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Hardness and Thermal Studies of ZnS Doped KCl_xBr_{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. From the microhardness studies to calculate the hardness value of the grown crystals, thermal studies reveal endothermic and exothermic temperature of the grown crystals.***

Keywords: ZnS, mixed, microhardness, thermal studies

1. 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.

2. 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.

Microhardness Studies

Good quality crystals are needs for various applications, not only with good optical performance but also with good mechanical behavior. The hardness of a material is a measure of the resistance it offers to local deformation. The microhardness characterization is extremely important as far as the fabrication of the devices is concerned. Pure and doped KCl and KBr crystals were tested for their microhardness 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 [1]. The measurements were carried out on (100). Plans at room temperature and the indentation time was kept as 10 s for each load(p), several indentations were made and the average value of the diagonal length(d) was used to calculate the microhardness of the crystals. The hardness of the crystals is calculated using the relation

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

Where
H_v is the Vicker’s hardness number,
P is the applied load in kg and
‘d’ the average diagonal length of the impression in mm.

The microhardness measurement is carried out on the grown crystals to estimate the mechanical properties. 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. Microhardness characterization is extremely important

and control of the hardness testing machine and evaluation of test data are handled by Shimadru HMV- 2 Vicker's

Microhardness measurements are made using a Vicker's microhardness tester fitted with a diamond pyramidal indentor. The hardness of a material is defined as the resistance it offers to the motion of dislocations, deformation or damage under an applied stress. Hardness testing provides useful information on the strength and deformation characteristics of materials. It is correlated with other mechanical properties like elastic constant and yield stress. A relationship between indentation hardness and plastic and work-hardening capacity of a material [2]. Vicker's microhardness 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. Indentation test is done in air at room temperature. The applied load is varied as 25g, 50g and 100g for a constant indentation period of 10 s. The Vicker's hardness number H_v is calculated using the relation. Diagonal lengths'd' of indented impressions obtained for various loads are measured. The average value of the diagonal lengths of the indentation marks in each trial is calculated. Hardness of the crystal is calculated using the relation.

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

Where P is the applied load in kg and 'd' the average diagonal length of the impression in mm. The hardness of the materials, a graph of log P versus log d is plotted. The slope of the best linear fit gives Mayer's work hardening co-efficient 'n'.

Table 5.3.1: 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 $KCl_{0.2}KBr_{0.8}$ mixed crystal ZnS doped	9.5114	13.5564	20.6809
$KCl_{0.5}KBr_{0.5}$ mixed crystal ZnS doped	6.8575	11.5064	19.0960
$KCl_{0.8}KBr_{0.2}$ mixed crystal	32.3811	59.1431	74.2527

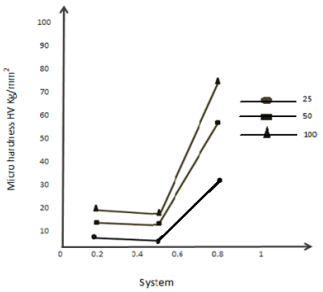


Figure 5.3.1: Variation Vicker's micro hardness value of all the grown crystals

The Vicker's microhardness values for the grown crystals are provided in Table 5.3.1. The variations of microhardness with composition for KCl_x Br_{1-x} were shown in figure 5.3.1. In the case of mixed and ZnS added 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 KCl_x Br_{1-x} mixed crystals is good compared to the ZnS doped mixed crystals.

Table 5.3.2: The log p and log d values for all grown crystals

System	log p			log d		
	25	50	100	25	50	100
Pure KCl crystal	1.3979	1.6989	2	1.8265	1.8948	1.9688
Pure KBr crystal	1.3979	1.6989	2	1.8919	1.9434	2.0321
ZnS doped $KCl_{0.2}KBr_{0.8}$ mixed crystal	1.3979	1.6989	2	1.8440	1.9175	1.9763
ZnS doped $KCl_{0.5}KBr_{0.5}$ mixed crystal	1.3979	1.6989	2	1.9150	1.9531	1.9936
ZnS doped $KCl_{0.8}KBr_{0.2}$ mixed crystal	1.3979	1.6989	2	1.5782	1.5976	1.6988

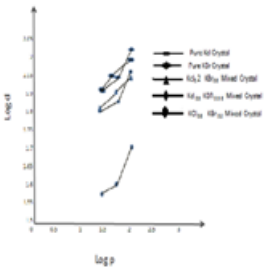


Figure 5.3.2: Plot of log p vs log d value of all the grown crystals

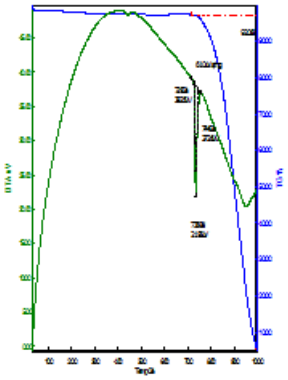
The log p and log d values for all grown crystals are provided in Table 5.3.2.We also draw the figure 5.3.2 between log p and log d for all mixed crystals. For the mixed crystals log p and log d values increased linearly.

Thermal Analysis

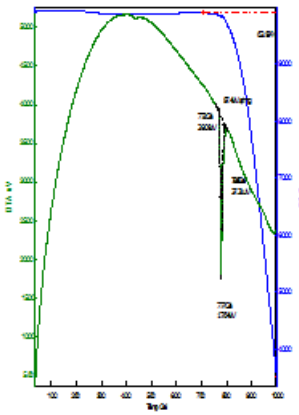
Thermogravimetric and differential thermal analysis give information regarding phase transition, crystallization and different stages of decomposition of the crystal system. Thermogravimetric analysis is an analytical technique in which the weight change of a substance is recorded as a function of temperature. The weight change may due to dehydration or decomposition. When weight of a sample is plotted against temperature, a curve characteristic of the substance is obtained. Such a curve is called a thermo gravimetric curve or thermogram. 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.DTA is a thermoanalytic technique similar to differential scanning calorimetry. In DTA the material under study and an inert reference are made to undergo identical thermal cycles,

while recording any temperature difference between sample and reference. This differential temperature is then plotted against time or temperature. Changes in the sample either exothermic or endothermic can be detected relative to the inert reference. Thus a DTA curve provides data on the transformations that have occurred such as glass transitions, crystallization, melting and sublimation. The area under a DTA peak is the enthalpy change and it not affected by the heat capacity of the sample [3].

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 [70]. Thermo gravimetric (TG) and differential thermal analysis (DTA) for the crystal samples were caved out in air atmosphere by a STA 1500 Thermal Analysis of the grown crystals. TGA is commonly used to determine the characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles. Thermal stability, oxidation, and combustion, all of which are possible interoperations of TGA traces. The TGA instrument continuously weighs a sample as it is heated to temperatures of up to 1000^{o}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. The data can be adjusted using curve smoothing and first derivatives are often also plotted to determine pointes of inflection for more in-depth interpretations. 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. TGA can be used to evaluated 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. Beyond this temperature the materials will begin to degrade. When the TGAs were run under a air atmosphere, there is no oxidation of the substrate. This phenomenon arises from a rapid temperature change. 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. 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.



(a)



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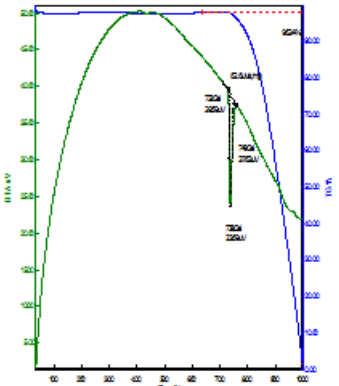

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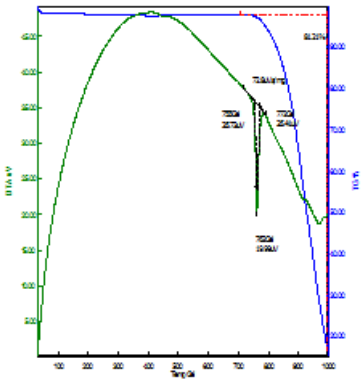
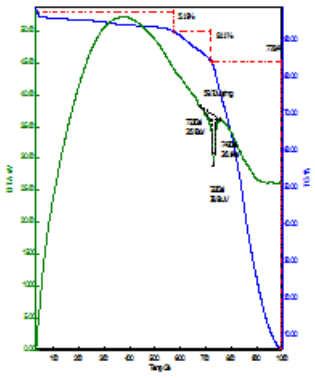


(d)



(e)

Figure 5.6.1: TG and DTA curve of

a) Pure KCl crystal
b) Pure KBr crystal
c) ZnS doped $KCl_{0.2}KBr_{0.8}$ mixed crystal
d) ZnS doped $KCl_{0.5}KBr_{0.5}$ mixed crystal
e) ZnS doped $KCl_{0.8}KBr_{0.2}$ mixed crystal

Table 5.6.1: Endothermic and Decomposition of all grown Crystals

System	Endothermic°C	Start the Decomposition °C
Pure KCl crystal	777	724
Pure KBr crystal	738	725
ZnS doped $KCl_{0.2}KBr_{0.8}$ mixed crystal	762	749
ZnS doped $KCl_{0.5}KBr_{0.5}$ mixed crystal	735	718
ZnS doped $KCl_{0.8}KBr_{0.2}$ mixed crystal	732	710

Thermal analysis of the grown crystals have been carried out by obtaining thermogravimetric (TG) and differential thermal analysis (DTA) curves and are shown in fig 5.6.1 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 5.6.1. Thermogravimetric and differential thermal analysis give information regarding phase transition, crystallization and different stages of decomposition of the crystal system [4].The thermogravimetric analysis of KCl and KBr mixed crystal was carried out between 100^0C and 1000^0C in air atmosphere at a heating rate using TG/DTA analyzer. The thermogram and differential thermogravimetric traces are shown in figure 5.6.1. The nature of weight loss indicates the decomposition point of the material. 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 KCl, KBr, $KCl_{0.2}KBr_{0.8}$, $KCl_{0.5}KBr_{0.5}$, $KCl_{0.8}KBr_{0.2}$ samples. The curved portions indicate the temperature at which weight change due to dehydration or decomposition occurs. The steep weight loss is observed the temperature range from 724°C to 790°C, from 725°C to 778°C, from 749°C to 775°C from 718°C to 753°C, from 710°C to 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 KCl, KBr, $KCl_{0.2}KBr_{0.8}$, $KCl_{0.5}KBr_{0.5}$, $KCl_{0.8}KBr_{0.2}$ 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.

In the present study, the crystals of pure and ZnS doped KCl_xBr_{1-x} mixed crystals 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 microhardness measurements were carried out on the grown crystals to estimate the mechanical properties. The microhardness measurements were made using Vicker's microhardness 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-Vis-Spectrum to study the absorbance and transmission of all grown crystals. The morphology of all the grown samples was analyzed from SEM images. Various types of separation occur in brittle and tough material. In the case of brittle fracture, crystallites are split are identified in the SEM images of KCl and KBr mixed crystal. The SEM picture show square plate structure of the grains. The thermal properties were studied from TG/DTA analysis. 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 [5].

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