Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(17):258-263
(http://derpharmachemica.com/archive.html)

Growth and Characterization of Zns doped KCl_x Br_{1-x} Mixed Crystals

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ABSTRACT

Mixed crystals of ZnS doped KCl_x Br_{1-x} crystals have been successfully grown from aqueous solution by slow evaporation technique. Mixed crystals were grown in a period of three weeks. The lattice parameters were determined by PXRD analysis. FTIR analysis was used to confirm the presence of various functional groups in the grown crystals. From the microhardness studies to calculate the hardness of the grown crystals.

Key words: ZnS, PXRD, FTIR, lattice parameter, microhardness.

INTRODUCTION

The crystal grower - especially if he develops a proficiency in relating structure, bonding and other chemo-physical considerations to properties of interest - is in a key position in determining the direction and success of solid state research and - ultimately - technology" [1]. Single crystals have long-range order. Towards the middle of last century a deeper understanding developed regarding the correlation of the structure of crystals and mechanical, thermal, electrical and magnetic properties of solids [2]. The whole volume of a crystal can be constructed by moving a building block of the smallest acceptable size along its edges. This block consisting of atoms or a group of atoms is called a unit cell [3]. X- ray crystallography used to determine the structure of large bio molecules such as proteins [4].

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.

G. Selvarajan [5] have reviewed Lattice parameters and thermal parameters from the X-ray powder diffraction data of NaCl, KBr and KI. Toshihiko Kataoka [6] synthesized the temperature and concentration dependence of the critical resolved shear stress (CRSS) for KCl and KCl-KBr solid solutions was measured from 4.2 K to 293 K.

MATERIALS AND METHODS

The Analytical Reagent (AR) grade KCl and KBr and dissolved double distilled water were taken for the 100ml beaker. Super saturated solutions of KCl_xBr_{1-x} were prepared for (0.5). The KCl and KBr doped mixed crystals were grown by a desired molecular ratio of 0.5 mol % of ZnS and taken in a beaker and allowed to crystallize by slow evaporation method. The weighted salt is poured in to the beaker to make up 40 ml of aqueous solution by added distilled water totally five (two pure, one doped mixed) crystals were grown in identical conditions .A magnetic

stirrer is used to mix the salt with distilled water. Then the beakers are allowed to evaporate using porously sealed polyethylene sheet. The beakers are placed in a open atmosphere. Nucleation occurs for all crystals within four days. The end member crystals were grown for comparison purposes. Small tiny transparent crystals were obtained in the beaker. The resulting solutions was left for slow evaporation method and the high quality single crystals of pure KCl, KBr and ZnS doped KCl_x Br_{1-x} crystals were harvested after three weeks.

The formed crystals were carefully harvested from the beakers. The crystals are dried using filter paper. Growth of pure and ZnS doped KCl_x Br_{1-x} crystals by slow evaporation technique is reported. The grown crystals are characterized by powder XRD, FTIR, microhardness analysis.

RESULTS AND DISCUSSION

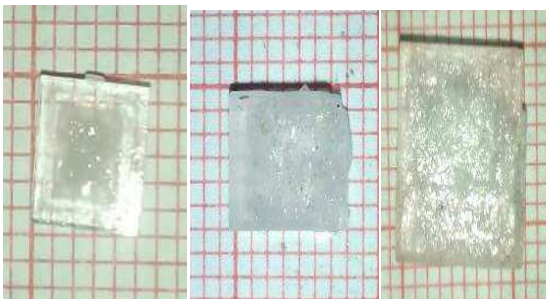

Figure 1: Photograph of all the grown crystals

Table 1 PXRD Intensity for different 2θ peaks for pure KCl crystal

for pure KCl				
Intensity %	Angle in degrees(2θ)	d spacing (Å)	Miller indices(hkl)	Lattice parameters(Å)
100.00	28.4410	3.13830	(200)	
15.56	40.6097	2.22163	(220)	
4.76	50.2655	1.81518	(222)	a =6.2766
7.88	58.6945	1.57301	(400)	
4.97	66.3985	1.40797	(420)	

Table 2 PXRD Intensity for different 2θ peaks for pure KBr crystal

for pure KBr				
Intensity %	Angle in degrees(2θ)	d spacing (Å)	Miller indices (hkl)	Lattice parameters (Å)
4.81	23.3765	3.80546	(111)	
100.00	27.0572	3.29557	(200)	
14.05	38.6155	2.33164	(220)	
1.85	45.6254	1.98839	(311)	a =6.5911
3.79	47.7675	1.90410	(222)	
9.85	55.7286	1.64949	(400)	
1.21	61.2036	1.51441	(331)	
9.04	62.9496	1.47654	(420)	

Table 3: PXRD Intensity for different 2θ peaks for mixed crystal

for $KCl_{0.5}KBr_{0.5}ZnS$				
Intensity %	Angle in degrees (2θ)	d spacing (Å)	Miller indices(hkl)	Lattice parameters (Å)
7.11	23.7144	3.75200	(111)	
100.00	27.4618	3.24794	(200)	
61.67	39.2751	2.29398	(220)	
2.19	46.4277	1.95588	(311)	a =6.4959
13.86	48.6096	1.87307	(222)	
4.87	56.7357	1.62258	(400)	
1.24	62.3886	1.48846	(331)	
12.09	64.1928	1.45091	(420)	

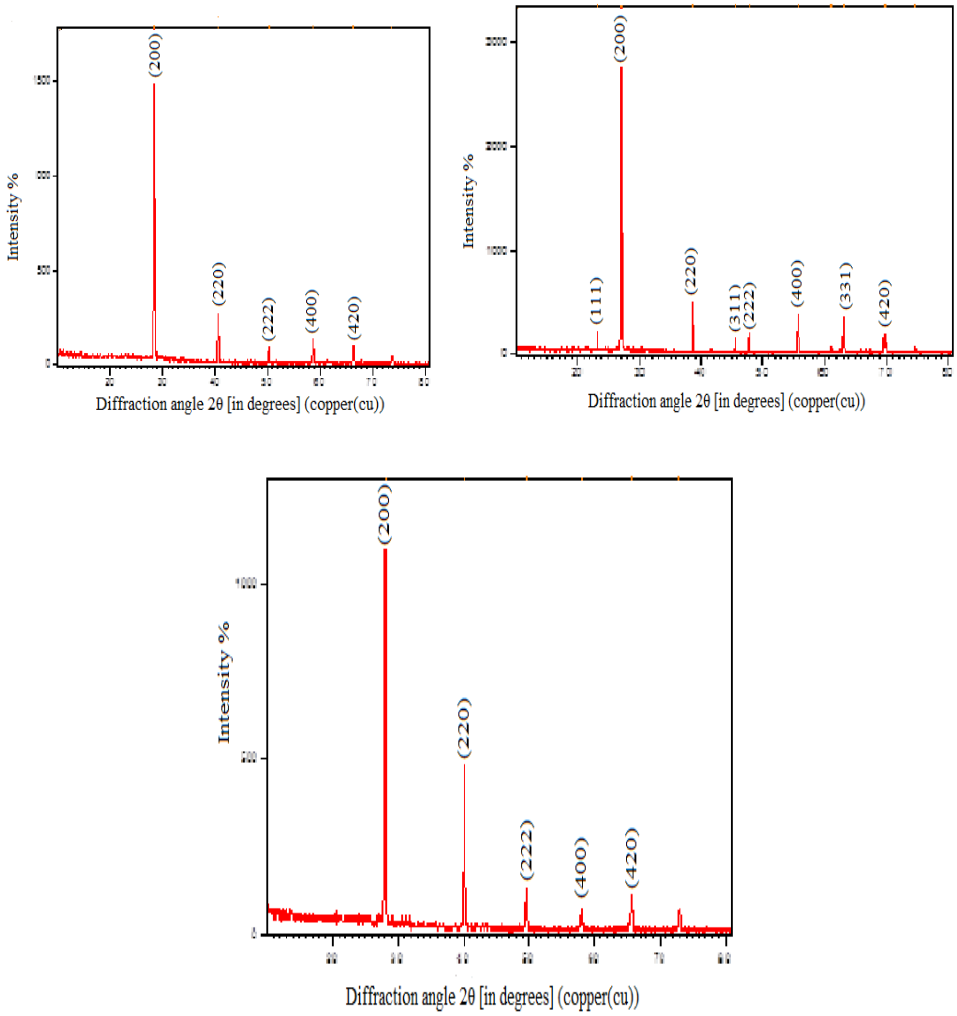

Figure 2: PXRD Patterns of all grown crystals

In order to establish that KCl and KBr mix properly and yield only a cubic phase, Power X-ray diffraction (PXRD) characterization of KCl_xBr_{1-x} samples for x=0.5 The Tables 1 to 3 to give the diffracted X-ray intensity versus angle (2θ) data for these samples. The PXRD patterns show 100% intensity for reflections from (200) planes. Further, it is seen that the d-separation between two adjacent (200) planes [7] shows a regular variation with the continuous addition of KCl and KBr. The intensity of all grown crystals change according to the KCl and KBr concentration.
Figure 2 give the PXRD patterns for the five samples as above. For determination of unit cell parameters, each reflection must be indexed to a specific hkl [8].

Table 4: Lattice parameter for mixed crystals

Composition	Lattice parameter(Å)
Pure KCl	6.2766
Pure KBr	6.5911
ZnS doped $KCl_{0.5}$ $KBr_{0.5}$ mixed crystal	6.4959

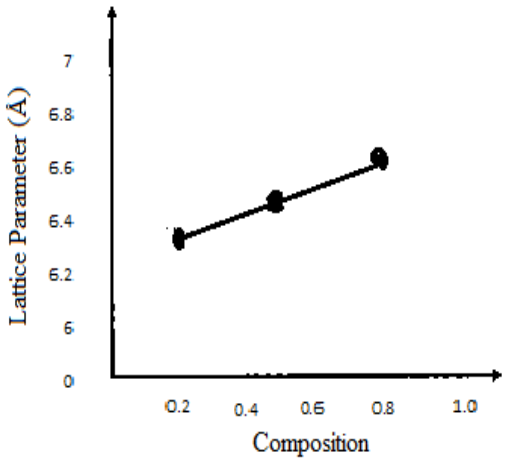

Figure 3: Curve of molar percent changing for crystal toward lattice parameter

The PXRD shows the lattice parameter values are 6.2766 Å, 6.5911 Å,6.4959 Å for pure KCl, KBr and 0.5 mol% of, ZnS doped $KCl_{0.5}$ $KBr_{0.5}$ mixed crystal samples. The lattice parameter for the grown crystals are provided in Table 5. The ZnS doped KCl_x Br_{1-x} mixed crystal values increases with lattice parameter increases linearly. As can be seen in figure 3 by changing the composition percentage of the elements, the parameter of the mixed crystal lattice will be changed as well.

Table 5: Lattice parameters for pure and mixed crystals

System	Lattice parameters	Vegard's law	Retger's rule
Pure KCl	6.2766	-	-
Pure KBr	6.5911	-	-
$KCl_{0.5}$ $KBr_{0.5}$	6.4959	6.4339	6.4377

The lattice parameters of pure and mixed crystals are provided in Table 5.From the pure crystals lattice parameter through we calculate the lattice parameter of the mixed crystals of Vegard's law and Retger's rule values.

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. The IR spectroscopy is the individual frequencies the radiation is absorbed and transmitted [9].Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities.

Force constant of the grown crystals were determined from the FTIR transmission data using the formula.

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

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

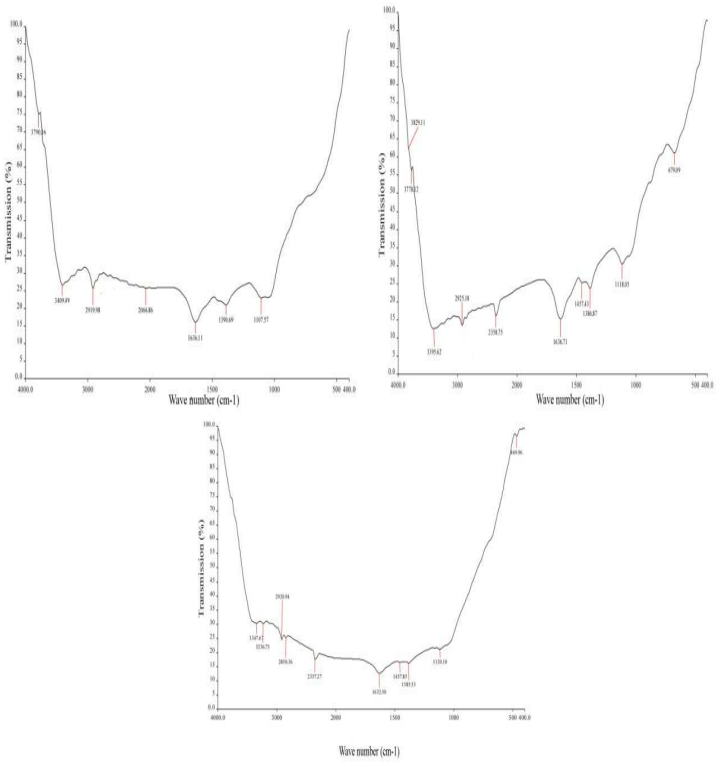

Figure 4: FTIR spectrum of grown crystals

The wave number peak values are noted for the FTIR spectrum of pure and ZnS doped mixed crystals are shown in figure 4. The FTIR spectra of KCl and KBr are found to be complex as result of the presence of various functional groups in the mixed crystals and are shown in this figure.

Table 8: Wave number and force constant of all the grown crystals

System	Wave number cm^{-1}	Absorption maximum Wave number cm^{-1}	Force constant $X10^{2}$ N/cm
Pure KCl	2919.98	3409.49	6.5022
Pure KBr	2925.18	3395.62	6.4494
ZnS doped $KCl_{0.5}$ $KBr_{0.5}$ mixed crystal	2852.80	3371.31	6.3574
	2922.10	3420.58	6.5445

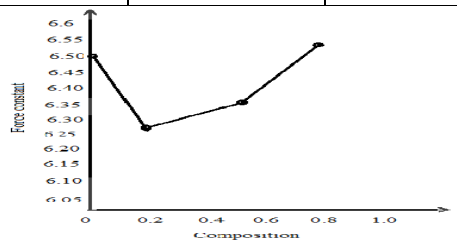

Figure 3: Force constant of all the grown crystals

The $\bar{\nu}$ values of the peaks correspond to chlorine and bromine are provided in Table 8. The increases of force constant depend for maximum absorption of wave number increases. The force constant values are 6.502 $X10^{2}$ N/cm, 6.4494 $X10^{2}$ N/cm, 6.3574 $X10^{2}$ N/cm, for pure and ZnS doped mixed crystal. In the present study, the mixed crystals observe not just a single frequency but two frequencies close to those of the pure crystals [10]. The force constant thus determined are found to vary non- linearly with composition is shown in figure 3.

MICROHARDNESS

Table 9 : Microhardness values for all grown crystals

System	Micro Hardness pure kg /mm ^{2}		
	25	**50**	**100**
Pure KCl crystal	10.3091	15.0542	21.4133
Pure KBr crystal	7.6291	12.0333	15.9972
ZnS doped $KCl_{0.5}KBr_{0.5}$ mixed crystal	6.8575	11.5064	19.0960

In the case of mixed and ZnS doped crystals, the hardness value gets increased with increase in indenter loads no cracks have been observed up to 100g. For mixed the hardness value gets increased when the load is increased. The mechanical strength of the crystals is good the ZnS doped mixed crystals.

CONCLUSION

In the present study, the crystals of pure and ZnS doped KCl_xBr_{1-x} mixed crystal were grown by slow evaporation technique. 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 X-ray diffraction 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. 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. FTIR spectral studies confirmed the presence of various functional group in the grown doped crystals. Identifying the functional groups of the grown crystal by FTIR studies. The Force constants value varies non linearly with composition. The mechanical strength of the crystals calculated from the microhardness study.

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