

PREPARATION OF TERNARY CHLORIDES OF A_2MCl_4 (A = K, Cs, Li) (M = Sr, Ba) Using Solution Method

Dr. (Mrs.) Bertha Abdu Danja¹

¹Department of Chemical Sciences, Faculty of Science, Federal University Kashere, Gombe State, Nigeria

Abstract: Ternary chlorides may be prepared conveniently from aqueous solutions or acetic acid, provided they are congruently soluble in the solvent or they may be prepared by heating together appropriate amount of anhydrous halides. The synthetic route followed here starting from the binary chlorides of alkali metal (ACl) and alkaline earth metal (MCl_2) chlorides made use of preparation from solutions. Attempt was made to prepare the following ternary chlorides K_xSrCl_y , Cs_xSrCl_y , Li_xSrCl_y , K_xBaCl_4 and Rb_xSrCl_y from solution. Stoichiometric amount of the binary chlorides were used to grow the crystals in solutions. One solid state reaction was carried out with one group of educts. The results obtained showed that the ternary chlorides are harder to prepare in water solution than in solid state, and therefore the research recommend using water free solvents in future work to prepare these ternary chlorides in solution.

Key Words: Chlorides, Ternary, solution method, crystals preparations, X-ray, powder diffraction

I. Introduction

Since the beginning of last century people have focused research on the crystal structure and the thermal properties of ternary chloride systems [1]. Ternary chlorides may be prepared conveniently from aqueous solutions or acetic acid, provided they are congruently soluble in the solvent or they may be prepared by heating together appropriate amount of anhydrous halides [II]. The synthetic route followed here starting from the binary chlorides of alkali metal (ACl) and alkaline earth metal (MCl_2) chlorides, made use of preparation from solutions as found in literatures [III & IV]. Attempt is made to prepare the following ternary chlorides K_xSrCl_y , Cs_xSrCl_y , Li_xSrCl_y , K_xBaCl_4 and Rb_xSrCl_y from solution. From literature some ternary chlorides have already been prepared, such as K_2SrCl_4 prepared in the University of Karlsruhe using solid state reaction [I, V, VI & VII]. It crystallized in a trigonal/rhombohedral crystal system in the space group $R\bar{3}c$. Na_2MgCl_4 is also found in literature which crystallized in an orthorhombic crystal system in the space group $pbam$ [VIII & IX]. Most of the examples of ternary chlorides crystals prepared from solutions so far are those of trivalent or even higher valents metals, the divalent ternary chlorides reported in literature are from solid state reactions [X & XI]. Therefore the aim of this work is to prepare ternary chlorides of the alkali and alkaline earth metals from solutions.

II. Experimental

II.1 REAGENTS: Reagent used includes $SrCl_2$, KCl, CsCl, $BaCl_2$, RbCl, NaCl and concentrated HCl.

2.2. PREPARATION OF CRYSTALS

Three types of solution methods were used

2.2.1 Stoichiometric amount of the binary chlorides ACl (A = K, Li, Na and Cs) and MCl_2 (M = Sr, Ba) in the ratio 2:1 were weighed, dissolved in water and heated to evaporate the water. The concentrated solution was allowed to cool down with formation of crystals.

2.2.2. A_xMCl_y were prepared by dissolving the educts (in a ratio 2:1) ACl (A = K, Cs, Rb) and MCl_2 (M = Sr, Ba,) in HCl (2m) and allowed to evaporate slowly without heating. Crystals formed were observed under a microscope. The product was divided into two portions; one heated in an oven at 100°C/h for 48hrs then cooled down slowly at 1°C/h. The second portion was washed with alcohol and rinsed with Acetone.

2.2.3. 2mmole of ACl (A = K, Li, Cs, Rb) and 1mmole of MCl_2 (M = Sr and Rb) in the ratio 2:1 were weighed and dissolved in a small amount of conc. HCl (approx. 100ml), then boiled for some minutes after which the heating temperature was reduced and the solution evaporated slowly to dryness. The compound formed was observed under a microscope. This was put in an oven at 500°C for 1 day and cooled down slowly.

2.2.4. One of the reactions above was tried using solid state reaction. The phase diagrams for the three alkali metal and the corresponding alkaline earth metals were checked and that of RbCl and $SrCl_2$ at 1:1 and 1:2 ratio

look feasible to prepare. These two were prepared using solid state reaction. Stoichiometric amount of the salts in the above ratios were weighed and put in quartz ampoules in the glove box. The ampoules were put in the oven at 750°C for 7 days. After which the ampoules were opened in a glove box, samples for powder diffraction were prepared also in the glove box and powder diffraction pattern were measured.

2.3. X-ray Powder Diffraction:

The X-ray powder diffraction was detected using a D5000-diffractometer which is from the company Braun (München). The measurements were always done for 30 minutes. The patterns obtained were compared with theoretical patterns of the binaries and the expected ternary compounds.

III. Results And Discussion

From the three solution methods used the products looked similar. Two phases were seen under the microscope, one grown on top of the other. One phase looked powder like while the other phase under the microscope looked crystalline. The crystals were separated and used for x-ray powder diffraction. The theoretical pattern of K_2SrCl_4 did not fit into the measured pattern as can be seen in fig 1 but the theoretical pattern of one of the educts i.e. KCl fit some peaks very well (fig2), hence KCl was present in the product. The theoretical pattern of $SrCl_2$ in fig3 did not fit well into the peaks, suggesting that there is no $SrCl_2$ educts present but Comparing the diffraction pattern with the hydrate of $SrCl_2$ it is clear that the products obtained contain $SrCl_2$ in its hydrate form (fig4). After heating this product the X-ray diffraction pattern were repeated as seen in fig 5-7, and the peaks from the hydrate were seen to have disappeared. But one can still see some peaks that can not be accounted for by any of the educts, suggesting a new compound have been produced.

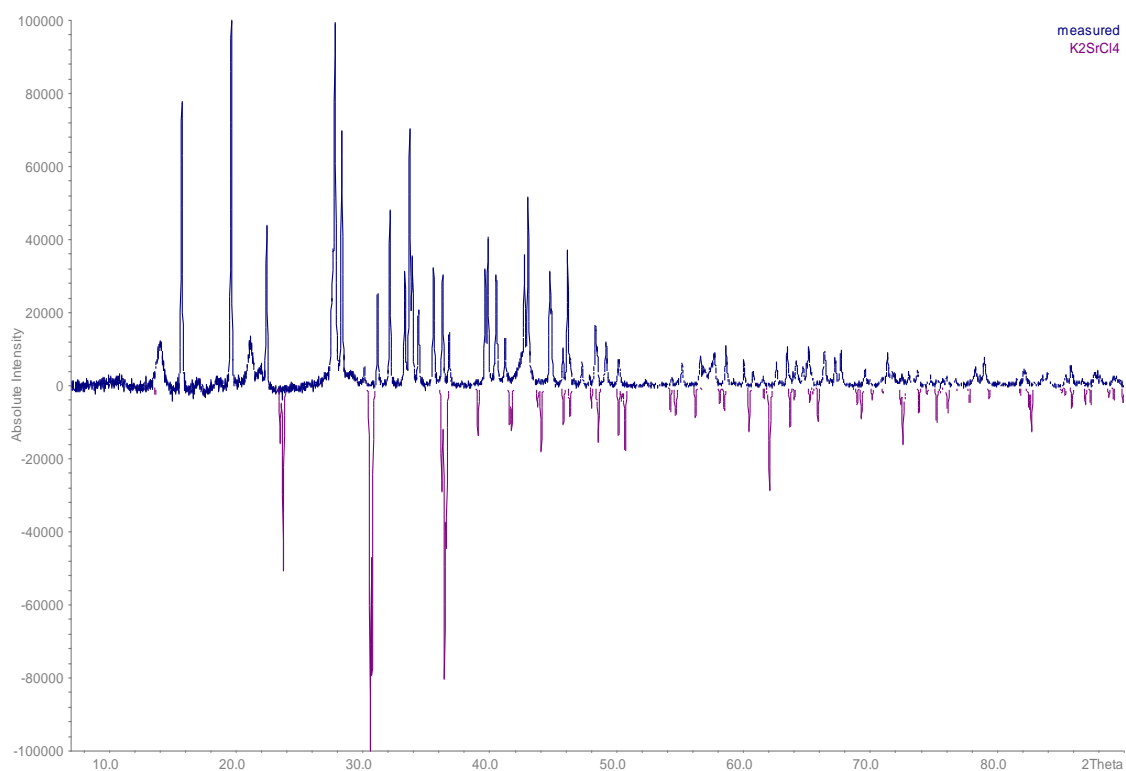


Figure 1 Measured powder diffraction pattern compared with K_2SrCl_4

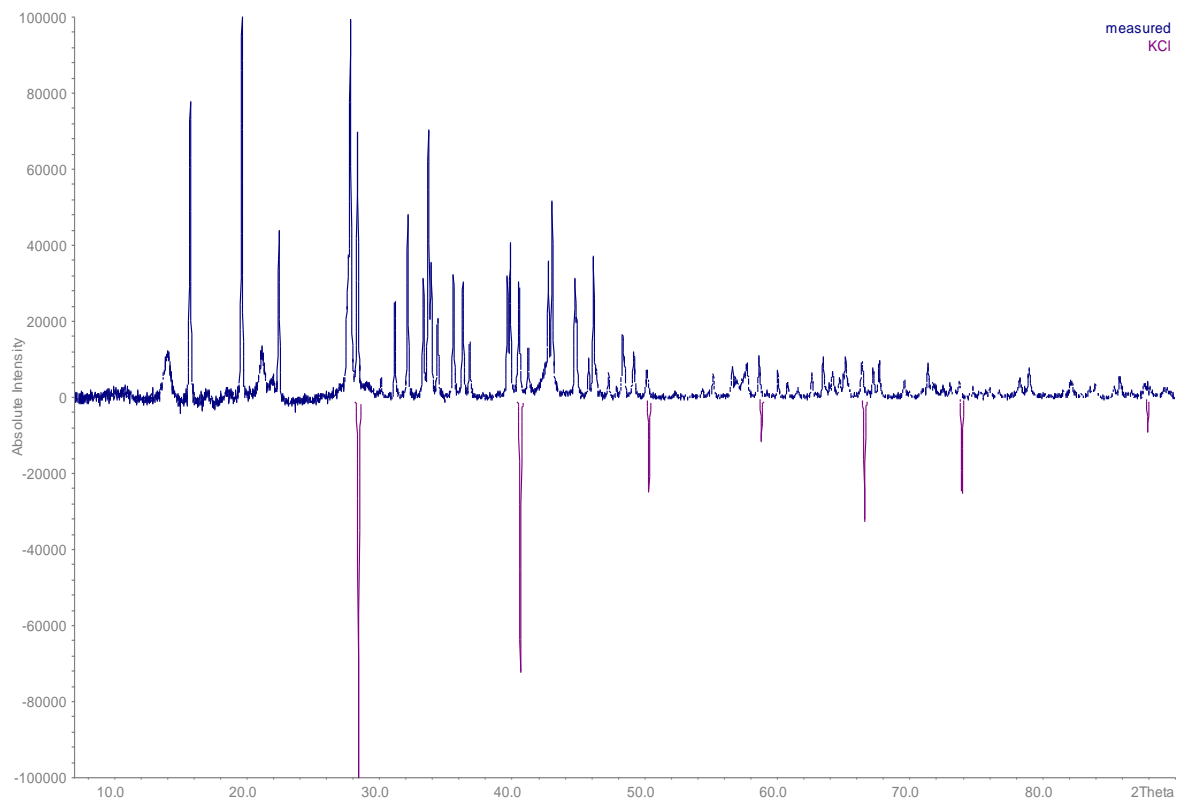


Figure 2 Measured powder diffraction pattern compared with KCl educts

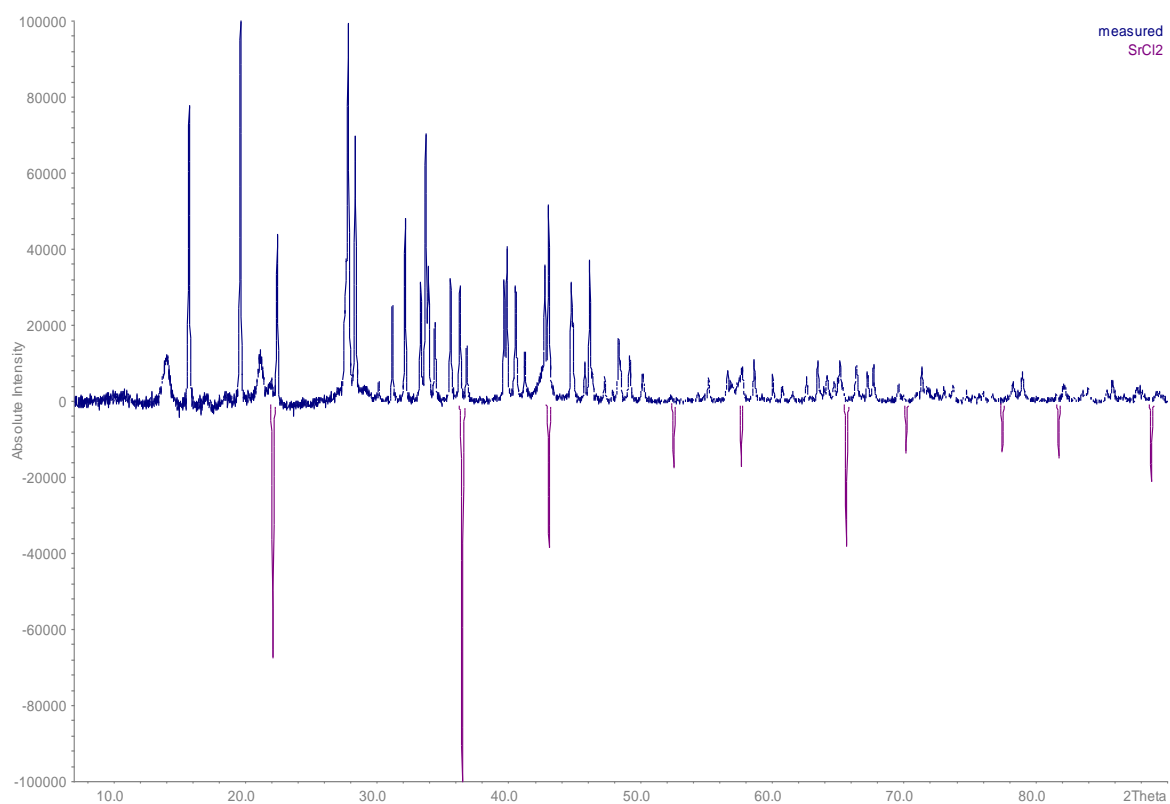


Figure 3 Measured powder diffraction pattern of product obtained compared with theoretical $SrCl_2$ educts

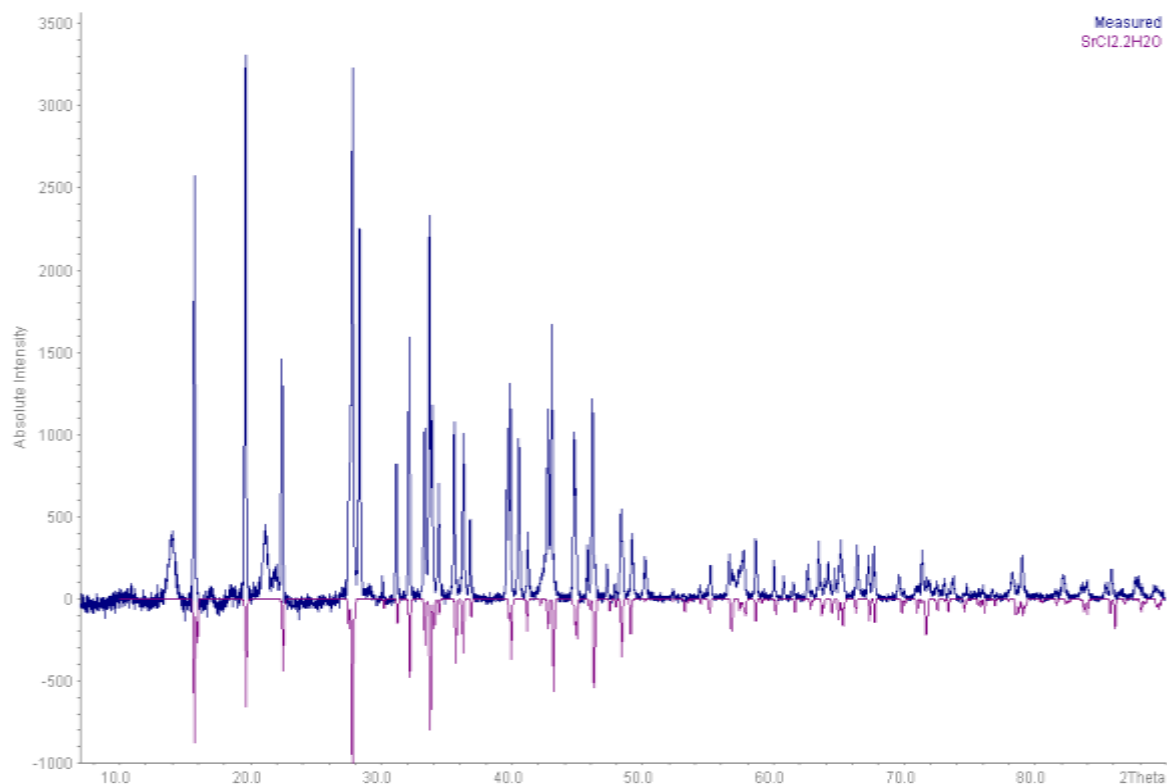


Fig 4 Measured powder diffraction pattern of product obtained compared with theoretical $SrCl_2 \cdot 2H_2O$.

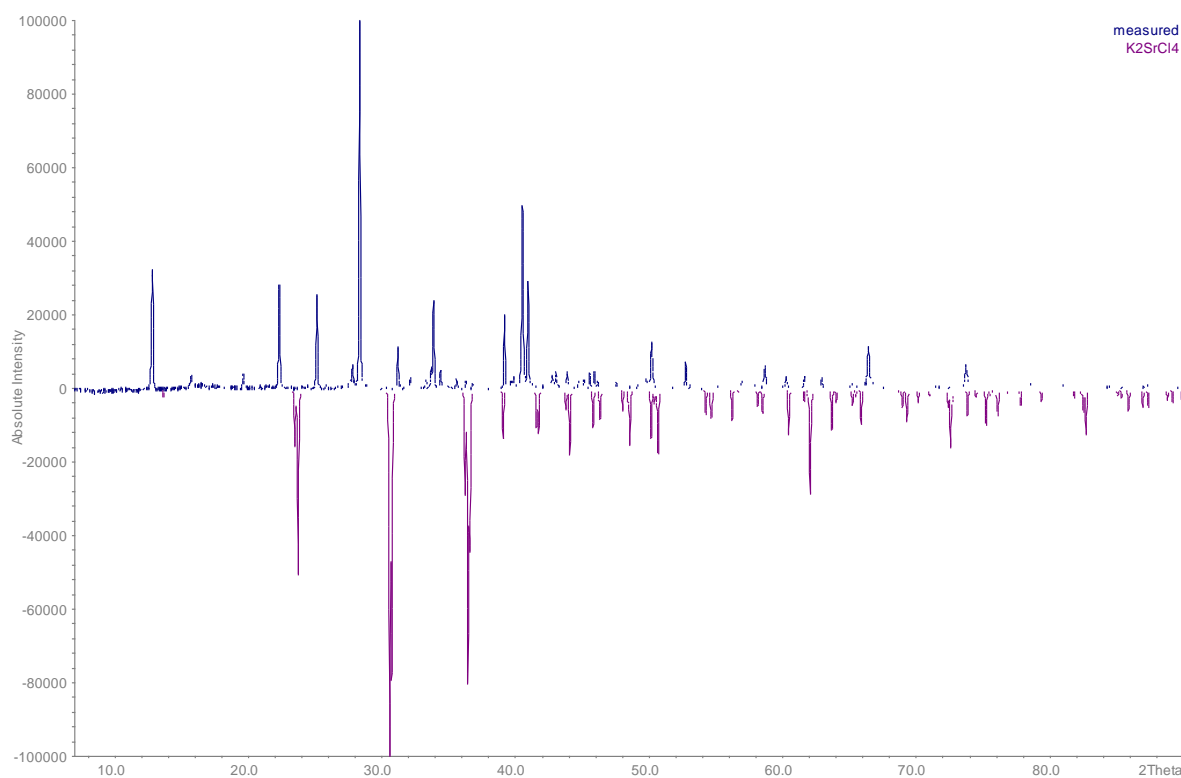


Figure 5 Powder pattern of product from reaction of $KCl + SrCl_2$ after heating to get rid of water. Above measured and below theoretical pattern for K_2SrCl_4 .

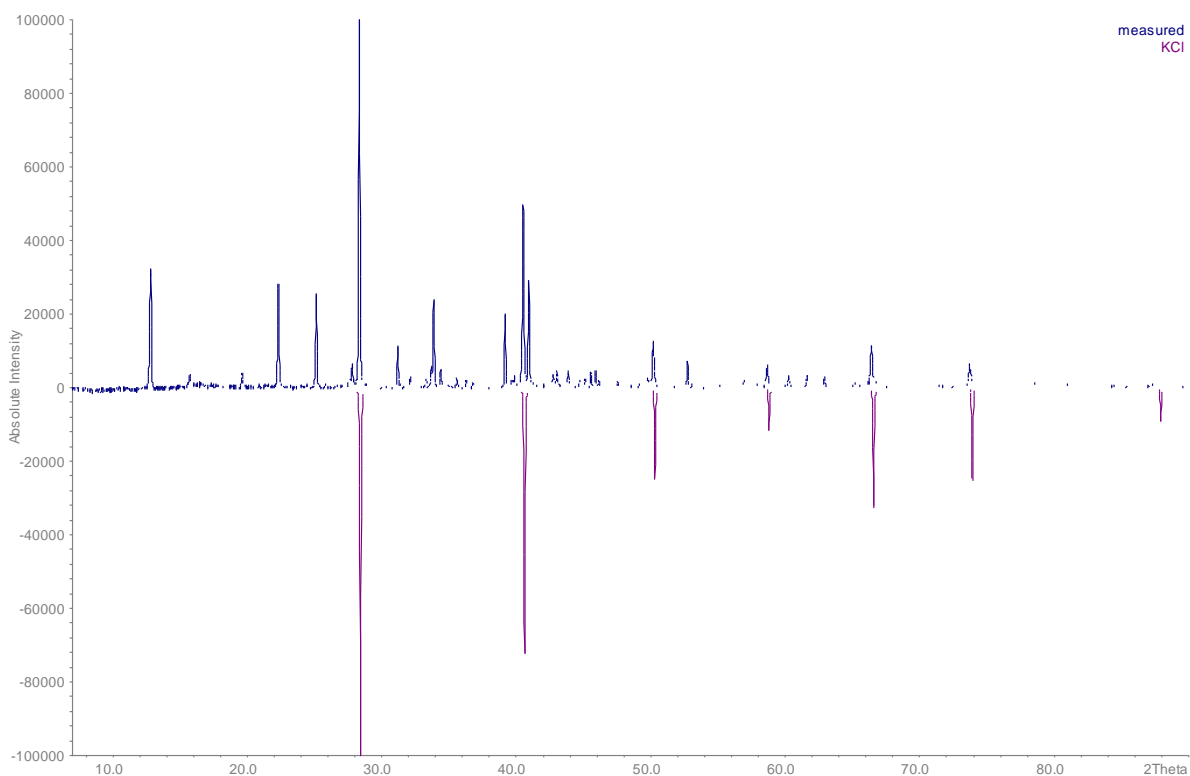


Figure 6 Powder pattern of product from reaction of $KCl + SrCl_2$ after heating to get rid of water. Above measured and below theoretical pattern for KCl .

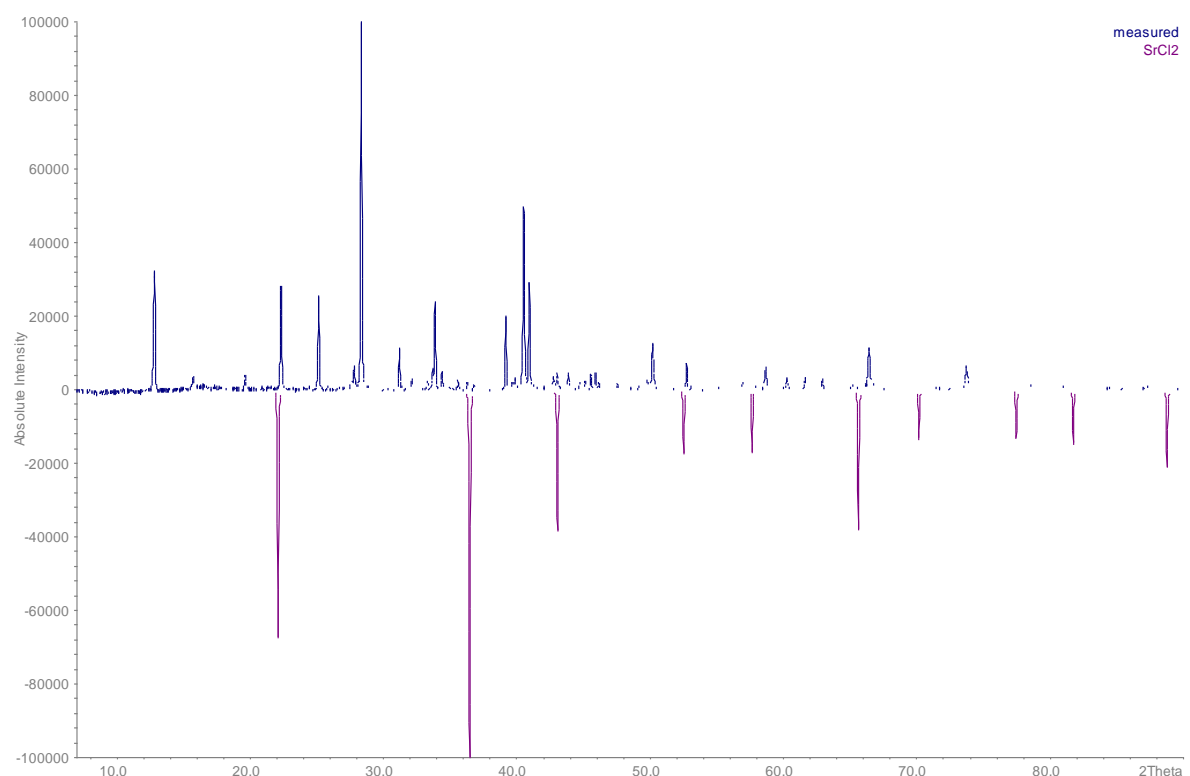


Figure 7 Powder pattern of product from reaction of $KCl + SrCl_2$ after heating to get rid of water. Above measured and below theoretical pattern for $SrCl_2$.

The powder pattern obtained from the other trials was similar to the ones given above in term of the the products obtained, which were always containing one of the educts.

3.2. Result from solid state reaction:-

The results of the 1:1 ratio reaction of RbCl and $SrCl_2$ showed the present of RbCl educts but $SrCl_2$ was absent as can be seen from the X-ray powder diffraction pattern in fig 7 and 8. Those peaks that did not fit into the RbCl can be seen to fit into the $RbSrCl_3$. One can conclude that the products obtained was a mixture of the expected ternary chlorides $RbSrCl_3$ and RbCl.

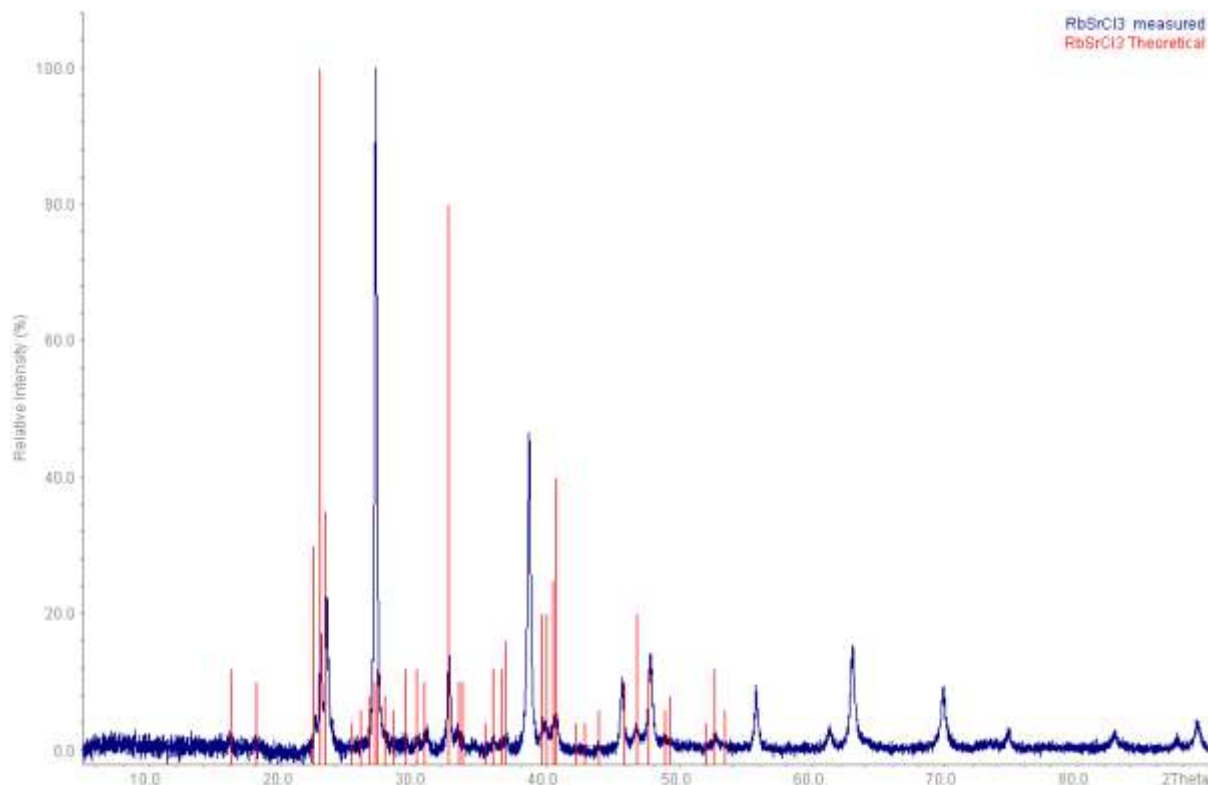


Figure 8 X-ray powder diffraction pattern of expected $RbSrCl_3$ compared with the theoretical pattern.

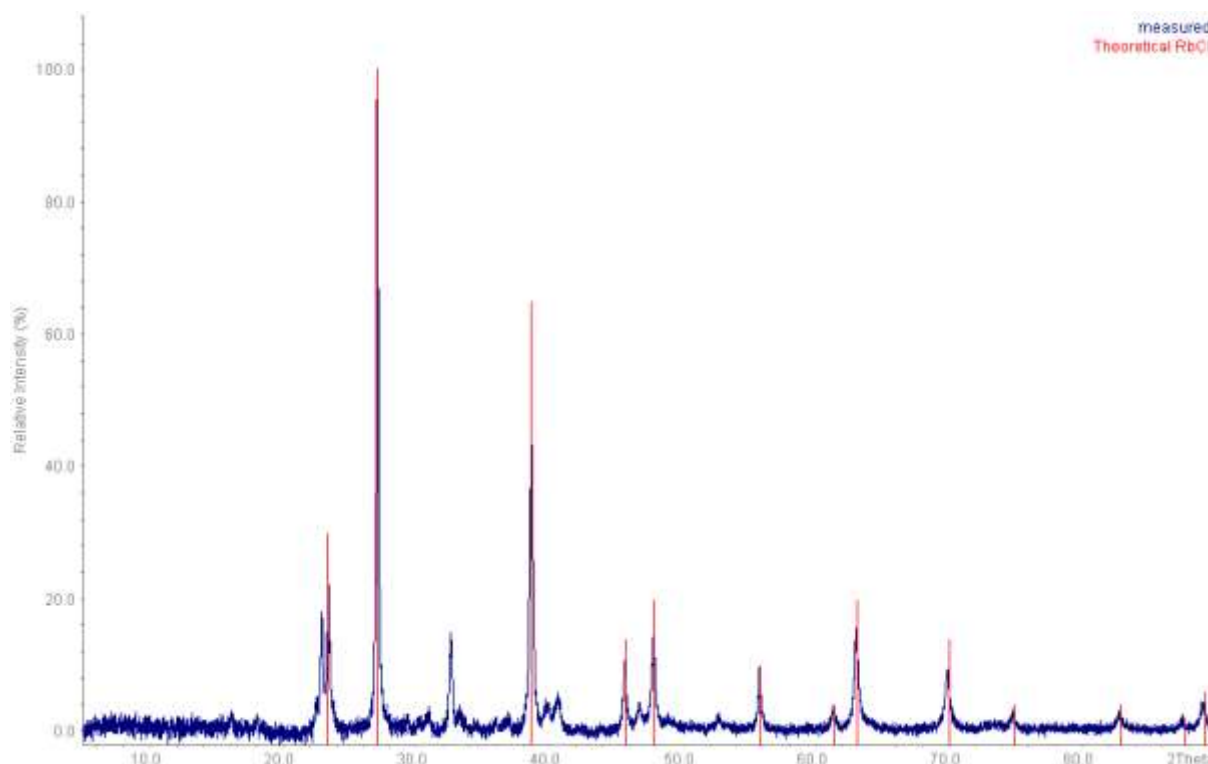


Figure 9 X-ray powder diffraction pattern of expected $RbSrCl_3$ compared with RbCl.

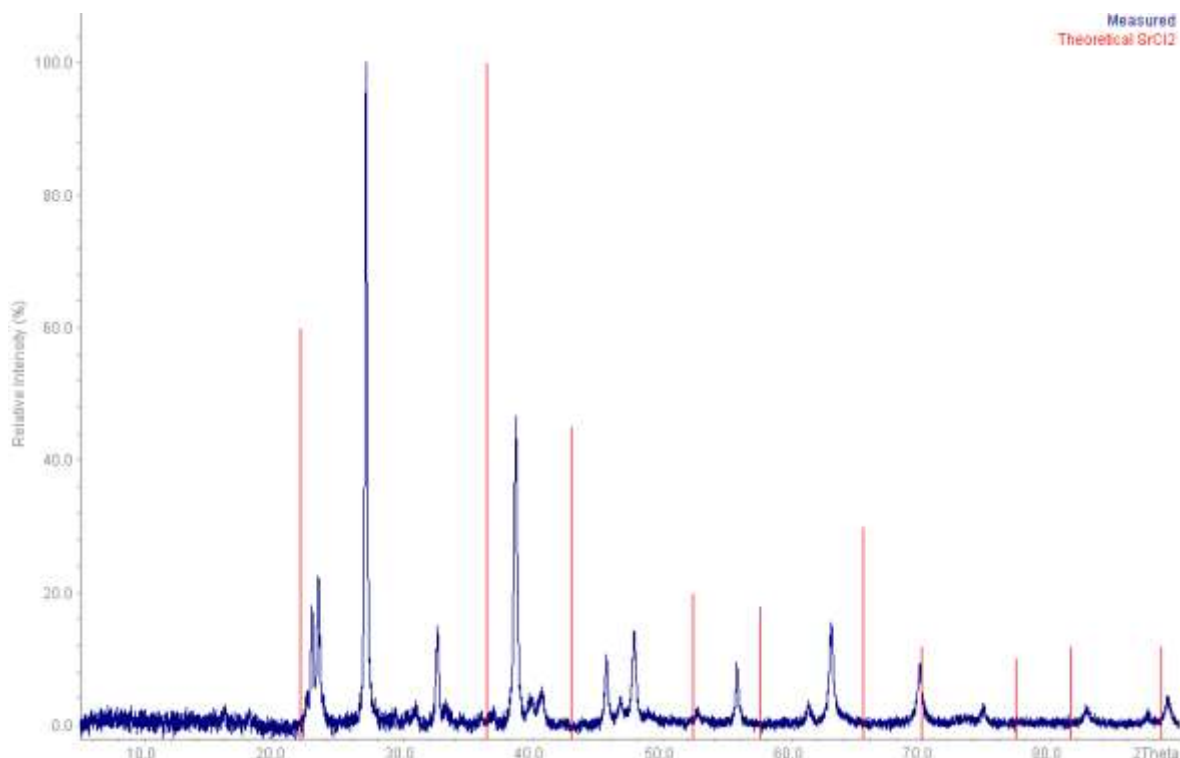


Figure 10 X-ray powder diffraction pattern of expected $RbSrCl_2$ compared with $SrCl_2$.

IV. Discussion

The preparation of these ternary chlorides were not successful in water solution, as can be seen from the products obtained, in most cases the educts were still seen in the final products. Gerd Meyer (Ref 1) used the third method to prepare Caesium Praseodymium Chloride and Potassium Dysprosium Chloride, but the same method proved difficult with divalent metals in this research. One may conclude that the stability of the monovalent and divalent in solution are higher than the ternary, hence the difficulty in prepare these ternaries using the same methods, but may not be the same with higher valent binaries. Some ternary Chlorides could be prepared conveniently from aqueous solutions, provided they are congruently soluble in those solvents (Zheng and Seifert). The nature of the higher valent metal seems to play a role here, Zheng and Seifert used the Lanthanides whose binary Chlorides are not as soluble and stable in water solution as the divalent metals. This may account for why the most of divalent ternary Chlorides already synthesised are either by using solid state reaction or hydrothermal methods. The two phases observed grew from the walls of the evaporating dish and their shape also could suggest good tendency for crystal growth, which could mean with proper choice of solvents these crystals, may be prepared by solution methods. The results of the solid state reaction showed most of the peaks as seen above fit the $RbCl$ educts with the exception of some few which may belong to some new unknown compound. The $SrCl_2$ theoretical pattern did not fit into the peaks, which means some kind of reaction has taken place, but not as expected.

V. Conclusion

It can be concluded here that the divalent metals are more stable in water solution in their binary form than in their ternary form which agrees with literature [XI1]. To grow good ternary chlorides crystals of these divalent metals may be water free solvent may offer a solution to this problem or hydrothermal method. In this work, no good and pure phase crystal was successfully prepared by these solution methods, to get these ternary chlorides, solid state reaction method was employed and only a mixture of the ternary and one of the educts was obtained. The conclusion of this research is that water free solvents should be tried for growing such ternary chlorides in solution for further research.

Acknowledgements

I acknowledge the staff of University of Siegen Inorganic Chemistry II working group under the leadership of Prof. Wickleder, for their contribution during this work, which was carried out in their laboratory.

Literature

- [1]. Flick. K. Ternäre chloride des Formeltypes A_2MCl_4 mit $A = K, Rb, Cs$ and $M = Eu, Ba, Pb$ als strukturverwandte des Th_3P_4 - Typs. Ein Beitrag zum problem kreis inkommensurabet modulierter structuren. Dissertation Universität Karlsruhe (1990), 1.161
- [2]. Kanno. R, Takeda. Y, Murata.K and Yamamoto. O. Crystal structure of double chlorides, Na_2mCl_4 ($m = Mg, Cr, Cd$) correlation with ionic conductivity. Solid state Ionics (1990), 39, 233-244
- [3]. Gerd Meyer – Ternary Chlorides and Bromides of the rare earth elements; Inorganic Synthesis (1983), 22, 1-10
- [4]. Seifert, H.J. Why do ternary compounds exist? Thermo analytical investigations on binary systems of metal Chlorides. Journal of Thermal Analysis (1988), 33(1), 147-55.
- [5]. Seifert, H.J. Stability of Ternary Chlorides in the system sodium Chloride/manganese dichloride. European journal of Solid and Inorganic Chemistry (1989), volume. Date 1988, 25(5.6), 463-70.
- [6]. Seifert, H.J., Kraeme.R. Ternary Chlorides in the systems $ACl/DyCl_3$ ($A=Cs, Rb, K$). Zeitschrift für Anorganische und Allgemeine Chemie(1994), 620(9), 2543-8.
- [7]. Seifert, H.J., Sandrock.J., Uebach.J. Thermo chemical and structural investigation on the systems $NaCl/TbCl_3$ and $NaCl/DyCl_3$.Int. Herald A oeye symp. (1995) 69-76
- [8]. Roffe. M and Seifert .H. J. Ternary chlorides in the systems $ACl/HoCl_3$ ($A = Cs, Rb, K$) Journal of Alloys and compounds (1997), 257(1 - 2), 128 - 133.
- [9]. Seifert .H.J Retarded solid state reactions III. Journal of Thermal Analysis (1997) 49(3), 1207 -1210.
- [10]. Zheng. Chagoui and Seifert. H.J Ternary chlorides in the system $ACl/TmCl_3$ ($A= Cs, Rb, K$) Jorunal of solid state chemistry (1998) 135(1) 127-131.
- [11]. Mccarthy, Lauffenburger, Skonezny and Ruhrer. Crystal structure of Dicesium Dichlorotetra-aquo chromium (III) chloride. Inorganic chemistry (1981), 20, 1566-1570.
- [12]. Ito. Hiroshi; Hasegawa. Yasuo and Ito Yasuhiko. Densities of Eutectic mixtures of molten Alkali chlorides below 673k. Journal of chemical Engineering Data (2001), 46(5), 1203 - 1205.