Scientific Research

Growth of $KCl_{1-x}Br_x$ Mixed Crystals with Different Composition Percent and Study of KBr Concentration Effect on Optical Characteristics of Mixed Crystals

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ABSTRACT

In the present research, mixed crystals $KCl_{1-x}Br_x$ ($x = 0.1, 0.3, 0.5, 0.7$ & 0.9) were grown by Czochralski method. Then some analysis such as chemical etching, XRD, and absorbing spectrum were established on the irradiated crystals by γ-ray. The results of this research show that configuration of defects in mixed crystals in contrast with pure crystals is different. Somehow that type and percentage of cumulative composition cause to changing in lattice parameter and lattice defect density in alkali halide crystals and finally change optical properties of crystal.

Keywords: Alkali Halide; Crystal Growth; Czochralski; Seed; Mixed Crystal; Etching; Color Center; Lattice Defect; X-Ray Diffraction; Absorbing Spectrum

1. Introduction

The alkali halide crystals have always been at the center state of solid-state physics. Mixed crystals have aroused considerable interest, curiosity and have motivated extensive investigations because of their wide applications. The solid solutions of alkali halides indeed constitute a very interesting study. There are several reasons for this choice. Alkali halide mixed crystals are of the completely disordered substitutional type. Haribabu and Subbarao have reviewed the aspects of the growth and characterization of alkali halide mixed crystals [1]. Sirdeshmukh and Srinivas have reviewed the physical properties [2]. Several more reports are available on binary mixed crystals of alkali halides [3-5]. However, very limited reports are available on ternary and quaternary mixed crystals of alkali halides [6,7]. The study of alkali halide solutions from view pointed existent Essence in them and their roles on optical properties indicate that intensity of pigmentation, dislocation density and post of different bands of color centers are nonlinearly changed with dose of compound and lattice constant has linear changes with amount of compound. The conclusions of these studies indicate that structure of defects for mixed crystals is different in contrast with their pure position. The difference of atomic size between mixed crystals cause to local stresses in lattice and this defeat change crystal properties,

its lattice parameters [8-10]. In addition, mixed alkali halides found their applications in optical, opto-electronic and electronic devices.

In view of this, in the present study alkali halide $KCl_{1-x}Br_x$ mixed crystals of a different composition was grown by Czochralski (Cz) technique and various studies like X-ray diffraction, Etching and optical absorption have been carried out on the grown mixed crystals.

In the recent years, decides has established studies about X-ray diffraction, absorption spectrum, thermo luminescence, spin-electron resonance and etc on mixed crystals of source. Our results were compared with results of references [11,12] and this comparison indicated that is received similar results about XRD and absorption. Also in this article we also evaluated etching samples and severity of pigmentation in crystal with same dose against the source of gamma.

2. Description of Experimentation

$KCl_{1-x}Br_x$ alkali crystals have grown by Cz method. At first, the pure salt powder KCl, KBr (Merck) has weighed with definite weight ration. In order to uniformity we mix the present combination. Then the combination of two alkali halides has been pour in crucible and put in the furnace and heats the salt powder to 100 degrees above the melting point. After contact of seed with molten surface, growth conditions are controlled with observing proper cervical (pulling rate 7 mm/h) until to reach crystal

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defects to a minimum.

After cervical operation with decreasing temperature and of pulling rate to appropriate size, diameter can be increased. **Figure 1** shows a view of grown crystal by Cz method.

Then we cleave mixed crystals along lattice constant with appropriate dimensions by XRD device (Model: DB-AXS).

Some pieces of cleaved crystals were irradiated under 15 KGy γ radiations. Then absorption curve is measured by spectrophotometer (Cary 17D Models) in wave length range 180 - 900 nm.

The pieces of the crystals with new surfaces were washed by acetic acid solution and diluted $FeCl_3$ until very fine crystalline defects be larger and visible. It should be mentioned that solution used in the place of defects acts faster than other parts of crystal, because etching causes to places of defects be older. After washing with etching solution, crystals are accurately washed with acetone and become dry by blowing of hot air. After this work, crystal is prepared to set under a microscope for study now it can be obtained the better time for etching by analyzing etched crystals under microscope in the various times. Then photos are taken from useful parts of crystal. At all of pictures sharp pyramids are seen which is related to dislocations.

2.1. XRD Analysis on Mixed Crystals $KCl_{1-x}Br_x$

Miller indices which are related to mixed single crystals are specified according to American Society for Testing and Materials (ASTM) standard with particular indices and quantities. XRD results have been shown in **Figure 2** for crystals.

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. Moreover, due to the fact that the ionic radius of Br and Cl elements are considered to be 1.95 and 1.81 Angstroms; it can be concluded that by increasing the ionic radius in mixed crystal the lattice constant will also increase. This means that lattice constant increase with increasing of KBr molar percent. It is worth noting that these outcomes have confliction with others outcomes [12-14].

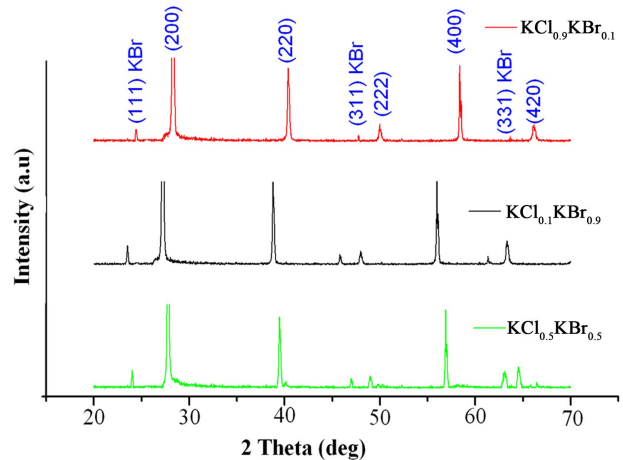**Figure 1. View of grown crystal by Cz method with pulling rate 7 mm/h.**
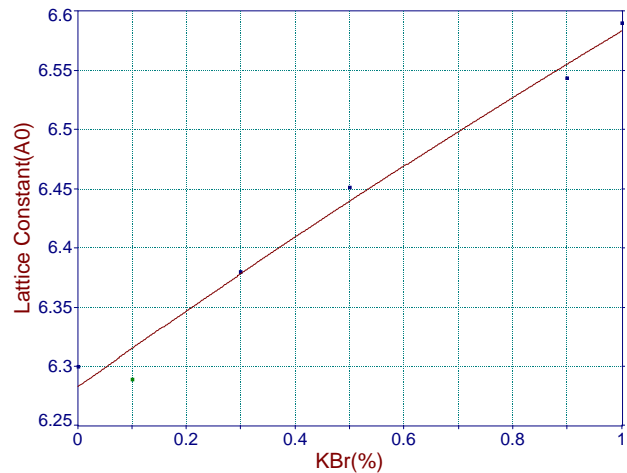

Figure 2. XRD results for crystals.

Figure 3. Curve of molar percent changing for KBr toward lattice constant.

$$a = \sqrt{d_{hkl}^2 \left(h^2 + k^2 + l^2 \right)} \qquad (1)$$

$$a_{ss} = c_1 a_1 + c_2 a_2 \qquad (2)$$

As for Equation (1) and Vegard Rule (2) and also as for resulting of XRD and relative distance value between planes for mixed crystals in which ionic radius difference is less than 15 percent can be obtain lattice constant. These results (in **Table 1**) are different from the others [15,16].

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Table 1. Lattice constants for grown crystals.

Crystal	Experimental
KCl	6.30
$KCl_{90}Br_{10}$	6.33
$KCl_{70}Br_{30}$	6.36
$KCl_{50}Br_{50}$	6.45
$KCl_{30}Br_{70}$	6.47
$KCl_{10}Br_{90}$	6.57
KBr	6.59

2.2. Determination of $KCl_{1-x}Br_x$ Feature by Etching Method

By experimentation upon mixed crystals pieces, we can understand that due to increasing of disorder, dislocations density is more than similar non-mixed crystals. By pluralization of mixed crystals analyses, we will understand that irregularity of the intermediate crystals cause to increasing of dislocations [17]. The results of this analysis are available in **Figure 4** and **Table 2**.

As for **Table 2**, whereas for crystals which have optical application density is less than 10^7 $1/cm^2$ [18], dislocation density of grown crystal is order of 10^5 $1/cm^2$. Grown crystals quality is suitable for optical devices.

As for **Figure 5** with changing of complex concentration percent, dislocation density changes to non-linear from the pluralization of mixed crystals analysis would be foundation existence of irregularity in the middle crystals cause to increasing of dislocations. It is for recombination value of center F electrons increase in vicinity of dislocations. From analysis of dislocation density can be deducted that intensity of center F decreases in middle crystals. Of course by analyzing of crystals absorption spectrum can be seen above results.

2.3. Determination of Optical Absorption Features $KCl_{1-x}Br_x$

When the radiation transmits within the layer of solid, solution and gas, some frequencies may be selectively eliminate by absorption process. Absorption process is process in which electromagnetic energy transfer into atoms, ions and manufacturer electron molecules.
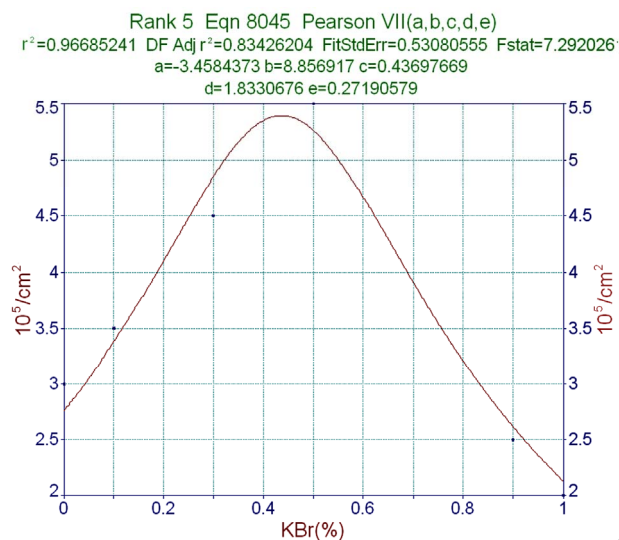
Absorption cause to raise these particles from room temperature or ground state to one or multi excited energy. Of course we should know that absorption is scale of radiation power reduction. Absorption centers are colored centers which the most important of them is colored center F.

The significant feature of colored crystals is generation of distinct color in alkali halide crystals. Of course the crystal should exhibit against of ionizer radiation such as X-ray or γ-ray. Substantially this color is related to absorption band F [10].

In mixed crystals, prominent band F is in visible zone.
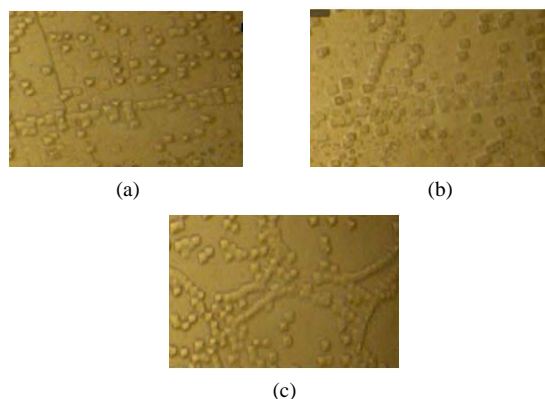
Figure 4. Optical microscopic picture provided of (a) $KCl_{0.1}Br_{0.9}$; (b) $KCl_{0.9}Br_{0.1}$; (c) $KCl_{0.5}Br_{0.5}$ crystals.

Table 2. Dislocations density for grown crystals.

Crystal	Dislocation density $1/cm^2$
KCl	2.96×10^5
$KCl_{90}Br_{10}$	3.43×10^5
$KCl_{70}Br_{30}$	4.67×10^5
$KCl_{50}Br_{50}$	5.41×10^5
$KCl_{30}Br_{70}$	3.91×10^5
$KCl_{10}Br_{90}$	2.62×10^5
KBr	2.41×10^5

Rank 5 Eqn 8045 Pearson VII(a,b,c,d,e)
r^2=0.96685241 DF Adj r^2=0.83426204 FitStdErr=0.53080555 Fstat=7.292026
a=-3.4584373 b=8.856917 c=0.43697669
d=1.8330676 e=0.27190579

Figure 5. Curve of molar percent changing for KBr toward dislocation density.

According to Mollow theorem, constitution place of top for band F is related to crystal's lattice constant.

On the other hand asymmetry and deformation of band F is for existence of aggregated centers in crystal which is associated with decreasing of center F density.

According theorem (Allard & Etzel, 1959) parameters like radiation temperature (upper than 2000 K), radiation

intensity, optical bleaching and impurity in lattice crystal are effective were brought in **Figure 6** and **Table 3** of course these resulting are opposite of other results [11].

Since dislocation density in mixed crystals is due to increasing of disorder in contrast with non-mixed crystals and value of center F electrons recombination is increased in the vicinity of dislocations, the concentration of censers F will decreased and this is due to the irregularity in the vicinity of dislocation, the potential for keeping the electron center F is weak.

Therefore electron and whole recombination is done easier and centers F are destroyed earlier. It can be expected that the color intensity of mixed crystals due to reduction of centers F recombination reduced and at the ratios of middle to reach it's minimum [19-21].

As we see in **Figure 7** in intermediate molar ratio due to disorder in the vicinity of dislocations, optical intensity decrease and F center reach to its minimum. Of course we should know that these disorders cause to reduce F center's potential for maintaining the electron.

Whereas in mixed crystals as KBr with increasing of ionic radius lattice constant linearly are increased, we consider that band F appearance place in mixed crystal are changed as well as. As for increasing of KBr molar percent we expect to band F appearance place tend toward higher wavelengths. See **Figure 8**.

By investigation of analysis related to absorption and etching, we can understand that in intermediate molar ratios F center intensity reach to its minimum. Therefore, we can expect that mixed crystal's pigmentation is deducted by decreasing of F centers. Thus, the crystals should be placed against of γ source (15 KGy) and then we investigate their pigmentation intensity. As we see in **Figure 9**, mixed crystal $KCl_{50}Br_{50}$ has been colorless in contrast with other crystals.
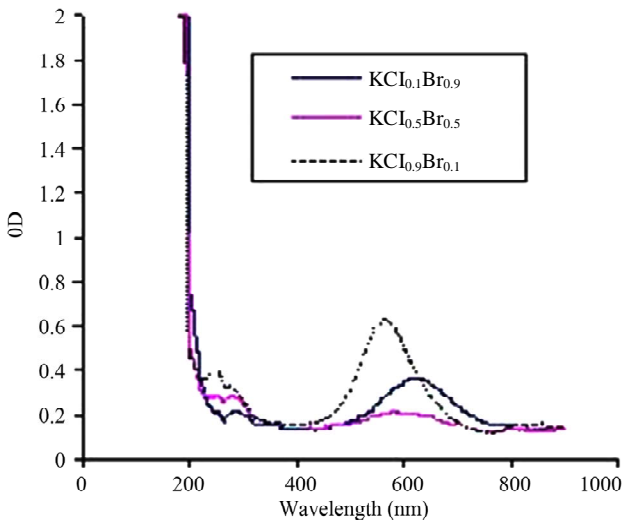
Table 3. F center emergence location for grown crystals.

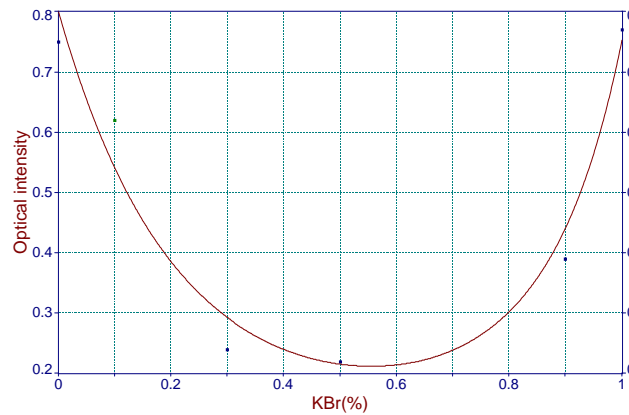| Crystal	F-band (nm)
KCl	549
$KCl_{90}Br_{10}$	563
$KCl_{70}Br_{30}$	582
$KCl_{50}Br_{50}$	599
$KCl_{30}Br_{70}$	608
$KCl_{10}Br_{90}$	619
KBr	620

Figure 7. Curve of molar percent changing for KBr toward optical density.
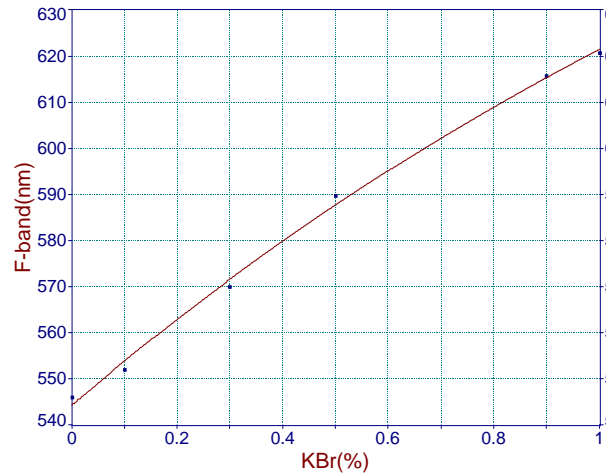
Figure 8. Curve of molar percent changing for KBr toward F center emergence location.
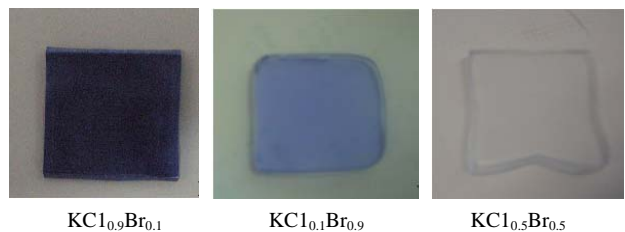

Figure 6. Curve of absorption spectrum for mixed crystals $KCl_{1-x}Br_x$.

$KCl_{0.9}Br_{0.1}$ $KCl_{0.1}Br_{0.9}$ $KCl_{0.5}Br_{0.5}$

Figure 9. View of crystals pigmentation against of γ source.

3. Conclusions

The results of XRD measurement, absorbing spectrum and etching process indicate that structure of solid mixed crystals defects is different of pure component in the same crystals. Therefore, existence of additive component causes to disorder in crystalline lattice. This disorder exhibit itself by nonlinear changing in lattice parameter, changing in point defects, and optical properties. By the way dislocation density of grown crystals is order of 10^5 $1/cm^2$ and consequently grown crystals quality is suitable for optical devices.

It is taken that with analysis of peak observation band according to concentration percentage and non-linear changing observation for absorption band, we can relatively predict peak absorption wavelength with specific percentage of compositions component.

Whereas in mixed crystal $KCl_{50}Br_{50}$ F center intensity is minimized in contrast with other mixed crystals, we consider the pigmentation intensity of this crystal which is less than others by γ source.

Write "Magnetization (A/m)" or "Magnetization (A·m^{-1})", not just "A/m". Do not label axes with a ratio of quantities and units. For example, write "Temperature (K)", not "Temperature/K".

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