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SYNTHESIS OF CuCl

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ABSTRACT

The reaction of Cu metal with CCl₄ has been found to produce very pure and stoichiometric CuCl. CuCl prepared in this way is not photosensitive and does not exhibit the severe hygroscopicity of earlier preparations. Details of the synthesis and I.R. absorption measurements on the resultant CuCl are given. Preliminary experiments on the use of this reaction to produce other metal chlorides are also discussed.

Introduction

Cuprous chloride has sustained a high level of interest over the years because it exhibits a number of interesting properties. Recently, high pressure experiments that describe an a.c. magnetic susceptibility anomaly (1-3) have appeared in the literature. An excellent paper by Wilson (4) summarizes these experiments. CuCl has traditionally been prepared by solution of Cu metal in concentrated HCl, with the CuCl then being precipitated from this solution by diluting it with H_2O . This was followed by very careful drying and melting. At times this entire operation was carried out in a dark room and the final product was stored in a light tight dry box to protect it from photo-darkening and hygroscopicity. Other techniques required special apparatus to handle the Cl_2 gas which was reacted with Cu metal. In order to prepare ultra-pure and stoichiometric CuCl, which we hoped would result in reproducible physical measurements, we sought a method that would avoid the use of HCl and H₂O (5). Other experimenters attempted to remove H₂O and HCl by zone refining or vapor transport. We have felt that zone refining and/or vapor transport do not necessarily remove those impurities. Further, the use of those techniques, unless excess Cu metal is present, could result in disproportionation and non-stoichiometry of the resultant CuCl. The use of carbon tetrahalides to scavenge H₂O during

crystal growth of a number of metal halides has been reported extensively by R. C. Pastor, et al (6). Their method was to purify the prepared metal halides by pyrolysis with carbon tetrahalide during crystal growth of the desired halide.

Experimental

For the synthesis of CuCl, our approach was to use readily obtainable ultra-pure copper metal and carbon tetrachloride. The direct reaction of these components in a sealed and evacuated silica tube has only carbon as a by-product which can be kept mechanically separated from the resultant CuCl. Typically, very pure and stoichiometric CuCl was prepared in the following way. A 20% excess of Cu metal (\sim 1.5 gm) and a measured amount of CCl $_4$ (\sim 0.5 cc) for the reaction 4Cu + CCl₄ \rightarrow 4CuCl + C were contained in an evacuated and sealed silica tube (6 mm I.D. imes 8 mm O.D. imes \sim 10 cm long). The CCl₄ was frozen in liquid N₂ before sealing. It was found advantageous to insert a plug of pure SiO₂ wool about midway in the tube. This prevented the C that is, formed at the reaction end from falling into the CuCl. The prepared tube was placed in a temperature gradient furnace on a suitable support in such a way that the tube was inclined, at \sim 30°, with the Cu metal at the hot (455°C) and low end. After a reaction time of about 16 hours at this temperature, it is seen that solid CuCl has accumulated at the cool end; probably transported there during the reaction by residual CCl_4 vapor. While this product is colorless and transparent, we find that the reaction to CuCl is not quite complete. Two optical absorption bands have been observed in the infrared region, centered around 83 meV (670 cm⁻¹) and 125 meV (1010 cm⁻¹) [Fig. 1(a)]. The peak absorption coefficient is $\sim 5 \text{ cm}^{-1}$. We do not give any microscopic reason for these two bands, but it is possible that this is a result of C-Cl bonding in the CuCl matrix. The tube inclination is now inverted, with the Cu metal at the high and hot end and the temperature is raised to 650-700°C. After \sim 16 hours at this temperature, it is seen that CuCl has collected as a red, transparent liquid at the cooler end. Carbon accumulates mainly on the Cu metal at the hot end where reaction has taken place. Furnace power is shut off and the CuCl allowed to crystallize. The temperature gradient of the furnace, and its uncontrolled cooling rate, appeared to be adequate to produce (essentially) water clear, colorless single crystals.

An infrared absorption spectrum of such a sample is given in Fig. 1(b). As in 1(a), the phonon and multiphonon absorption dominates the spectrum of lowest energies. (The sample in 1(b) is \sim 7 times as thick as in 1(a), therefore the cutoff appears at higher photon energy.) As clear evidence for the purity of CuCl grown by this process, the transmitted light intensity is only limited by the reflection losses at the surface. Given the thickness of the sample, we can rule out any impurity absorption exceeding an absorption coefficient K of \sim 0.1 cm⁻¹. On the high energy end, not shown here, the fundamental absorption across the band gap sets in around 3 eV, increasing exponentially with energy from K = 1.5×10^{-2} cm⁻¹ at 3.00 eV.



FIG. 1 Optical density in the infrared region of two samples of CuCl reacted from Cu+CCl₄ at different temperatures.

The well-known photo-sensitivity of CuCl does not appear in our material. Samples left under a fluorescent light for months showed no discoloration at all. Further, the hygroscopic nature of CuCl prepared by traditional techniques is dramatically reduced. We did not find it necessary to take any precautions against moisture during the physical measurements. Finally, we find the stoichiometry of our pure CuCl, after a total Cu analysis of two samples, to be an average $Cu_{1.0007}Cl_{0.9993}$. The total quantitative analysis for Cu was done by dissolving the samples and weighing the Cu after electro-deposition from the solution. The solution was then analyzed for remaining Cu by atomic absorption spectrometry.

We have produced other metal chlorides in this way. NiCl₂, FeCl₂, AgCl and EuCl₂ were prepared with reaction temperatures adjusted depending on the reactivity of the specific metal with CCl₄, and the vapor pressure or melting point of the chloride produced. In the case of $EuCl_2$ we find that Eu metal reacts with CCl_4 at low temperature (near room temperature) to produce EuC_2 . Clearly, one must use sufficient Eu metal to first complete the carbide reaction and have an excess remaining to produce $EuCl_2$.

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