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Microhardness And Dielectric Studies of Ternary Mixed Alkali Halide Crystals Grown by Aqueous Solution Method

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ABSTRACT

Single crystals of ternary mixed alkali halides $(KCI)_x(KBr)_{0.9-x}(NaI)_{0.1}$ *of different compositions were grown by slow evaporation technique. All the crystals were grown under identical conditions. The crystals obtained were checked by XRD pattern. EDAX data has been taken for the samples to know the elemental analysis. Microhardness measurements have been carried out using Zwick hardness tester fitted with a Vicker diamond pyramidal indenter. The dielectric constant and dielectric loss measurement were made using LCR meter which operates in the range IkHz to 10 MHz . It is observed that the formation of a ternary mixed crystal is accompanied by an increase in hardness and it varies non-linearly with composition. From the hardness measurement, the Elastic stiffness constant* (C_{11}) *of the crystals for various loads have been estimated. In order to investigate the nature of defects, dielectric loss and dielectric constant measurements have been done which showed that the mixed crystals are more defective, containing a high concentration of dislocations, low angle grain boundaries and vacancies as compared to the end products.*

Key Words: Microhardness, dielectric constant, dielectric loss, Elastic stiffness constant.

INTRODUCTION

Alkali halide mixed crystals are widely used as laser window materials, neutron monochromators, infrared transmitters etc., But the use of pure simple alkali halides is limited by the mechanical systems and hence there exist the need to strengthen them. The mixed and impurity added crystals of alkali halides are found to be harder than the end members and so they are more useful in these applications. Also it is a known fact that alloys are more useful than the pure simple metals in device fabrications. In view of this, it becomes necessary and useful to prepare binary and ternary mixed crystals regardless of miscibility problem and to characterize them by studying their physical properties. In the present research work, single crystals of ternary mixed alkali halides $(KCl)_x(KBr)_{0.9-x}(NaI)_{0.1}$ of different compositions were grown by slow evaporation technique and studies of microhardness and dielectric constant have been carried out.

MATERIALS AND METHODS

Experimental

Ternary mixed crystals of $(KCI)_x(KBr)_{0.9-x}(NaI)_{0.1}$ were grown by slow evaporation technique from aqueous solution using Analog grade samples of KCI, KBr and NaI as the starting materials for the growth of the crystals. Well-defined optically transparent crystals were obtained. All the crystals were grown under identical conditions.

Grown crystals were cleaved and subjected to microhardness and dielectric constant measurements.

RESULTS AND DISCUSSION

1. Microhardness studies

Micro hardness measurements were carried out using Zwick 3212 hardness tester fitted with a Vicker's diamond pyramidal indenter. All the indentation measurements were carried out on the freshly cleaved samples. The indentation was made by varying the load from 5 to 100 gm and the time of indentation was kept at 10 sec. The indented impressions were approximately square. The crystal surfaces were indented at different sites. Diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope. Several indentations were made on each sample. The average value of the diagonal lengths of indentation mark was used to calculate the hardness.

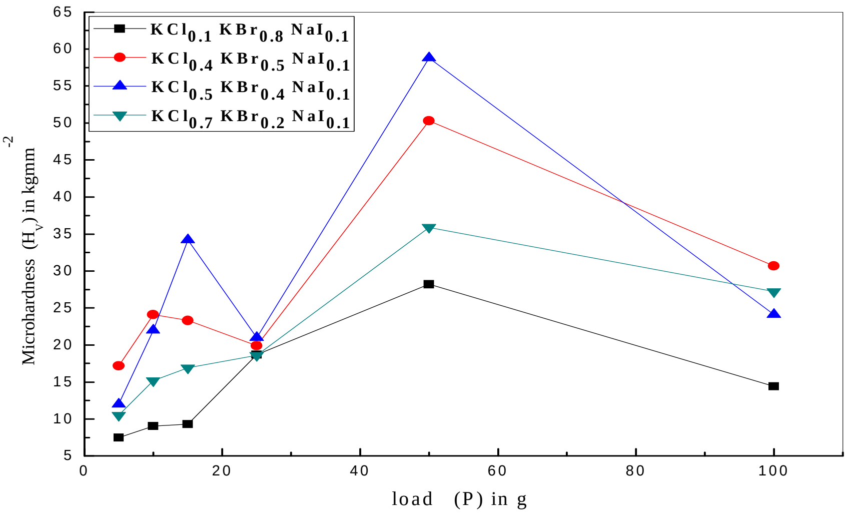


Fig.1 Variation of microhardness with load

The Microhardness is calculated using the expression (1)

$$\mathbf{H_v = 1.8544P/d^2}\ \text{Kg mm}^{-2}$$

where P is the applied load in Kg and d the average diagonal length of the Vickers impression in mm after unloading.

It is observed that the formation of mixed crystals is accompanied by an increase in hardness and it varies non-linearly with composition. Although hardness has been defined in several ways, it is now generally accepted that it is the resistance offered to dislocation motion. There are several contributions to the resistance to the dislocation motion and they can be classified into two types (i) the intrinsic resistance which depends on some structure insensitive physical parameter of the crystal and (ii) a disorder parameter which depends on the concentration of the imperfections.

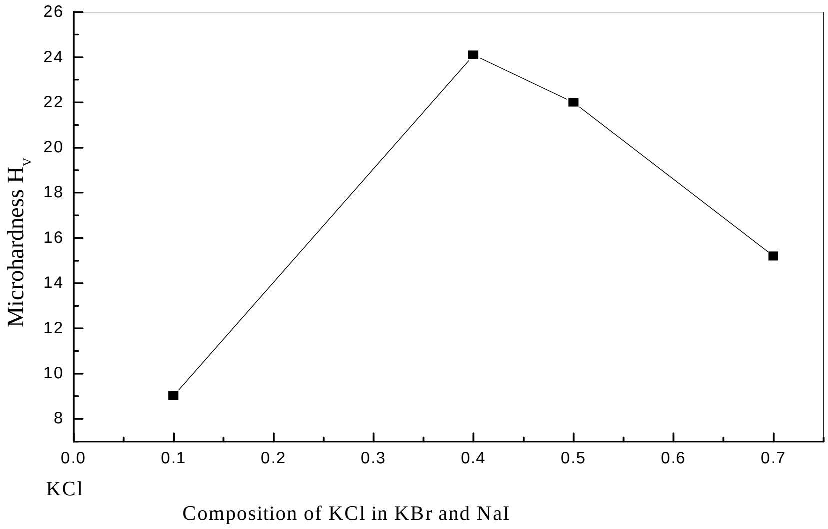


Fig.2 Variation of microhardness with composition

The non-liner variation of microhardness with composition is due to the presence of imperfections. These imperfections can be vacancies, impurity-vacancy pairs, dislocations, low-angle grain boundaries etc. The studies made by others on ionic conductivity of mixed crystals (2) shows that conductivity is high for mixed crystals as compared to the end crystals. Since ionic conductivity is solely due to the presence of charged vacancies, these results therefore indicate that mixed crystals contain excess of vacancies. The results on dislocation morphology (3) shows that the low-angle grain boundaries and dislocations are more in mixed crystal compared to pure crystals. Also Tiller's eutectic crystallization mechanism may be responsible for the origin of low- angle grain boundaries in mixed crystal (4). Thus vacancies, dislocations and grain boundaries appear to be the dominant imperfections in mixed crystals and these may be responsible for the observed non-linear variation of microhardness in them.

Table.1 Pauling ionic radii IN Å

Ion	**Ionic size Å**
Cl^-	1.81
Br^-	1.95
I^-	2.16
K^+	1.33
Na^+	0.95

It is well known that lattice strains are developed in mixed crystals due to the difference in the size of the atoms or ions.

The size of different ions (5) is shown in table.1.

Therefore internal strain arising out of the difference in ionic sizes may be responsible for the formation of various types of imperfections such as vacancies, dislocations, low angle grain boundaries and other defects, which in turn are responsible for the non-linear variation of microhardness. The results also suggest that the microhardness in mixed crystals depends upon the difference in the size of the ions and not on the nature of the ions substituted.

To know hardness of the materials, a graph of log P versus log d is plotted. The slope of the best linear fit graph gives Mayer's work hardening co-efficient, 'n'. The n values for different composition are shown in table.2. According to Onitsch (6) and Hanneman (7) the 'n' value falls below 1.6 for hard materials and more than 1.6 for soft materials. The values obtained imply that the mixed crystals belong to hard materials category.

Table.2 Work hardening co-efficient

Composition	**'n' Value**
$KCl_{0.1}\,KBr_{0.8}\,NaI_{0.1}$	0.33
$KCl_{0.4}\,KBr_{0.5}\,NaI_{0.1}$	0.38
$KCl_{0.5}\,KBr_{0.4}\,NaI_{0.1}$	0.36
$KCl_{0.7}\,KBr_{0.2}\,NaI_{0.1}$	0.32

Table.3 Values of Elastic stiffness constant

Load (p) in g	C_{11} for $KCl_{0.1}$ $KBr_{0.8}\,NaI_{0.1}$ ($\times10^{14}$ Pa)	C_{11} for $KCl_{0.4}$ $KBr_{0.5}\,NaI_{0.1}$ ($\times10^{14}$ Pa)	C_{11} for $KCl_{0.5}$ $KBr_{0.4}\,NaI_{0.1}$ ($\times10^{14}$ Pa)	C_{11} for $KCl_{0.7}$ $KBr_{0.2}\,NaI_{0.1}$ ($\times10^{14}$ Pa)
5	33.8	145.3	77.4	61.2
10	47.0	262.1	223.5	117.0
15	49.4	247.1	483.7	140.8
25	168.0	187.5	206.0	166.6
50	345.1	950.0	1248.0	526.5
100	106.4	400.0	262.0	324.0

The elastic stiffness constant (C_{11}) for various compositions as well as for different loads have been estimated using Wooster's empirical formula $C_{11}= H_v^{7/4}$ .The C_{11} values are shown in table.3.These values gives an idea about the tightness of bonding between neighboring atoms(8).Among the investigated combinations, atoms are more tightly bound to their neighboring atoms in the sample $KCl_{0.5}$ $KBr_{0.4}$ $NaI_{0.1}$.

Among the investigated samples, the sample $KCl_{0.5}$ $KBr_{0.4}$ $NaI_{0.1}$ is answering for a higher value of C_{11} for all the loads from 5gm to 50gm.

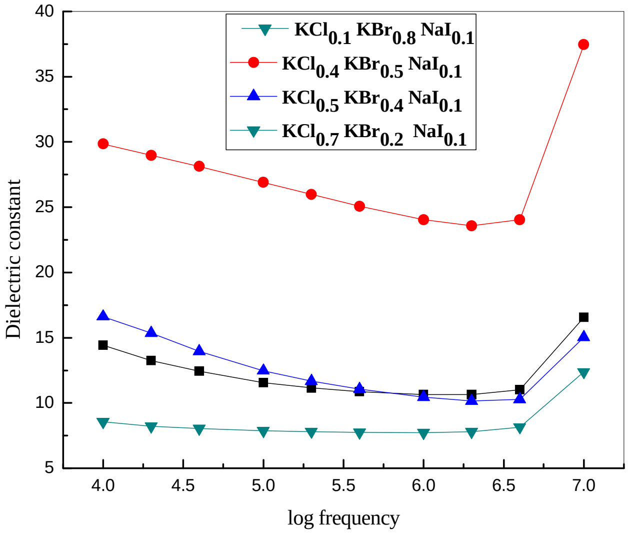
2. Dielectric studies and a.c. Conductivity (σ_{ac})

The samples were ground to proper thickness and polished. The final dimensions of the samples were about 1.5 to 2 sq.cm.in area and 0.1 to 0.3 cm. in thickness. Each sample was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A 4275A, multi frequency LCR meter (Hewlett-Packard) was used to measure capacitence (C) and dissipation factor (D) of the sample as a function of frequency. The dielectric constant (ε_r) ,dielectric loss (tanδ) and ac conductivity were calculated from C and D using the relations,

$$\varepsilon_r = C\, d/\varepsilon_o\, A, \qquad \tan\delta = D\, \varepsilon_r \qquad \text{and} \qquad \sigma_{ac} = \varepsilon_o\, \varepsilon_r\, \omega \tan\delta$$

Glossary of symbols

C – Capacitance of a capacitor
d – Plate separation
A – Area of plate
D – Dissipation factor
ω -- Angular frequency
ε_r – Dielectric Constant
ε_o - Permittivity of free space.



σ_{ac} - A.C. Conductivity

Fig.3 Variation of dielectric constant (ε_r) with frequency

The variation of dielectric constant (ε_r) with logfrequency at room temperature is shown in Fig.3. It is observed that the value of dielectric constant is more at lower frequency. It decreases with increasing frequency. Generally the dielectric constant of a material is related to electronic, ionic, dipolar and space charge polarization. All these are active at low frequencies. In fact the nature of variation of dielectric constant with logfrequency indicates the type of polarization present.

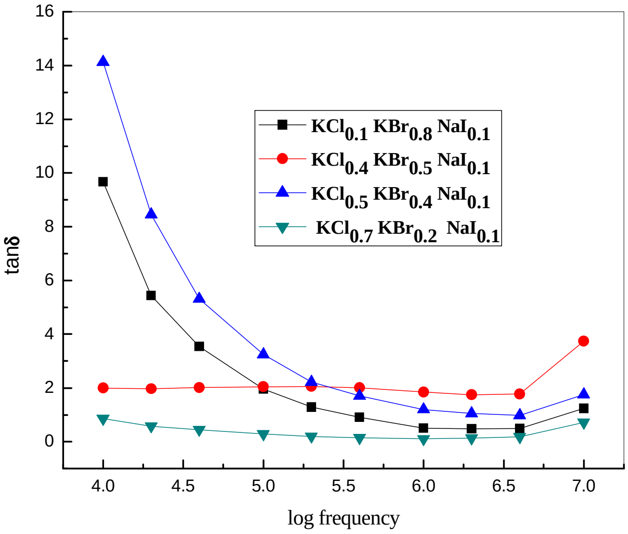


Fig.4 variation of dielectric loss with frequency

The space charge polarization contribution will depend on the purity and perfection of the crystals. Its influence is negligible at very low temperatures and is noticeable in the low frequency region. The dipole orientational effect can sometimes be seen in some materials even upto 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz. The dielectric loss is very high at lower frequency for certain compositions but falls to moderately low values at higher frequencies.

Recollecting our data the larger values of dielectric constant at low frequencies may be ascribed to space charge polarization due to charged defects in the material. This is supported by the fact that tanδ has very large values at low frequencies and also the tanδ varies with logfrequency indicating that it is due to D.C. conduction.

The variation of σ_{ac} with frequency is shown in figure 5.

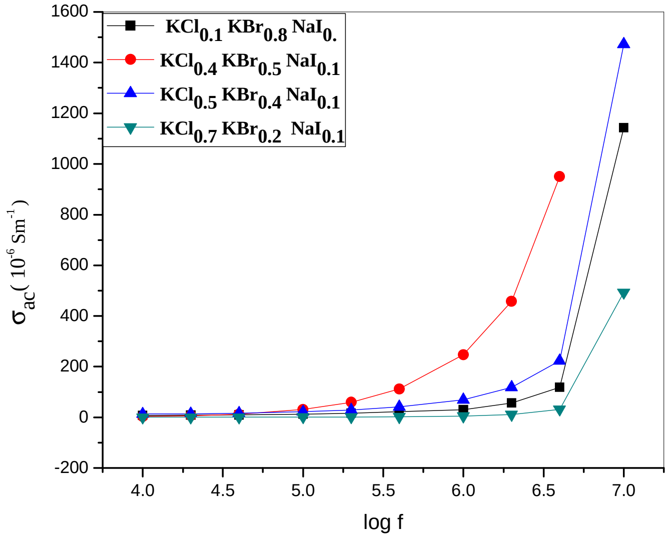


Fig.5 variation of AC conductivity with frequency

The variation of σ_{ac} with frequency for all the investigated samples is almost constant upto 100 KHz. Later it has shown exponentional variation with frequency in agreement with the reported results (9).

CONCLUSIONS

Good optically transparent ternary mixed alkali halide crystals $(KCI)_x(KBr)_{0.9-x}(Nal)_{0.1}$ of different compositions were grown by slow evaporation from aqueous solution. Elemental analysis have been confirmed by EDAX. Microhardness has varied non-linearly with composition. Microhardness is more in ternary mixed crystals than in the pure and binary mixed crystals. The increase in hardness in mixed crystals has been attributed to the internal strains arising out of the difference in ionic sizes, which is responsible for the formation of dislocations, low-angle grain boundaries and other defects. Among the investigated combinations, atoms are more tightly bound to their neighboring atoms in $KCl_{0.5}$ $KBr_{0.4}$ $NaI_{0.1.}$

The value of the dielecric constant in mixed $(KCI)_x$ $(KBr)_{0.9-x}$ $(Nal)_{0.1}$ crystals is more than the pure components. Dielectric constant varies non-linearly with composition. Large value of dielectric constant at low frequencies in the present study confirms the purity of the sample, secondly, as due to the space charge polarization.The ac conductivity results indicate that conduction mechanism is due to hopping.

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