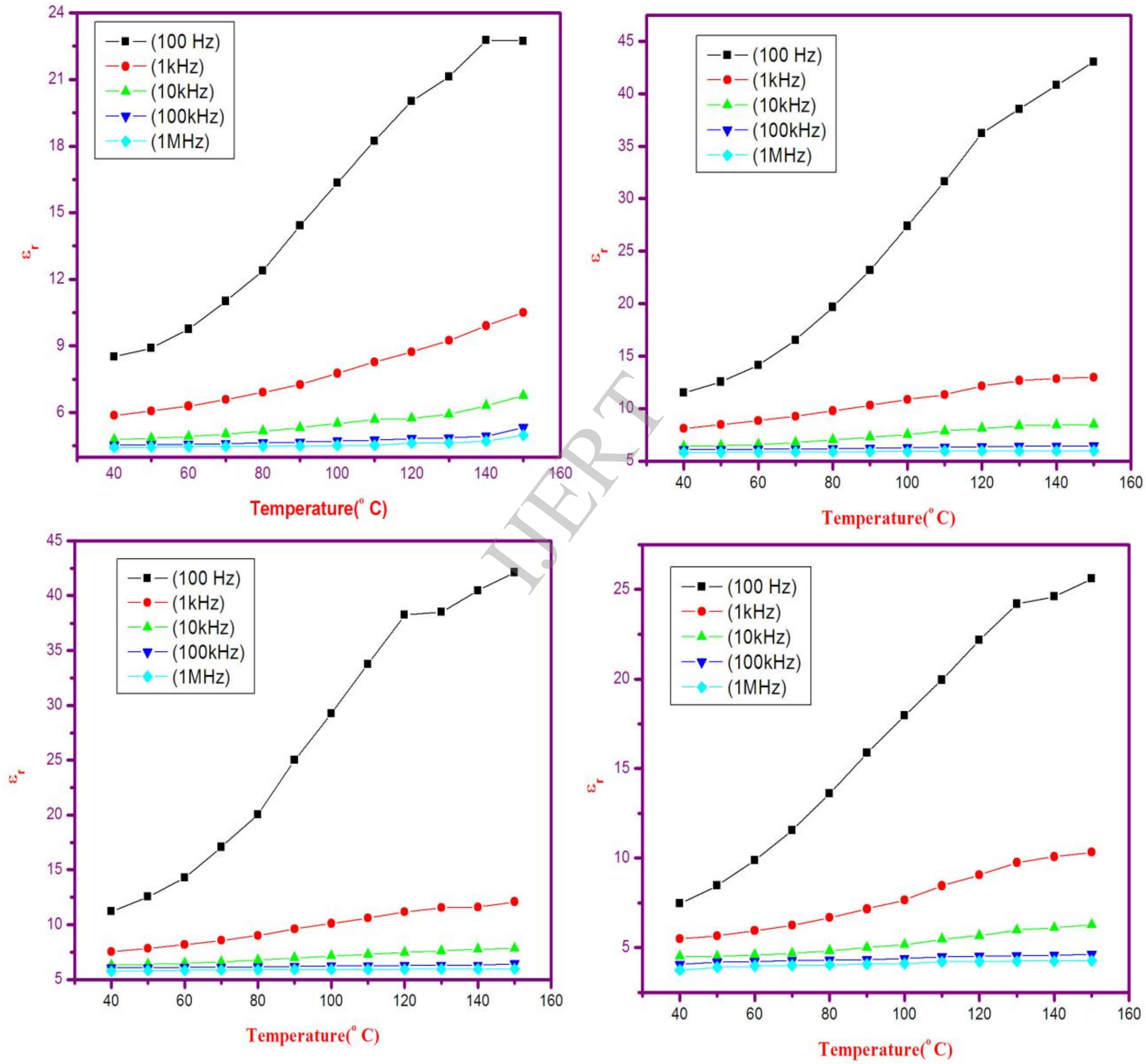

Figure 5: Variation of Dielectric constant with temperature for different frequencies for a) $NaPb_2Br_5$ b) $NaPbBr_3$ c) Na_2PbBr_4 and d) Na_3PbBr_5 single crystals

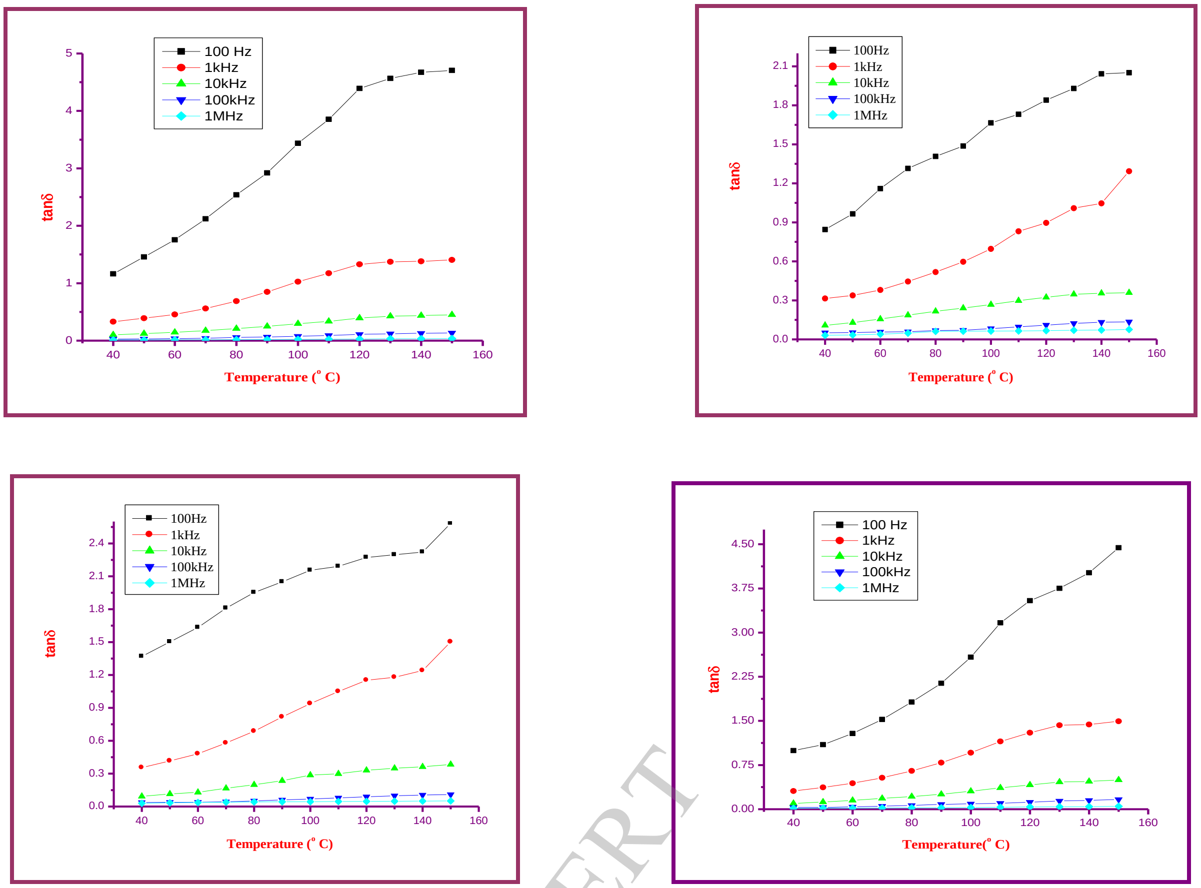

Figure 6: Variation of Dielectric loss factor with temperature for different frequencies for a) Na Pb_2Br_5 b) $NaPbBr_3$ c) Na_2PbBr_4 and d) Na_3PbBr_5 single crystals

3.9 AC and DC conductivities

The AC and DC conductivities observed in the present study for the four crystals are shown in Figures 7 and 8. The increase of conductivity with the increase in temperature observed in the present study is similar to that observed for some crystals.

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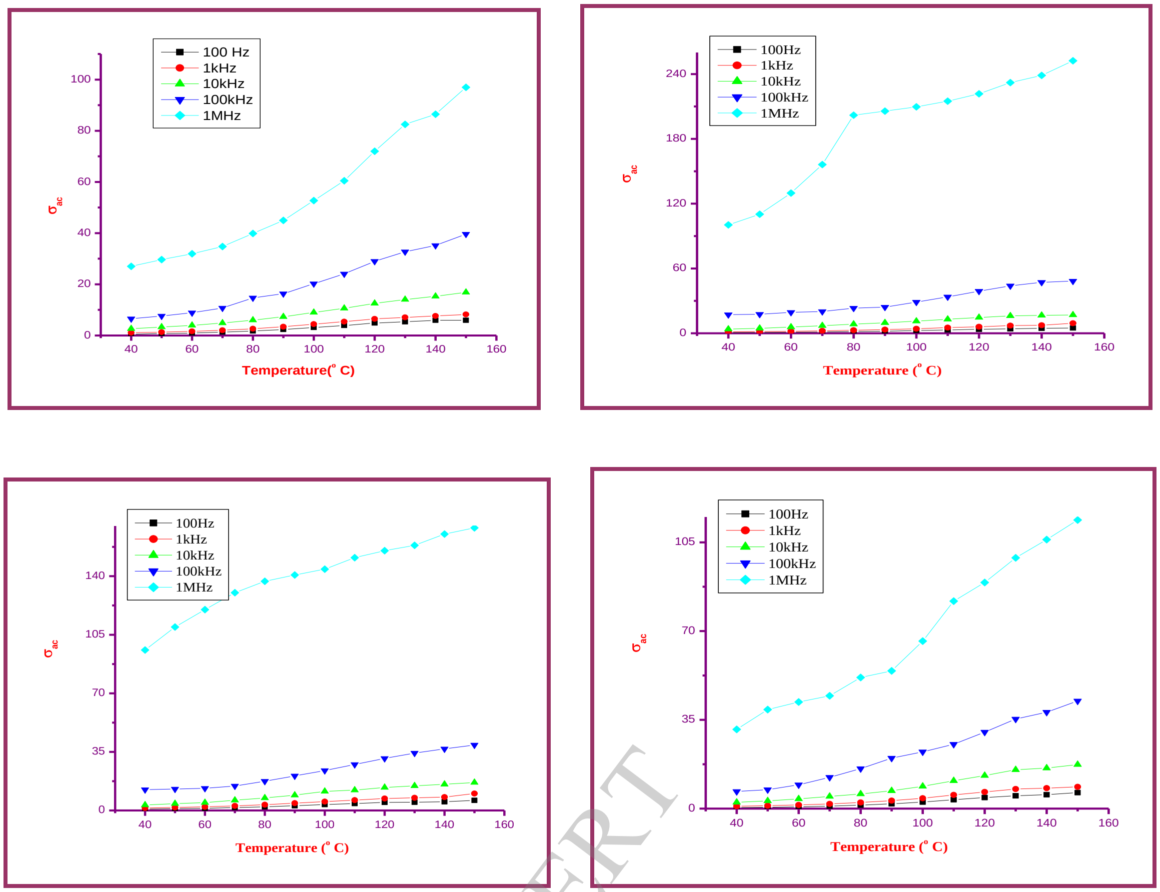

Figure 7: Variation of AC conductivity with temperature for different frequencies for a) Na Pb_2Br_5 b) $NaPbBr_3$ c) Na_2PbBr_4 and d) Na_3PbBr_5 single crystals

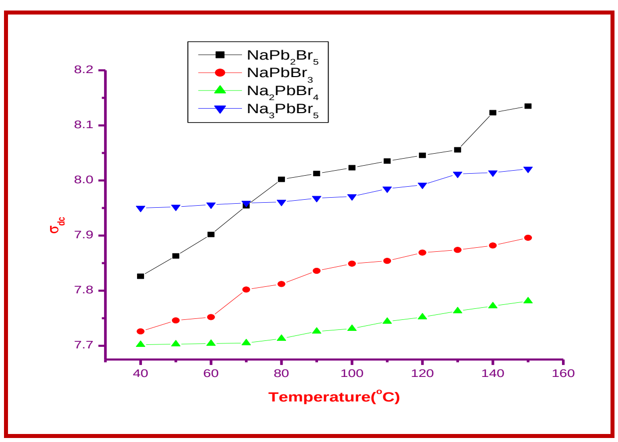

Figure 8 : Temperature dependence of DC conductivity (*10^{-5} mho/m) for sodium lead bromide crystal

Conclusion

All the four single crystals ($NaPb_2Br_5$, $NaPbBr_3$, Na_2PbBr_4 and Na_3PbBr_5) were grown by slow evaporation method. They were thermally stable upto more than 500^{o}C and have a phase transition occurring at ~370^{o}C. The results obtained from the chemical characterization studies (XRD, AAS and EDAS measurements) indicate that the crystal grown are not the ternary mixed (as attempted to grow at room temperature) but Na doped $PbBr_2$ crystals. The transmittance observed for all the four grown crystals is significantly more than that observed for $PbBr_2$.Hence, the results obtained in the present study indicate that even though the crystals grown are not properly mixed they exhibit superior optical characteristics required for acousto-optical (AO) devices

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