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Growth and Characterization of Pure ZnS Doped KCl$_x$Br$_{1-x}$ Mixed Crystals

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ABSTRACT

In the present study high quality single crystals of KCl$_x$ Br$_{1-x}$ (Composition x=0.2, 0.5, 0.8) were, grown by the slow evaporation technique under room temperature. The structural properties have been studied by powder X-ray Diffraction (XRD) analysis. The Fourier Transform Infrared (FTIR) spectrum is taken for all the samples to study the spectroscopic properties of the grown crystals. The micro hardness measurements were carried out on the grown crystals to estimate the mechanical properties. The optical properties of the grown samples were determined from UV-Visible absorption and transmission spectra. The thermal properties were studied from Thermogravimetric/Differential Thermal Analyzer (TG/DTA) analysis.

Keywords: Alkali halide, Crystal growth, Mixed crystals, XRD, Lattice parameter, FTIR, Micro hardness, UV, TG/DTA

INTRODUCTION

A crystal is a solid, composed of atoms or other microscopic particles arranged in an orderly repetitive array [1]. In crystallography, crystal structure is a description of the ordered arrangement of atoms, ions or molecules in a crystalline material [2]. Crystallography is the experimental science of determining the arrangement of atoms in the crystalline solids. X-ray crystallography is used to determine the structure of large bio molecules such as proteins [3]. Armington et al. [4], studied the micro hardness measurements done in KCl, KBr and in difference compositions of KCl-KBr mixed crystals show that it varies nonlinearly with composition. A.K. Mishra et al. [5], synthesized the X-ray characterization of mixed KCl$_x$Br$_{1-x}$ Single crystals. The distance 'd' between adjacent (100) planes has been found to vary in a linear way with the change of x for different KCl$_x$Br$_{1-x}$ crystals, studied through X-ray Diffraction (XRD) analysis. Neelakandapillai et al. [6] have reported the single crystals were grown from aqueous solution. All the grown crystals were characterized by XRD and Vicker's micro hardness measurement. All mixed crystals were able to index with single lattice parameter and all the grown crystals belong to hard category materials. Selvarajan and Mahadevan [7] have reviewed the observed lattice parameters showed the existence of three phases in solid solutions each nearly corresponds to NaCl, KBr and KI. Lesly Fathima and Neelakandenpillai [8] obtained the mixed and doped crystals of alkali halides are found to be harder than the end number crystals and so they are more useful in applications. So, it is necessary to prepare binary and ternary mixed crystals regardness of their miscibility problem. The grown crystals are characterized by measuring their physical properties. In the present work KCl$_x$Br$_{1-x}$ crystals have been grown for various values of x. The Fourier Transform Infrared (FTIR) spectrum was recorded for all the grown crystals.

DESCRIPTION OF EXPERIMENTATION

Slow evaporation technique

The high quality single crystals of KCl$_x$Br$_{1-x}$ can be grown by the slow evaporation method under room temperature. In this method, the saturated solution is kept at a particular temperature and colligation in to the atmosphere. This evaporation technique has the advantage to grow crystals at a fixed temperature. This technique needs a vessel for keeping the supersaturated solution in which the crystal grows. The heights, radios volume of the vessel are chosen by crystal size. The vessels are allowed to evaporate and closed tightly using a porously sealed cover.

Crystal growth technique

The low temperature solution growth technique. It consists of a large tank heated at the base using an infrared lamp. The IR lamps are energized through a relay switch. The control is affected by a Jumo contact thermometer coupled to an on-off controller, which has a controlling accuracy of ± 0.01°C. The temperature of the constant temperature bath is converted into a signal by a suitable sensor. The controller is contacted with an on-off switch. It gets activated when the process variable crosses the set point. There are only two stable states in an on off controller. "On" state is enabled when the temperature is below the set point. As the desired set point is arrived, the controller goes to the "off" state. To get change in the state, the temperature must cross the set point. Set point variations, which occur due to electrical noise interference and process disturbances, seriously affect the practical applications of the controller. Contrary to this, a proportional controller continuously manipulates the process variable so that the heat input is in balance with the heat demand.

The controller consists of a power supply, processor, booster and proportional controllers. In the present investigation, the growth instrument was modified by replacing the infrared lamp using a programmable controller heater.

Alkali halide crystals

The alkali halide crystals have importance in past six decades. They have been "model crystals" for testing many solid-state theories. In recent decades, they have also proved useful in several applications ranging from X-ray monochromators to tunable lasers. The use of pure simple alkali halides is limited by the mechanical systems and hence there exist the need to strengthen them two methods of improving the hardness of alkali halides is Solid solution hardening, Impurity hardening. Two compounds or elements are said to form a continuous solid solution if a single lattice parameter as measured by X-ray powder photographs, can be assigned to the solid solution at all compositions. In the present work, all the compositions are assigned single lattice parameter and it indicates that they form continuous solid solutions.

Solution preparation

The Analytical Reagent (AR) grade KCl and KBr and dissolved double distilled water were taken for the 100 ml beaker. The 40 ml super saturated solutions of two pure and three 0.5 mol % of ZnS doped KCl_xBr_{1-x} mixed crystals and distilled water are taken in a beaker. Then it is crystallize by slow evaporation method. The solutions are stirrer with heated for 2 h by using magnetic stirrer. Then the beakers are allowed to evaporate and closed tightly using a porously sealed polyethylene sheet with open atmosphere. Nucleation occurs for all crystals within 4 days and small tiny transparent crystals were obtained. The high quality crystals were harvested after three weeks. The crystals are dried using filter paper. The grown crystals are characterized by powder XRD, FTIR, UV, micro hardness and Thermogravimetric/Differential Thermal Analyzer (TG/DTA) analysis (Figure 1).
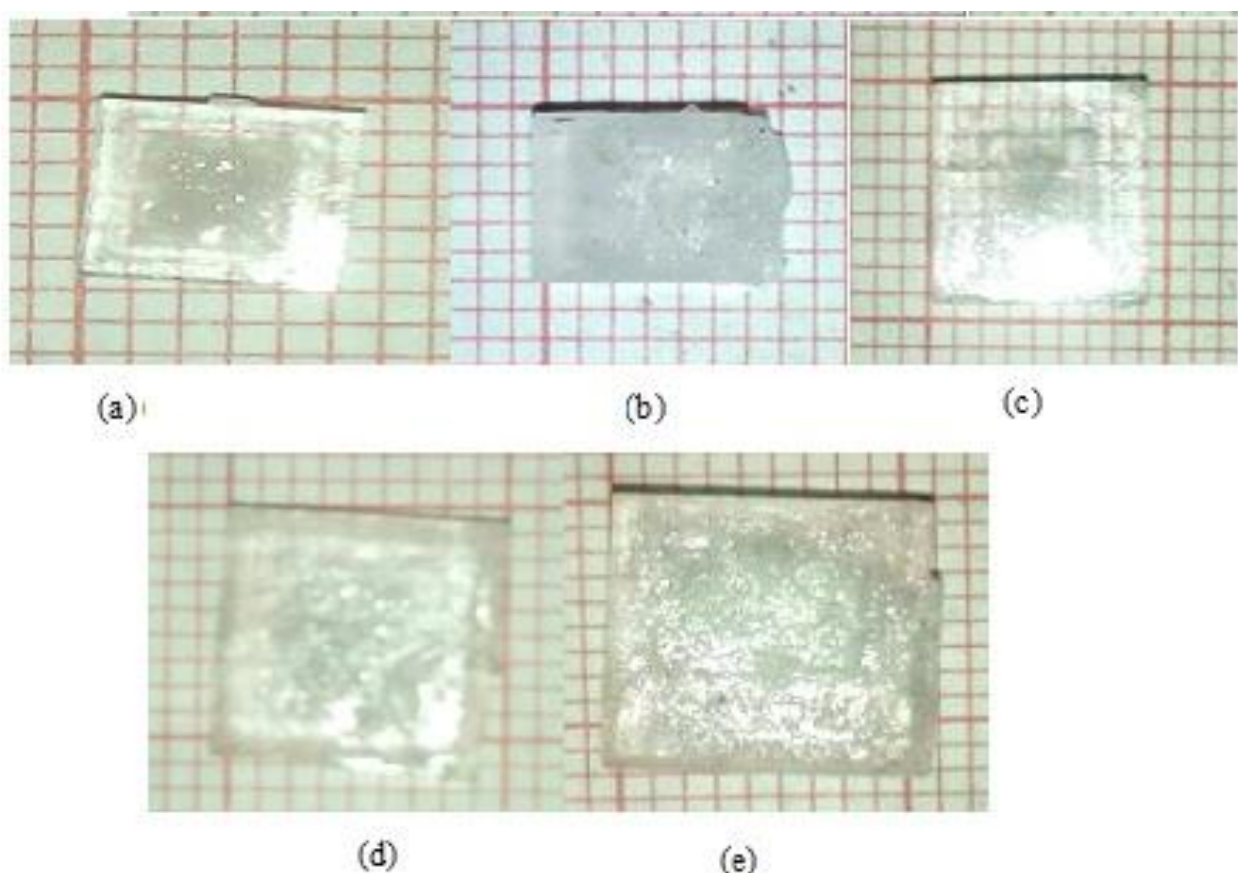

Figure 1: Photographs of all the grown crystals mixed crystals. (a) KCl, (b) KBr, (c) $KCl_{0.2}KBr_{0.8}$, (d) $NKCl_{0.5}KBr_{0.5}$, (e) $KCl_{0.8}KBr_{0.2}$

Characterization techniques

Alkali halide mixed crystals are of the completely disordered substitutional type. To identify the material, the peaks of the XRD pattern can be compared with the standard available data for the confirmation of the structure. High resolution Guinier Powder X-ray Diffraction (PXRD) used for phase analysis as well as the Miller indices values used to calculate the lattice parameters. The main goal of IR spectroscopic analysis is to identify the chemical functional groups in the sample and to identity of a pure compound or to detect the presence of specific impurities. The FTIR spectra have been recorded by using IFS Brukkker 66V spectrophotometer energy limited middle IR region in the range of 400 cm^{-1}-4000 cm^{-1} in order to find the presence of various functional groups. The FTIR spectroscopy improved the quality of IR spectra and minimized the time. The IR spectroscopy is the individual frequencies the radiation is absorbed and transmitted [9]. Pure and doped KCl and KBr crystals were tested for their micro hardness properties using a Shimadzu HMV-2 Vicker's indentation hardness were measured as the ratio of applied load to the surface area of the indentation. UV spectroscopy of the wavelength of absorption peaks can be correlated with the type of bonds in a given molecule and it is used determining the functional groups within a molecule.

The UV-Visible absorbance spectra were recorded in the wavelength region 200-800 nm using Varian Cary 5E UV-Vis-NIR Spectrophotometer. UV-Vis spectroscopy measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules. Ultraviolet spectroscopic studies are optical absorption and transmission spectra were recorded for the mixed crystals by slow evaporation technique. TG and DTA give information regarding phase transition, crystallization and different stages of decomposition of the crystal system TG and DTA for the crystal samples were carved out in air atmosphere by a STA 1500 Thermal Analysis of the grown crystals. The crystals may lose its devise performance due to the heat generated during the cutting and polishing of the crystal, it is essential to study the thermal behavior and stability of the grown crystals.

RESULTS AND DISCUSSION

Structural studies

High resolution Guinier PXRD used for phase analysis as well as the Miller indices values used to calculate the lattice parameters. It can record lower diffraction angle (starting from 10) with very little background and good resolution.

The XRD data were collected from powdered samples using PXRD monochromated CuK_α radiation with current 20 mA and voltage 30 kV. To identify the material, the peaks of the PXRD diffraction pattern can be compared with the standard data for the structure is confirmed. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy by Bragg's Equations:

$$n\lambda = 2d\sin\theta$$

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$a = \sqrt{d_{hkl}^2(h^2 + k^2 + l^2)}$$

Where, d is the interplanar spacing, hkl is the Miller indices, a is the lattice parameter.

Table 1: PXRD Intensity for different 2θ peaks for pure crystals

For pure KCl					For pure KBr				
Intensity %	Angle in degrees (2θ)	d spacing (Å)	Miller indices (hkl)	Lattice parameters 'a' (Å)	Intensity %	Angle in degrees (2θ)	d spacing (Å)	Miller indices (hkl)	Lattice parameters 'a' (Å)
100	28.441	3.1383	-200		4.81	23.3765	3.80546	-111	
15.56	40.6097	2.22163	-220		100	27.0572	3.29557	-200	
4.76	50.2655	1.81518	-222		14.05	38.6155	2.33164	-220	
7.88	58.6945	1.57301	-400	6.276	1.85	45.6254	1.98839	-311	6.5911
4.97	66.3985	1.40797	-420		3.79	47.7675	1.9041	-222	
					9.85	55.7286	1.64949	-400	
					1.21	61.2036	1.51441	-331	
					9.04	62.9496	1.47654	-420	

Table 2: PXRD Intensity for different 2θ peaks for mixed crystals.

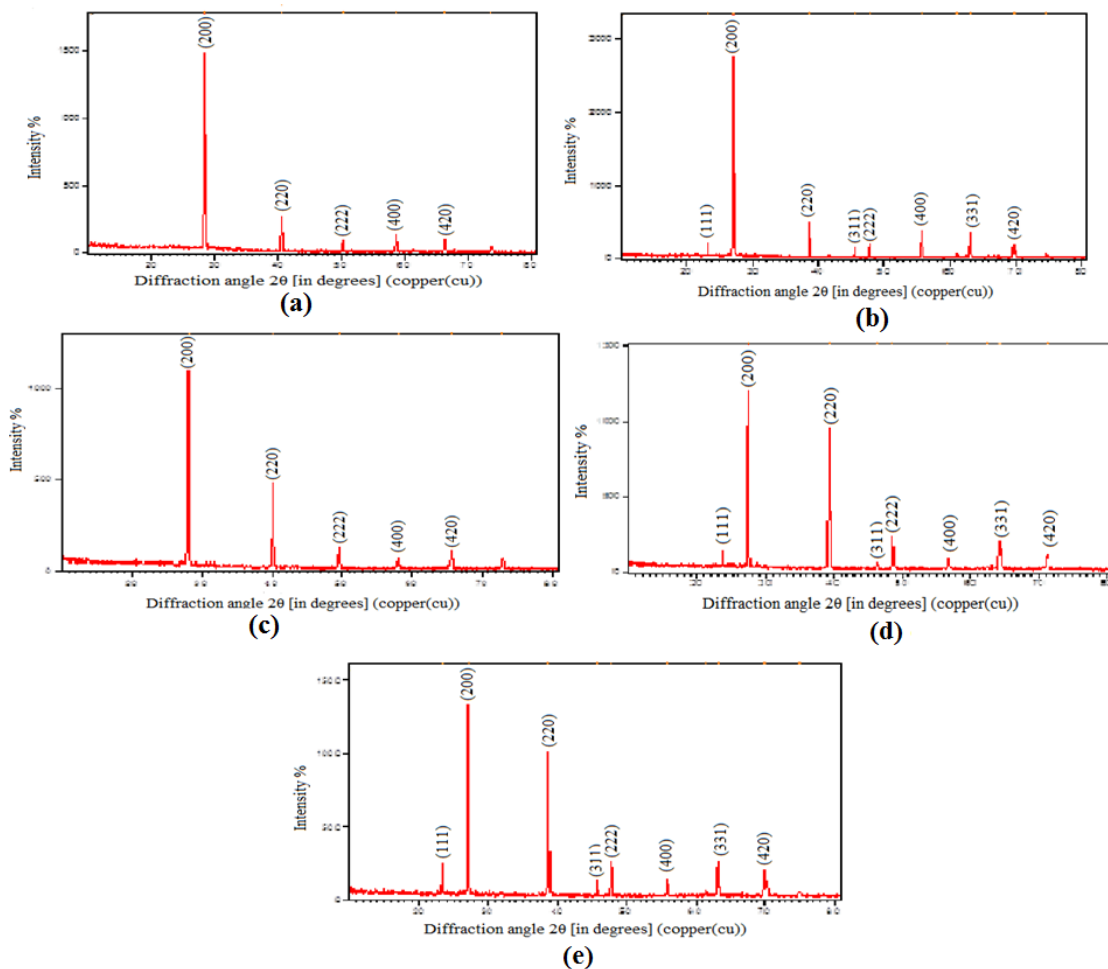| For KCl$_{0.2}$ KBr$_{0.8}$ ZnS					For KCl$_{0.5}$ KBr$_{0.5}$ ZnS					For KCl$_{0.8}$ KBr$_{0.2}$ ZnS				
Intensity %	Angle in degrees (2θ)	d spacing (Å)	Miller indices (hkl)	Lattice parameters 'a' (Å)	Intensity %	Angle in degrees (2θ)	d spacing (Å)	Miller indices (hkl)	Lattice parameters 'a' (Å)	Intensity %	Angle in degrees (2θ)	d spacing (Å)	Miller indices (hkl)	Lattice parameters 'a' (Å)
100	28.0493	3.18123	-200		7.11	23.7144	3.752	-111		14.08	23.4088	3.80029	-111	
34.83	40.1109	2.24809	-220		100	27.4618	3.24794	-200		100	27.0991	3.29058	-200	
8.69	49.6312	1.83688	-222		61.67	39.2751	2.29398	-220		65.53	38.7093	2.3262	-220	
4.64	58.0725	1.58837	-400	6.3625	2.19	46.4277	1.95588	-311		7.16	45.7373	1.98378	-311	
5.92	65.7815	1.41967	-420		13.86	48.6096	1.87307	-222	6.4959	14.29	47.9069	1.89889	-222	6.5812
					4.87	56.7357	1.62258	-400		7.07	55.8846	1.64526	-400	
					1.24	62.3886	1.48846	-331		2.48	61.4821	1.50821	-331	
					12.09	64.1928	1.45091	-420		15.03	63.1836	1.47164	-420	

Figure 2: PXRD Patterns of all grown crystals mixed crystals. (a) KCl, (b)KBr, (c) KCl$_{0.2}$ KBr$_{0.8}$, (d) KCl$_{0.5}$ KBr$_{0.5}$, (e) KCl$_{0.8}$ KBr$_{0.2}$

The Tables 1-2 to give the diffracted X-ray intensity versus angle (2θ) data for these samples. The peak positions at diffraction angle 2θ x-axis and intensity (counts) y-axis. The intensity change from two pure KCl, KBr and three doped KCl$_x$Br$_{1-x}$ mixed crystals concentration. In order to establish that KCl and KBr mix properly yield only a cubic phase and PXRD characterization of KCl$_x$Br$_{1-x}$ samples for composition x=0.2, 0.5 and 0.8. The d spacing corresponding to the diffraction angles. Figure 2 give the PXRD patterns for the 5 samples as above.

Table 3: Inter planar spacing for mixed crystals

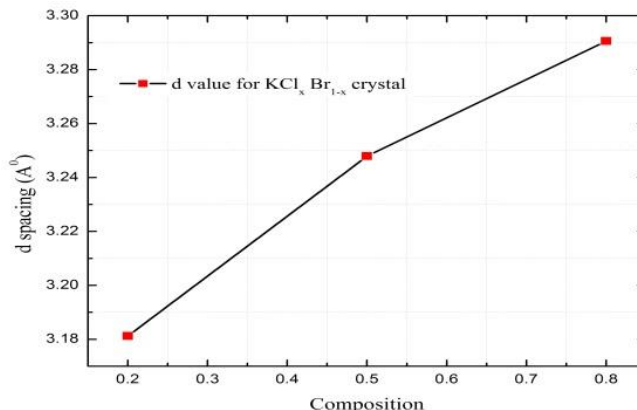| Composition	Intensity %	Miller indices (hkl)	d spacing (Å)
KCl			3.1383
KBr			3.29557
KCl$_{0.2}$KBr$_{0.8}$	100	-200	3.18123
KCl$_{0.5}$ KBr$_{0.5}$			3.24794
KCl$_{0.8}$ KBr$_{0.2}$			3.29058

Figure 3: Variation of d-spacing for KCl$_x$Br$_{1-x}$

The inter planar spacing for the grown crystals are provided in Table 3. The peak intensity is recorded the most intense peak is (200) plane and Miller indices identify diffraction angle peaks. The PXRD patterns show 100% intensity for reflections from (200) planes the inter planar spacing vary (increase) in a linear way with the change of composition x is 0.2, 0.5, 0.8 for different $KCl_x Br_{1-x}$ crystals, studied through XRD. The graph is obtained linear, indicating good mobility of KCl and KBr, leads to the formation of mixed cubic lattices and change of lattice size in a regular fashion with variation of composition. The Figure 3 shows variation of d (200) parameter for $KCl_x Br_{1-x}$, when x is varied as 0.2, 0.5 and 0.8.

Table 4: Lattice parameter for mixed crystals

Composition	Lattice parameter (Å)
KCl	6.2766
KBr	6.5911
KCl0.2 KBr0.8	6.3625
KCl0.5 KBr0.5	6.4959
KCl0.8 KBr0.2	6.5812
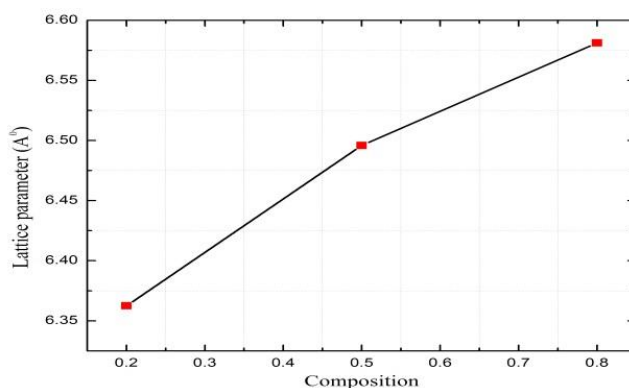
Figure 4: Curve of molar percent changing for crystal toward lattice parameter

The lattice parameters for the grown crystals are provided in Table 4. The composition increases with lattice parameter increases (change) linearly. From the XRD pattern of the mixed crystals the d values corresponding to 2θ values and the miller indices values were used to calculate the lattice parameter values. As can be seen in Figure 4 by changing the composition percentage of the elements, the parameter of the mixed crystal lattice will be changed as well. The bulk composition of the mixed crystal is determined by Vegard's law:

$$a = xa_1 + (1 - x) a_2$$

The bulk compositions of the mixed crystals were also verified by Retger's rule using the Equation:

$$a^3 = xa_1^3 + (1 - x) a_2^3$$

Where, a is the lattice parameters of the mixed crystal, x is the composition of KCl, (1–x) is the composition of KBr a_1 is the lattice parameters of pure KCl, a_2 is the lattice parameters of pure KBr.

Table 5: Lattice parameters for pure and mixed crystals

System	Lattice parameters	Vegard's law	Retger's rule
KCl	6.2766	-	-
KBr	6.5911	-	-
$KCl_{0.2} KBr_{0.8}$	6.3625	6.5282	6.5306
$KCl_{0.5} KBr_{0.5}$	6.4959	6.4339	6.4377
$KCl_{0.8} KBr_{0.2}$	6.5812	6.3395	6.342

The lattice parameters obtained in the present study along with those estimated from Vegard's law and Retger's rule are provided in Table 5. From the pure crystals lattice parameter through us calculate the lattice parameter of the mixed crystals. The ZnS doped mixed crystals lattice parameter values increases the Vegard's law and Retger's rule values decreases.

Spectroscopic studies

The conventional IR spectrometers all not of much use for the far IR region (20-400 cm^{-1}) as the sources are weak and detectors insensitive. FTIR has made this energy limited region more accessible. FTIR has made the middle infrared region more useful (400-4000 cm^{-1}). The advent of FTIR created renewed interest in the field of IR spectroscopy. It is one of the most widely used analytical tools available today. The rapidly increasing demand for routine analysis of a wide range of compound and data handling capabilities generated this interest. Infrared spectroscopy is an important technique in organic chemistry. The FTIR analyses identify the chemical functional groups in the sample. To identify of a pure compound or to detect the presence of specific impurities.
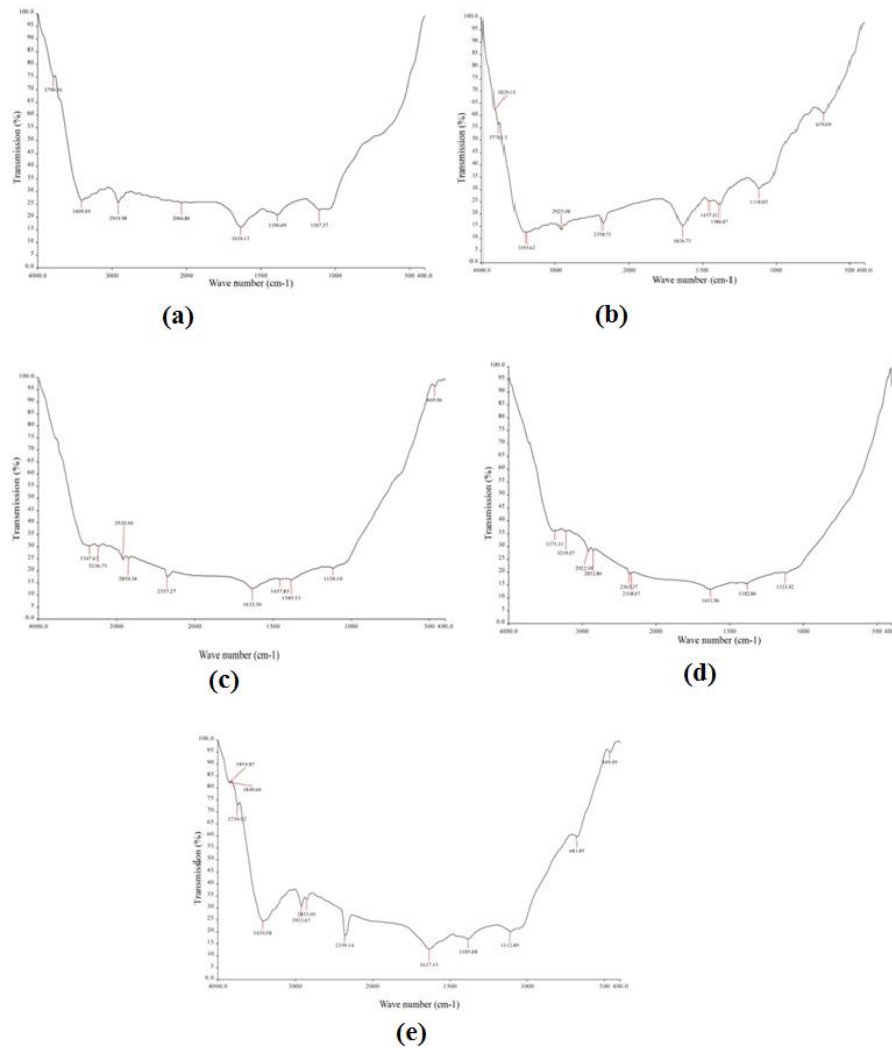
Figure 5: FTIR spectrum of mixed crystals. (a) Pure KCl, (b) pure KBr, (c) $(KCl)_{0.2}(KBr)_{0.8}$, (d) $(KCl)_{0.5}(KBr)_{0.5}$, (e) $(KCl)_{0.8}(KBr)_{0.2}$

The wave number peak values are noted for the FTIR spectrum of pure and ZnS doped mixed crystals are shown in Figure 5. FTIR spectrum with wavelength or wave number (number of waves per unit length) as the x-axis and absorption intensity or present transmittance as the y-axis. The transmittance intensities ranges from 0-100% T. In the present study, the mixed crystals observe not just a single frequency but two frequencies close to those of the pure crystals. Force constant of the grown crystals were determined from the FTIR transmission data using the formula:

$$\bar{v} = 5.3 \times 10^{-12} \sqrt{\frac{k_f}{\mu}}$$

Where, $\bar{v}$ is the wave number corresponding to the absorption maximum, k_f is the force constant, μ is the reduced mass.

Table 6: Wave number and force constant of all the grown crystals

System	Wave number (cm^{-1})	Absorption maximum Wave number cm^{-1}	Force constant($\bar{v}$) X10^2 N/cm
KCl	2919.98	3409.49	6.5022
KBr	2925.18	3395.62	6.4494
KCl$_{0.2}$ KBr$_{0.8}$	2850.36 2920.94	3347.67	6.2685
KCl$_{0.5}$ KBr$_{0.5}$	2852.80 2922.10	3371.31	6.3574
KCl$_{0.8}$ KBr$_{0.2}$	2855.05 2923.67	3420.58	6.5445

The $\bar{v}$ values of the peaks correspond to chlorine and bromine are provided in Table 6. It is found that the pure KCl and KBr has only one peak and the mixed crystals have two peaks are nearer. The increases of force constant depend for maximum absorption of wave number increases. The force constant thus determined are found to vary non-linearly with composition. The force constant thus determined are found to vary non-linearly with composition is shown in Figure 6.
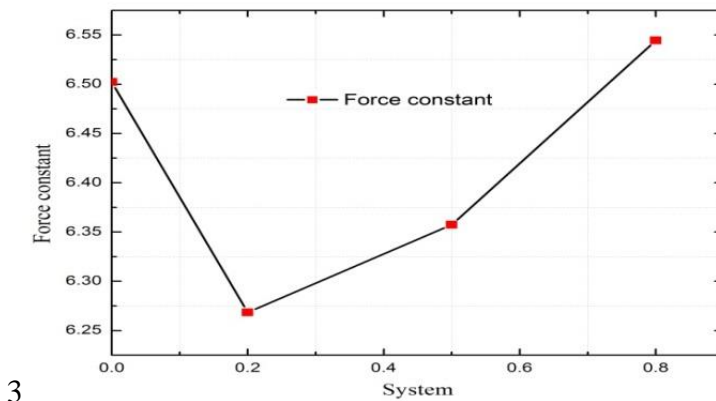
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Figure 6: Force constant of all the grown crystals

Mechanical studies

Micro hardness measurements were made using a Vickers micro hardness tester fitted with a diamond pyramidal indentor. Micro hardness is defined as the ratio of the load applied to the surface area of the indentation. The hardness tester has been designed for different load ranges so that the measuring unit is automatically lowered to the specimen. Test-area height can be varied as required. Vickers micro hardness measurements are done on all the fourteen crystals grown using Zeitz Wetzler hardness test fitted with a diamond pyramidal indentor and attached with Leitz incident light microscope. The Vickers hardness number H_V of Diamond Pyramid Number (DPN) is defined as defined as:

$$H_v = 2 p \sin (\alpha/2)/d^2$$

Where, α is the apex angle of the indenter ($\alpha = 136°$). The Vicker's micro hardness of the crystal is calculated using the relation:

$$H_v = 1.8544 \ (P/d^2) \ kg/mm^2$$

$$d = L_1 + L_2/2$$

Where, H_v is the Vicker's hardness number, P is the applied load in kg and d the average diagonal length of the indentation mark impression in mm. The applied load was varied as 25, 50 and 100 g for a constant indentation period of 10 sec. Micro hardness is defined as the ratio of the load applied to the surface area of the indentation.

Table 7: Micro hardness values for all grown crystals

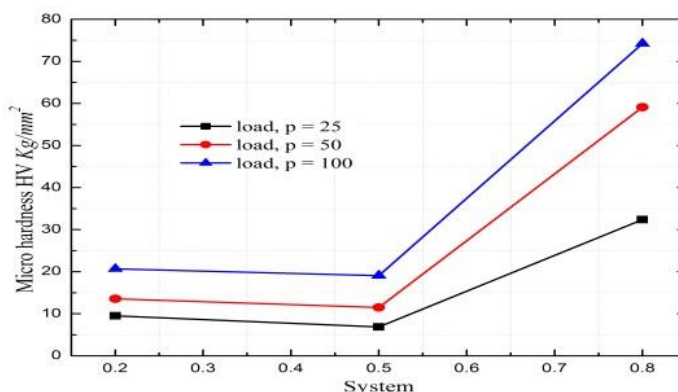| System	Micro hardness pure (kg/mm^2)		
	25	50	100
KCl	10.3091	15.0542	21.4133
KBr	7.6291	12.0333	15.9972
KCl$_{0.2}$ KBr$_{0.8}$	9.5114	13.5564	20.6809
KCl$_{0.5}$ KBr$_{0.5}$	6.8575	11.5064	19.096
KCl$_{0.8}$ KBr$_{0.2}$	32.3811	59.1431	74.2527

Figure 7: Variation Vickers micro hardness value of all the grown crystals

The Vicker's microhardness values for the grown crystals are provided in Table 7. The theoretical and experimental value of micro hardness H_v are same. The graph was plotted between the system along the X-axis and the hardness number H_v along Y-axis. The hardness value gets decreased then increased with increase in applied loads up to 100 g. For mixed the hardness value gets increased when the load is increased. The mechanical strength of the ZnS doped crystals is weak. The variation of micro hardness with composition for KCl$_x$ Br$_{1-x}$ was shown in Figure 7.

Table 8: The log p and log d values for all grown crystals

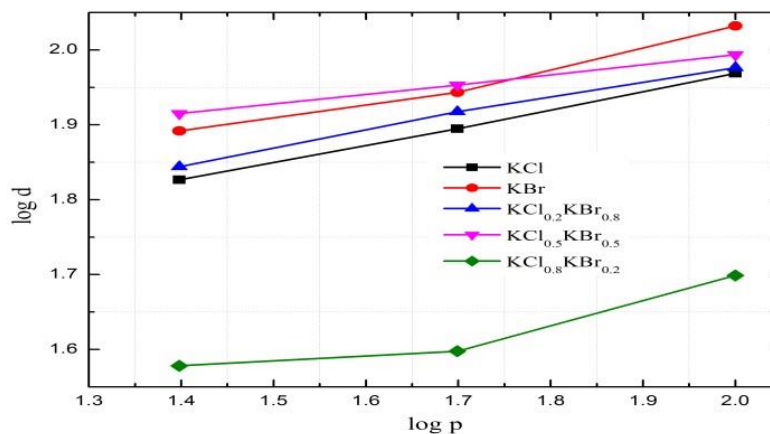| System	log p			log d		
	25	50	100	25	50	100
KCl				1.8265	1.8948	1.9688
KBr				1.8919	1.9434	2.0321
$KCl_{0.2} KBr_{0.8}$	1.3979	1.6989	2	1.844	1.9175	1.9763
$KCl_{0.5} KBr_{0.5}$				1.915	1.9531	1.9936
$KCl_{0.8} KBr_{0.2}$				1.5782	1.5976	1.6988

Figure 8: Plot of log p vs log d value of all the grown crystals

The log p and log d values for all grown crystals are provided in Table 8. For the mixed crystals log p and log d value of the pure KCl, KBr crystals increased simultaneously. The $KCl_{0.8} KBr_{0.2}$ very low value and also $KCl_{0.2} KBr_{0.8}$, $KCl_{0.8} KBr_{0.2}$ increased linearly. But the $KCl_{0.5} KBr_{0.5}$ value is increased then slightly increased. We also draw the Figure 8, a graph is plotted between log p vs log d for all mixed crystals.

Optical studies

An unknown compound can be identified with the help of UV spectroscopy. UV-Visible spectroscopy refers to the absorption spectroscopy in the UV-Visible spectral region. Ultraviolet spectroscopic studies i.e., optical absorption and transmission spectra were recorded for the mixed crystals by slow evaporation technique. It uses light in the visible and adjacent ranges. Fluorescence deals with transitions from the excited state to the ground state, while the absorption measures transitions from ground state to the excited state. The wavelength of absorption peaks can be correlated with the type of bonds in a given molecule and it is used determining the functional groups within a molecule. Organic compounds with a high degree of conjugation absorb light in the UV or visible regions of the electromagnetic spectrums.

UV-Visible spectrum of absorbance and transmittance of all grown crystals are shown as Figure 9. The wavelength x-axis and transmittance y-axis. The spectra were recorded in the wavelength ranging from 200-800 nm. The absorbance and transmittance curves are opposite to each other. The absence of strong absorption in the region between 218-800 nm in UV-Visible spectrum is useful for Opto-electronic application. The Band gap energy is calculated as:

$$E=h\nu, \nu =c/\lambda, E=hc/\lambda$$

Where, h is the plank's constant (6.626×10^{-34} Js), c is the speed of light in vacuum (3×10^8 ms^{-1}) and λ is the cut of wavelength of light.

The UV-Visible spectra recorded for pure and $KCl_x Br_{1-x}$ mixed crystals in shown in Figure 9 and it gives the UV-Visible absorbance and transmittance spectra of pure and $KCl_x Br_{1-x}$ mixed crystals. The wavelength x-axis and transmittance y-axis. The cut-off wavelengths were observed from the absorption spectra. The low optical absorption and high transmittance (100%). The transmittance absorbance percentages of pure and mixed crystals are almost same. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region. The absorbance and transmittance of all grown crystals are provided in Table 9.

Table 9: Band gap energy of all the grown crystals

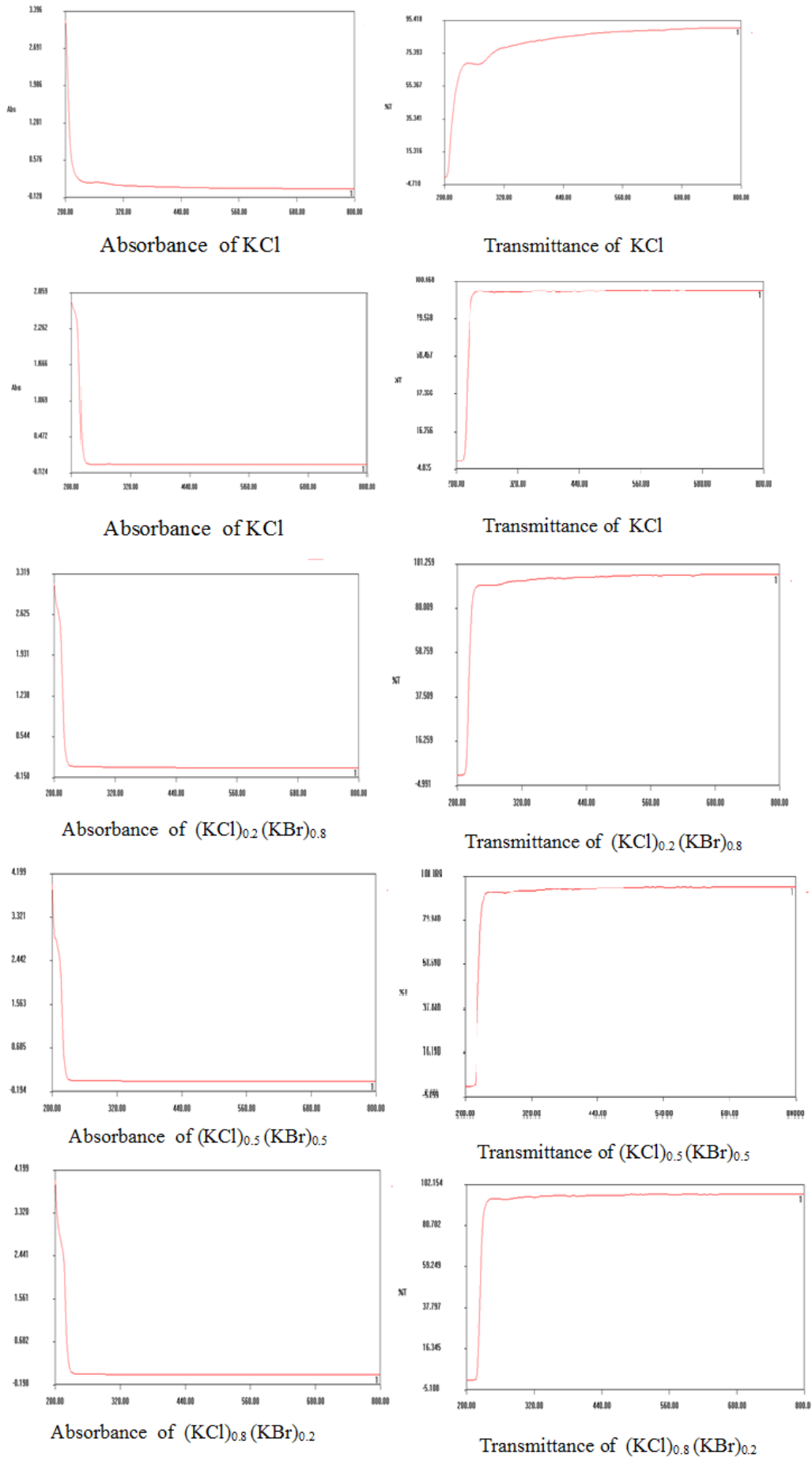| System	λ_{cut} (nm)	Eg (eV)
KCl	218.5	5.6788
KBr	222.5	5.5767
$KCl_{0.2} KBr_{0.8}$	230	5.3949
$KCl_{0.5} KBr_{0.5}$	228	5.4422
$KCl_{0.8} KBr_{0.2}$	228.5	5.4303

Figure 9: UV-Visible Spectrum of absorbance and transmittance of all grown crystals

Thermal studies

Thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature, or as a function of time [10]. Thermogravimetric analysis is an analytical technique in which the sample weight change of a substance is recorded as a function of temperature due to dehydration or decomposition. When sample weight of a sample is plotted temperature is thermo gravimetric curve or thermogram. TGA can be used to evaluate the thermal stability of a material. In a desired temperature range, if a species is thermally stable, there will be no observed mass change. Negligible mass lose corresponds to little or no slope in the TGA trace. TGA also gives the upper use temperature of a material. DTA is a thermo analytic technique similar to differential scanning calorimetry. The crystals may lose its devise performance due to the heat generated during the cutting and polishing of the crystal, it is essential to study the thermal behavior and stability of the grown crystals.
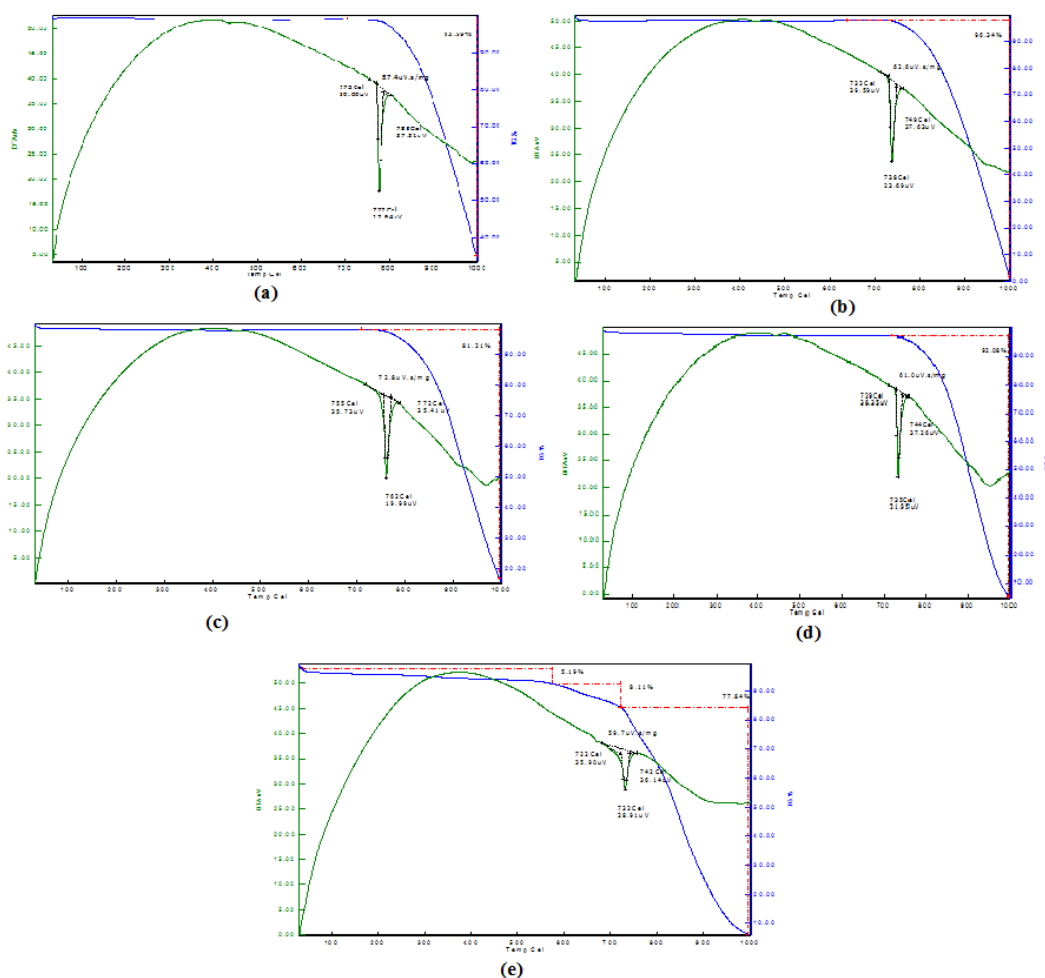

Figure 10: TG and DTA curve of mixed crystals. (a) KCl, (b) KBr, (c) $KCl_{0.2}KBr_{0.8}$, (d) $KCl_{0.5}KBr_{0.5}$, (e) $KCl_{0.8}KBr_{0.2}$

In our present study, we have recorded TG thermo gram of pure as well as 0.5 mol % ZnS doped KCl_xBr_{1-x} mixed crystals, in order to understand the effect of ZnS addition on the stability of the pure crystal. The recorded thermograms are shown in Figure 10. The thermogravimetric analysis of KCl and KBr mixed crystal was carried out between 100°C and 1000°C in air atmosphere at a heating rate using TG/DTA analyzer. The TGA instrument continuously weighs a sample as it is heated to temperatures of up to 1000°C for coupling with FTIR and mass spectrometry gas analysis. As the temperature increases, various components of the sample are decomposed and the weight percentage of each resulting mass change can be measured. Results are plotted with temperature on the X-axis and mass loss on the Y-axis. Thermogravimetric analysis may be presented by mass versus temperature curve, referred to as the thermogravimetric curve, or rate of mass loss versus temperature curve, referred to as the differential thermogravimetric curve. When the time and temperature are plotted, a dramatic slope change in the first derivative plot is concurrent with the mass loss of the sample and the sudden increase in temperature seen by the thermocouple (Table 10).

Table 10: Endothermic and decomposition of all grown crystals

System	Endothermic (°C)	Start the decomposition (°C)
KCl	777	724
KBr	738	725
$KCl_{0.2}KBr_{0.8}$	762	749
$KCl_{0.5}KBr_{0.5}$	735	718
$KCl_{0.8}KBr_{0.2}$	732	710

Thermal analyses of the grown crystals have been carried out by obtaining TG and DTA curves and are shown in Figures 1-5. The nature of weight loss indicates the decomposition point of the material.

From the TGA curve the weight loss of the sample with temperature is obtained. The endothermic and decomposition of all grown Crystals are provided in Table 1. In the DTA, the strong endothermic peaks located 777°C, 738°C, 762°C, 735°C, 732°C depict the crystallization of some of the phases of the decomposed material. The curved portions indicate the regions of thermal stability of KCl_xBr_{1-x} mixed crystals and the compound formed from it. The grown crystals are losing their weight gradually and slowly up to 724°C, 725°C, 749°C, 718°C, 710°C for gain samples. The curved portions indicate the temperature at which weight change due to dehydration or decomposition occurs. The temperature at steep weight loss is observed the temperature range from 724-790°C, from 725°C-778°C, from 749°C-775°C, from 718°C-753°C, from 710°C-722°C which may be due to the loss of physically absorbed water and significant dehydration or decomposition of samples respectively. From 790°C, 778°C, 775°C, 753°C, 722°C onwards a steady decrease in weight is observed up to 1000°C which may due to the final stage of decomposition of the samples. A small variation in the temperature range has been observed in the TGA curve of KCl and KBr mixed crystal samples. From the DTA curve it is clearly observed that the pure and doped crystal samples loses its texture at 382°C, 411°C, 407°C, 411°C, 355°C respectively. Hence it is concluded from this study that KCl is thermally more stable than KBr.

CONCLUSION

In the present study, the crystals of pure and ZnS doped KCl_xBr_{1-x} mixed crystal were grown by slow evaporation technique under room temperature. The grown crystals are stable, harder and transparent than end member crystals. The grown crystal possessed a large number of planes as observed in pure KCl and KBr crystal. The structural properties have been studied by powder XRD analysis. From the X-ray diffraction pattern of the mixed crystals the d values corresponding to 2θ values and the miller indices values were used to calculate the lattice parameter values. Identifying the crystal structure by PXRD. The PXRD pattern reveals that all the mixed crystals can be assigned a single lattice parameter. From the variations observed in the calculated lattice parameter values the presence of potassium halides in the grown crystals has been confirmed. The FTIR spectrums are taken for all the samples to study the spectroscopic properties of the grown crystals. Force constant of the grown crystals were determined from the FTIR transmission data. The Force constants value varies non-linearly with composition. FTIR spectral studies confirmed the presence of various functional groups in the grown doped crystals. Identifying the functional groups of the grown crystal by FTIR studies. The micro hardness measurements were carried out on the grown crystals to estimate the mechanical properties. The micro hardness measurements were made using Vicker's micro hardness tester. The work-hardening co-efficient values simply that all the grown crystals belong to hard category materials. The optical properties of the grown samples were determined from UV-Visible absorption spectra. UV-Visible spectrum to study the absorbance and transmission of all grown crystals and band gap energy were calculated. The thermal properties were studied from TG/DTA analysis. Determining thermal stability using TG analyzer. Thermal analysis revealed the thermal stability of the grown crystals and shown the suitability of the crystals for device fabrication. Thermal stability of the grown crystal were studied by Thermogravimetric (TG) and Differential Thermal Analysis (DTA) and found that the grown crystals are suitable for decrease fabrication for frequency conversion applications.

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