Mechanochemical Reactions of Alkali Metal-Halides—The Systems AX/BX/(H₂O) with A, B = Na, K, Rb, Cs and X = Cl, Br, I

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Solid solutions $(K, Rb)X$ with $X = Cl$, Br, I are obtained by grinding mixtures of KX and RbX in a ball mill. The reaction can be accelerated by adding a small amount of water. When grinding CsCl and NaCl or CsBr and NaBr together with a stoichiometric amount of water in the ratio $1:2:2$ double salts $Cs(Na \cdot H_2O)_2X_3$ $(X = Cl, Br)$ are obtained. Above 40°C or 70°C, respectively they are partially dehydrated, yielding solid solutions $Cs_{1-x}(Na \cdot H_2O)_xX$. For both phases the enthalpies of formation from the binary halides were measured by solution calorimetry. They are negative. © 1990 Academic Press, Inc.

1. Introduction

For systematic investigations about the existence of ternary compounds it can be important to prepare such compounds at ambient temperature. An example is KMn Cl₃ (*1*), which crystallizes from the melt with the cubic perovskite structure and later undergoes several non-reconstructive phase transitions to distorted perovskites. At ambient temperature the Gd FeO₃-type structure exists, but is only metastable; however, a partial transition to the stable NH₄CdCl₃-type structure requires several years (*2*). One way to yield such compounds in a more convenient way might be the mechanochemical synthesis by grinding mixtures of the binary precur-

sor compounds in a mortar or in a ball mill.

Some years ago, Yariv and Shoval (*3*) investigated the grinding of CsCl with other alkali metal halides at ambient atmosphere, in order to get information about possible problems which may arise during the application of CsCl as a matrix for the preparation of disks for IR-spectroscopy. They found, that by grinding a mixture of CsCl and NaCl in atmospheric ambient a solid solution $Cs_{1-x}(Na \cdot H_2O)_xCl$ was formed, first described by Plyushchev et al. (*4*), who precipitated it from aqueous solutions. Similar solid solutions were obtained by grinding CsBr or CsI with NaBr or NaI, respectively. The water required for the mechanochemical process was adsorbed from the atmosphere during grinding.

These two investigations were the starting

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point for a study to find out the basic features of the mechanochemical reactions taking place among two different alkali metal halides as a model for other, more complicated ternary systems AX/MX_n. The investigations, described here, were conducted with anhydrous mixtures AX/BX (A, B = Na–Cs; X = Cl, Br, I) in a ball mill, which is a closed system. In a second series a small amount of water was added, because it is assumed that traces of water might have a catalytic effect. Furthermore a discrete hydrated double salt $Cs(Na \cdot H_2O)_2Cl_3$, is known (5). This compound has been previously precipitated from aqueous solutions; in the present study we tried to obtain it by mechanochemical treatment. We also tried to establish whether CsBr and CsI form hydrated double salts with NaBr and NaI, respectively, analogous to the chloride salt.

2. Experimental

Materials.—The alkali metal halides (p.A.-quality, Fa. Merck) were dried at 150°C.

Ball-mill: The ball-mill (model S1, Fa. Retsch) consisted of a 50 ml agate cell equipped with seven agate balls ($\varnothing$ 10 mm).

X-ray powder patterns: Philips goniometer PW 1050/25 equipped with a proportional counter and a vacuum attachment. During exposure (CuK_α-radiation) the samples were in He-atmosphere. NaCl (a = 5.63919 Å) and Al_2O_3 (a = 4.7592 Å; c = 12.9800 Å) were used as inner-standards; cell dimensions were calculated with the least-squares program of Warczewski (6).

DTA-measurements were performed with a home-made device for samples of ~0.5 g; degradation curves (TG and DTG-registration) were recorded with the thermobalance TG-750 of Stanton Redcroft.

The apparatus used for solution calorimetry was a home-made isoperibolic calorimeter; samples of 3–6 g were dissolved in a volume of 1.3 l yielding virtually ideal solutions with a dissolution ratio of 1 : 3500 mol.

3. The Formation of Mixed Crystals (A, B)X by Grinding

When grinding mixtures of alkali metal halides AX and BX (A, B = Na, K, Rb, Cs; X = Cl, Br, I) a reaction occurs only, if the two salts form mixed crystals which are stable at room temperature. That is the case for the systems KCl/RbCl, KBr/RbBr and KI/RbI (7). For samples of ~2 g the reaction was completed after 220 h for the chlorides, 172 h for the bromides, 70 h for the iodides. The extent of the reaction was identified by X-ray-diffractograms. An example is shown in Fig. 1.

Similar results are known from literature for the systems KCl/KBr (8, 9) and NaCl/NaBr (10).

The reaction was considerably accelerated by adding a drop of water (30 mg H_2O for 2 g mixture). In the presence of water all the reactions were completed after one hour grinding. Such a catalytic effect of water was also noticed in two other kinds of solid-state-reactions:

a) Mixtures were exposed to a pressure of 10 kbar for 10 min. With dry mixtures no reaction occurred. In the presence of some water, the mixed-crystals-formation was complete for the bromide and iodide mixtures, whereas KCl + RbCl reacted only in part.

b) Pressed disks of KBr/RbBr mixtures were annealed in closed quartz ampoules for one day. Mixed crystals were formed at 500°C. In the presence of a catalytic amount of water the reaction occurred already at 300°C. Such an effect is known from other investigations in the systems $ACl/LnCl_3$ (11).

The 'catalytic effect' of water might be explained by a process analogous to the 'zone melting': in the drop a concentrated solution is obtained from which mixed crystals are recrystallised. With time the drop is migrating through the whole sample. However, at
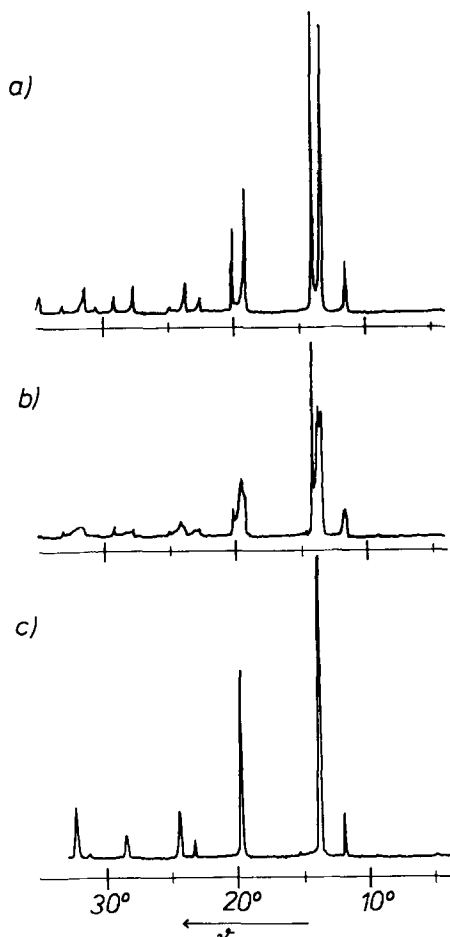
FIG. 1. X-ray patterns for the formation of solid solutions (K, Rb)Cl. a) KCl + RbCl, unground; b) after 14 h grinding; c) after 20 h grinding.

elevated temperature this model will not be applicable any longer.

4. The Double Salts Cs(Na · H$_2$O)$_2$Cl$_3$ and Cs(Na · H$_2$O)$_2$Br$_3$

CsCl, NaCl and H$_2$O in the molar ratio 1 : 2 : 2 were ground in a closed ball mill. The wet mixture became hard after ~24 h and the X-ray pattern showed only the peaks, found by Chou et al. (*12*) for CsCl · 2Na Cl · 2H$_2$O, which they had prepared from an

aqueous solution. For a mixture of 3.51 g NaCl, 5.05 g CsCl and 1.1 ml H$_2$O the reaction was completed after a grinding period of 24 h. Smaller amounts needed shorter grinding periods.

The same procedure applied for a 1 : 2 : 2-mixture of CsBr, NaBr and H$_2$O did not directly result in a complete reaction. However, after one week aging of the ground mixture at room temperature, an X-ray diffractogram showed only the peaks of the double salt. The compound is isostructural with Cs(Na · H$_2$O)$_2$Cl$_3$.

Monoclinic unit cell (space group I2/c): a = 14.285(3) Å; b = 6.097(1); c = 11.075(2); B = 91.30(2); Z = 4.

All experiments to obtain an analogous double salt with iodide failed.

Both compounds are formed exothermally from the binary ingredients. The corresponding reaction enthalpies ΔH^R can be calculated from the solution enthalpies of the binary compounds:

$$\Delta H^R = \Delta H^L(CsX + 2NaX) - \Delta H^L \text{ (complex)}$$

The measured solution enthalpies of the complex salts are:
ΔH^L (double chloride) = +46.6 ± 0.8 kJ · mol^{-1}; ΔH$_{298}^L$ (double bromide) = 47.1 ± 0.3 kJ · mol^{-1}. The ΔH^L-values for the binary compounds were taken from literature (*13*): ΔH^L (double chloride) = 46.6 ± 0.8 kJ · = 4.5 kJ · mol^{-1}; ΔH^L(CsBr) = 26.25 kJ · mol^{-1}; ΔH^L(NaBr) = −0.2 kJ · mol^{-1}.

The final results are:
ΔH^R(Cs(Na · H$_2$O)$_2$Cl$_3$) = −13.5 kJ · mol^{-1};
ΔH^R(Cs(Na · H$_2$O)$_2$Br$_3$) = −21.3 kJ · mol^{-1}.

As demonstrated by thermoanalytical measurements both compounds are losing water already at ~40°C (X = Cl) and ~60°C (X = Br) forming solid solutions of (NaX · H$_2$O) in CsX:

$$Cs(Na · H_2O)_2X_3 \rightarrow Cs(Na · H_2O)_zX_{1+z} + (2 − z)NaX + (2 − z)H_2O$$
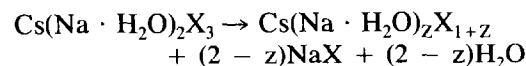
Such solid solutions can be obtained directly
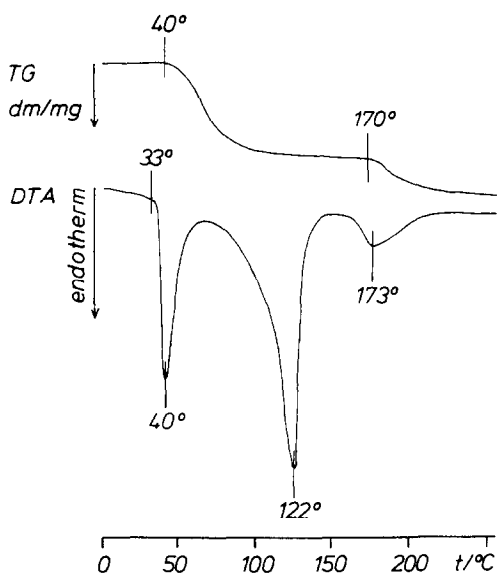
FIG. 2. TG- and DTA-curves of $Cs(Na \cdot H_2O)_2Cl_3$.

by grinding adequate mixtures of CsX, NaX and H_2O (*14*).

Experiments, to get hydrated solid solutions of KX or RbX in CsX failed. DTA- and TG-curves of $Cs(Na \cdot H_2O)_2Cl_3$ are shown in Fig. 2. According to the thermogravimetric weight loss curve in the first step 8.5% water are released in a temperature range from 40 to 120°C; in the second step (173 to 250°C) 2.8% H_2O are lost. The total loss is 11.3% (H_2O calculated for $Cs(Na \cdot H_2O)_2Cl_3$ = 11.2%). The DTA-curve must be interpreted as follows: at ~40°C water is released from the double salt, forming a saturated solution which boils at ~120°C. The generated solid solution loses the rest of the water at ~175°C. (Arkhipov et al. (*15*) had found in the degradation curve of a specimen of the solid solution with 14.6 mass-% NaCl one endothermic peak with a maximum at 190°C).

The DTA curve of $Cs(Na \cdot H_2O)_2Br_3$ is similar to that of the chloride compound, but the evolution of water begins later at about 64°C. The three endothermic peak

maxima appear at 72, 104 and 162°C. The TG shows that in the temperature range 65–110°C the sample lost 5.12% of its weight, forming a solid solution and NaBr. The former loses 2.18% H_2O in the temperature range 140–250°C. The total weight-loss is 7.8%. (H_2O calculated for $Cs(Na \cdot H_2O)_2Br_3$ = 7.9%).

5. Discussion of the Results

The present results show that reactions of solid alkali metal halides occurring during grinding, yield only stable phases. Thus, mixed crystals (A, B)X are only formed if they are stable at ambient temperature. That is the case for all systems where A = K, B = Rb. It is not possible to prepare metastable phases, for instance mixed crystals (K, Na)Cl which are only stable at elevated temperatures, because of an extended miscibility gap below ~500°C (*7*). The reaction can be accelerated considerably by a small amount of water as catalyst. In this case it can be assumed that the reaction occurs in a film of water formed on the surface of the crystalites. For our final aim, to prepare ternary lanthanoide halides by grinding, it might be of importance to investigate also reactions between alkali metal halides and hydrates of compounds LnX_3.

The double salt $Cs(Na \cdot H_2O)_2Cl_3$ and also the solid solutions $Cs_{1-x}(Na \cdot H_2O)_xCl$ are unique for the systems CsCl, NaCl, H_2O and CsBr, NaBr, H_2O. The known structure of the double salts and also the assumed coordination in the solid solution is based on the CsCl-structure in which Cs-ions are substituted by Na^+-ions situated in the centre of the cube faces (1,1,0). The empty cube-centres are filled with water. A calculation of the madelung part of lattice energy by Prof. G. Meyer from Hannover yielded a gain of $31 \text{ kJ} \cdot \text{mol}^{-1}$ in Coulomb energy by transferring $\frac{1}{3}$ of the positive charges from (1,1,1) to (1,1,0) (MAPLE for CsCl = 686.2 kJ · mol^{-1}; for $Cs_{0.66}Na_{0.33}Cl$ = 717.2 kJ ·

mol^{-1}). That must be the principal reason for the stability of both phases. It should be pointed out that the more negative formation enthalpy of the bromide double salt corresponds with its higher dehydration temperature.

Acknowledgments

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