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Microhardness studies on $Na_xK_{1-x}Cl$ single crystals grown from aqueous solution

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ABSTRACT

The mixed and impurity added crystals of alkali halides are found to be harden than the end members and so they are more useful. So, it is necessary and useful to prepare binary and ternary mixed crystals of alkali halides and characterize them by measuring their physical properties. In the present work, we have grown $Na_xK_{1-x}Cl$ crystals for various values of x by slow evaporation method. Vicker's microhardness was measured for all the grown crystals. The results show that these mixed crystals belong to the hard category of materials. Details are presented.

Keywords: Alkali halides, mixed crystals, crystal growth, microhardness.

INTRODUCTION

In recent decades, alkali halide crystals have proved useful in several applications ranging from X-ray monochromators to tunable lasers. The use of pure simple alkali halides is limited by the mechanical systems and hence they exist the need to strengthen them. The mixed and impurity added crystals of alkali halides are found to be more harder than the end members and they are more useful in these applications. There has been lot of work done to grow alkali halide mixed crystals from the melt but only limited work has been done to grow alkali halide mixed crystals from the aqueous solutions.

As regards mechanical properties, hardness testing provides useful information on this strength and deformation characteristic of materials [1]. As hardness properties are basically related to the crystal structure of material, microhardness studies have been applied to understand with plasticity of the substance [2]. Many investigators have used the microhardness indentation to study glide, deformation, anisotropy cracks, grain boundary hardening, state of dispersions of impurity, quench dislocation mobility.

In the present study, we have measured the microhardness of pure and doped (zinc sulphide) mixed crystals of $Na_xK_{1-x}Cl$ from aqueous solutions. Results are reported and discussed here.

MATERIALS AND METHODS

2.Experimental details

Analytical Reagent (AR) grade NaCl and KCl substance along with doubly distilled water were used for the growth of single crystals. An aqueous solution of the salt with desire molecular ratio was prepared at supersaturated concentration and seed crystals were used to grow the sample crystals. The temperature and volume were kept constant respectively at 32°C and 25ml for all the crystals. 1N solution of 2.5ml ZnS was added to the 25ml supersaturated solution. In the present study total of fourteen crystals (five pure mixed crystals, five doped mixed crystals, two pure end members and two doped end members) for various values of x viz. 0.2, 0.4, 0.5, 0.6 and 0.8

were grown in identical conditions. The bulk compositions and the dopant concentration of all the grown crystals were determined from the EDAX data.

Vicker's microhardness measure-ments were done on all the fourteen crystals grown using Leitz Wetzler hardness tester fitted with a diamond pyramidal indentor and attached with Leitz incident light microscope. Indentation test was done in air at room temperature. Different loads (25g, 50g and 100g) were used for indentation. The 'd' values were measured and the average value of the diagonal lengths of the indentation marks in each trial was calculated. Hardness of the crystal was calculated using the relation [3-4].

$H_v=1.8544\ (P/d^2)$ kg/mm^2. Where 'P' the applied load in 'kg' and 'd' the average diagonal lengths of the Vicker's impression in 'mm' after unloading.

The Meyor's work hardening co-efficient 'n' can determine by plotted logP vs logd. The slope of the best linear fit graph gives 'n' value.

The elastic stiffness constant (C_{11}) for various compositions as well as different loads have been estimated using Wooster's empirical formula.

$C_{11}=H_v^{7/4}$

RESULTS AND DISCUSSION

Microhardness values of pure mixed and ZnS added mixed crystals along with pure and ZnS added end member crystals are given in Table.1. The estimated composition of pure mixed and ZnS added mixed crystals are also provided in the table.1

Table 1 Microhardness values for pure and ZnS added Crystals along with estimated composition

System	Estimated composition	d			Hv		
		25	50	100	25	50	100
Undoped mixed crystals							
NaCl	NaCl	66.668	74.483	81.251	9.515	15.25	27.4
KCl	KCl	79.765	90.728	106.495	7.285	10.65	16.3
$NaCl_{0.2}\ KCl_{0.8}$	$NaCl_{0.135}\ KCl_{0.865}$	83.505	105.953	117.663	6.65	8.255	13.3
$NaCl_{0.4}\ KCl_{0.6}$	$NaCl_{0.248}\ KCl_{0.752}$	55.298	66.68	83.995	15.15	20.8	26.2
$NaCl_{0.5}\ KCl_{0.5}$	$NaCl_{0.339}\ KCl_{0.661}$	77.553	87.835	109.538	7.705	11.95	15.4
$NaCl_{0.6}\ KCl_{0.4}$	$NaCl_{0.602}\ KCl_{0.398}$	53.825	65.488	70.395	15.95	21.55	37.35
$NaCl_{0.8}\ KCl_{0.2}$	$NaCl_{0.91}\ KCl_{0.099}$	53.88	72.853	94.405	15.8	17.4	20.7
ZnS doped mixed crystals							
NaCl	NaCl	51.08	61.755	79.489	17.75	24.3	29.35
KCl	KCl	57.783	68.635	84.998	13.85	19.7	25.5
$NaCl_{0.2}\ KCl_{0.8}$	$NaCl_{0.191}\ KCl_{0.772}$	51.565	65.515	86.09	15.55	21.6	23.95
$NaCl_{0.4}\ KCl_{0.6}$	$NaCl_{0.386}\ KCl_{0.614}$	69.463	85.853	98.44	9.585	12.55	19.05
$NaCl_{0.5}\ KCl_{0.5}$	$NaCl_{0.443}\ KCl_{0.557}$	52.74	66.423	75.715	16.7	20.85	32.3
$NaCl_{0.6}\ KCl_{0.4}$	$NaCl_{0.601}\ KCl_{0.399}$	85.035	102.858	125.895	6.485	9.085	15.45
$NaCl_{0.8}\ KCl_{0.2}$	$NaCl_{0.697}\ KCl_{0.303}$	51.06	64.948	86.99	17.75	21.95	24.01

The variation of hardness value with load for pure and ZnS doped mixed. Crystals are shown in Fig.1. and Fig.2 respectively.

The hardness number increases as the load increases. The hardness number of the mixed crystals are found to be greater than those for end member crystals. It reveals that the mixed alkali halides are harder than the pure alkali halides. Also hardness number of the ZnS added mixed crystals are greater than the pure mixed crystals except $Na_{0.4}K_{0.6}Cl$ and $Na_{0.6}K_{0.4}Cl$ crystals. In both the cases, the decrease in hardness value when doped may be due to the creation of imperfections.

The hardness number varies non-linearly with composition. The non-linear 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 results on dislocation morphology[5] shows that the low angle grain boundaries and dislocations are more in mixed crystals compared to pure crystals. Also Tiller's eutectic crystallization mechanism may be responsible for the origin of low angle grain boundaries in mixed crystals [6]. The 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 micro hardness in them.

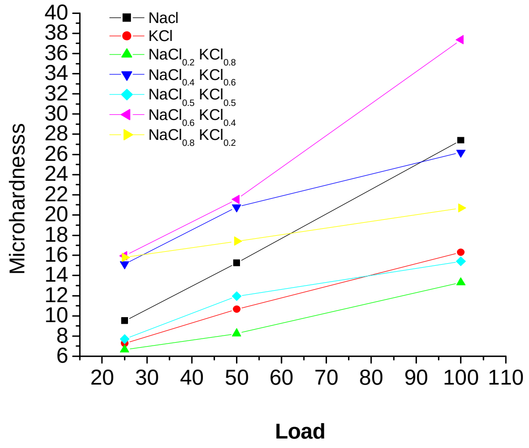

Fig . 1. Variation of hardness value with load for pure mixed crystals.

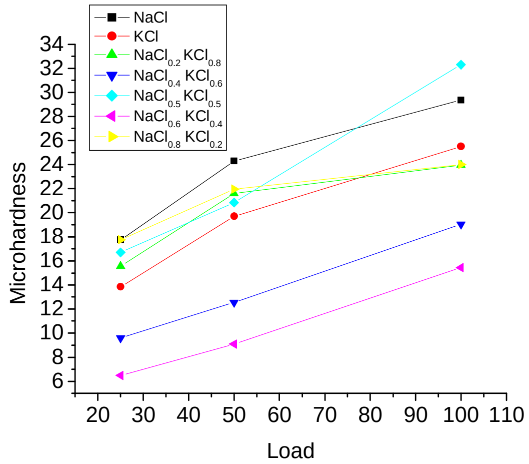

Fig .2. Variation of hardness value with load for ZnS doped mixed crystals

Table 2 Work hardening and stiffness constant values for pure and ZnS added crystals

System		**C_{11}= ($H_v^{7/4}$)**		
	n	**25**	**50**	**100**
Undoped mixed crystals				
NaCl	0	51.548	117.685	328.143
KCl	0.208	32.304	62.786	132.229
$NaCl_{0.2}$ $KCl_{0.8}$	0.247	27.538	40.203	92.628
$NaCl_{0.4}$ $KCl_{0.6}$	0.301	116.338	202.587	303.408
$NaCl_{0.5}$ $KCl_{0.5}$	0.249	35.633	76.806	119.718
$NaCl_{0.6}$ $KCl_{0.4}$	0.193	127.301	215.542	564.298
$NaCl_{0.8}$ $KCl_{0.2}$	0.404	125.213	148.239	200.885
Zns doped mixed crystals				
NaCl	0.319	153.496	265.957	370.096
KCl	0.278	99.435	184.211	289.365
$NaCl_{0.2}$ $KCl_{0.8}$	0.369	121.767	216.418	259.289
$NaCl_{0.4}$ $KCl_{0.6}$	0.251	52.214	83.681	173.707
$NaCl_{0.5}$ $KCl_{0.5}$	0.26	137.96	203.44	473.627
$NaCl_{0.6}$ $KCl_{0.4}$	0.283	26.354	47.541	120.4
$NaCl_{0.8}$ $KCl_{0.2}$	0.384	153.496	225.592	260.427

The size of sodium (Na^+) and potassium (K^+) ions are 0.95 Å and 1.33 Å [7] respectively. Sirdeshmukh [8] and Srinivas [8] pointed out in their review paper that the replacement of an ion by another ion of different size ("size effect") in mixed crystals in a highly non-linear composition variation in properties like the Debye-Waller factor, the dislocation, density and hardness. SubbaRao and Haribalbu[9] pointed out that in a mixed crystal, lattice interaction as well as the disorder due to size effect contribute to the hardness.

Work hardening co-efficient (n) and the stiffness constant(C_{11}) values for pure and doped mixed crystals along with pure and doped end member crystals are provided in Table.2. According to Onitch[10] that if n>2, the microhardness number increases as the load is increased and he showed that if n>2, the materials belong to soft category, if n<2, the materials belong to hard category. In the present work it is found that the 'n' values of all the grown crystals are less than 2 So, if that should they belong to hard materials category.

The elastic stiffness constant (C_{11}) values give an idea about the tightness of bonding between neighbouring atoms [11]. Among all the samples, the atoms are more tightly bound to their neighbouring atoms in the samples $Na_{0.6}K_{0.4}Cl$ and ZnS doped $Na_{0.5}K_{0.5}Cl$.

CONCLUSION

The hardness number of mixed and doped mixed crystals are found to be greater than those for end member crystals. The work hardening -coefficient values shown that all the grown crystals belong to hard category.

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