Statham[5] investigated complexes of the types shown in Fig. 4.

They were unable to secure any evidence for the two predicted geometrical isomers. On the other hand, racemates containing coördinated sulfur[6] and coördinated nitrogen[7] as the centers of asymmetry have been proven to exist.

Certain conjectures about the relative coördinating power of tertiary nitrogen, chloride and carboxylate oxygen atoms toward palladium(II) and platinum(II) may be derived from the methods required for the preparation of the complexes of bidentate and tetradentate EDTA. The formation of two metal–nitrogen bonds in the initial reaction of EDTA with the anions $[MCl_4]^=$ implies that the strength of the metal–nitrogen bonds is comparable to that of the metal–chlorine bonds. The failure of the two free carboxylate groups to displace the remaining chloride groups, despite the increased stability expected from the formation of two additional chelate rings, is interpreted as meaning that chloride attaches itself more firmly to these metal ions than does oxygen. The introduction of an external driving force (removal of chloride with silver ion) allows the oxygen atoms to coördinate to the metal. This interpretation is in accord with the observations of others.[8]

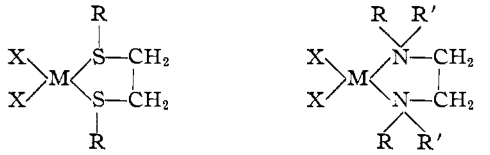

Fig. 4.—(M = Pt^{II} or Hg^{II}).

Acknowledgment.—The authors wish to express their gratitude to the Bersworth Chemical Company whose financial support made this work possible.

---

(5) G. M. Bennett, A. N. Mosses and F. S. Statham, *J. Chem. Soc.*, 1668 (1930).

(6) F. G. Mann, *ibid.*, 1745 (1930).

(7) J. R. Kuebler, Jr., and J. C. Bailar, Jr., This Journal, **74**, 3535 (1952).

(8) N. V. Sidgwick, *J. Chem. Soc.*, 433 (1941).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE WATSON LABORATORY OF INTERNATIONAL BUSINESS MACHINES]

Preparation of Pure Potassium Metaniobate

BY ARNOLD REISMAN, FREDERIC HOLTZBERG, SOL TRIEBWASSER AND MELVIN BERKENBLIT

RECEIVED OCTOBER 7, 1955

Potassium metaniobate has been prepared in laboratory quantities by two procedures. The first method involves the fusion of potassium carbonate with niobium pentoxide and yields large polycrystalline aggregates exhibiting a slight degree of reduction. After leaching and grinding, a product of greater than 99.9% purity is obtained. Digesting the powder derived from the first process, in a flux of potassium carbonate, yields very finely crystallized, non-reduced, strain-free potassium metaniobate after water extraction. A rapid quantitative method for assaying the Nb_2O_5 content of potassium metaniobate has also been described

Introduction

Several compounds of the perovskite type are exceedingly interesting because of their ferroelectric properties. Potassium metaniobate was first characterized as a ferroelectric by Matthias, *et al.*,[1] who found a curie transition at 425° and a phase transformation at 215°. In order to complete a study of dielectric properties correlated with X-ray diffraction measurements it was felt desirable to obtain the pure material in a non-reduced strain-free state. Laboratory quantities of the *meta* salt were needed for crystal growing and the preparation of ceramics.

Starting with reagent grade Nb_2O_5 one would expect that the usual difficulties encountered in niobium analysis, could be circumvented, since one would not be faced with the problem of separating the compound from tantalum. It was expected, therefore, that a straightforward rapid analytical scheme could be devised to establish the purity of $KNbO_3$.

Joly[2] first reported the preparation of potassium metaniobate in 1877. The method was based on the fusion of stoichiometric quantities of K_2CO_3 and Nb_2O_5 with an unspecified amount of CaF_2 as a flux. All attempts to reproduce his experiments in this Laboratory have proved unsuccessful. More recently Matthias,[3] Vousden[4] and others[5,6] have prepared $KNbO_3$ by fusion of either KOH or K_2CO_3 with Nb_2O_5, in the absence of a flux. These procedures were successful in producing a few small crystals for X-ray studies and dielectric measurements, but were not readily adaptable to the preparation of laboratory quantities of the pure niobate, because the range of compositions and the methods of purification were not clearly defined.

A recent phase equilibrium study[7] of the system K_2CO_3–Nb_2O_5 indicates that $KNbO_3$ (I) can be contaminated by $2K_2O{\cdot}3Nb_2O_5$ (II) or $3K_2O{\cdot}Nb_2O_5$ (III), depending on the mole ratios of the original reactants. Separation of I from II could not be effected because of their similar solubilities. Fusion of stoichiometric quantities of K_2CO_3 with Nb_2O_5 often showed the presence of II in the reaction mixtures. It is evident from the phase diagram that any volatilization of K_2CO_3 or K_2O during the reaction would result in the appearance of II.

Uncertainty exists concerning the state in which

---

(1) B. T. Matthias, E. A. Wood and A. N. Holden, *Phys. Rev.*, **76**, 175 (1949).

(2) A. Joly, *Ann. Sc. de l'Ecole norm.*, **16**, #2, 25 (1877).

(3) B. T. Matthias, *Phys. Rev.*, **75**, 1771 (1949).

(4) P. Vousden, *Acta Cryst.*, **4**, 373 (1951).

(5) E. A. Wood, *ibid.*, **4**, 353 (1951).

(6) A. V. Lapitskii, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 379 (1952).

(7) A. Reisman and F. Holtzberg, This Journal, **77**, 2115 (1955).

II is present at room temperature,[8] but its product or products are soluble and relatively stable in cold aqueous solution. In boiling water there is appreciable decomposition with liberation of hydrated Nb_2O_5 which contaminates the insoluble potassium metaniobate. Fortunately, a means of separating I from the hydrated Nb_2O_5 was found, which depends upon the stability of the water-soluble fraction in a dilute solution of potassium carbonate (*p*H 11.5) even after prolonged boiling.

Experimental Procedure

The niobium pentoxide used in these experiments was purchased from the Fansteel Metallurgical Company, and was reported to contain a maximum of 0.2% Ta_2O_5 as the major contaminant. Analysis of the oxide by the Tannin fractional precipitation technique showed no detectable trace of tantalum. Mallinckrodt analytical grade potassium carbonate dried at 300° for one hour to remove moisture was used to supply the K_2O in the reaction mixtures.

Preparation of Potassium Niobate Powder.—Charges containing 50.05–50.2 mole % K_2CO_3 were weighed in platinum crucibles with the Nb_2O_5 at the bottom. The reaction mixtures were placed in a furnace at 800° and the furnace temperature increased to 1075° at 5°/min. After soaking for one hour to allow for the complete evolution of CO_2 the temperature was lowered to 840° at 2°/min. and then to room temperature at 10°/min. The potassium metaniobate obtained by this procedure is polycrystalline and exhibits a color range from yellow to pale blue. The blue color has been attributed to a slight reduction of the niobate.[7] The contents of the crucible were tapped out, crushed sufficiently to pass a number 8 sieve, and leached twice for one hour in hot 2% potassium carbonate solution using 400 ml. of solution for 75 g. of charge. The leached niobate was washed five times with 250 ml. of boiling water, dried and ground in a mullite mortar.

Preparation of Crystalline Potassium Niobate.—Sufficient potassium carbonate was added to the niobate powder obtained by the first procedure to produce a melt containing 57.5 mole % K_2CO_3. The charges were heated to 960° at 10°/min., a temperature approximately 20° below the liquidus.[7] Soaking for 20 hours at this temperature was found adequate to obtain equilibrium. The temperature was lowered at 1°/min. allowing two-hour annealing periods at each of the transition points. The contents of the crucible were purified as previously described except that no mechanical grinding was employed. Pale yellow, transparent crystals of the niobate were obtained ranging in size from 40 to less than 400 mesh, the size range depending within limits on the length of digestion time.

Strain in crystalline materials results in a broadening of the X-ray diffraction maxima. In most cases the strain can be removed by proper annealing techniques. With ferroelectric materials the problem is further complicated by the twinning associated with the domain structure. Microscopic examination with polarized light, of the finely crystalline metaniobate, showed the individual crystallites to be predominantly single domain. It has been found that grinding produces a multidomain structure which cannot be readily removed by annealing.

Samples of (a) crystalline $KNbO_3$, (b) ground crystalline $KNbO_3$, (c) powdered $KNbO_3$ and (d) annealed powdered $KNbO_3$ were examined with X-rays using a G.E. X R D 3 diffractometer and Cu Kα radiation. The pattern obtained with (a) showed clearly resolved maxima while all of the others gave poor diffraction patterns. Lattice constants obtained with (a) were found to agree with the more recent literature values for $KNbO_3$ at room temperature.[11,12]

Analysis of Potassium Niobates.—By fusing any of the water-insoluble potassium niobates with sufficient potassium carbonate to give a melt composition of greater than 75 mole % K_2O, a completely water-soluble reaction mixture is obtained. Furthermore if enough carbonate is employed to raise its composition to 90 mole % or more, the water-soluble mixture will be stable even when hot, because of the presence of sufficient excess carbonate. Addition of concentrated NH_4OH (15 *M*), to the solution, followed by addition of concentrated HCl (12 *M*), results in quantitative flocculation of $Nb_2O_5 \cdot x(H_2O)$ which can be readily filtered and washed.

0.2–0.4 gram of dry niobate is weighed in a 15-cc. gold crucible. Ten times this weight of potassium carbonate is placed over the niobate and the charge is heated with a hand torch until a clear melt results. The contents of the crucible are swirled during cooling in order to produce a thin layer of solid which is readily dissolved. The contents are brought into solution with 100 ml. of hot distilled water. At this point a slight turbidity may be present, but this will not affect the analysis. The volume of the solution is brought up to 200 ml. and 50 ml. of NH_4OH is added with stirring. A watch glass is placed over the beaker and 50 ml. of HCl is added through the lip by means of a pipet in order to prevent splattering as CO_2 is liberated. The beaker and contents are placed on a hot plate for a few minutes and, after CO_2 evolution has ceased, the watch glass and walls of the beaker are washed down. The flocculent, white precipitate is allowed to digest on the hot plate for 20 minutes at boiling temperatures. In order to avoid bumping of the contents, the mixture should be stirred prior to digesting. The precipitate is then filtered through Whatman 41H filter paper using a vacuum filtrator. Filtration is greatly aided by placing a few small pieces of 41H paper in the apex of the filter cone. Filter pulp was not found to be as satisfactory. The precipitate is washed with 800 ml. of boiling water delivered by a wash bottle, care being taken to break up the precipitate with the stream of wash water. The paper and precipitate are transferred to a previously ignited and weighed porcelain crucible, and heated over a bunsen burner until charring of the paper is complete. The crucible and contents are then ignited at 1000° for one hour and the precipitate is weighed as Nb_2O_5.

In order to check the validity of the method, Nb_2O_5 was used as a control and analysis data for the Nb_2O_5, crystalline and powdered $KNbO_3$ showed reproducibility to be better than 2 pts./1000. Both the fine crystals, and powdered niobate gave an Nb_2O_5 analysis of 99.9% of theoretical.

New York, N. Y.

---

[8] The actual compound with which I is in equilibrium at room temperature is uncertain. It has been shown to be in equilibrium with $3K_2O \cdot Nb_2O_5$[7] in solid liquid equilibria, but either undergoes a phase transformation or decomposition below the eutectic. Schoeller[9] has reported that the compound $4K_2O \cdot 3Nb_2O_5$ is present at room temperature, and de Marignac[10] has reported that in water solution $4K_2O \cdot 3Nb_2O_5 \cdot 16H_2O$ is present.

[9] W. R. Schoeller, "The Analytical Chem. of Tantalum and Niobium," Chap. 2, Chapman & Hall, Ltd., London, 1937.

[10] J. C. de Marignac, *Ann. Chim. Phys.*, **8**, 20 (1866).

[11] P. Vousden, *Acta Cryst.*, **4**, 375 (1951).

[12] G. Shirane, R. Newnham and R. Pepinsky, *Phys. Rev.*, **96**, 581 (1954).