Mechanochemical Synthesis of Ternary Potassium Transition Metal Chlorides

Roland H. Pawelke,^[a] Michael Felderhoff,^[a] Claudia Weidenthaler,^[a] Borislav Bogdanovíc,^[a] and Ferdi Schüth^{*[a]}

Dedicated to Professor Bernt Krebs on the Occasion of His 70th Birthday

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Abstract. Ternary halide systems $KM^{II}Cl_3$ ($M^{II} = Ti$, Cr, Mn, Fe, Co, Ni, Cu, Zn) have been prepared by mechanochemical synthesis. Furthermore, $TiCl_2$ was converted to Ti_7Cl_{16} by mechanochemical treatment. For most samples, the X-ray powder diffraction patterns

Introduction

The scientific interest in ternary halides of transition metals is usually focused on their structural and electronic properties [1-9]. Apart from that, these materials can be considered as intermediates for the synthesis of more sophisticated hydrogen storage compounds than current systems [10-12] of ternary composition. At present, this reaction is already an established procedure for the access to ternary non-commercial boron and aluminium hydrides, as shown in Eq. (1a) and (1b).

 $CaCl_2 + 2 NaAlH_4 \longrightarrow Ca(AlH_4)_2 + 2 NaCl$ (1a)

$$\operatorname{ZnCl}_2 + 2 \operatorname{LiBH}_4 \longrightarrow \operatorname{Zn}(\operatorname{BH}_4)_2 + 2 \operatorname{LiCl}$$
 (1b)

These metathesis reactions proceed under wet-chemical conditions, as well as mechanochemical synthesis conditions [13-15], the exchange is favoured thermodynamically by the formation of alkali halide.

Since we are interested in the synthesis of multinary hydrides, we explored the synthesis of reactive ternary halides as possible starting materials for the formation of hydrides.

A straightforward way to a ternary halide system A-M^{II}-X comprising a monovalent cation A (e.g. alkali metal, NH_4^+ or NR_4^+), a divalent metal cation M^{II} and the respective halide anion X – is the synproportionation of two binary chlorides AX and $M^{II}X_2$ at appropriate proportion.

 [a] Max-Planck-Institut f
ür Kohlenforschung Kaiser-Wilhelm-Platz 1 could either be assigned to isotypic structures or were found in accordance with reference data. The monochloride systems of Ti, Co and Zn were extended to their double chloride stoichiometry $\rm K_2M^{11}Cl_4.$

 $AM^{II}X_3$ ternary halides systems [16–24] have usually perovskite-type structure [25–27].

If prepared by the common ceramic approach, the reactants are brought into a reaction vessel und kept at temperatures which are sufficiently high for substantial ion mobility until thermodynamic equilibrium is reached.

Mechanochemical syntheses have some advantages, because they are usually less time consuming and less laborious than the classical ceramic procedures. In addition, if it is desired to use the reaction products for further conversions, the smaller particle sizes and higher defect concentrations brought about by mechanochemical synthesis are favourable, since such materials have higher reactivity. Unlike common chemical synthesis methods, the energy amount needed for reaction is not delivered by heat or electromagnetic radiation but by mechanical work [28, 29].

Since these reactions are usually carried out in a ball mill, mechanochemical syntheses are also referred to as ball milling. Mechanochemical activation may be understood as an inverse *Jahn-Teller* effect [30], with the excess energy delivered by pressure and shear forces being stored by the formation of non-equilibrium, non-stoichiometric defects, structural distortions and additional intergrain boundaries.

Mechanochemically activated materials can undergo polymorphic phase transitions and/or amorphization [31]. In the case of multiple reactants, the formation of new compounds may be favoured. Compared to a ceramic solid state reaction, the saving on reaction time by a mechanochemical process can be substantial: we found that the synthesis of orthorhombic K_2CoCl_4 via ball milling is finished within 3 h, whereas the ceramic preparation takes one week at 400 °C [32].

Unfortunately, this method does not allow the synthesis of crystals suitable for X-ray single-crystal analysis. However, if structure determination is not in the centre of inter-

^{*} Prof. Dr. F. Schüth Fax: +49-208-306 2995 E-Mail: schueth@mpi-muelheim.mpg.de

⁴⁵⁴⁷⁰ Mülheim an der Ruhr, Germany

est, this setback is compensated by economy of time and the simplicity of the preparation method. The easy scalability of ball milling processes is an additional advantage to mention.

The number of examples of mechanochemically prepared ternary halide systems is surprisingly low: only the syntheses of various fluoride perovskites [33, 34], cryolite/chiolite [35] and some lithium transition 3d-metal chloride spinels [36] have been reported.

We prepared ternary systems with $KM^{II}Cl_3$ composition from potassium chloride and 3d-transition metal chlorides $M^{II}Cl_2$ ($M^{II} = Ti$, Cr, Mn, Fe, Co, Ni, Cu, Zn) by ball milling; double chlorides of titanium, cobalt and zinc were also prepared. The reaction products were analyzed by Xray powder diffraction (XRD) methods.

Experimental Section

Commercial chemicals were obtained from Sigma-Aldrich in anhydrous quality and at least 99.5 % purity. Ti_7Cl_{16} was prepared by thermal disproportionation of TiCl₃ (26 mmol) at 600 °C in a quartz glass tube in an argon stream for 5 hours (isolated yield 85%).

A Fritsch Pulverisette P7 classic line ball mill was used with 12 mL steel-vials with six balls of the same material (10 mm diameter). Some experiments were carried out with Si₃N₄ balls and vials to study the possible influence of iron abrasion, without noticeably different results of the synthesis after adaptation of the ball-to-powder ratio necessary due to the lower density of the ceramic balls. Loading and extraction procedures were performed in an argon-filled glove box (O₂ < 2 ppm, H₂O < 1 ppm) because some of the compounds were hygroscopic. However, this may not be necessary in all cases.

For the syntheses of KM^{II}Cl₃, 1 mmol of transition metal chloride $M^{II}Cl_2$ ($M^{II} = Ti$, Cr, Mn, Fe, Co, Ni, Cu, Zn) and a corresponding amount of KCl were non-stop ball milled for 3 hours at 800 rpm. In a few cases, we prepared the double chlorides with $K_2M^{II}Cl_4$ stoichiometry. The ball to powder ratio was approximately 120:1. This high ratio is due to the screening character of this investigation, the reactions take also place at the common ratio of approximately 40:1. The isolated yield was ~80%, in all cases no XRD-indications of residual starting material were observed.

Depending on the chemical composition of the samples, the XRD patterns for qualitative phase analysis were collected either on a Stoe STADI P transmission diffractometer with a primary monochromator (Mo $K\alpha_1$) and a linear position sensitive detector or on a X'Pert Pro instrument (PANalytical company) (Cu $K\alpha_1$) equipped with an X'Celerator detector. For the measurements, the samples were filled into glass capillaries (0.5 mm diameter) in a glove box, which were sealed to prevent contact with air.

The measured patterns were evaluated qualitatively by comparison with entries from the PDF-2 powder pattern database [37].

Results and Discussion

The XRD powder analysis of the reaction products confirmed the conversion of the starting materials; the results are summarized in Table 1.

 Table 1. Survey of the different phases obtained by mechanochemcal reaction.

MII	KM ^{II} Cl ₃	Fig.	Ref. Lit	$K_2 M^{11} Cl_4 \\$	Fig.	Ref.
Ti ^{a)} Ti ^{b)} Cr Mn Fe Co Ni Cu	KTiCl ₃ KTiCl ₃ rew phase ^{c)} KMnCl ₃ KFeCl ₃ new phase ^{d)} KNiCl ₃ KCuCl ₃	2 2 4 5 5 6 5 5	[38] [38] [39] [40] [42] [43]	new phase ^{e)} K ₂ CoCl ₄	3 - 7 - -	 [32, 41]
Zn	new phase	8	-	K_2ZnCl_4	8	[44, 45]

a) Ti_7Cl_{16} ; b) $TiCl_2$; c) potentially similar to KCuCl₃ structure; d) similar to KNiCl₃ structure, shifted to lower angles; e) phase composition and structure not finally assigned, potentially K_3MoCl_6 structure [46].

During our experimental series, we found ourselves confronted with a several month-lasting shortage on commercial TiCl₂; when we decided to prepare the material by ourselves according to Eq. (2), we obtained exclusively Ti_7Cl_{16} (Fig. 1b).



Figure 1. Powder diffraction patterns of Ti_7Cl_{16} (a) calculated pattern according to structure data given by *Krebs* and *Henkel* [47] (b) synthesized material Ti_7Cl_{16} , (c) mixture of $TiCl_2$ and Ti_7Cl_{16} after 2 h ball milling of $TiCl_2$.

This result is surprising because in literature, the formation of Ti_7Cl_{16} is considered rather a special case. Ti_7Cl_{16} has been prepared in a chemical transport reaction, em-



ploying Al_2Cl_6 as transport auxilliary, with gaseous TiAlCl₆ being the active transport species [48, 49]. Our results indicate that such an aluminium transport species is not necessary and the formation of Ti₇Cl₁₆ can be explained solely by disproportionation of Ti-Cl compounds [48].

Curious about the structural relationship between $TiCl_2$ [50, 51] and Ti_7Cl_{16} , we subjected commercial $TiCl_2$ to 2 h of ball milling under our standard conditions: Ti_7Cl_{16} was obtained from $TiCl_2$ by mechanochemical treatment (Fig. 1c), although some residual $TiCl_2$ was still present in the sample.

The transformation proceeds presumably via Eq. (3), but due to the ill-resolved diffraction peaks of the sample, the titanium phase could not be identified precisely.

8 TiCl₂
$$\xrightarrow{\text{Ball}}$$
 Ti₇Cl₁₆ + Ti (3)

We used Ti₇Cl₁₆ for the preparation of the ternary potassium mono chloride and the double chloride (1/7 Ti₇Cl₁₆ \approx TiCl_{2.3}). The monochloride reaction product was found to fit with the hexagonal KTiCl₃ structure solved by *Jongen* et al. rather well, although precise assignment is difficult due to the broad and ill-resolved reflections of the ball-milled sample (Fig. 2) [38]. We repeated the preparation of the monochloride with commercial TiCl₂. The powder pattern is very similar to the pattern of hexagonal structure of KTiCl₃ (Fig. 2c).



Figure 2. Powder diffraction patterns: (a) simulated pattern of hexagonal $KTiCl_3$ (b) measured pattern of the product of the reaction KCl + 1/7 Ti_7Cl_{16} (c) powder diffraction pattern obtained from the reaction of KCl with commercial $TiCl_2$.

The reaction of two equivalents of KCl with Ti_7Cl_{16} yielded the pattern shown in Figure 3. It can either been explained by a mixture of KTiCl₃ and a second phase, or

by the formation of a new $K_x Ti_y Cl_z$ modification with a structure similar to monoclinic $K_3 MoCl_6$ [46].



Figure 3. Measured diffraction pattern obtained from the reaction of two equivalents of KCl (respective to titanium) with Ti_7Cl_{16} . The pattern is compared to K_3MoCl_6 [01-073-0358] peak positions.

When we proceeded to the CrCl₂ based system, we were unable to assign the diffraction peaks (Fig. 4) to any known structure or powder pattern in the K-Cr-Cl system. However, extension of the search to other systems revealed a possible correlation to the monoclinic structure of KCuCl₃. For simulation of the powder pattern in Figure 4, the Cusite in the crystal structure was simply replaced by a Cr cation. A further refinement of the new KCrCl₃ structure would require both better quality of the sample and correspondingly better quality of the diffraction data. Higher sample quality with respect to crystallinity is hardly possible due to the limitations imposed by the preparation method.



Figure 4. Powder diffraction patterns of (a) unidentified K-Cr-Cl phase from equimolar reaction of KCl with $CrCl_2$ and (b) simulated pattern using a KCuCl₃-type structure with Cu^{II} replaced by Cr^{II} .

The $KM^{II}Cl_3$ phases for $M^{II} = Mn$, Fe, Ni and Cu are in accordance with reference diffraction data (Fig. 5, Tab. 1):



Figure 5. Powder diffraction patterns of a) KMnCl₃ [01-076-0970] b) KFeCl₃ [01-070-1637] c) KNiCl₃ [01-071-1764] and d) KCuCl₃ [01-072-0261].

The KCoCl₃ sample had a diffraction pattern similar to the KNiCl₃-structure (Fig. 6).



Figure 6. Comparison of measured pattern after ball-milling of KCl with CoCl₂ (a) and (b) simulated pattern calculated from the hexagonal KNiCl₃ structure.

In order to gather as much information about the compound as possible, this material was reacted with a further amount of KCl, because the formation of ternary halides takes place in a stepwise manner [52] as shown in Eq. (4) and K_2CoCl_4 [32] has the next confirmed structure in the K-Co-Cl system.

$$CoCl_2 \xrightarrow{+ KCl} KCoCl_3 \xrightarrow{+ KCl} K_2CoCl_4$$
 (4)

We obtained K_2CoCl_4 (Fig. 7) from this reaction; with the close connection to the KNiCl₃ structure, this sufficiently supports the postulate of a new phase in the K-Co-Cl system.



Figure 7. Powder diffraction pattern of K_2CoCl_4 recieved stepwise according to Eq (4). The powder pattern was calculated from the structure data given by *Mashiyama* [41], the shift is due to different data collection temperatures.

Basically the same initial situation was encountered in the K-Zn-Cl system. No crystalline compound with the composition KZnCl₃ has been observed yet, the reaction product of KCl with ZnCl₂ yields a powder pattern consisting of numerous reflections. This pattern is not fitting any known K-Zn-Cl structure (Fig. 8) and so far, the search for an isostructural compound was not successful. By analogy to the KCoCl₃/K₂CoCl₄ system, the KZnCl₃ sample



Figure 8. The upper powder diffraction pattern represents the unidentified phase received by the equimolar reaction of KCl with $ZnCl_2$. The lower diffraction pattern belongs to K_2ZnCl_4 [45], which was obtained by reaction of the unidentified material with a further equivalent of KCl.



was reacted further with an additional amount of KCl, the reaction yielded K_2ZnCl_4 [44, 45] (Fig. 8).

The formation of K_2ZnCl_4 from the intermediate phase does not prove the single phase nature of the intermediate, but on the other hand, there is no need to argue otherwise; final certainty about this could probably only be achieved by structure solution from the powder pattern for which, however, the data quality is clearly insufficient, again due to the limitations associated with the mechanochemical synthesis.

The existence of new (metastable) phases in ternary systems may be expected, because the enthalpy gain from the synproportionation of two binary chlorides to a ternary system is rather small ($\sim 0.6 - 20 \text{ kJ mol}^{-1}$, usually much less than 1 % of the total lattice enthalpy). But enthalpy values have significance only at 0 K; at higher temperatures, the Gibbs enthalpy has to be considered as the sole criterion for stability ("high" relative to 0 K) [52].

A small endothermic formation enthalpy overruled by a sufficient negative entropy term $T\Delta S$ can still result in a negative Gibbs enthalpy: the synproportionation enthalpy for K₂CoCl₄ from KCl and KCoCl₃ according to Eq. (4) is almost zero (0.6 kJ mol⁻¹)! Nevertheless the reaction proceeds to K₂CoCl₄, due to the considerable entropy gain provided by the transition from linked to isolated coordination polyhedra [52].

Conclusion

This study proves, that ball milling is a versatile and useful tool in solid state chemistry, especially as a preparative method. Mechanochemical synthesis gave easy access to a number of known and previously unknown ternary halides, and it is expected that also numerous other compounds will be accessible via related pathways. The disadvantages of the method with respect to structural investigation are the small particle sizes and high defect concentrations induced by the ball milling, which seriously impedes structural analysis. It is typically not possible to produce single crystals sufficiently big for structural analysis. The quality of the powder diffraction data is also insufficient for structure solution, so that only comparison to known structure types can give indications with respect to the structure of new compounds. However, the results of our investigations may induce work to produce higher quality samples of some of the phases described and thus further promote knowledge on these and related compounds. On the other hand, the very weakness of the mechanochemical synthesis pathway turns into a strength, when the products of this preparation method are to be converted to other compounds, such as the multinary hydrides discussed in the introduction. Work in this direction is going on in our laboratory, and possibly, novel hydride storage materials can emerge from this line of work.

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References

- J. Legendziewicz, J. Cybinska, M. Guzik, G. Boulon, G. Meyer, Opt. Mater. 2008, 30, 1655–1666.
- [2] J. A. Schlueter, J. L. Manson, U. Geiser, *Inorg. Chem.* 2005, 44, 3194–3202.
- [3] N. Gerlitzki, S. Hammerich, G. Meyer, Z. Anorg. Allg. Chem. 2004, 630, 2431–2433.
- [4] S. Emori, N. Koga, F. Yamada, *ITE Lett. Batteries, New Technol. Med.* 2004, 5, 267–270.
- [5] S. Kaluza, M. Suchanska, R. Belka, S. Lesniewski, *Ferroelectrics* 2002, 273, 143–148.
- [6] G. Schilling, G. Meyer, Z. Anorg. Allg. Chem. 1996, 622, 759-765.
- [7] M. Hagemann, H. J. Weber, Appl. Phys. A: Mater. Sci. Process. 1996, 63, 67–74.
- [8] A. K. Banerjee, A. C. Verma, S. K. Roy, J. Indian Chem. Soc. 1995, 72, 1–3.
- [9] G. H. Rao, K. Barner, I. D. Brown, J. Phys.: Condens. Matter 1998, 10, L757–L763.
- [10] B. Bogdanovíc, U. Eberle, M. Felderhoff, F. Schüth, Scr. Mater. 2007, 56, 813–816.
- [11] S.-i. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev.* 2007, 107, 4111–4132.
- [12] A. Züttel, Naturwissenschaften 2004, 91, 157-172.
- [13] M. Fichtner, C. Frommen, O. Fuhr, Inorg. Chem. 2005, 44, 3479-3484.
- [14] Y. Nakamori, H. Li, K. Miwa, S.-i. Towata, S.-i. Orimo, *Mater. Trans.* 2006, 47, 1898–1901.
- [15] M. Mamatha, B. Bogdanovíc, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schüth, C. Weidenthaler, J. Alloys Compd. 2006, 407, 78–86.
- [16] D. A. Porter, A. Harrison, D. Visser, R. C. B. Copley, A. E. Goeta, J. A. K. Howard, K. S. Knight, *Physica B* 1998, 241–243, 385–386.
- [17] I. N. Flerov, M. V. Gorev, K. S. Aleksandrov, A. Tressaud, J. Grannec, M. Couzi, *Mater. Sci. Eng.*, R 1998, R24, 81–151.
- [18] V. Luana, A. Costales, A. M. Pendas, M. Florez, V. M. G. Fernandez, *Solid State Commun.* 1997, 104, 47–50.
- [19] V. Luana, A. Costales, A. M. Pendas, Phys. Rev. B: Condens. Matter 1997, 55, 4285–4297.
- [20] A. Boumriche, J. Y. Gesland, A. Bulou, M. Rousseau, J. L. Fourquet, B. Hennion, *Solid State Commun.* 1994, 91, 125–128.
- [21] M. T. Anderson, K. B. Greenwood, G. A. Taylor, K. R. Poeppelmeier, Prog. Solid State Chem. 1993, 22, 197–233.
- [22] D. Visser, A. Harrison, J. Magn. Magn. Mater. 1992, 116, 80-82.
- [23] C. Ridou, M. Rousseau, J. Bouillot, C. Vettier, J. Phys. C 1984, 17, 1001–1007.
- [24] J. F. Ackerman, G. M. Cole, S. L. Holt, *Inorg. Chim. Acta* 1974, 8, 323–343.
- [25] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature* 2002, 418, 164–167.
- [26] H. Tanaka, M. Misono, Curr. Opin. Solid State Mater. Sci. 2001, 5, 381–387.
- [27] C. J. Howard, Acta Crystallogr. 2005, A61, 93-111.
- [28] V. V. Boldyrev, K. Tkacova, J. Mater. Synth. Process. 2000, 8, 121–132.
- [29] J. F. Fernandez-Bertran, Pure Appl. Chem. 1999, 71, 581-586.
- [30] J. J. Gilman, Science 1996, 274, 65.
- [31] N. Z. Lyakhov, T. F. Grigoryeva, A. P. Barinova, J. Therm. Anal. Calorim. 2005, 82, 741-746.
- [32] W. J. Vermin, G. C. Verschoor, D. J. W. Ijdo, Acta Crystallogr. 1976, B32, 3325–3328.

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- [33] J. Lee, H. Shin, J. Lee, H. Chung, Q. Zhang, F. Saito, Mater. Trans. 2003, 44, 1457–1460.
- [34] J. Lee, Q. Zhang, F. Saito, Chem. Lett. 2001, 700-701.
- [35] G. Scholz, O. Korup, Solid State Sci. 2006, 8, 678-684.
- [36] I. Solinas, H. D. Lutz, J. Solid State Chem. 1995, 117, 34-38.
- [37] ICDD-PDF-2 Database, Newton Square, PA, USA, 2007.
- [38] L. Jongen, T. Gloger, J. Beekhuizen, G. Meyer, Z. Anorg. Allg. Chem. 2005, 631, 582-586.
- [39] A. Horowitz, M. Amit, J. Makovsky, L. Ben Dor, Z. H. Kalman, J. Solid State Chem. 1982, 43, 107–125.
- [40] M. Amit, A. Zodkevitz, J. Makovsky, Isr. J. Chem. 1970, 8, 737-740.
- [41] H. Mashiyama, J. Phys. Soc. Jpn. 1991, 60, 180-187.
- [42] D. Visser, G. C. Verschoor, D. J. W. Ijdo, Acta Crystallogr. 1980, B36, 28-34.
- [43] R. D. Willett, C. Dwiggins, Jr., R. F. Kruh, R. E. Rundle, J. Chem. Phys. 1963, 38, 2429–2436.

- [44] I. Mikhail, K. Peters, Acta Crystallogr. 1979, B35, 1200-1201.
- [45] J. Kusz, D. Kucharczyk, Appl. Crystallogr. 1995, 16, 268-272.
- [46] Z. Amilius, B. Van Laar, H. M. Rietveld, Acta Crystallogr. 1969, B25, 400-402.
- [47] B. Krebs, G. Henkel, Z. Anorg. Allg. Chem. 1981, 474, 149-156.
- [48] H. Schaefer, R. Laumanns, Z. Anorg. Allg. Chem. 1981, 474, 135-148.
- [49] H. Schaefer, R. Laumanns, B. Krebs, G. Henkel, Angew. Chem. 1979, 91, 343–344; Angew. Chem. Int. Ed. Engl. 1979, 18, 325–326.
- [50] N. C. Baenziger, R. E. Rundle, Acta Crystallogr. 1948, 1, 274.
- [51] E. L. Gal'perin, R. A. Sandler, *Kristallografiya* **1962**, *7*, 217–219.
- [52] H. J. Seifert, H. Fink, G. Thiel, J. Uebach, Z. Anorg. Allg. Chem. 1985, 520, 151–159.

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