Polymorphism in KCl–RbCl and KCl–KBr Solid Solutions at High Pressure*

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The pressure-induced polymorphic transition in solid solutions of KCl–RbCl and KCl–KBr systems was investigated by dilatometry over the temperature interval 25–800°C. This transition is similar to the $Fm3m \rightleftarrows Pm3m$ phase change which occurs in the component salts at high pressure. However, the transition is broader, i.e., occurs over a larger pressure interval, than was found in the pure component salts. Data for the mean transition pressure (P_{tr}^m) and total volume change (ΔV_{tr}) for this transition in these solid solutions are given for the temperature range 200–800°C. As an approximation, P_{tr}^m has been treated in the same manner as the transition pressure for a pure salt to calculate $P\Delta V$, ΔS, and ΔE for the polymorphic transition in these solid solutions. These properties change in a continuous, but nonlinear, manner upon substitution of RbCl and KBr into the KCl structure. Both cationic substitution (Rb^+ for K^+) and anionic substitution (Br^- for Cl^-) increase the interatomic spacing by approximately the same amount. However, cationic substitution (the smaller ions) has a greater effect on the transition properties than does anionic substitution.

I. INTRODUCTION

It is well-known that the alkali halides occur in two crystalline forms. The halides of cesium normally have the CsCl-type structure, space group $Pm3m$ (CsF excepted). Halides of lithium, the smallest of the alkali metals, have been observed only in the "rock salt" form, space group $Fm3m$. Halides of the alkali metals of intermediate size (Na, K, and Rb) normally have the $Fm3m$ structure, but in many cases these salts transform to the $Pm3m$ form at elevated pressure (1–4).[1] The normal occurrence of the phases in this class of compounds is, in general, in accordance with the relative stability of these structure types as is predicted from radius ratio considerations (10, 11).

Trends associated with atomic number or size of the ions are known to exist in some of the thermodynamic properties of this $Fm3m \rightleftarrows Pm3m$ transition. For example, some of the cesium salts undergo this polymorphic transition when heated at atmospheric pressure. The rubidium salts undergo this change at ordinary temperatures but at pressures of 4–6 kb, the potassium salts likewise at pressures from

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[1] The literature on the phase transition in this class of compounds is extensive. For further information the reader is referred to papers by Tosi and Fumi (5), Schumacher (6), Tosi (7), Klement and Jayaraman (8), and Darnell and McCollum (9).

18–20 kb, while the rock salt form of NaCl transforms to the CsCl structure at a pressure of 300 kb (12). In a recent paper Darnell and McCollum (9) have found other trends in this polymorphic transition in this group of salts, e.g., the transition volume of the rubidium chloride, bromide, or iodide is greater than for the corresponding potassium salt. Furthermore, the entropy change, $\Delta S(Fm3m \rightarrow Pm3m)$, is positive for the potassium salts but negative for the rubidium salts (and CsCl). Indeed such trends in this polymorphic transition should not be surprising since similar trends in the temperature, volume, and entropy of the melting of the $Fm3m$ phase of these salts (i.e., $Fm3m \rightarrow$ liquid) are known (13).

In order to gain more insight into the polymorphic transition in this class of compounds we have therefore examined this phase transition in the very nearly ideal solid solutions of the KCl–RbCl (cation substitution) (14) and KCl–KBr (anion substitution) (15) systems. This is analogous in some respects to the work of Menary, Ubbelohde, and Woodward (16), Wood and co-workers (17–19), Krogh-Moe (20, 21), and Rao et al. (22) on the effect of ionic substitution upon the thermally induced (atmospheric pressure) $Pm3m \rightleftarrows Fm3m$ transition in CsCl.

II. EXPERIMENTAL

A. Materials

The salts KCl, KBr, and RbCl used in these measurements were Mallinckrodt analytical reagent grade. These salts were out-gassed for a period of 24 hr under high vacuum ($p < 10^{-6}$ Torr) at 150°C. The component salts for a given solid solution were weighed, with a precision necessary to yield mole ratios known to within one part in one thousand, and then mixed in a molten state. This molten salt solution was rapidly chilled by pouring it into a thin layer (1 mm) on the bottom of a Pt crucible. The resulting solid solution was then homogenized by keeping it for several hours at a temperature $\sim 100°$ below the temperature of the solidus curve (23). These solid solutions were pulverized and then compressed into pellets 0.6 by 1.5 cm at a pressure of 2 kb. X-ray powder patterns show this technique gives solid solutions with a uniform composition. Lattice parameters (a_0, one atmosphere) were calculated from an average of five separate back reflections.

The results obtained here are in excellent agreement with the lattice parameters reported for the component salts KCl, KBr, and RbCl by Swanson et al. (24, 25), as well as for the solid solutions of KCl–RbCl reported by Havighurst et al. (26), and the KCl–KBr system reported by Oberlies (27). As is well-known in the literature (26, 27) the lattice parameters of these two binary solid solutions varies linearly with mole fraction (x) of the component salts, i.e.,

$$a_0(\text{solid solution}) \cong x_1 a_{0_1} + (1 - x_1) a_{0_2}. \tag{1}$$

B. Apparatus and Procedure

The experimental methods used to measure the transition pressure and transition volume of these solid solutions of KCl–RbCl and KCl–KBr were, in general, similar to the methods employed for the component salts (9). The equilibrium transition pressure (P_{tr}) for the component salts KCl, RbCl, and KBr was determined from an average of the pressures at which the phase transition initiates upon compression