

LETTERS TO THE EDITOR

ON THE MICROHARDNESS INDUCED BY IMPURITY IONS IN THE NaCl AND KCl SINGLE CRYSTALS

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SMALL concentrations of divalent cations are known to be much more effective than the monovalent ions in raising the microhardness of alkali halide crystals¹⁻⁶. Although the interactions of the dislocations with the defect structure of the crystal have a decisive role in the hardening mechanism, the nature of monovalent and divalent impurity ions in modifying the dislocation content of the crystal is not completely resolved. Therefore, systematic studies were carried out on NaCl and KCl crystals doping them with such impuri-

ties to investigate the effect of dopant ions on dislocation density and microhardness; and the results are reported briefly.

The doped NaCl and KCl crystals were grown from supersaturated solution of their salts (AR grade, BDH) in a beaker covered with a lid and dopant ions were added in requisite quantities. The beaker was then placed in an oven maintaining a constant temperature of 35° C. Slow evaporation resulted in cubic, transparent crystals.

Only crystals grown in the central part of the beaker bottom and that too of nearly the same size were selected to ensure uniform growth conditions. The crystals were washed with acetone to remove the mother liquor. The washing agent was so selected to prevent salting and dissolution. The crystals were cleaved gently with fine blade to avoid stresses. {001} faces of the crystals were etched with suitable etchants

TABLE I

Variation of dislocation density and microhardness in NaCl and KCl crystals on doping with various divalent impurities

Crystal	Impurity	Ionic Size (Å)	Diff in ionic sizes of impurity and host ions		Impurity Conc. (PPM) (± 5)	Dislocation* Density (dislo/cm ²)	Micro-hardness (kg/mm ²)
			Δr	Δr%			
Pure KCl	Nil	1.33	Nil	Nil	Nil	3	10.1
Doped KCl	Ca ²⁺	0.94	-0.39	-29%	50	3	13.2
					100	3.1	14.4
					200	3	15.2
Doped KCl	Sr ²⁺	1.10	-0.23	-17%	50	3.1	12.4
					100	3	13.3
					200	3	14.6
Doped KCl	Ba ²⁺	1.29	-0.04	-3%	50	2.9	10.9
					100	3	11.2
					200	3	12.3
Pure NaCl	Nil	0.96	Nil	Nil	Nil	8	19.6
Doped NaCl	Ca ²⁺	0.94	-0.02	-2%	50	8	21.4
					100	8	22.8
					200	8	24.2
Doped NaCl	Sr ²⁺	1.10	+0.16	+17%	50	8.4	22.2
					100	8.4	23.2
					200	8.6	24.6
Doped NaCl	Ba ²⁺	1.29	+0.35	+37%	50	9	23.3
					100	9.4	24.4
					200	9.9	25.1

*The dislocation density values given above for KCl correspond to $\times 10^4$ and that for NaCl to $\times 10^5$.

and viewed under microscope (Carl-Zeiss NU-2). Flame photometry or a suitable chemical method (e.g. titration) was used to analyse the compositions. The dislocations built in the lattice are therefore expected to be influenced by the impurity ions substituting the host ions and distorting the lattice.

Table 1 shows that in pure KCl and KCl crystals doped with Ca^{2+} , Sr^{2+} and Ba^{2+} , the dislocation density remains practically the same; however these divalent ions increase the microhardness. All these divalent ions have much smaller ionic radii than the host ions and therefore can easily be accommodated in the lattice without producing the lattice distortions. In pure NaCl and NaCl crystals doped with Ca^{2+} impurity the dislocation density is also seen to be unchanged, even though microhardness in this crystal increases. In NaCl crystals doped with Sr^{2+} and Ba^{2+} , the dislocation density increases raising the microhardness. The increase in dislocation density in Ba^{2+} doped NaCl is comparatively greater than that of Sr^{2+} doped NaCl crystals. This rise could be correlated with the corresponding large differences in ionic sizes existing between the host ion (Na^+ : 1.96 Å) and the impurity ions (Sr^{2+} : 1.10 Å°, Ba^{2+} : 1.29 Å°). It is also seen from table 1 that when the impurity ions are smaller than the host ions (e.g. NaCl doped with Ca^{2+} or KCl doped with Ca^{2+} , Sr^{2+} and Ba^{2+}) no lattice strains are caused with no change in dislocation content, but the microhardness increases. For each divalent ions introduced into the lattice, a positive ion vacancy is created. The impurity ions and the vacancies could be present as individual defects independent of one another or impurity—vacancy complexes or larger aggregates.

All these defects hinder the dislocation motion and increase the microhardness of the crystals.

Divalent impurities form high solid solutions with alkali halides; however the monovalent ions can be substitutionally dissolved in the alkali halide crystals to a larger extent, especially when the ionic radii do not differ much. Table 2 shows that in NaCl crystals doped with K^+ ions, the increase in dislocation density is higher compared to that in pure NaCl crystal. Subsequent increase in the concentration of the dopant results in a corresponding increase in the dislocation density and microhardness. The difference between the ionic radii of the Na^+ ions and the substituting K^+ ions is as large as 42% causing lattice distortions and increasing dislocation density along with the microhardness.

In KCl crystals any extent of KBr can be dissolved as these two salts exhibit complete mutual solubility with an interchange of Cl^- ions by Br^- ions. The Br^- ions are only 7% larger than Cl^- ions. From the table 2, it is seen that the dislocation density and the microhardness increase with rise in KBr concentration, these being optimum for the 50:50 composition wherein the substitution of Cl^- ions by Br^- ions is also optimum. On either side of the solubility curve either Cl^- or Br^- ions predominate and the lattice strains being reduced, the dislocation density and microhardness too fall. The dislocation density and the microhardness in NaCl doped with K^+ ions is comparatively more than that in KCl-KBr where in Cl^- ions are substituted by the Br^- ions.

Thus, these studies suggest that in NaCl and KCl crystals, the dopant ions with large ionic radii (more

TABLE 2

Variation of dislocation density and microhardness in NaCl and KCl crystals on doping with various monovalent impurities

Crystal	Impurity	Ionic size (Å)	Diff in ionic sizes of impurity and host ions		Impurity Conc. (PPM/mol. wt)	Dislocation* Density (dislo/cm ²)	Microhardness (kg/mm ²)
			Δr	$\Delta r\%$			
Doped NaCl (from KCl)	K^+	1.33	+0.37	+ 42%	50 ± 5	9	24.8
					100 ± 5	9.5	26.4
					200 ± 5 (PPM)	10.8	28.2
Doped KCl (from KBr)	Br^-	1.95	+ 0.14	+ 8%	0.1	8	16.1
					0.3	16	21.8
					0.5	24	25.2
					0.7	14	19.8
					0.9 (mol. wt)	6	14.2

* Dislocation density values are $\times 10^5$ for NaCl and $\times 10^4$ for KCl.

than $\pm 7\%$) increase the microhardness by increasing the dislocation density due to lattice strains. Multi-valent dopants create ion vacancies which provide obstacles to the dislocation motion thereby raising the microhardness of the crystals.

12 January 1982

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THE CRYSTAL STRUCTURE OF SULPHAMOXOLE

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SULPHAMOXOLE (2-*p*-aminobenzene sulphonamido-4,5-dimethylloxazole, $C_{11}H_{13}N_3O_3S$) is a well known antibacterial drug. The crystal structure of sulphamoxole is reported in this paper as part of our programme on the crystal and molecular structure studies of sulphonamides¹⁻³.

Large yellow coloured crystals of sulphamoxole were obtained by slow evaporation at room temperature from its solution in methanol. The crystals belong to monoclinic space group $P2_1/c$ with $a = 7.93(2)$, $b = 12.88(1)$, $c = 13.38(3)$ Å, $\beta = 106.1^\circ(5)$, $d_m = 1.378(5)$, $d_c = 1.373$ gcm⁻³ with $Z = 4$.

Three-dimensional x-ray intensity data were recorded on multiple films by Weissenberg technique. The structure was solved by the direct method and successive difference Fourier technique; 250 reflexions with $E > 1.30$ were used for sign determination. The co-ordinates of the atoms as read from the E -map and individual isotropic temperature factors were refined by structure factor least squares refinement. The present R value is 0.175. The intramolecular bond distances and angles are listed in table 1. The packing of the molecules in the unit cell is shown in figure 1.

The bond lengths and angles are in good agreement with the values observed in other sulphonamides e.g. sulphisoxazole⁴, sulphisomidine¹, sulphadiazine³, sulphadimethoxine², etc. The planes of both the rings are

TABLE I

Intramolecular bond distances (a) and angles (b)

(a)	C1—C2	1.43 Å
	C1—S8	1.76
	C1—C6	1.40
	C2—C3	1.39
	C3—C4	1.39
	C4—C5	1.40
	C4—N7	1.40
	C5—C6	1.39
	S8—O9	1.49
	S8—O10	1.46
	S8—N11	1.56
	N11—C12	1.30
	C12—O13	1.37
	O13—C14	1.42
	C14—C15	1.35
	C14—C18	1.52
	C15—N16	1.40
	C15—C17	1.49
	N16—C12	1.33
(b)	C2—C1—C6	121.1°
	C2—C1—S8	121.4
	C6—C1—S8	117.5
	C1—C2—C3	120.0
	C2—C3—C4	119.3
	C3—C4—C5	119.8
	C3—C4—N7	118.7
	C5—C4—N7	121.6
	C4—C5—C6	122.8
	C5—C6—C1	116.7
	C1—S8—O9	105.7
	C1—S8—O10	109.8
	C1—S8—N11	102.6
	N11—S8—O9	110.9°
	N11—S8—O10	107.9
	O9—S8—O10	118.8
	S8—N11—C12	119.8
	N11—C12—O13	132.3
	N11—C12—N16	117.5
	N16—C12—O13	110.0
	C12—O13—C14	107.7
	O13—C14—C15	105.0
	O13—C14—C18	120.9
	C15—C14—C18	134.1
	C14—C15—N16	110.9
	C14—C15—C17	133.7
	N16—C15—C17	115.0
	C15—N16—C12	106.3

inclined at an angle of approx. 55° . The dihedral angle 30° along S—N bond seems to be very small as compared to other sulphonamides. The tetrahedral geometry around sulphur is also distorted, as angles