

## **FORMATION OF CARNALLITE TYPE DOUBLE SALTS BY GRINDING MIXTURES OF MAGNESIUM AND ALKALI HALIDES WITH THE SAME ANIONS\***

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### **Abstract**

The formation of carnallite type double salts by grinding mixtures of hydrated magnesium halide and alkali halides with the same anions was investigated by X-ray diffraction, infrared spectroscopy and thermal analysis. Carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ), cesium-carnallite ( $\text{CsMgCl}_3 \cdot 6\text{H}_2\text{O}$ ), bromo-carnallite ( $\text{KMgBr}_3 \cdot 6\text{H}_2\text{O}$ ) and cesium-bromo-carnallite ( $\text{CsMgBr}_3 \cdot 6\text{H}_2\text{O}$ ) were formed by grinding mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl or CsCl and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr or CsBr, respectively. Hydrated solid solutions of magnesium in potassium or cesium halides were obtained from that portion of potassium and cesium halides which did not take part in the formation of the double salt.

**Keywords:** cesium halide, grinding, hydrated double salt, magnesium halides, mechanochemical reactions

### **Introduction**

In previous publications [1–3] we showed that grinding mixtures of sodium and cesium halides gave rise to mechanochemical reactions in which hydrated double salts or hydrated solid solutions were formed. By grinding in a closed ball mill mixtures of NaCl with CsCl or NaBr with CsBr in the presence of water, with the molar ratio 2:1:2, hydrated double salts  $\text{Cs}[\text{Na}(\text{H}_2\text{O})]_2\text{Cl}_3$  and  $\text{Cs}[\text{Na}(\text{H}_2\text{O})]_2\text{Br}_3$  were formed, respectively. If the amount of NaCl or NaBr was not sufficient for the formation of the double salts, solid solutions  $\text{Cs}_{1-x}[\text{Na}(\text{H}_2\text{O})]_x\text{Cl}$  or  $\text{Cs}_{1-x}[\text{Na}(\text{H}_2\text{O})]_x\text{Br}$  were obtained [2–3]. The hydrated solid solutions were also formed by grinding mixtures of these halides in an open system with a mortar and a pestle [4]. Under these conditions the water was adsorbed from the atmosphere. Similarly, by

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grinding mixtures which contained relatively small amounts of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with great amounts of potassium or cesium halides, hydrated solid solutions were obtained [5–7]. However, a possible formation of hydrated double salts by grinding mixtures which contained relatively large amounts of magnesium halides with the alkali halides were not investigated.

It is well known that the hydrated double salt carnallite or bromo-carnallite crystallizes from an aqueous solution containing  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{KCl}$  or  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{KBr}$ , respectively [8]. In a previous study [9] we showed that such hydrated double salts were formed with rubidium and cesium halides. The formation of carnallite type double salts, with the general formula  $\text{M}^1\text{MgX}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{M}=\text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Li}(\text{H}_2\text{O})^+, \text{and } \text{NH}_4^+$ ;  $\text{X}=\text{Cl}^-, \text{Br}^-, \text{and } \text{I}^-$ ) were studied by Emons [10]. The crystal structure of carnallite and several carnallite type double salts were previously described [11–14]. In the present paper we describe the formation of carnallite type double salts by grinding magnesium and alkali halides with the same anions.

## Experimental

### Materials

Cesium halides were of a 'suprapur' grade, supplied by Merck. The other halides were analytical-grade, supplied by Merck, BDH, Hopkin & Williams and Baker. The alkali halides were dried at  $110^\circ\text{C}$ . The magnesium halides,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ , were equilibrated over 70% sulfuric acid [15, 16].

### Grinding

Mixtures of magnesium and alkali halides (total amount 200 mg) were manually ground in an agate mortar and pestle, covered by a polyethylene bag. The bag prevented the adsorption of atmospheric water during the grinding. 200 and 300 rounds of the pestle were used. Unless otherwise stated, the ground mixtures were examined immediately after grinding.

### Methods

X-ray powder diffractions were recorded using a Philips PW-1730 and PW-1820 with  $\text{CuK}_\alpha$  radiation, 35 kV–40 mA, and a curved graphite monochromator. Data were collected from  $15$  to  $70^\circ 2\theta$ . Silicon was used as an internal standard for calibration.

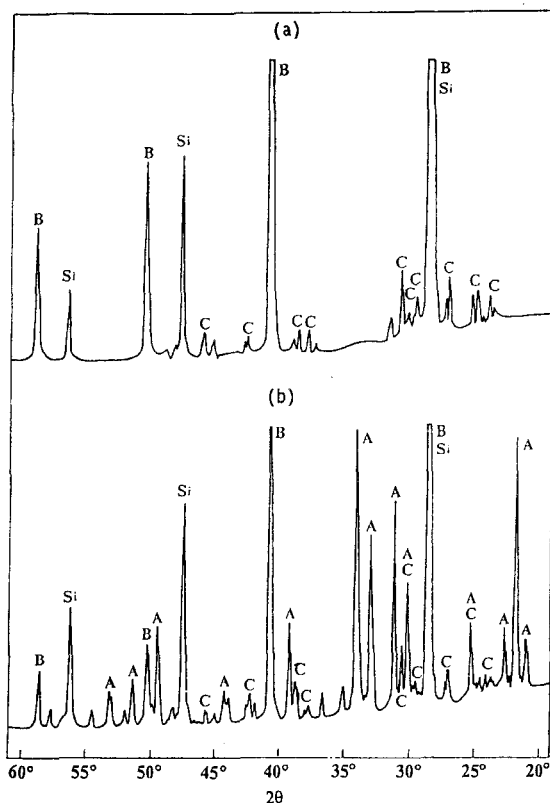
Simultaneous DTA and TG measurements were carried out in a Stanton Redcroft apparatus (STA 780). Alumina crucibles were used both for the specimen and for the reference material, which was calcined alumina. The samples were heated from room temperature to  $700^\circ\text{C}$  and cooled back to room temperature. The heating rate was  $10^\circ\text{C min}^{-1}$ . Measurements were performed in flowing air. The temperature was measured near the sample holder.

IR spectra were recorded by a Nicolet FT-IR spectrometer. The samples were examined in Nujol (to prevent any reaction between the KBr matrix and the double salts during the preparation of disks).

## Results

### *X-ray powder diffraction*

X-ray diffractograms of the ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl or CsCl and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr or CsBr in different amounts are shown in Figs 1–4. The diffractograms of the ground mixtures show new peaks (signed in the figures by C) in addition to the peaks of magnesium and alkali halides (signed in the figures by A and B, respectively). These new peaks can be attributed to hydrated double salts of magnesium and alkali halides. The principal peaks of the potassium double salts were detected in ground mixtures containing  $\geq 5\%$  mag-



**Fig. 1**  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{KCl}$ . X-ray diffractograms of a ground mixture (200 rounds of pestle) containing 10% (a) and 73% (equimolar) (b) of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl. A =  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , B = KCl, C =  $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ , Si = Silicon for calibration

**Table 1** XRD data of a pure ground potassium or cesium halide and of the portion of potassium and cesium halides which did not take part in the formation of the double salts in equimolar ground mixtures of potassium or cesium halides with magnesium halides (300 rounds of pestle)

Ground pure halide			Ground mixture			Ground pure halide			Ground mixture			
<i>hkl</i>	<i>d</i> -value/nm	intensity/%	<i>d</i> -value/nm	intensity/%	<i>hkl</i>	<i>d</i> -value/nm	intensity/%	<i>hkl</i>	<i>d</i> -value/nm	intensity/%	<i>d</i> -value/nm	intensity/%
KCl												
2 0 0	3.146	100	MgCl <sub>2</sub> ·6H <sub>2</sub> O/KCl	100	CsCl	1 1 0	2.919	100	MgCl <sub>2</sub> ·6H <sub>2</sub> O/CsCl	100	2.904*	100
2 2 0	2.225	57		35**		1 1 1	2.382	14		48**	2.381	48**
2 2 2	1.816	25		8**		2 0 0	2.061	16		9	2.058	9
4 0 0	1.573	7		5		2 1 0	1.844	13		21	1.840*	21
4 2 0	1.407	18		8		2 1 1	1.683	25		38**	1.683	38**
						2 2 0	1.457	6		4	1.456	4
						3 0 0	1.374	5		11	1.373	11
KBr												
1 1 1	3.803	12	MgBr <sub>2</sub> ·6H <sub>2</sub> O/KBr	15	CsBr	1 1 0	3.039	100	MgBr <sub>2</sub> ·6H <sub>2</sub> O/CsBr	100	3.031*	100
2 0 0	3.292	100		100		1 1 1	2.479	4		42**	2.476	42**
2 2 0	2.333	58		38**		2 0 0	2.149	20		10	2.146	10
3 1 1	1.989	6		24**		2 1 0	1.921	6		6	1.921	6
2 2 2	1.905	14		10		2 1 1	1.754	43		34**	1.750*	34**
4 0 0	1.649	9		9		2 2 0	1.519	18		9	1.518	9
3 1 1	1.514	2		4		3 0 0	1.432	3		7	1.433	7

\* - Pronounced shifts in the *d*-values

\*\* - Pronounced changes in the relative intensities

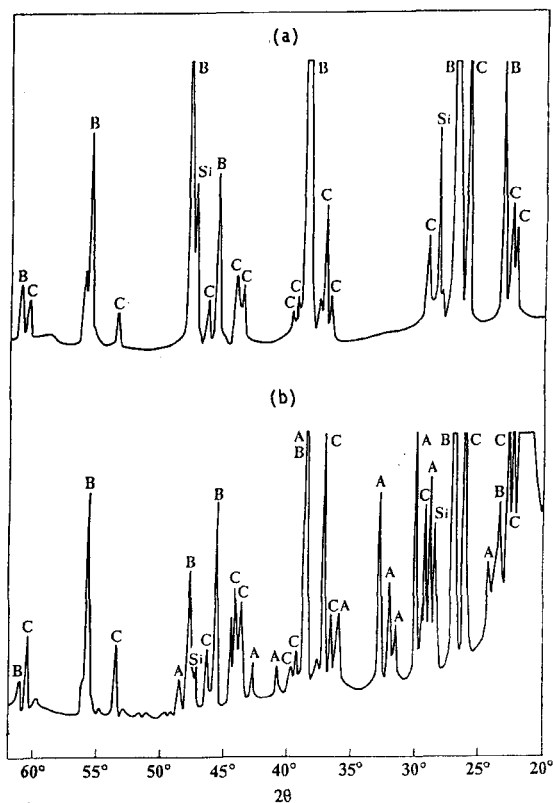
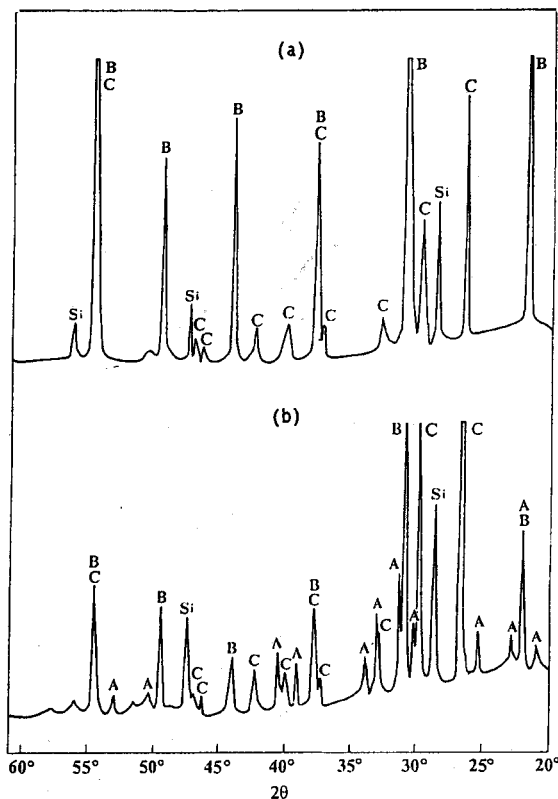


Fig. 2  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}/\text{KBr}$ . X-ray diffractograms of a ground mixture (200 rounds of pestle) containing 20% (a) and 71% (equimolar) (b) of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr. A =  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ , B = KBr, C =  $\text{KMgBr}_3 \cdot 6\text{H}_2\text{O}$ , Si = Silicon for calibration

nesium halide, whereas those of cesium double salts were observed in ground mixtures containing  $\geq 10\%$  magnesium chloride or  $\geq 20\%$  magnesium bromide. They were not detected with smaller concentrations of magnesium halides. In equimolar ground mixtures cesium double salts were the principal phase, whereas potassium double salts appeared together with considerable amounts of the original halides. The relative amounts of the chloride double salts were smaller than those of the bromide double salts in both cesium and potassium ground mixtures.

Peaks of magnesium halides were observed only when the ground mixtures contained almost 50 mol% of these halides, whereas peaks of potassium or cesium halides were detected in all the diffractograms. Some of the peaks of potassium and cesium halides in the ground mixtures showed small shifts to lower  $d$ -values and changes in their relative intensities when compared to those of the original halides (Table 1). No new peaks of hydrated double salts were observed



**Fig. 3**  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{CsCl}$ . X-ray diffractograms of a ground mixture (200 rounds of pestle) containing 10% (a) and 55% (equimolar) (b) of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with CsCl.

A =  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , B = CsCl, C =  $\text{CsMgCl}_3 \cdot 6\text{H}_2\text{O}$ , Si = Silicon for calibration

in the diffractograms of ground mixtures of magnesium and sodium halides, indicating that no hydrated double salt of magnesium and sodium halide was obtained.

The effect of grinding on the formation of the double salts in the ground mixture of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with CsCl is demonstrated in Fig. 5. The intensity of the principal peak of the hydrated double salt increased significantly with the number of the pestle rounds. For comparison, similar mixtures were left without grinding in the open air for periods up to 3 h. They showed only small new peaks of hydrated double salts.

### *IR spectroscopy*

The locations of the water bands in the IR spectra of equimolar ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl or CsCl and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr or CsBr are summarized in Table 2. For comparison, the locations of the water bands in

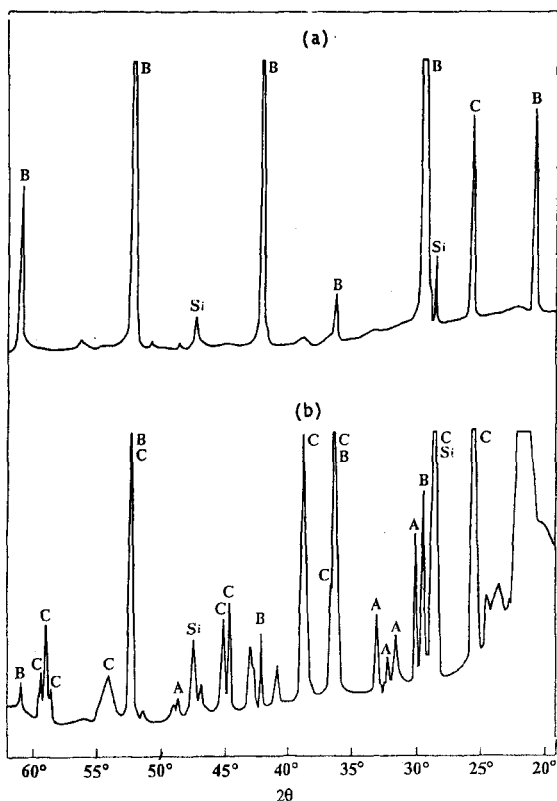
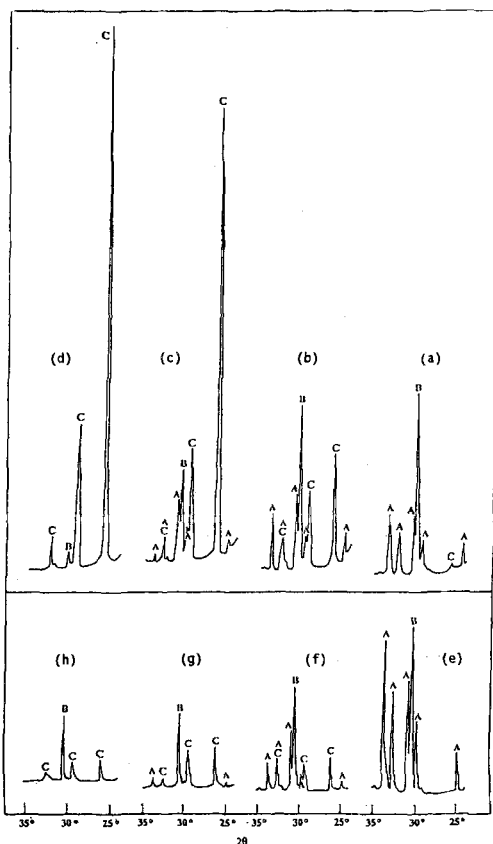


Fig. 4  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}/\text{CsBr}$ . X-ray diffractograms of a ground mixture (200 rounds of pestle) containing 20% (a) and 58% (equimolar) (b) of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with CsBr. A =  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ , B = CsBr, C =  $\text{CsMgBr}_3 \cdot 6\text{H}_2\text{O}$ , Si = Silicon for calibration

ground mixtures of potassium or cesium halides with 1% magnesium halide [6] are also included in the table. The spectra of these ground mixtures are characterized by five relatively sharp water bands, two stretching vibrations (asymmetric and symmetric), one deformation vibration and two librational modes. On the other hand, only broad deformation bands were observed in the spectra of ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with NaCl or  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with NaBr.

### Thermal analysis

DTA curves of ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with NaCl, KCl and CsCl and of ground mixtures of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with NaBr, KBr and CsBr are shown in Fig. 6. The thermal curves of ground mixtures of magnesium and sodium halides were similar to those of the pure magnesium halides, indicating that no new hydrated phases were obtained. On the other hand, the thermal curves of ground



**Fig. 5**  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{CsCl}$ . X-ray diffractograms of an equimolar mixture of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{CsCl}$ : Upper part, after grinding with 25 (a); 50 (b); 200 (c) and 300 (d) rounds of pestle; Lower part, without any grinding, after allowing the mixtures to be in contact for half an hour (e), 1 h (f), 2 h (g) and 3 h (h). A =  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , B =  $\text{CsCl}$ , C =  $\text{CsMgCl}_3 \cdot 6\text{H}_2\text{O}$

mixtures of magnesium and potassium or cesium halides differed from those of the pure magnesium halides, indicating that new hydrated phases were formed. TG curves showed that the DTA endothermic peaks were associated with mass-loss. Thermo-IR-spectrometry study showed that the mass loss below  $300^\circ\text{C}$  was due to loss of hydration water. Above this temperature, in ground mixtures of magnesium and potassium halides, the mass loss was due to hydrolysis of the hydrous complexes. In the ground mixtures of magnesium and cesium halides the mass loss was also due to sublimation of excess of the latter salt. At high temperature endothermic peaks of phase transition of the excess cesium halides were also observed. In the cooling curves exothermic peaks were observed for these phase transitions.



## Discussion

### *Carnallite type double salts*

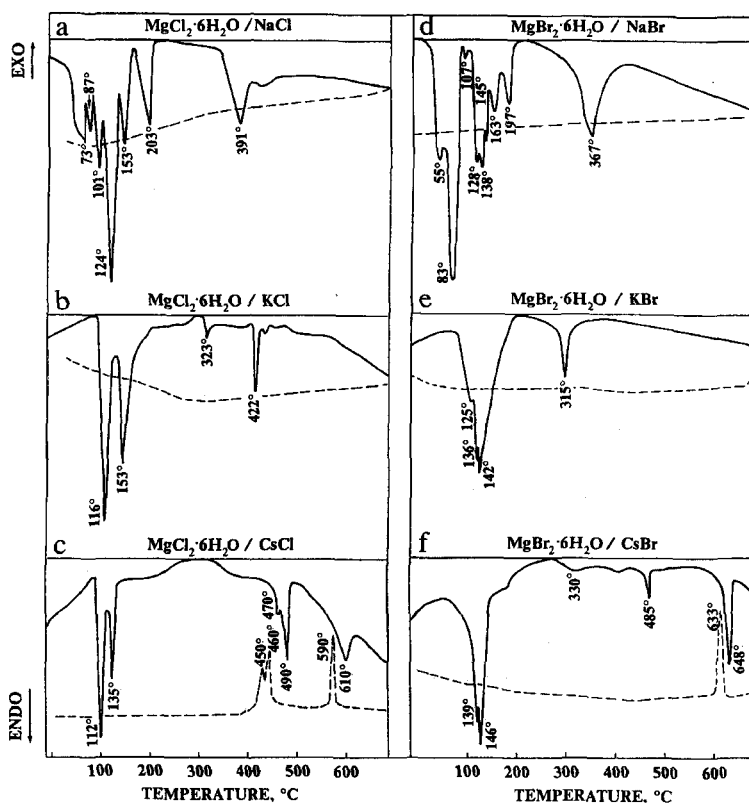
The new peaks which are observed in the diffractograms of the ground mixture of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl (Fig. 1) are similar to those of carnallite in the JCPDS data, indicating that this double salt was formed during the grinding of the mixture. The  $d$ -values of the new peaks in the diffractograms of the mixture of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with CsCl (Fig. 3) are similar to those of cesium carnallite, which were calculated from the lattice constants published by Waizumi *et al.* [13]. The  $d$ -values of the new peaks in the diffractograms of ground mixture of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr or CsBr (Figs. 2 and 4) are in good agreement with those of potassium- and cesium-bromo-carnallite, respectively, which were calculated from the lattice constants published by Emons *et al.* [14]. It may be concluded that carnallite ( $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) and bromo-carnallite ( $\text{KMgBr}_3 \cdot 6\text{H}_2\text{O}$ ) were formed by grinding mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr, respectively, whereas cesium-carnallite ( $\text{CsMgCl}_3 \cdot 6\text{H}_2\text{O}$ ) and cesium-bromo-carnallite ( $\text{CsMgBr}_3 \cdot 6\text{H}_2\text{O}$ ) were formed by grinding  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with CsCl and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with CsBr, respectively.

### *Hydrated solid solutions*

While the concentrations of magnesium halides in the mixtures were small, no hydrated double salts were identified by X-ray diffraction. In addition, magnesium halides were not detected in the ground mixtures. This is an indication that solid solutions of magnesium in the potassium or the cesium halides were formed. The formation of hydrated solid solutions in similar ground mixtures was previously proven by IR spectroscopy and thermal analysis [5–6].

Potassium and cesium halides that did not take part in the formation of the double salts in the ground mixtures, showed shifts in some of their  $d$ -values and changes in their relative intensities, compared to those of the original halides. Maximum changes were obtained in the equimolar ground mixtures (Table 1). Similar small changes have been previously shown to be due to the formation of hydrated solid solutions of sodium in cesium halides [2, 3].

Emons *et al.* [18] studied the thermal decomposition of carnallite below  $200^\circ\text{C}$  by DTA. In the first heating cycle, the DTA curve shows a single endothermic peak at  $167^\circ\text{C}$  which is due to incongruent melting. When this double salt was cooled and reheated, it showed an additional peak at  $116^\circ\text{C}$  which increased with the cycles of heating and cooling. They attributed the lower temperature peak to the crystallization of new phases, such as KCl and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . Based on this observation, we assume that the first two endothermic DTA peaks shown in our DTA curve of the ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl (Fig. 6) are due to the presence of both, hydrated solid solutions of magnesium in the potassium halides and carnallite double salt, respectively, obtained during the grinding.



**Fig. 6** DTA curves of ground mixtures (200 rounds of pestle) containing 10% of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with NaCl (a), KCl (b) and CsCl (c) and of ground mixtures containing 20% of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with NaBr (d), KBr (e) and CsBr (f)

**Table 2** The locations (in  $\text{cm}^{-1}$ ) of the water bands in the IR spectra of equimolar ground mixtures of potassium or cesium halides with magnesium halides (300 rounds of pestle) recorded in Nujol, in comparison with ground mixtures of potassium or cesium halides with 1% magnesium halide [6]

Assignment	Ground mixture							
	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} / \text{KCl}$		$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} / \text{CsCl}$		$\text{MgBr}_2 \cdot 6\text{H}_2\text{O} / \text{KBr}$		$\text{MgBr}_2 \cdot 6\text{H}_2\text{O} / \text{CsBr}$	
	equimolar	1%	equimolar	1%	equimolar	1%	equimolar	1%
Stretching as.	3400	3400	3397	3386	3400	3410	3403	3400
sym.	3236	3235	3256	3250	3234	3235	3236	3240
Bending	1634	1640	1638	1640	1634	1632	1632	1632
Librational-	618	630	620	625	610	604	605	608
modes	459	500	469	510	459	470	459	478

According to Emons [10] and Emons *et al.* [19] the other carnallite type double salts also show a single endothermic peak below 200°C. Therefore, it is assumed that the first two endothermic DTA peaks observed in the DTA curves of the ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with CsCl (Fig. 6) may also be ascribed to the presence of both, hydrated solid solutions of magnesium in the cesium halides and cesium-carnallite double salt, respectively. These two phases were also observed by X-ray diffraction.

The DTA curves of ground mixtures of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr and CsBr below 200°C show only one large peak accompanied by shoulders. It is assumed that the principal peak in these curves is due to the melting of the bromo-carnallite or the cesium-bromo-carnallite double salts, respectively. The shoulders can be attributed to the presence of hydrated solid solutions of magnesium in the potassium or cesium halides, respectively.

From the relative intensities of the first and second DTA peaks it seems that the portions of the hydrated solid solution in ground mixtures of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  with KCl or CsCl are greater than the portions of the hydrated solid solution in ground mixtures of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  with KBr or CsBr. This is in agreement with the X-ray diffraction data.

### *Coordinated water in the double salts and the solid solutions*

The appearance of five water bands in the spectra (Table 2) especially the librational modes is characteristic of 'coordination water' packed with a high degree of order [17]. In a previous publication we showed that in ground mixtures of potassium or cesium halides with 1% magnesium halide, similar water bands were characteristic of hydrated solid solutions [6]. It appears that five water bands are also characteristic for carnallite type double salts, but the locations of the librational modes are slightly different from those of the hydrated solid solutions. It should be noted that in the equimolar ground mixtures, both hydrated double salts and hydrated solid solutions are present and their bands may overlap (Table 2).

According to Waizumi *et al.* [13], carnallite is constructed from isolated  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  octahedra occupying the vacancies of the corner sharing  $[\text{KCl}_6]$  network. Hydrated double salts or hydrated solid solutions were not formed in ground mixtures of magnesium and sodium halides, as indicated by XRD and from the broad water bands in their spectra. This can be understood by the fact that the relatively small vacancies in a hypothetical corner sharing  $[\text{NaCl}_6]$  network are not large enough to accommodate  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  octahedra.

### *The mechanochemical process*

Increased amounts of double salts were obtained by increasing the number of rounds of the pestle (Fig. 5, upper part). This is an indication that the hydrated double salts were obtained mechanochemically. In a previous publication [4] we

showed that a hydrated solid solution was formed in ground mixtures of NaCl and CsCl by a mechanochemical process, in which planes of NaCl and water molecules, adsorbed from the atmosphere, combined with planes of CsCl due to sliding of their crystal planes under the effect of shearing, caused by the grinding process. Twenty four h of grinding by ball mill were required to complete the formation of the hydrated solid solutions, whereas for the formation of the double salt an additional aging period of 7 days after the grinding was needed [2, 3]. However, the carnallite type double salts were formed immediately after a short time of grinding, indicating a different mechanochemical process.

Although the salt mixtures containing the hydrated magnesium halides remained solid during the grinding in a closed system, it seems that microdrops of liquid water were released from the solid hydrated particles of the magnesium halides. Magnesium and potassium, or cesium halides, were dissolved in this water and, in fact, the microdrops were saturated solutions of these salts. The hydrated double salts precipitated from these concentrated solutions. Thus, the microdrops served as a medium for the dissolution of the original halides and the precipitation of the double salts. The pressure of the pestle on each halide particle or microdrop changed during the grinding, due to the non-homogeneous pressure applied during the grinding process. Therefore, the solubility products of the salts also changed. This is known as effect of 'pressure solutions' [20]. The involvement of liquid water may explain the high rate of this mechanochemical process.

Carnallite type double salts were also obtained by allowing mixtures of both magnesium and potassium or cesium halides to come in contact in the open air without any grinding (Fig. 5, lower part). In the latter system, the reaction proceeded in the hygroscopic water adsorbed from the atmosphere by the magnesium salts. Only small amounts of the double salts were formed under these conditions. It appears that the grinding process highly increases the amounts of the hydrated double salts and speeds up their formation.

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