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PHASE EQUILIBRIA IN SOLID SOLUTIONS OF ALKALI HALIDES AT HIGH PRESSURE

by

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INTRODUCTION

Seventeen of the twenty alkali halides have the NaCl (fcc) type structure while three of them have the CsCl (bcc) type structure at atmospheric pressure. Slater(1) first discovered that RbBr and RbI exhibit a phase transition at pressure of about 5 kilobars. Jacobs(2) showed by high pressure X-ray diffraction studies that this phase transition in RbI, which normally has the NaCl type structure, was to the CsCl type structure. Other researchers(3,4,5,6,7) have discovered phase transitions in all but four of the NaCl type alkali halides. In all cases examined by high pressure X-ray diffraction the high pressure polymorph has been shown to have the CsCl type of structure(2,6,8).

It is of particular interest that all the rubidium halides undergo this NaCl to CsCl type structure change at a pressure of 5 to 6 kilobars(1,4,9) whereas the potassium halides undergo this phase transition at pressures from 18 to 20 kilobars(4,6). From this, it would appear that the cation plays a predominant role over the anion in determining the pressure at which this phase transformation occurs. This is of special interest since the PΔV work carried out during the transition can be related to difference in lattice energies of the two crystalline forms as calculated from the Born-Mayer model(9).

We have carried out pressure-volume measurements on binary solid solutions(10) of certain of the alkali halides which exemplify cation substitution, for example in the KCl-RbCl system, and anion substitution in the KCl-KBr system, in order to learn more of the role of the cation and of the anion on these pressure induced structure changes.

EXPERIMENTAL

Solid solutions were prepared from analytical reagent grade salts dried at 125°C. The salts were mixed thoroughly then melted and further mixed in the molten state. Samples of approximately 1/2 inch diameter by 1 1/2 inch length were cast and then encapsulated in lead foil for the high pressure studies. The high pressure apparatus is a piston-cylinder device similar to one described by Darnell(11). The pressure-volume measurements were carried out at 100°C since the kinetics of these solid-solid phase transformations is much more rapid and the transition pressures more reproducible than at room temperature. The pressure versus change in volume of the system, relative to Bridgman's(3) data for iron, was measured to 40 kilobars. The pressure at which the phase change occurs was calculated from an average of the pressure of the transition taken with increasing pressure and with decreasing pressure.

RESULTS AND DISCUSSION

The phase transformations in the solid solutions of KCl-RbCl occur at about the same rates and with the same hysteresis (difference in pressure of phase transformation with increasing pressure and with decreasing pressure after subtracting off piston friction) as for the pure salts comprising the system. There was no discernable difference in the P-V curve between successive compressions of the 50-50 mixtures. Furthermore, the relative intensities of the X-ray diffraction lines are essentially the same in the 50-50 mixtures before and after compression, thus indicating no tendency in segregation or of ordering due to the compression. Apparently these salts are completely miscible in the high pressure CsCl structure as they are in the normal NaCl structure(10). Figures 1 and 2 show the variation in transition pressure at 100°C for the KCl-RbCl and KCl-KBr systems, respectively. In the KCl-RbCl system the transition pressure behaves almost linearly with a slight negative deviation from additivity, while in the KBr-KCl system there is a slight positive deviation. The pressure-composition curve for this solid-solid transition is very similar in shape to the melting curve for this system. The substitution of a Rb^+ ion for a K^+ ion changes the average lattice parameter(12), melting point(10), and transition pressure in the KCl-RbCl system. However changing the anion as in the KCl-KBr system results in essentially no change in the transition pressure of this solid-solid transformation but does effect the melting temperature and the lattice parameter(12).

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Figure 1.

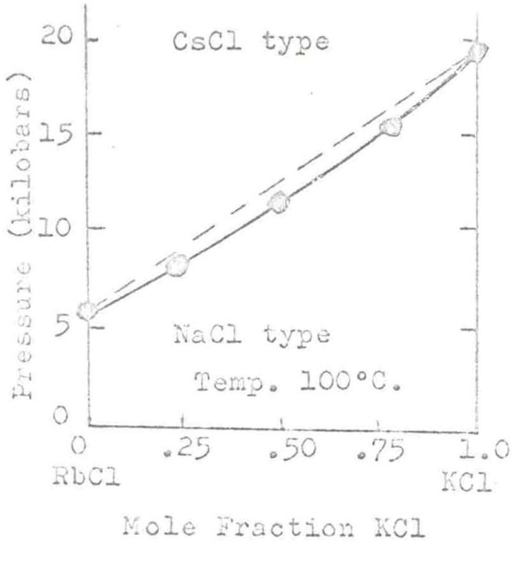
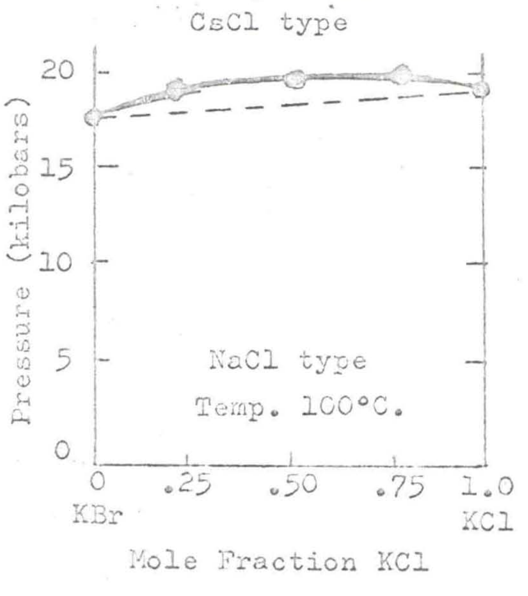


Figure 2.



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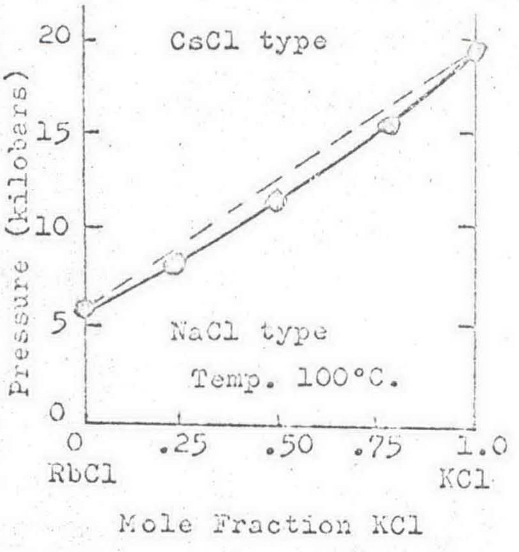

Figure 2.