JOURNAL OF SOLID STATE CHEMISTRY 117, 34–38 (1995)

Nonceramic Preparation Techniques for Ternary Halides AB_2X_4 with A = Mg, Mn, Zn; B = Li, Na; X = Cl, Br[1]

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Received June 6, 1994; in revised form November 7, 1994; accepted November 10, 1994

Two alternative techniques for synthesizing ternary halides AB_2X_4 were studied and compared to the classical "ceramic" method. Tribochemical reaction of LiCl with $ZnCl_2$ has been proved to be an easy method for synthesizing the stable spinel-type room-temperature modification of Li_2ZnCl_4 as well as olivine-type Na_2ZnCl_4 and Na_2ZnBr_4. Reaction times and activation energies decrease in the order $Li_2ZnCl_4 > Na_2ZnCl_4 > Na_2ZnBr_4$. On the other hand, $MgCl_2$ and $MnCl_2$ do not react mechanochemically with LiCl and NaCl at all. In addition, it is possible to synthesize ternary halides as Li_2MnCl_4 and Li_2ZnCl_4 by dehydration of appropriate hydrates. The modification of Li_2ZnCl_4 obtained by this method depends on the dehydration conditions.

INTRODUCTION

The most common and successful preparation technique in solid state chemistry is undoubtedly the ceramic method, i.e., annealing the starting materials in evacuated, sealed ampoules at elevated temperatures, in order to get sufficiently high diffusion rates at which reaction can take place. However, in certain cases, the high temperatures employed in the ceramic method may be disadvantageous, especially when phase transition from a high-temperature polymorph to a room-temperature one proceeds only slowly. Such a case is Li_2ZnCl_4, which normally can only be obtained in the metastable olivine-type modification (1). The aim of our investigations was to synthesize ternary halides AB_2X_4 (A = Mg, Mn, Zn; B = Li, Na; X = Cl, Br) using alternative preparation methods, for example, the nonthermal tribochemistry or the dehydration of appropriate hydrates, in order to establish whether novel, stable, or metastable polymorphs are formed.

EXPERIMENTAL

The starting materials were LiCl, NaCl, NaBr, $ZnCl_2$, $ZnBr_2$ (all Fluka 4N), $MgCl_2 \cdot 6H_2O$ (Janssen, 4N), and $MnCl_2 \cdot 4H_2O$ (Reidel de Haen, p.A.). They were all dried or dehydrated at 400°C in an HX (X = Cl, Br) stream and handled in an argon glove box to exclude the presence of atmospheric moisture.

For tribochemical investigations, three experimental series were carried out using a Retsch S2 planetary mill as triboreactor. In the first series, stoichiometric amounts of the binary halides with catalytic amounts of water (20 μl) were employed. In the second, thoroughly dried reactans were used without adding water. In the third, binary $MgCl_2$, $MnCl_2$, and $ZnBr_2$ were ground separately in order to study the formation of structural defects depending on the milling time.

For the dehydration experiments, two hydrates $Li_2ZnCl_2 \cdot 2H_2O$ and $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$ were synthesized from aqueous solution as described by Jacobi and Brehler (2) and Benrath (3). Both starting materials and the reaction products were characterized by X ray diffraction, analytical methods (ion–coupled plasma), and infrared spectroscopy, respectively.

Subsequently, the dehydration process and the formation of anhydrous ternary halides were studied by thermoanalytic methods, high-temperature X ray diffraction, and Raman spectroscopy.

Thermoanalytic measurements were performed on a Mettler-Toledo TG 5 and on a Perkin–Elmer DSC 7 with heating rates of 5 and 10°C/min, respectively.

For the X ray and high-temperature X ray diffraction studies, Guinier powder technique, e.g., an Enraf-Nonius Guinier-Simon FR 553 camera, was used. Raman spectra were performed with a Dilor Omars 89 multichannel spectrograph using an Ar^+-laser with 514.5 nm radiation for excitation; infrared reflection spectra were recorded with a Bruker IFS 113v Fourier transform interferometer using pressed pellets.

RESULTS AND DISCUSSION

Tribochemical Preparations

In the system LiCl–$ZnCl_2$, complete reaction is yielded after milling 84 hr at 100°C. Complete formation of olivine-

[1] This work is dedicated to Professor Heinrich Oppermann on the occasion of his 60th birthday.

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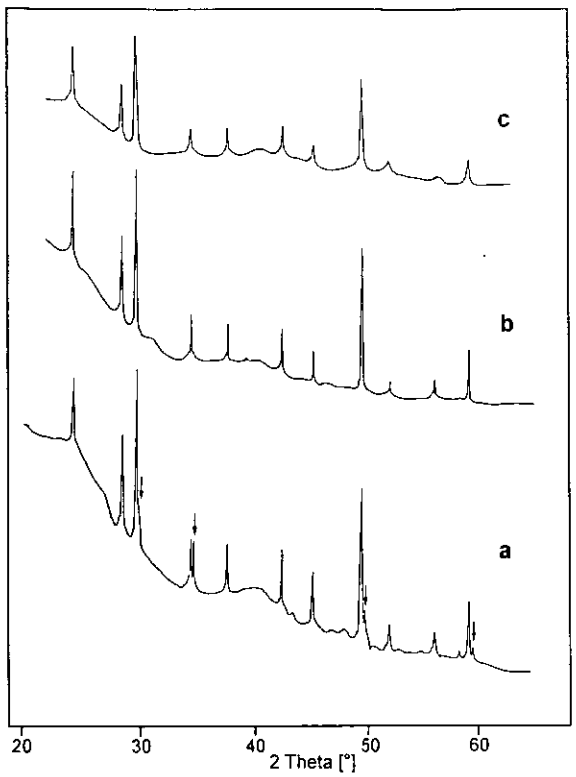

FIG. 1. X ray powder diffraction patterns (densitograms of Cu$K\alpha_1$, Guinier photographs) of thermally synthesized (c) and tribochemically prepared Li_2ZnCl_4 after grinding for 15 hr at 70°C (a) and 84 hr at 100°C (b) (↓, LiCl).

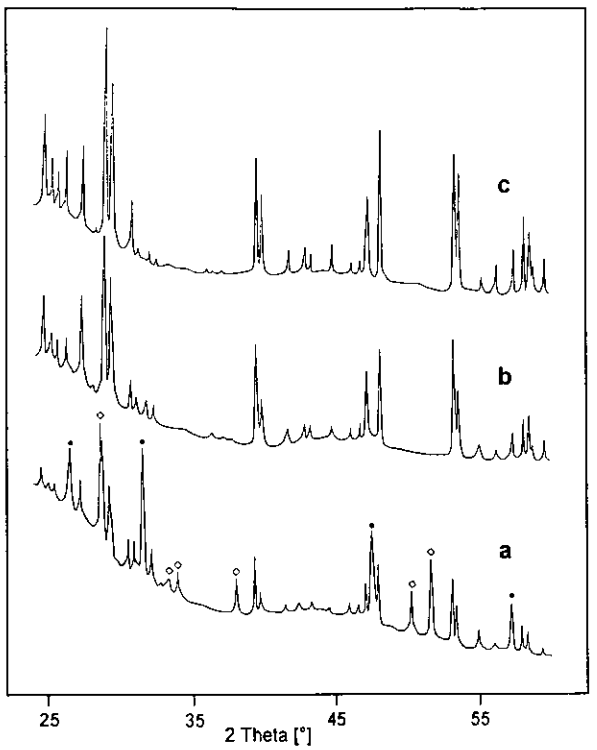

FIG. 2. X ray powder diffraction patterns (Cu$K\alpha_1$, see Fig. 1) of thermally synthesized (c) and tribochemically prepared Na_2ZnBr_4 after grinding for 10 (a) and 23 hr (b) (◇, $ZnBr_2$; ●, NaBr).

type Na_2ZnCl_4 and Na_2ZnBr_4, however, already takes place at room-temperature after 30 and 23 hr, respectively. Figures 1 and 2 show the X-ray powder diffraction patterns of stoichiometric amounts of LiCl and $ZnCl_2$ and NaBr and $ZnBr_2$ after different milling times, including the patterns of samples prepared by the ceramic method.

Monophase Li_2ZnCl_4 can obviously be obtained in its low-temperature modification (spinel-type) under moderate conditions and in much less time than by annealing the olivine-type polymorph at about 200°C. The purity of the tribochemically prepared Li_2ZnCl_4 has been analyzed by IR reflection spectroscopy (see Fig. 3). No contamination with unreacted material was detected. An accelerating effect of catalytic amounts of water as suggested by Severin *et al.* (4) has not been established. Evidently, a strong decrease in activation energy (and, hence, increase in reaction rate) exists within the zinc halides $Li_2ZnCl_4 > Na_2ZnCl_4 > Na_2ZnBr_4$.

Analogous experiments with the $LiCl–MgCl_2$, $LiCl–MnCl_2$, as well as the $NaCl–MgCl_2$ and $NaCl–MnCl_2$ systems remained unsuccessful also after 100 hr grinding. These results caused us to investigate the tribochemical behavior of AX_2 (A = Mg, Mn, Zn; X = Cl, Br). While $MgCl_2$ and $MnCl_2$ became amorphous within 60

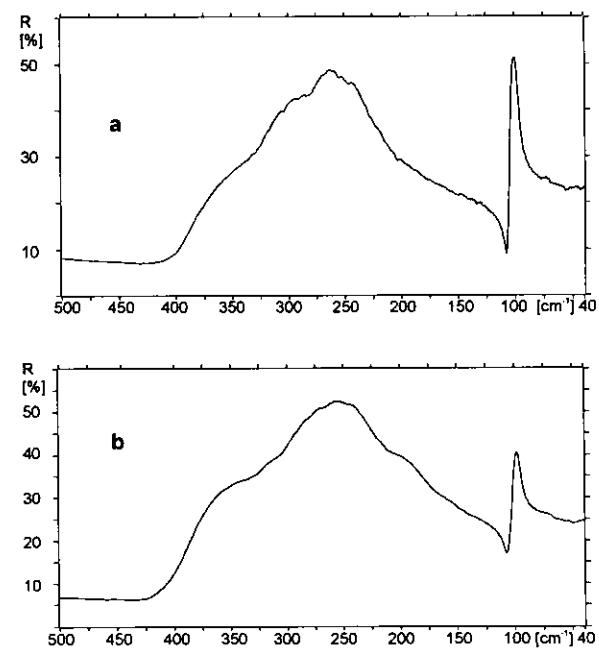

FIG. 3. IR reflection spectra of mechanochemically (a) and thermally (b) prepared spinel-type Li_2ZnCl_4.

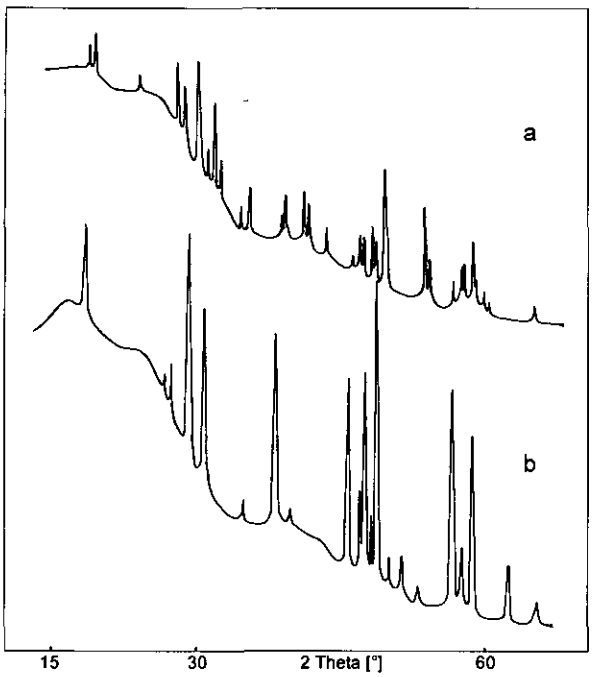

FIG. 4. X ray diffraction pattern (Cu$K\alpha_1$, see Fig. 1) of $ZnCl_2$ before (a, orthorhombic polymorph) and after grinding for 90 hr (b, tetragonal modification).

hr grinding, $ZnCl_2$ and $ZnBr_2$ do not show any decrease in X ray reflection intensities even after a mechanical activation of 90 hr. $ZnCl_2$ transforms from the orthorhombic modification ($Pna2_1$) (5) to the tetragonal form ($I\bar{4}2d1$) (6) during the impact stress. Figure 4 shows the X ray diffraction pattern of $ZnCl_2$ before and after grinding for 90 hr.

Considering tribochemical kinetics (7) an amorphization mechanism can be excluded here. Thus we assume a diffusion-controlled mechanism to be effective in these systems. The increase in reactivity going from the

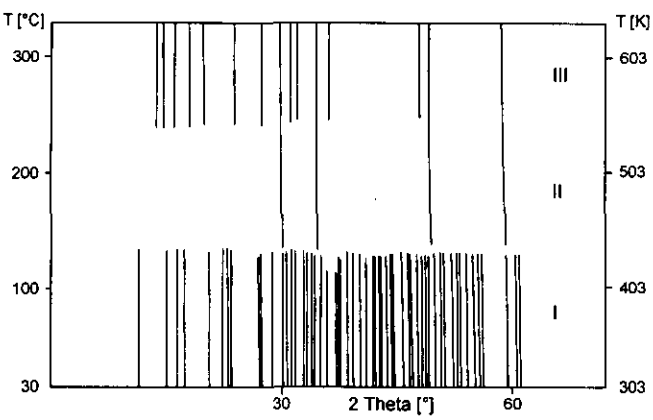

FIG. 5. High-temperature X ray diffraction patterns (Cu$K\alpha_1$) taken in an open capillary of $Li_2ZnCl_4 \cdot 2H_2O$ (I), LiCl (II), and olivine-type Li_2ZnCl_4 + LiCl (III).

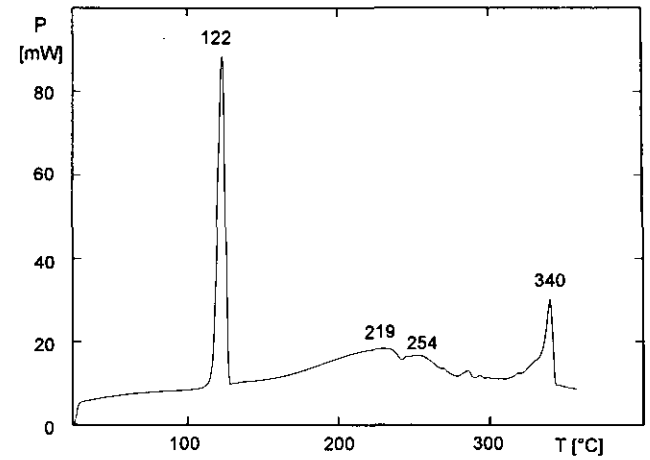

FIG. 6. DSC diagram of $Li_2ZnCl_4 \cdot 2H_2O$ (open crucible, heating rate: 10°C/min).

LiCl–$ZnCl_2$ to the NaBr–$ZnBr_2$ systems is obviously caused by the increased diffusion rates of Zn^{2+} ions into the respective MX (M = Li, Na; X = Cl, Br). On the other hand, formation of the inverse spinel-type Li_2MCl_4 (M = Mg, Mn) was not achieved by tribochemical methods. The reason is not known thus far. One possibility is that these ternary chlorides are thermodynamically not stable at ambient temperature.

Dehydration of $Li_2ZnCl_4 \cdot 2H_2O$ and $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$

Dehydration of $Li_2ZnCl_4 \cdot 2H_2O$ was found to depend on the experimental conditions, such that three cases have to be distinguished.

(i) When heating up in an open capillary, dehydration starts at 130°C dissolving the salts in the liberated water. Instantaneously, LiCl is precipitated from the solution, whereas ternary olivine-type Li_2ZnCl_4 is not formed before reaching 240°C (see Fig. 5). In the DSC thermograms, four peaks are detected (see Fig. 6). The first at 122°C is due to the loss of water, the last at 340°C represents the melting of the solid phases. (ii) In closed capillaries, dehydration temperature increases to 150°C and spinel-

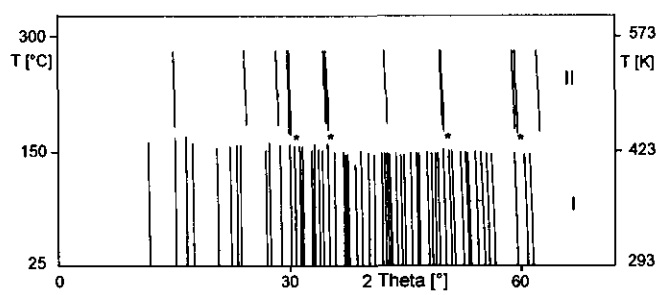

FIG. 7. High-temperature X ray diffraction pattern (Cu$K\alpha_1$) taken in a closed capillary of $Li_2ZnCl_4 \cdot 2H_2O$ (I); spinel-type Li_2ZnCl_4 + LiCl (II); *, reflections due to LiCl.

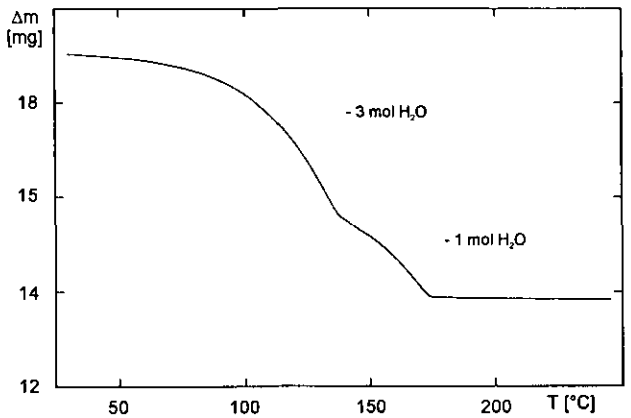

FIG. 8. TG thermogram of $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$ (open crucible, heating rate: 5°C/min).

type Li_2ZnCl_4 is formed beside LiCl. The phase transition to the olivine-type form could not be observed since the capillary was destroyed by the increased water pressure (see Fig. 7). (iii) Dehydration of $Li_2ZnCl_4 \cdot 2H_2O$ over P_2O_5 at room temperature also yields the olivine-type modification.

In contrast to $Li_2ZnCl_4 \cdot 2H_2O$, $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$ loses its water in two steps (see Figs. 8 and 9). The first, in the temperature range 50 to 137°C (TG, DSC peak: 95°C, both open crucibles), is equivalent to 3 mol water and, hence, a hitherto unknown monohydrate is formed. During the second step, between 137 and 175°C (DSC peak: 161°C) the last mol water is delivered (see Fig. 8). The high-temperature X ray diffraction pattern is shown in Fig. 10. The tetrahydrate first dehydrates to the monohydrate, which contains possibly less lithium than the reactant because there are additional reflections of LiCl. However, the pattern of the monohydrate is not equal to that of $MnCl_2 \cdot H_2O$ (8). Above 157°C further dehydration

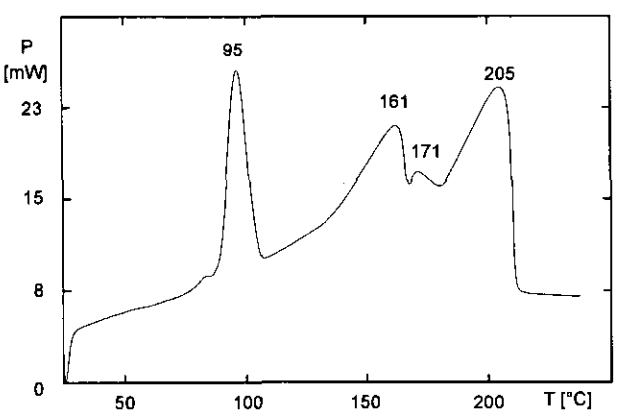

FIG. 9. DSC diagram of $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$ (open crucible, heating rate: 10°C/min).

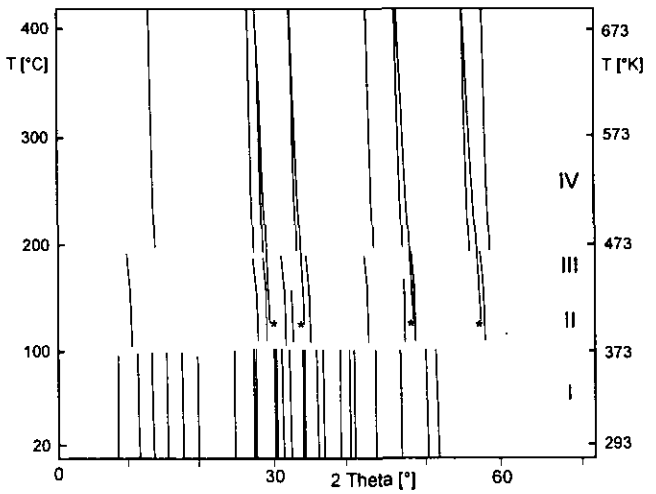

FIG. 10. High-temperature X ray diffraction pattern ($CuK\alpha_1$) of $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$ (I), monohydrate + LiCl (II), dehydrated compound + LiCl (III), and Li_2MnCl_4 + LiCl (IV); *, reflections due to LiCl.

takes place, yielding an anhydrous compound with an only slightly changed pattern compared to that of the monohydrate. This phase decomposes at 190°C (DSC peak: 205°C) to spinel-type Li_2MnCl_4.

The Raman spectra, taken at different temperatures (see Fig. 11), display evident similarity among the mono-

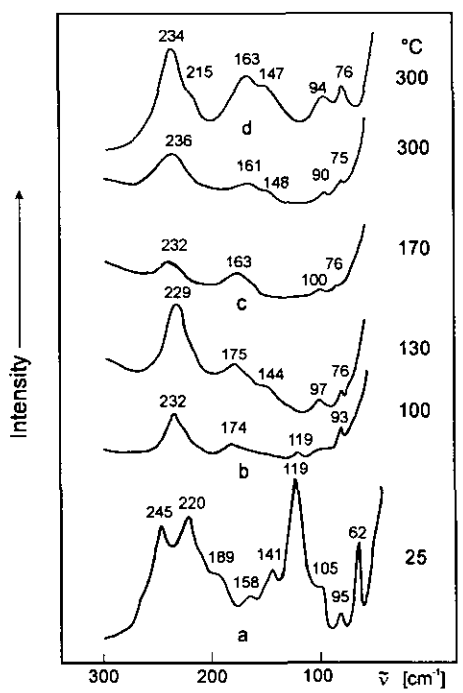

FIG. 11. Raman spectra of $Li_{2.28}Mn_{0.86}Cl_4 \cdot 4H_2O$ (a) and its dehydration products (b–c) taken from 25 to 300°C, and of thermally synthesized Li_2MnCl_4 at 300°C (d); (b) monohydrate; (c) dehydrated compound.

hydrate (Fig. 11b), the anhydrous compound mentioned above (Fig. 11c), and spinel-type Li_2MnCl_4 (Fig. 11d), presuming some structural correspondence of these compounds.

CONCLUSION

Both tribochemistry and dehydration experiments have been successfully employed for synthesizing ternary halides AB_2X_4 (A = Li, Na; B = Zn; X = Cl, Br). The formation of the stable or the metastable polymorph of Li_2ZnCl_4 depends strongly on the preparation method and the reaction conditions. Spinel-type Li_2MnCl_4 cannot be synthesized mechanochemically, but by dehydration of the tetrahydrate.

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