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Structure and FTIR studies on KCl_xBr_{1-x} single crystals grown from aqueous solutions

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ABSTRACT

Mixed and doped crystals of alkali halides are found to be harder than the end member crystals and so they are more useful in applications. So, it is necessary to prepare binary and ternary mixed crystals regardless of their miscibility problem. The grown crystals are characterized by measuring their physical properties. In the present work KCl_xBr_{1-x} crystals have been grown for various values of x. Bulk compositions of the grown mixed crystals were measured by taking EDAX. The FTIR spectrum was recorded for all the grown crystals.

Keywords: Alkali halides, mixed crystals, Two-mode behavior, FTIR

INTRODUCTION

In recent years alkali halide crystals have several applications viz, a radiation detectors, and also as laser host materials [1]. But their applications are limited by their mechanical strength. Mixed and doped crystals of alkali halides are found to be harder than the end member crystals and so they become more useful in their applications in optical, optoelectronic and electronic devices [2]. So, it is necessary to grow mixed crystals (both binary and ternary) regardless of their miscibility problem and characterize them by measuring physical properties.

Haribabu and Subbarao [3] have reviewed the aspects of growth and characterization of alkali halide mixed crystals. Sirdeshmukh and Srinivas [4] have reviewed the physical properties. Limited work has been done in infrared studies on alkali halide mixed crystals. Kruger et al [5] were the first to record the IR spectra of alkali halide mixed crystals. They studied the NaCl-KCl system. Mitsuichi [6] recorded the IR spectra of mixed crystals in the KCl-KBr and KCl-RbCl systems. The KCl-KBr system was also studied by Ferraro et al [7], Angress et al., have recorded IR spectra for the KCl-RbCl and KBr-RbBr systems. In all these studies it has been observed that the frequency of transverse optical mode varies linearly with composition. Feretel and Perry [8] obtained the IR frequency from the reflectivity data for the KCl-KBr system and reported a slightly non-linear dependence on composition.

An interesting observation was made on by Fertel and Perry [8] in their study of the KI-RbI system. For the system they observed not just a single frequency as in the case of pure crystals but two frequencies close to these to the pure crystals. Angress et al., [9] observed two frequencies in the KCl-RbBr system. This is a new phenomenon and referred to as “two mode behaviour”.

Chang and Mitra [9] obtained a criterion to predict whether a given mixed crystal of type AB_xC_{1-x} will exhibit a one-mode or two-mode behaviour. The criterion is

$m_B > \mu_{AC}$ one-mode behaviour
$m_b < \mu_{AC}$ two –mode behaviour
Where m_A is the mass of atom B and μ_{AC} is the reduced mass of AC.

MATERIALS AND METHODS

2.Experimental details

KCl_xBr_{1-x} single crystals were grown from aqueous solution. Analar grade KCl and KBr salts and doubly distilled water were used in the present study. A supersaturated solution of KCl_xBr_{1-x} was prepared in a desired molecular ratio and taken in a beaker and allowed to crystallize by slow evaporation. The temperature and volume were kept constant at 32^{o}C and 40 ml respectively for all the crystals. Small tiny transparent crystals were obtained in the beaker due to evaporation and the crystals were harvested after three weeks.

Totally five mixed crystals of compositions x = 0.2, 0.4, 0.5, 0.6 and 0.8 along with two end member crystals (KCl and KBr) were grown in identical conditions in the present study.SEM picture were taken for all the grown crystals to measure the size of the grain.

EDAX data was collected to estimate the composition of the mixed crystals. FTIR spectrum were 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 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 and μ is the reduced mass.

RESULTS AND DISCUSSION

The photograph of all the grown crystals is shown in Fig. 1. Mixed crystals grown in the present study are found to be stable and harder than the end member crystals.

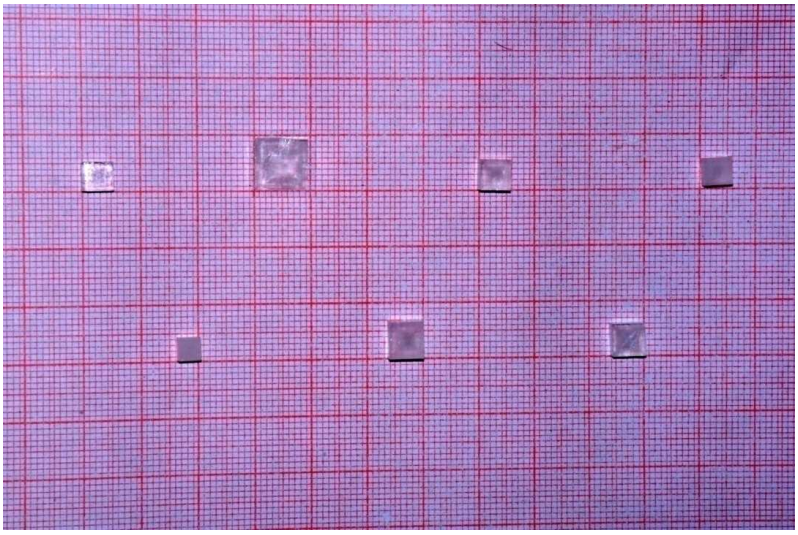

Figure 1 : Photograph of all the grown crystals

SEM pictures of all the samples were taken and the picture of $KCl_{0.5}$ $Br_{0.5}$ crystal is provided in Fig.2 for illustration.

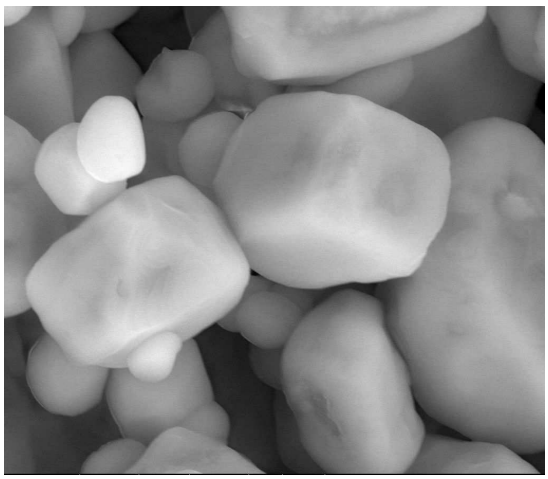

Figure 2 : SEM picture of the sample $KCl_{0.5}$ $Br_{0.5}$

The grain size of all the grown crystals are provided in Table 1. The shapes of all the grains are found to be square plates and the sizes of the grains vary from 2.8 μ m to 2.9 μ m for the pure crystal and from 12.86 μ m to 2.72 μ m for the mixed crystals. For $KCl_{0.5}$ $Br_{0.5}$ crystal, size is maximum and for $KCl_{0.4}$ $Br_{0.6}$ it is minimum.

Table 1: Grain Size of the grown crystals

System	Grain Size μ m	
	Maximum	Minimum
KCl	7.30	2.90
KBr	12.08	3.92
$(KCl)_{0.2}$ $(KBr)_{0.8}$	6.49	3.44
$(KCl)_{0.4}$ $(KBr)_{0.6}$	6.18	4.25
$(KCl)_{0.5}(KBr)_{0.5}$	12.86	6.84
$(KCl)_{0.6}$ $(KBr)_{0.4}$	8.39	2.72
$(KCl)_{0.8}$ $(KBr)_{0.2}$	8.30	3.43

Weight percentage and the estimated compositions of all the mixed crystals are provided in Table 2. Compositions calculated from the EDAX data exactly coincide with the compositions taken.

Table 2: Estimated Composition of all grown mixed crystals

System	Weight %			Estimated Composition
	K	Cl	Br	
$(KCl)_{0.2}$ $(KBr)_{0.8}$	18.10	2.52	46.39	$(KCl)_{0.1467}$ $(KBr)_{0.8533}$
$(KCl)_{0.4}$ $(KBr)_{0.6}$	22.5	8.93	40.16	$(KCl)_{0.3625}$ $(KBr)_{0.6375}$
$(KCl)_{0.5}(KBr)_{0.5}$	13.55	7.17	21.49	$(KCl)_{0.4594}(KBr)_{0.5406}$
$(KCl)_{0.6}$ $(KBr)_{0.4}$	22.8	16.83	15.07	$(KCl)_{0.66201}$ $(KBr)_{0.33799}$
$(KCl)_{0.8}$ $(KBr)_{0.2}$	15.13	16.33	4.9	$(KCl)_{0.8477}$ $(KBr)_{0.1523}$

The $\overline{\nu}$ values of the peaks correspond to chlorine and bromine are provided in Table 3. The FTIR spectrum of the crystals KCl and $KCl_{0.5}$ Br0.5 are provided in Fig.3 and Fig. 4 for illustration. It is found that the pure KCl has only one peak at 2923.13cm^{-1} and the mixed crystals have two peaks nearly at 2972 cm^{-1} and 2892 cm^{-1}. Similar result was observed by Fertel and Perry [8] in their study of KI-RbI system. They observed not just a single frequency but two frequencies close to those of the pure crystals. Angress [9] et al., also observed two frequencies in the KCl-RbBr system and this phenomenon is referred to as “two mode behaviour”.

Chang and Mitra [10] proposed a criteria that mixed crystals of type AB_xC_{1-x} will exhibit a one-mode or two mode behaviour if $m_B > \mu_{AC}$ or $m_B < \mu_{AC}$ respectively where on m_B is the mass of the atom B and μ_{AC} is the reduced mass of AC. In the present study, for the mixed crystals we observed not just a single frequency but two frequencies close to those of the pure crystals. So the two mode behaviour is exhibited for all the mixed crystals. The force constant thus determined are found to vary non- linearly with composition is shown in figure 5.

Table 3: Wave number and force constant of all the grown crystals

System	Wave number (cm^{-1})	Absorption Maximum Wave number (cm^{-1})	Force constant N/cm x 10^2
KCl	2923.13	3411.63	6.5103
KBr	2926. 23	3504.71	6.8652
$(KCl)_{0.2}$ $(KBr)_{0.8}$	2973.60 2892.86	3364.75	6.3278
$(KCl)_{0.4}$ $(KBr)_{0.6}$	2971.35 2896.06	3357.18	6.2994
$(KCl)_{0.5}(KBr)_{0.5}$	2972.88 2892.29	3307.77	6.1153
$(KCl)_{0.6}$ $(KBr)_{0.4}$	2970.65 2906.87	3351.61	6.2785
$(KCl)_{0.8}$ $(KBr)_{0.2}$	2973.35 2894.53	3368.20	6.3408

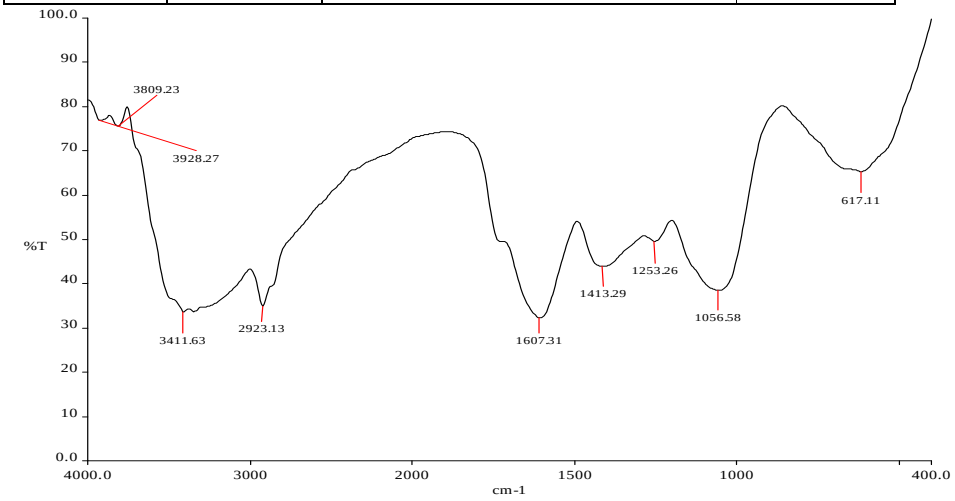

Figure 3 : The FTIR spectrum of the crystal KCl

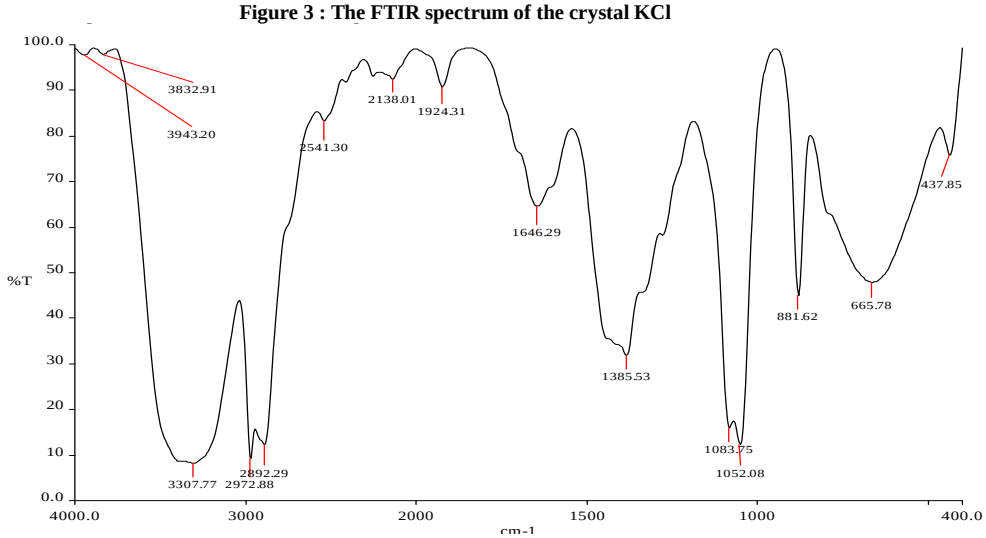

Figure 4 : The FTIR spectrum of the crystal $(KCl)_{0.5}(KBr)_{0.5}$

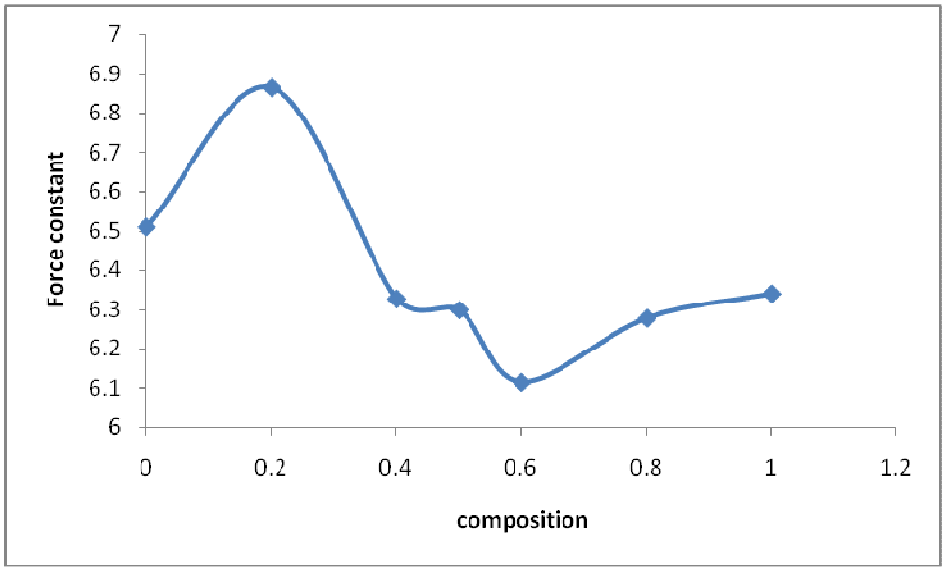

Figure 5 : Force Constant of all the grown crystals

CONCLUSION

Crystals grown in the present study are stable, harder and transparent than end member crystals. The SEM picture show square plate structure of the grains. The FTIR studies showed that two mode behaviour is observed in the mixed crystals. The force constants value varies non- linearly with composition.

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