

THE EFFECT OF ALKALI HALIDES ON THE THERMAL HYDROLYSIS OF MAGNESIUM CHLORIDE AND MAGNESIUM BROMIDE *

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ABSTRACT

DTA, TG and DTG curves were recorded for ground mixtures of hydrated MgCl_2 and MgBr_2 with NaCl , NaBr , KCl , KBr , CsCl and CsBr . Infrared spectra of the ground mixtures were recorded after they had been heated to several temperatures. Substitutional solid solutions of hydrated magnesium in potassium and cesium salts were formed during grinding of the salt mixtures. However, a solid solution of MgCl_2 is always obtained with KCl and CsCl , as a result of grinding the alkali chloride either with MgCl_2 or with MgBr_2 . Also, a solid solution of MgBr_2 is always obtained with KBr and CsBr , either from MgCl_2 or from MgBr_2 . Cesium halides form stable solid solutions with the magnesium halides, and thermal hydrolysis of the hydrated magnesium is prevented. The solid solutions formed with potassium halides are less stable than those formed with cesium salts and hydrated Mg is thermally hydrolyzed. The temperature at which this hydrolysis occurs in the presence of potassium halide is above 300°C , whereas in its absence this reaction occurs at temperatures below 250°C . No hydrated solid solution of Mg is formed with sodium halides during the grinding process and the thermal behavior of magnesium chloride or bromide in sodium chloride or bromide, respectively, is similar to the thermal behavior of the pure magnesium salt. The thermal behavior of MgBr_2 in NaCl is similar to that of pure MgCl_2 but the thermal behavior of MgCl_2 ground with NaBr shows some similarities with each of the two pure magnesium salts, the chloride and the bromide.

INTRODUCTION

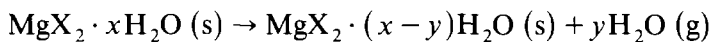
The thermal hydrolysis of hydrated magnesium salt is an important process which is applied in different industries. In a preliminary publication [1] we showed that the thermal hydrolysis of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ can be avoided by grinding this salt together with CsCl . The grinding of a mixture of these two salts gave rise to a mechanochemical reaction in which a solid solution

* Dedicated to Professor S. Seki on the occasion of his 70th anniversary.

of MgCl_2 and water molecules in CsCl were formed. A solid solution was also formed during the grinding of a mixture containing KCl and $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. However, the thermal stability of this solid solution was not as high as that of CsCl and thermal hydrolysis of MgCl_2 occurred to a small extent. This study was extended, and in the present publication we report the effects of various alkali chlorides and bromides on the thermal properties of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$. We also report on different solid solutions which are formed during the grinding of the two magnesium salts with some alkali halides.

The DTA and TG curves of hydrated magnesium halides (mainly chloride) have been widely investigated (see, e.g., refs. 2–8). The following reactions may occur during the course of the thermal analysis:

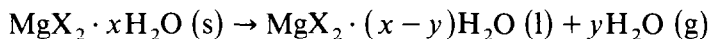
(1) *Dehydration*



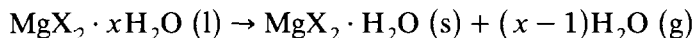
and



(2) *Melting of hydrate (accompanied by partial dehydration)*



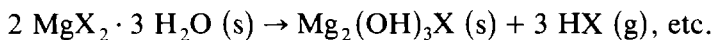
(3) *Boiling of the melt*



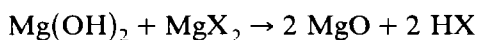
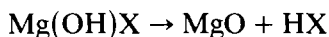
(4) *Thermal hydrolysis*



or



(5) *Dehydroxylation (by dehydrochloridization, dehydrobromidization or dehydration)*



Dehydration is usually represented in the DTA curves by endothermic peaks at temperatures below 200°C . Thermal hydrolysis and dehydroxylation are represented by endothermic peaks above 200 and 400°C , respectively. It should be noted that the reactions are not necessarily completed and that several reactions may occur simultaneously.

In the present investigation mixtures of magnesium and alkali halides were initially ground and then examined by DTA and TG. The same mixtures were examined by IR spectroscopy, after they had been thermally treated at various temperatures. The DTA (heating and cooling) curves, together with TG, were used to gain information on the occurrence of the various thermal reactions whereas IR analysis was used for identification of the reaction products.

EXPERIMENTAL

Materials

All the salts were of analytical grade. They were supplied by BDH and Merck. Cesium salts were of "Suprapur" grade.

Mixtures

For DTA runs, the mixtures contained 1.5 mg $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and 13.5 mg alkali halide, or 3.0 mg $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ and 12.0 mg alkali halide. Mixtures for the IR spectra contained either 1.5 or 15.0 mg magnesium salt and 135–150 mg alkali halide (1 or 10 wt.%, respectively). The mixtures were ground manually in an agate mortar. The pestle made 200 rounds before the mixtures were transferred to the DTA crucible or before they were pressed into disks for IR study.

DTA and TGA

Simultaneous TG, DTG and DTA measurements were carried out in a Stanton-Redcroft apparatus (STA 780). Alumina crucibles were used both for the specimen and the reference material, which was calcined alumina. The samples were heated from room temperature to 700°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. This should be taken into consideration when the present results are compared with previous results [1], in which the temperatures of the furnace body were quoted, which are higher than the temperatures of the sample.

Infrared spectra

Disks containing 1 and 10 wt.% magnesium salt in the different alkali halide matrices were used. The spectra were recorded on a Perkin-Elmer 597 spectrophotometer immediately after preparation of the disks and also after drying the disks at 105, 150, 190, 250, 300, 350, 400 and 450°C for 24 h.

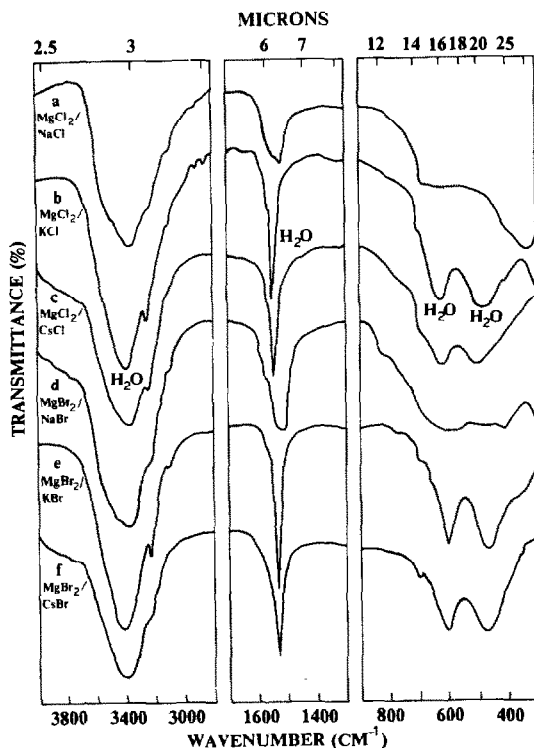


Fig. 1. IR spectra of 1% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ in NaCl (a), KCl (b) and CsCl (c) and of 1% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ in NaBr (d), KBr (e) and CsBr disks (f), after thermal treatment at 100°C .

Formation of solid solutions by grinding the salt mixtures

Infrared spectra of disks dried at 100°C

Figure 1 shows the IR spectra of 1% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ in NaCl, KCl and CsCl and of 1% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ in NaBr, KBr and CsBr matrices, after heating the disks at 100°C . The figure shows that the water absorption bands recorded in both Na salt matrices (NaCl and NaBr) are broad. On the other hand, in the spectra recorded with both K and Cs salt matrices, five relatively sharp water absorptions (four distinct bands and one shoulder) can be identified. The presence of five bands is characteristic for "coordination water" packed with a high degree of order [9]. In our previous study on the IR spectrum of Na salts in CsCl disks [10] we showed that the spectra of hygroscopic salts consisted of broad, overlapping H_2O bands whereas spectra of substitutional hydrated solid solutions consisted of five relatively distinct H_2O bands. These five bands can be identified in the spectra recorded in the K and Cs salt matrices (Table 1). It may therefore be concluded that MgCl_2 forms substitutional hydrated solid solutions in KCl and CsCl, but not in NaCl. Similarly, MgBr_2 forms substitutional hydrated solid solutions in KBr and CsBr, but not in NaBr.

TABLE 1

Characteristic absorption maxima (in cm^{-1}) of HOH bands in the infrared spectra of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ recorded in KCl, KBr, CsCl and CsBr disks

Assignment	KCl disk		KBr disk		CsCl disk		CsBr disk	
	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	$\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$
Stretching (as) (sym)	3400 br	3395 br	3410 br	3410 br	3386 br	3380 br	3400 br	3400
	3235 sh	3235 sh	3235 sh	3235 sh	3250 sh	3250 sh	3240 sh	3240 sh
Bending	1640	1638	1633	1632	1640	1640	1632	1632
Librational modes	630	630	605	604	625	625	605	608
	500 br	490 br	470 br	470 br	510	510	478	478

The IR spectra of MgCl_2 recorded in the bromide matrices (NaBr, KBr and CsBr) are very similar to those of MgBr_2 , in the same matrices. On the other hand, the spectra of MgBr_2 recorded in the chloride matrices (NaCl, KCl and CsCl) are very similar to those of MgCl_2 in the same matrices. The H_2O bands are broad in the spectra of the Na salt matrices, but distinct and relatively sharp in the other spectra. Their shapes may serve as a proof for the formation of substitutional solid solutions of hydrated Mg in the K and Cs matrices. Identification of the solid solution can be done from the locations of the five H_2O absorption bands. From Table 1 it is obvious that grinding either MgCl_2 or MgBr_2 hydrates in KCl or CsCl results in a substitutional solid solution of hydrated MgCl_2 in the alkali chloride, whereas grinding any of the magnesium salts in KBr or CsBr results in a solid solution of hydrated MgBr_2 in the alkali bromide.

Thermal reactions of the salts mixtures

Mg salts in NaCl or NaBr

The DTA, TG and DTG of both Mg salts ground with NaCl and NaBr, are shown in Figs. 2 and 3, respectively. The location of the DTA peaks and the principal thermal reactions, which are associated with these peaks, are given in Table 2. The assignment of the peaks is based on our previous study

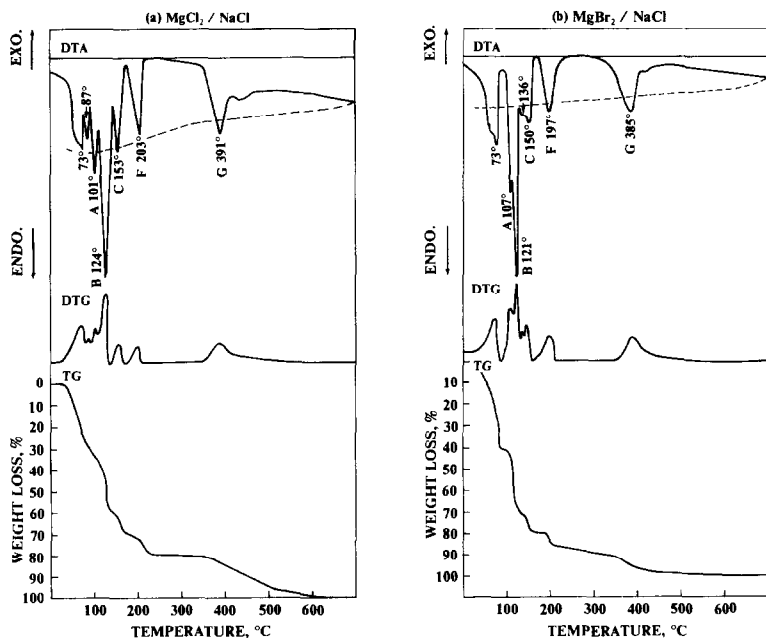


Fig. 2. DTA, DTG and TG of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b) ground with NaCl. Heating curves (—) and cooling curves (---).

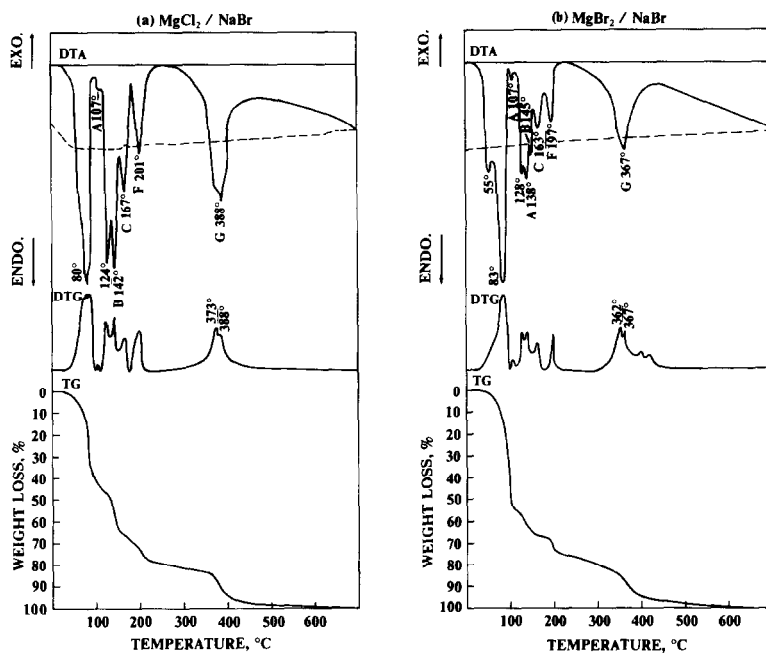


Fig. 3. DTA, DTG and TG of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b) ground with NaBr. Heating curves (—) and cooling curves (---).

of the kinetic analysis of thermal dehydration and hydrolysis of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ [8] and on similar work with $\text{MgBr} \cdot 6 \text{H}_2\text{O}$ which is now in preparation. For comparison, the temperatures of DTA peaks of non-dried $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ are also included in the table.

The endothermic peaks below 90 and 130°C in the DTA curves of NaCl and NaBr mixtures, respectively, are associated with weight losses of 30–40 and 45–55% from the total weight loss. Infrared spectra showed that the thermally treated mixtures lost free water. These peaks do not appear in the DTA curves of the pure magnesium halides. They are therefore assumed to be characteristic for the dehydration of sodium halides contaminated with magnesium halides. It should be noted that sodium halides become very hygroscopic on contamination with magnesium salts.

The DTA and DTG curves of the $\text{MgCl}_2/\text{NaCl}$ mixture at temperatures above 95°C, are very similar to those of the pure, non-dried $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ [8]. Peak E (Table 2 and Fig. 2a), which represents dehydration of the tetrahydrate magnesium salt, in the DTA curve of the pure salt, does not appear in the curve of the mixture. In a previous study we suggested that when non-dried $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ is thermally treated, the dihydrate is the principal dehydration product of the molten hexahydrate and is obtained during the appearance of peak C. Only small amounts of the tetrahydrate were obtained at this stage in the non-dried samples. The conversion of the

TABLE 2

Characteristic maxima (in °C) of endothermic peaks in DTA heating curves of pure $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ and of mixtures of both salts ground with NaCl and NaBr (10 and 20 wt.%, respectively)

Peak assignment	Principal thermal reaction	Pure $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	Pure $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$	MgCl ₂ in NaCl	MgBr ₂ in NaCl	MgCl ₂ in NaBr	MgBr ₂ in NaBr
	Drying of sodium halide			73, 87	73	80, 124 ^a	55, 83, 128
A	Drying and dehydration of magnesium halide	101	107, 140, 145	101	107	107	107, 138
B	Incongruent melting of $\text{Mg}(\text{H}_2\text{O})_6\text{X}_2$ and partial dehydration ^b	115	146	124	121	124 ^a , 142	145
C	Boiling of the melt	154	159	153	150	167	163
E	Boiling of $\text{Mg}(\text{H}_2\text{O})_4\text{X}_2$	184	185–190	ND	ND	ND	ND
F	Thermal hydrolysis	240	220, 232	203	197	201	197
G	Dehydrochloridization or dehydrobromidization	440–480	397	391	385	388	367

ND, not detected.

^a The peak is partly due to the drying of NaBr and partly to the melting of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2$, peak B.

^b Melting points of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ and $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ in the literature are 116–117 and 153–172°C, respectively.

tetrahydrate into the dihydrate was accompanied by the appearance of peak E. Since this peak is not observed in the DTA curve of the $\text{MgCl}_2/\text{NaCl}$ mixture, it may be assumed that during the thermal dehydration of the present mixture, the dihydrate is formed directly from the hexahydrate.

Peaks F and G are located at lower temperatures in the DTA curves of the $\text{MgCl}_2/\text{NaCl}$ mixture compared to their location in the DTA curve of the pure, non-dried $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. They are associated with weight losses of 12 and 20% of the total weight loss and represent thermal hydrolysis and dehydroxylation by dehydrochloridization, respectively. Since Cl^- is involved in these thermal reactions, the presence of excess NaCl is responsible for the shift of the peaks to lower temperatures.

The thermal analysis curves of the $\text{MgBr}_2/\text{NaCl}$ mixture are very similar to those of the $\text{MgCl}_2/\text{NaCl}$ mixture but not to those of the $\text{MgBr}_2/\text{NaBr}$ mixtures. It is therefore assumed that during grinding most of the MgBr_2 was converted into MgCl_2 .

Comparison between the DTA and DTG curves of $\text{MgBr}_2/\text{NaBr}$ mixtures at temperatures above 130°C and those of pure, non-dried $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ shows that they are similar. As with the chloride mixture, the tetrahydrate is not formed during thermal treatment and the hexahydrate is probably dehydrated directly to the dihydrate, and peak E does not appear in the curve. The thermal hydrolysis and the dehydrobromidization (weight loss of 14 and 19% from total weight loss) are shifted to lower temperatures due to the presence of excess Br^- .

The thermal analysis curves of $\text{MgCl}_2/\text{NaBr}$ mixtures have some features from the $\text{MgCl}_2/\text{NaCl}$ mixture and some from the $\text{MgBr}_2/\text{NaBr}$ mixture. The locations of peaks B and C are similar to those in the DTA curve of $\text{MgBr}_2/\text{NaBr}$. Peak G, on the other hand, is located at the same temperature as in the DTA curve of the $\text{MgCl}_2/\text{NaCl}$ mixture. Furthermore, the intensities of the peaks at 124 and 142°C are relatively very high, similar to the intensity of peak B in the DTA curve of the $\text{MgCl}_2/\text{NaCl}$ mixture. It is therefore assumed that the grinding of MgCl_2 in NaBr results only in partial substitution of Cl^- by Br^- in the $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ crystal.

Infrared spectra of 10% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ ground with NaCl and NaBr and of 10% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ ground with NaBr, after thermal treatment of the disks at various temperatures, are shown in Figs. 4 and 5. The IR spectra show that the principal thermal reaction below 200°C is the dehydration of the system, namely, the water absorption bands at $400\text{--}700$, 1620 and $3300\text{--}3500 \text{ cm}^{-1}$ become weaker.

The spectra of MgBr_2 ground with NaCl, after the various thermal treatments, are very similar to those obtained for MgCl_2 ground with the same salt [1]. An OH band at 3560 cm^{-1} , first observed after the thermal treatment of the disk at 250°C , persisted up to 400°C . At 450°C this band disappeared. A weak OH band appeared at 3625 cm^{-1} after thermal treatment at 450°C . It should be noted that the latter band was already

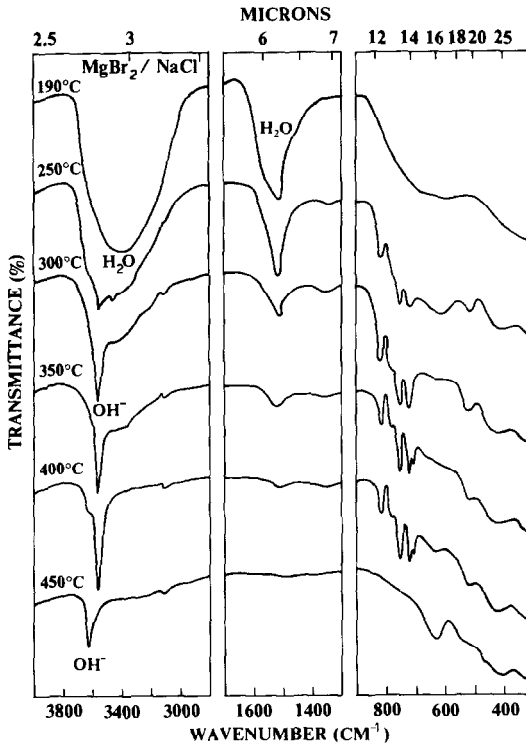


Fig. 4. IR spectra of 10% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ ground with NaCl and thermally treated as a disk at 190, 250, 300, 350, 400 and 450°C.

detected as a shoulder after heating the disk at 400°C. This band was also detected in the spectrum of a $\text{MgCl}_2/\text{NaCl}$ disk heated to 450°C; however, the intensity of the band was much weaker. Figure 4 also shows that at 400°C an Mg–O absorption appears at 410 cm^{-1} , which is characteristic of magnesium oxide. This is a proof of the occurrence of dehydroxylation at this stage of thermal treatment. The same phenomenon was observed with the $\text{MgCl}_2/\text{NaCl}$ mixture at this temperature.

The spectra of MgCl_2 ground with NaBr, recorded after the various thermal treatments, differ to some extent from those obtained for MgBr_2 ground with NaBr. After heating the disk at 250°C, the latter shows sharp OH bands absorbing at 3530 and 3590 cm^{-1} , whereas MgCl_2 in NaBr shows three absorptions at 3530 (weak), 3560 and 3615 cm^{-1} . After heating the disks at 450°C, both mixtures show the presence of MgO (absorbing at 410 cm^{-1} , not shown in the figure), indicating that a dehydroxylation process has occurred. The spectrum of $\text{MgBr}_2/\text{NaBr}$ shows that at this stage of the thermal treatment dehydroxylation was complete, as all the OH absorption bands disappeared. On the other hand, the spectrum of $\text{MgCl}_2/\text{NaBr}$ shows that at 450°C only two of the OH bands disappeared.

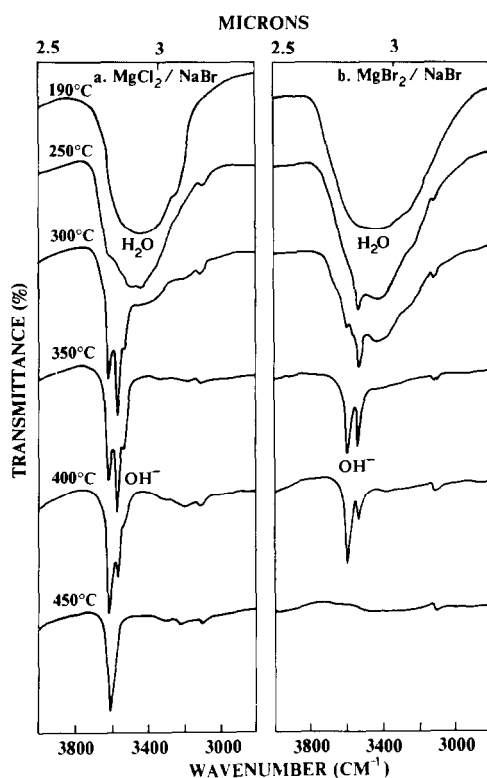


Fig. 5. IR spectra of 10% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of 10% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b), both salts in NaBr, thermally treated as disks at 190, 250, 300, 350, 400 and 450°C.

Only the 3615 cm^{-1} band persisted at this temperature, indicating that some of the hydroxyls are of a higher thermal stability than the bulk hydroxyls. Thus this mixture resembles the mixtures of both magnesium salts with NaCl. From the IR data it may be concluded that the thermal properties of the mixture $\text{MgBr}_2/\text{NaCl}$ are similar to those of the mixture $\text{MgCl}_2/\text{NaCl}$, but those of the mixture $\text{MgCl}_2/\text{NaBr}$ differ from those of the mixture $\text{MgBr}_2/\text{NaBr}$.

Mg salt in KCl or KBr

The DTA, TG and DTG of both Mg salts ground with KCl and KBr are shown in Figs. 6 and 7, respectively. They differ greatly from those of pure Mg salts, or from the Mg/Na salt mixtures. Instead of the four peaks which appear in the DTA curves of Mg/Na salt mixtures in the temperature range 100–200°C, there are only two peaks for the Mg/K salt mixtures. The IR spectra of the thermally treated disks show that the two endothermic peaks and weight loss below 250°C should be attributed to dehydration of the solid solution (the intensities of the peaks which are mentioned in Table 1 decrease with increasing temperature). The most significant difference be-

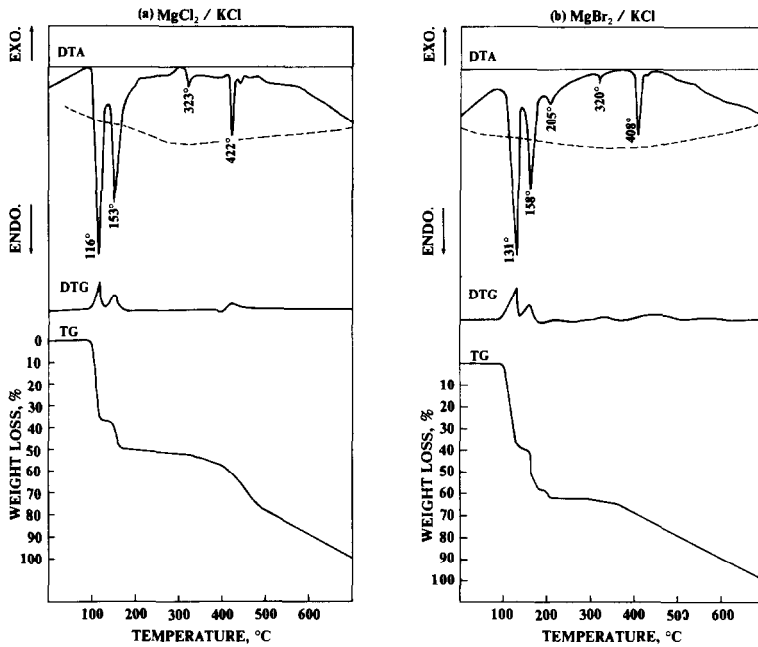


Fig. 6. DTA, DTG and TG of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b) ground with KCl. Heating curves (—) and cooling curves (---).

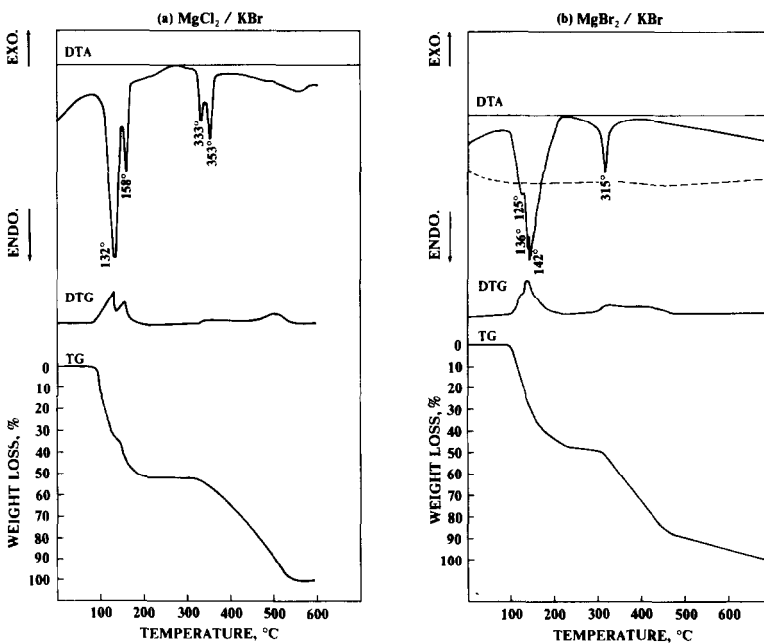


Fig. 7. DTA, DTG and TG of $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b) ground with KBr. Heating curves (—) and cooling curves (---).

tween the curves of Mg/K and Mg/Na salt mixtures is the location of the thermal hydrolysis endothermic DTA peak. It is located at about 197–203°C in the DTA curves of Mg/Na salt mixtures, and shifts to 315–333°C in those of Mg/K salt mixtures. Delay of thermal hydrolysis to temperatures above 300°C is also demonstrated by the weight loss curves. The slopes of the TG curves show that at this stage weight loss is smaller in the KCl mixtures compared to the KBr mixtures, indicating a higher thermal hydrolysis in the KBr matrix compared to the KCl matrix.

The last stage of thermal decomposition of the solid solutions is dehydroxylation. This is demonstrated in the IR spectra of the thermally treated disks by disappearance of the OH bands and appearance of an Mg–O band at 410 cm^{-1} , characteristic of magnesium oxide. In both KCl mixtures (MgCl_2/KCl and MgBr_2/KCl) this stage is represented in the DTA curves by an endothermic peak at 408–422°C. In the DTA curve of the MgBr_2/KBr mixture there is no endothermic peak which could be attributed to this reaction. However, from TG and DTG curves it is obvious that the weight loss, which started with the 315°C endothermic peak, continued up to 465°C. The dehydroxylation process may take place either by the mechanism of thermal escape of H_2O molecules (dehydration), or by the mechanism of thermal escape of HBr (dehydrobromidization). Since this stage is associated with a very large weight loss (35% of total) it seems reasonable to assume that the latter is the principal mechanism responsible for dehydroxylation. In MgCl_2/KBr the dehydroxylation reaction started slightly later (353°C), but extended up to 530°C (see TG and DTG curves in Fig. 7). The shift of the dehydroxylation peak to higher temperatures with increasing Cl content in the Mg/K salt mixtures (or decreasing Br content) is demonstrated by the shift of this peak from 408 to 422°C in the DTA curves of MgBr_2/KCl and MgCl_2/KCl mixtures, respectively. The weight loss in the TG curves which occurred at temperatures above 470°C might be due to slight sublimation of the alkali halide.

OH absorptions in the IR spectra of the Mg salts ground with KCl and KBr, after thermal treatment of the disks at various temperatures, are shown in Figs. 8 and 9, respectively. The spectra of MgBr_2 ground with KCl, after the various thermal treatments, are very similar to those obtained for MgCl_2 ground with the same salt. Two OH bands at 3560 and 3615 cm^{-1} are clearly observed in spectra recorded after heating the disks at 300 and 350°C. Although the molar concentration of MgBr_2 is smaller than that of MgCl_2 in the disks, the OH bands at 300°C are more intense in MgBr_2/KCl than in MgCl_2/KCl , indicating a higher degree of thermal hydrolysis in the first mixture. The OH bands disappear after 400 and 450°C treatments of the MgBr_2/KCl and MgCl_2/KCl disks, respectively. These observations indicate that bromide promotes both reactions, hydrolysis and dehydroxylation.

MgO formed at this stage of the thermal treatment, as the dehydrox-

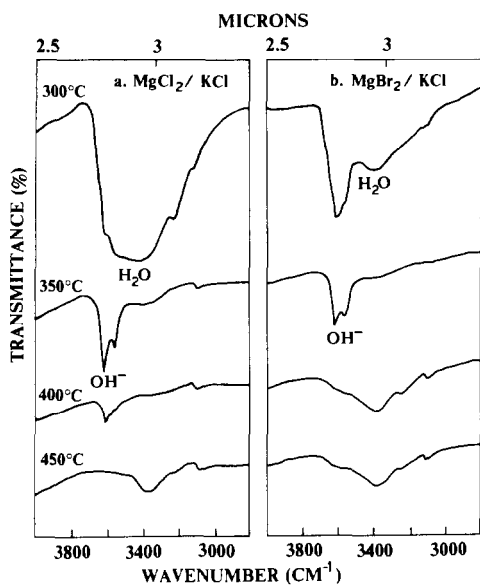


Fig. 8. IR spectra of 10% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of 10% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b), both salts in KCl, thermally treated as disks at 300, 350, 400 and 450°C.

ylation product, absorbs IR radiation at 410 cm^{-1} (not shown in the figures). It seems that in the MgBr_2/KCl system this oxide is of a poor degree of crystallinity, being rich with surface OH groups (absorbing at $3500\text{--}3600 \text{ cm}^{-1}$). Disks with a high surface-active MgO content adsorb water during the IR run, absorbing at 3390 (Fig. 8) and 1630 cm^{-1} (not shown in the figure).

The spectra of MgCl_2 ground with KBr, recorded after the various thermal treatments, differ from those of MgBr_2/KBr . After thermal treatment of MgCl_2/KBr mixtures at 300, 350 and 400°C, the IR spectra show the presence of a sharp OH absorption band at 3555 cm^{-1} . At 450°C this band disappears. Instead, broad absorptions at 3380 and $3520\text{--}3590 \text{ cm}^{-1}$ are observed, which are characteristic of adsorbed H_2O and surface OH groups (Fig. 9). At the same time absorption bands at 1630 (H_2O) and 410 cm^{-1} (MgO) also appear (not shown in the figure). These observations indicate that at this stage the MgO obtained has a poor degree of crystallinity.

The spectra of MgBr_2/KBr , after thermal treatment at 300 and 350°C, show two OH absorption bands. According to the IR spectra it is obvious that two types of OH groups are formed during thermal hydrolysis. The first, absorbing at 3506 cm^{-1} , is observed at lower temperatures (already detected at 250°C), whereas the second, absorbing at 3590 cm^{-1} , predominates at 350°C. Both bands disappear at 400°C. The IR spectra which are obtained after thermal treatment at 400 and 450°C are those of MgO,

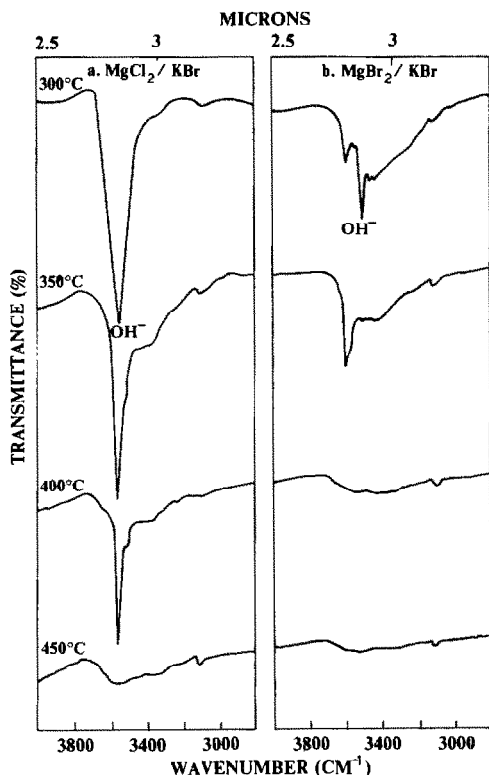


Fig. 9. IR spectra of 10% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a) and of 10% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b), both salts in KBr, thermally treated as disks at 300, 350, 400 and 450°C.

absorbing at 410 cm^{-1} . It may be concluded that the thermal properties of the MgBr_2/KCl mixture are similar to those of the MgCl_2/KCl mixture but those of the MgCl_2/KBr mixture differ from those of MgBr_2/KBr .

Mg salts in CsCl or CsBr

The DTA, TG and DTG of both Mg salts ground with CsCl and CsBr are shown in Figs. 10 and 11, respectively. They differ greatly from those of pure Mg salts, or from the Mg/Na salt mixtures. Only two peaks are observed in the dehydration region (below 200°C). According to IR spectra they represent dehydration of solid solutions of the magnesium halide in the cesium halide (intensities of peaks mentioned in Table 1 decrease with increasing temperature). No endothermic peak is observed in the temperature range $200\text{--}460^\circ\text{C}$. This is an indication of the absence of thermal hydrolysis of hydrated MgCl_2 or MgBr_2 at this temperature.

Both Mg salts in the CsCl matrix give similar DTA and TG curves. The dehydration is represented for both mixtures by peaks at $112\text{--}114$ and $135\text{--}138^\circ\text{C}$. Endothermic peaks at 470 , 490 and 610°C in the DTA curve of the $\text{MgCl}_2/\text{CsCl}$ mixture are not associated with peaks in the DTG curves

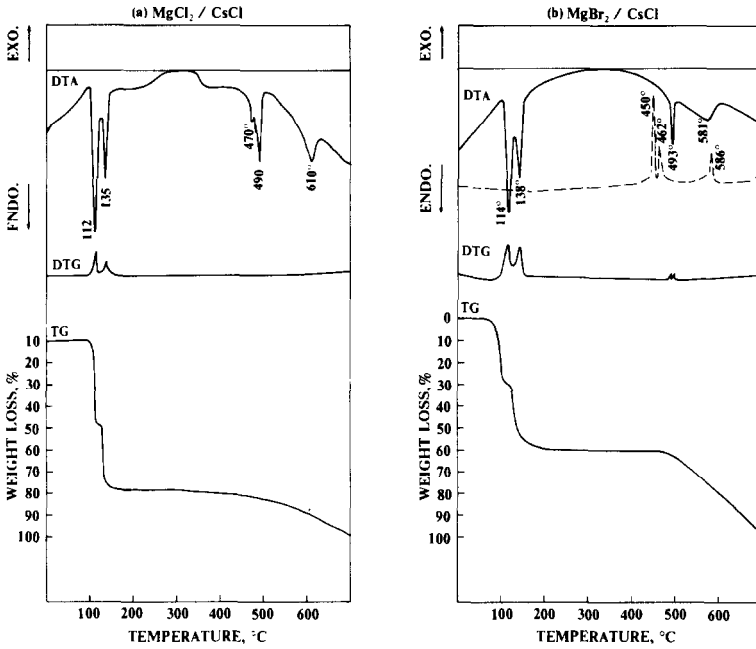


Fig. 10. DTA, DTG and TG of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (a) and of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ (b) ground with CsCl .

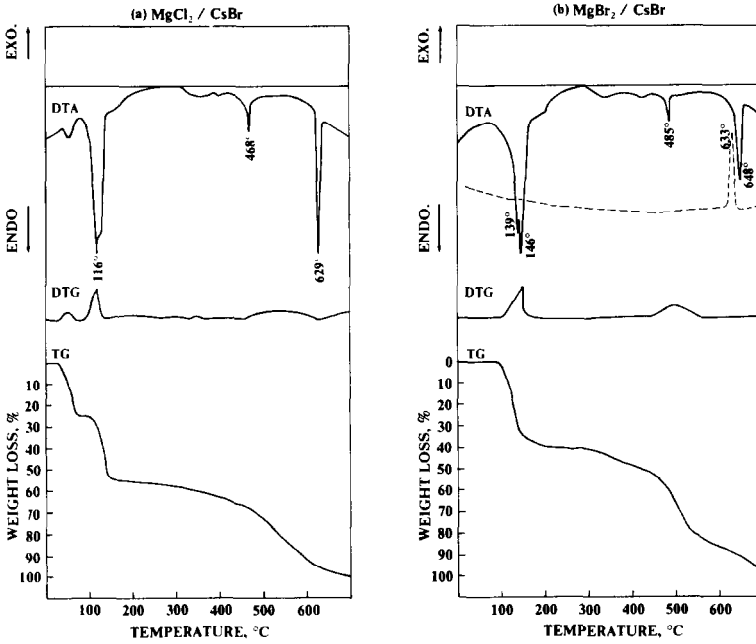


Fig. 11. DTA, DTG and TG of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (a) and of $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ (b) ground with CsBr .

and are assumed to be phase transitions rather than dehydroxylation. The reversible phase transitions are shown in the DTA cooling curves. They probably represent: (1) the solid state phase transition of excess CsCl; (2) the solid state phase transition of $\text{MgCl}_2/\text{CsCl}$ solid solution; and (3) melting of the system.

Only one peak (at 493°C) is observed in the heating curve of the $\text{MgBr}_2/\text{CsCl}$ mixture, in contrast to the two peaks which are observed in the DTA heating curve of the $\text{MgCl}_2/\text{CsCl}$ mixture. However, in the cooling curve two peaks are clearly detected. We therefore believe that in this case the solid phase transition of CsCl overlaps with the solid phase transition of the solid solution. The peak at 581°C may be attributed to the melting of the system.

The IR spectra of both Mg salts recorded after thermal treatment and the mixtures at various temperatures up to 450°C neither showed the presence of OH nor MgO. These observations confirm our interpretation of the DTA curve. It may be concluded that both Mg salts form stable solid solutions in CsCl, and thus thermal hydrolysis and dehydroxylation do not occur. Weight losses at temperatures above 470°C in the TG curves of $\text{MgCl}_2/\text{CsCl}$ and $\text{MgBr}_2/\text{CsCl}$ are mainly due to the sublimation of the Cs salt. In the first case only CsCl sublimates. In the latter CsBr may sublime as well.

There is a difference between the DTA curve of the $\text{MgCl}_2/\text{CsBr}$ and $\text{MgBr}_2/\text{CsBr}$ mixtures in the dehydration range (Fig. 11). The first shows

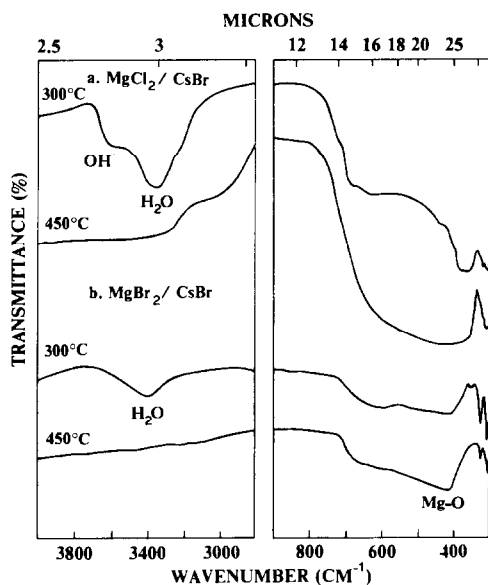


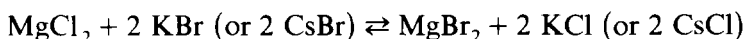
Fig. 12. IR spectra of 10% $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (a), and of 10% $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$ (b), both salts in CsBr, thermally treated as disks at 300°C and at 450°C .

one broad peak at 116°C and a shoulder at 127°C whereas the latter shows two sharp peaks at 139 and 146°C. The first also shows dehydration of "free" water at temperatures below 100°C. Other regions of both curves are very similar. The endothermic peaks at 468 and 485°C in the heating curves of MgCl₂/CsBr and MgBr₂/CsBr mixtures, respectively, are associated with thermal weight loss (27% of total), and do not appear in the DTA cooling curves. It should be mentioned that although the intensities of the water bands in the IR spectra decrease with increasing temperature, they persist at temperatures as high as 400°C. It seems that at 485°C the trace amount of water, which is still present in the system, reacts with Br⁻ to form HBr. This is supported by the appearance of MgO absorptions in the IR spectrum of both mixtures treated at 450°C (Fig. 12). This band is very weak in the spectrum of MgBr₂/CsBr but is strong in that of MgCl₂/CsBr. At 300°C the latter shows the presence of surface OH, giving a shoulder at 3580 cm⁻¹. This absorption disappeared at 350°C.

The weight loss above 525°C is due to sublimation of CsBr. The endothermic peak at 629–648°C describes a reversible phase transition and is attributed to the melting of the mixture. The reverse reaction which occurs during the cooling of the system appears as an exothermic peak in the cooling curve.

CONCLUSIONS

It seems from the present study that substitutional solid solutions of hydrated Mg²⁺ in KCl, KBr, CsCl and CsBr are formed during the grinding of MgCl₂ or MgBr₂ with the alkali halide. The existence of hydrated double salts of magnesium and alkali halides is well known. It seems probable that the double-salt structure is obtained in the present study during the grinding process, namely by a mechanochemical process. Under the present conditions (10 and 20 wt.% of MgCl₂ · 6 H₂O and MgBr₂ · 6 H₂O, respectively) a solid solution of magnesium chloride is always obtained with KCl and CsCl, as a result of grinding the alkali chloride either with MgCl₂ or with MgBr₂. Also, a solid solution of magnesium bromide is always obtained with KBr and CsBr, either with MgCl₂ or MgBr₂. This important observation indicates that if MgCl₂ is ground with any of the alkali bromides, or if MgBr₂ is ground with any of the alkali chlorides, the first stage of the mechanochemical process is the double decomposition between the alkali halide salt and the magnesium salt. The double decomposition reaction can be formulated as follows:



In the presence of alkali bromide the reaction will proceed from left to right. On the other hand, in the presence of excess of alkali chloride the

reaction will proceed from right to left. The thermal analysis of $\text{MgBr}_2/\text{NaCl}$ and of $\text{MgCl}_2/\text{NaBr}$ showed that grinding these mixtures also resulted in double decomposition. However, MgBr_2 undergoes this reaction to a higher extent than MgCl_2 .

The second stage of the mechanochemical process is the formation of the substituted solid solution. In a previous publication on the formation of a solid solution of Na halides in Cs halides we showed that the step in which the hydrated phase is formed is not an ion-exchange process, but must be a solid state dissolution of NaX in CsX crystals (where $\text{X} = \text{Cl}, \text{Br}$ or I), associated with the sliding of crystal planes under the effect of shearing, which is caused by the grinding [10]. A similar mechanochemical process seems to be responsible for the formation of the solid solution of the Mg salt. This is now under further investigation.

The formation of the solid solution may change the thermal properties of the hydrated magnesium salt. CsCl forms a stable solid solution of hydrated MgCl_2 which prevents thermal hydrolysis and dehydrochloridization of the hydrated magnesium salt. CsBr also forms a solid solution of hydrated MgBr_2 which prevents the thermal hydrolysis of hydrated magnesium, but allows some dehydrobromidization of the complex. Solid solutions of MgCl_2 in KCl , or MgBr_2 in KBr , only partly prevent the thermal hydrolysis. No endothermic peaks of hydrolysis were observed in DTA curves of these samples in the temperature range $200\text{--}300^\circ\text{C}$ but appeared at $315\text{--}333^\circ\text{C}$ and the intensities of the OH bands recorded in the IR spectra were relatively weak. Dehydrobromidization seems to be more effective than dehydrochloridization, as concluded from the intensities of the MgO absorptions in the IR spectra. The first always occurs at a lower temperature. No stable solid solutions are formed in NaCl or NaBr and the thermal properties of $\text{MgCl}_2/\text{NaCl}$ or $\text{MgBr}_2/\text{NaBr}$ mixtures are similar to those of pure $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ or $\text{MgBr}_2 \cdot 6 \text{H}_2\text{O}$, respectively.

The thermal properties of solid solutions of MgCl_2 in KCl and in CsCl are not dependent on whether they were prepared by grinding MgCl_2 or MgBr_2 with the excess alkali chloride. Very small shifts in the locations of the DTA peaks are observed due to isomorphous substitutions of Cl by Br in the solid solution. On the other hand, the thermal properties of solid solutions of MgBr_2 in KBr and in CsBr depend very much on whether they were prepared from MgCl_2 or MgBr_2 and the alkali bromide. This is in spite of the fact that the IR analysis of the ground mixtures reveals the formation of substitutional hydrated solid solutions of MgBr_2 in both cases. The discrepancy between the thermal and the spectroscopic methods may be explained if one assumes that the solid solution was formed only in part. In the case of MgBr_2 in alkali chlorides, the double decomposition and solid solution formation were almost completed. In the case of MgCl_2 in alkali bromides, additional reaction products are obtained during grinding which are not detectable in the IR analysis. These products affect the thermal

properties of the system. It is possible that this incomplete reaction with alkali bromides results in a solid solution with a high degree of isomorphous substitution of Br by Cl. In any case the present results show that in the mechanochemical system the affinity to form substitutional solid solutions of hydrated MgCl_2 in KCl or CsCl is higher than the affinity to form substitutional solid solutions of hydrated MgBr_2 in KBr or CsBr. They also show that MgCl_2 is less active in a double-decomposition mechanochemical reaction with alkali bromides compared to MgBr_2 with alkali chlorides.

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