A Method for the Preparation of Potassium Hexafluorovanadate(III) and Its Polymorphic Transitions

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In order to determine the best conditions for the preparation of potassium hexafluorovanadate(III), the reaction of V_2O_3 with KHF_2 was studied by means of thermogravimetric analysis, differential thermal analysis, and X-ray diffraction analysis. The reaction begins at about 225 °C and terminates at about 300 °C, and the decomposition of excess KHF_2 terminates at from 300 to 450 °C, depending on the amount of the mixture of V_2O_3 and KHF_2. Potassium hexafluorovanadate(III) is stable in air up to about 300 °C and is oxidized at temperatures higher than 300 °C. Potassium hexafluorovanadate(III) has four polymorphic forms, and the transition points are 158, 200, and 218 °C. The transition from δ to γ or from γ to β on cooling is hindered by adding a small amount of sodium ion.

Previously we measured the freezing points of the KCl–VF_3, $NaCl$–VF_3, KCl–$NaCl$(equimolar)–VF_3, KCl–KF–K_3VF_6, $NaCl$–NaF–Na_3VF_6, KF–NaF–K_2NaVF_6, and KCl–$NaCl$–K_2NaVF_6 systems and pointed out that compositions in the vicinity of the minimum melting point of the KCl–$NaCl$–K_2NaVF_6 system are suitable as an electrolyte for the electrorefining or electroextraction of vanadium.[1,2] Most regions of the KCl–$NaCl$–K_2NaVF_6 system, shown by hatching in Fig. 1b, can be prepared by the use of K_3VF_6, which can be more easily prepared than K_2NaVF_6. Several methods for the preparation of K_3VF_6 have been reported by several groups of workers,[3–5] but none of these methods are practicable from the viewpoint of cost. In a previous paper,[6] we reported that $(NH_4)_3VF_6$ can be prepared by fusing a mixture of V_2O_3 and NH_4HF_2 in an inert atmosphere. By analogy with this preparation of $(NH_4)_3VF_6$, K_3VF_6 may be expected to be prepared by fusing a mixture of V_2O_3 and KHF_2. This work was undertaken to determine the conditions for the preparation of K_3VF_6 from V_2O_3 and KHF_2, and also to examine the polymorphic transition of K_3VF_6.

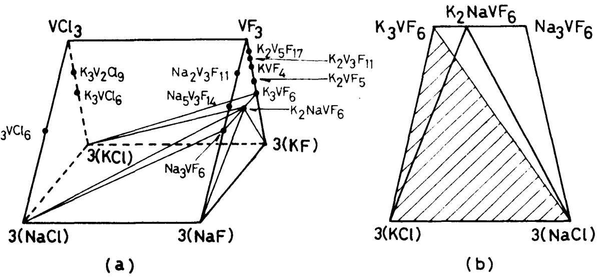

Fig. 1. (a) KCl–$NaCl$–VCl_3–KF–NaF–VF_3 system and (b) KCl–$NaCl$–K_3VF_6–Na_3VF_6 cross section.

Experimental

The vanadium(III) oxide used was prepared by the hydrogen reduction of V_2O_5 of a special reagent grade at 800—900 °C for 3 h. The potassium hydrogenfluoride and lithium fluoride used were of a special reagent grade, while the sodium hydrogenfluoride was reagent-grade. X-Ray diffraction patterns at elevated temperatures were taken with an X-ray diffractometer, Rigaku Denki Model SG-7, equipped with a high-temperature attachment, with a Ni-filtered Cu*Kα* radiation. The diffraction angles were corrected by using the diffraction angles of silicon. The differential thermal analysis curves were taken with an apparatus constructed in our laboratory by using 10 mg of a sample at a heating rate of 5 °C/min. The thermocouple used was calibrated by the transition temperatures of KNO_3(129 °C) and $KClO_4$(299 °C). The thermogravimetric analysis curves were taken with a microthermobalance, Shimadzu Model TG-20, by using 10 mg of a sample and at a heating rate of 5 °C/min.

Results and Discussion

X-Ray Diffraction Analysis. A mixture (2.5844 g) of V_2O_3 and KHF_2 in a molar ratio of 1 : 8 was placed in a platinum boat and heated at a given temperature for 30 min in a stream of argon (20 ml/min). Figure 2 shows a schematic diagram of the apparatus used for this experiment. The reaction product was identified by X-ray diffraction analysis at room temperature. Potassium hexafluorovanadate(III) was identified on the basis of the set of interplanar spacings for the low-temperature form of K_3VF_6 reported by Cretenet.[7] Table 1 shows the compounds identified in the product. The reaction of V_2O_3 with KHF_2 began at 225 °C and was completely terminated at 300 °C. The decomposition of the excess KHF_2 was almost terminated at 400 °C and completely terminated at 450 °C. As is shown in Table 1, $KF \cdot 2H_2O$ was detected in the products. The thermogravimetric study of $KF \cdot 2H_2O$ showed that $KF \cdot 2H_2O$ released the water of crystallization at 200—300 °C and that the residue was KF. Therefore, the $KF \cdot 2H_2O$ detected in the products is considered to have been formed while the substance

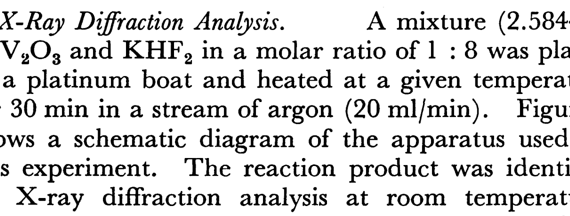

Fig. 2. Schematic diagram of the apparatus used for the preparation of K_3VF_6.
1. Nickel reaction tube, 2. platinum boat, 3. inlet of argon, 4. vinyl chloride tube, 5. copper cooling tube, 6. furnace, 7. outlet of argon.

was standing at room temperature by the reaction of KF with the moisture in air.

Differential Thermal Analysis. The differential thermal analysis curve for the reaction of V_2O_3 with KHF_2 is shown in Fig. 3. For comparison, the differential thermal analysis curve for the decomposition of KHF_2 is also shown in Fig. 3. Peaks a and b correspond to the transition(194 °C) and melting (225 °C) of KHF_2. Peak c is judged to correspond to the begining of the reaction of V_2O_3 with KHF_2 on the basis of the fact that the reaction of V_2O_3 with KHF_2 was observed with the naked eye to begin immediately after the melting of KHF_2, and the fact that K_3VF_6 was identified in the product obtained at 225 °C, as is shown in Table 1.

Thermogravimetric Analysis. The thermogravimetric analysis curve for the reaction of V_2O_3 with KHF_2 is shown in Fig. 4. For comparison, the thermogravimetric analysis curve for the decomposition of KHF_2 is also shown in Fig. 4. In curve a, the weight loss began at about 200 °C and terminated at about 300 °C; in curve b, while the weight loss also began at about 200 °C, it terminated at about 340 °C. The temperature at which the decomposition of excess KHF_2 terminated differs in Table 1 and Fig. 4. This can be ascribed to the difference in the weight of the samples used. The weight loss in the vicinity of 200 °C is considered to be due to the vaporization of HF from solid KHF_2, because the reaction of V_2O_3 with KHF_2 begins at about 225 °C.

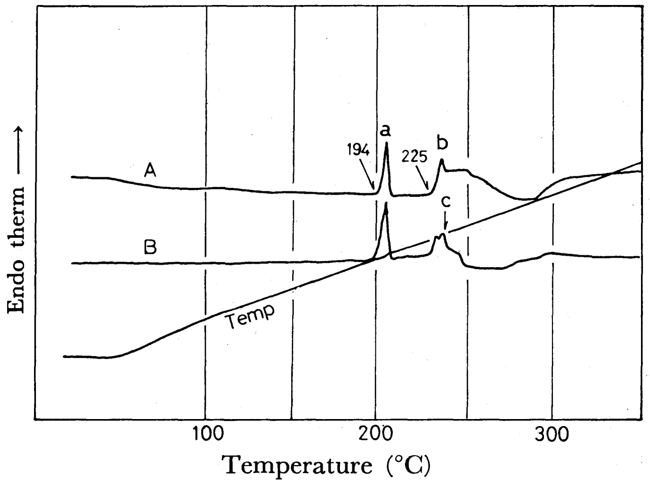

Fig. 3. DTA curves.
Curve A: KHF_2, curve B: a mixture of V_2O_3 and KHF_2 in a molar ratio of 1 : 8.

TABLE 1. RELATIONSHIP BETWEEN REACTION TEMPERATURE AND COMPOUNDS IN THE REACTION PRODUCT

Temperature (°C)	Compounds detected by X-ray diffraction analysis at room temperature
150	V_2O_3, KHF_2
200	V_2O_3, KHF_2
225	V_2O_3, KHF_2, K_3VF_6
250	V_2O_3, KHF_2, K_3VF_6
300	KHF_2, K_3VF_6, $KF\cdot 2H_2O$, KF
350	KHF_2, K_3VF_6, $KF\cdot 2H_2O$, KF
400	KHF_2, K_3VF_6, $KF\cdot 2H_2O$, KF
450	K_3VF_6, $KF\cdot 2H_2O$, KF
500	K_3VF_6, $KF\cdot 2H_2O$, KF
600	K_3VF_6, $KF\cdot 2H_2O$, KF

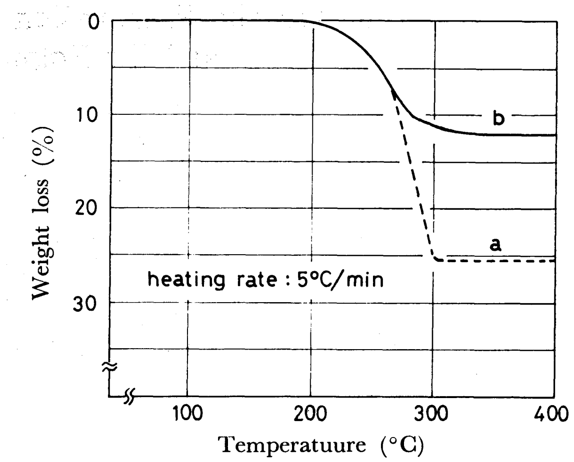

Fig. 4. TG curves.
Curve a: KHF_2, curve b: a mixture of V_2O_3 and KHF_2 in a molar ratio of 1 : 8.

From the results of the X-ray diffraction analysis, differential thermal analysis, and thermogravimetric analysis, it was found that the reaction of V_2O_3 with KHF_2 begins at about 225 °C and terminates at about 300 °C, and that the decomposition of excess KHF_2 terminates at 300—450 °C, depending on the weight of the mixture of V_2O_3 and KHF_2.

Molar Ratio of V_2O_3 to KHF_2. Since a part of the KHF_2 in a mixture decomposes without reacting with V_2O_3, an excess of KHF_2 is necessary for preparing

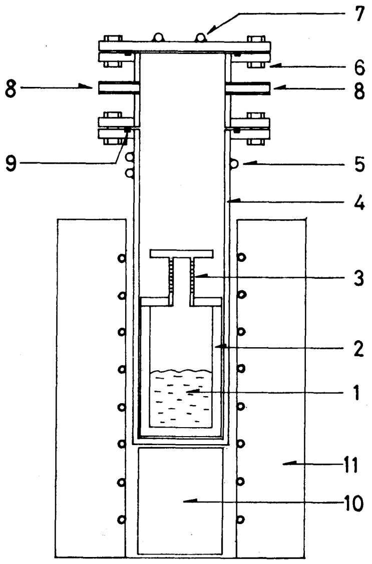

Fig. 5. Schematic diagram of the apparatus used for the preparation of K_3VF_6.
1: Mixture(about 300 g) of V_2O_3 and KHF_2, 2: graphite crucible(72 mm in inside diameter and 160 mm in height), 3: perforated lid, 4: stainless steel vessel, 5: copper cooling tube, 6: bolt and nut, 7: copper cooling tube, 8: inlet and outlet of argon, 9: O-ring.

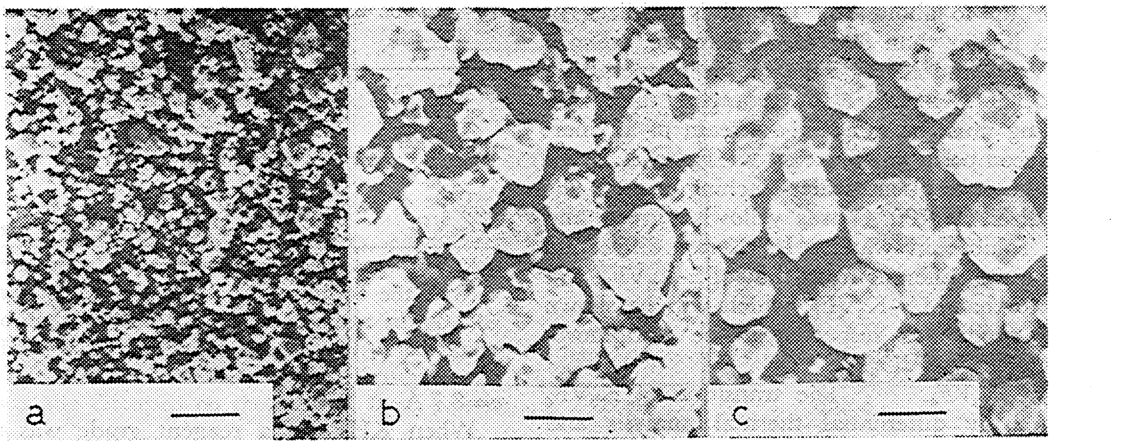

Fig. 6. Scanning electron micrographs of K_3VF_6. The bars represent 10 μm.
a: $V_2O_3/KHF_2=1/7$, b: $V_2O_3/KHF_2=1/8$, c: $V_2O_3/KHF_2=1/12$.

K_3VF_6 free from V_2O_3. In order to determine the lower limit of the excess of KHF_2, a 300-gram portion each of mixtures in the molar ratios 1 : 6, 1 : 6.5, 1 : 7, 1 : 8, 1 : 9, 1 : 10, 1 : 11, and 1 : 12 was heated at 600 °C in a stream of argon(200 ml/min) with the apparatus shown in Fig. 5. After having been cooled, the reaction products were leached with water, and the residue was examined with the naked eye and also analysed by an X-ray diffraction technique. Vanadium(III) oxide is black or brown, while the color of K_3VF_6 is bright green. When a reaction product was leached with water, the remaining V_2O_3 particles, if any, could be well discriminated from the K_3VF_6 in water with the naked eye. The mixtures in the molar ratios of 1 : 6 and 1 : 6.5 gave K_3VF_6 contaminated with V_2O_3, but those in the molar ratios of 1 : 7—1 : 12 gave K_3VF_6 free from V_2O_3. Figure 6 shows the scanning-electron micrographs of K_3VF_6 prepared from the mixtures of V_2O_3 and KHF_2 in the molar ratios of 1 : 7, 1 : 8, and 1 : 12. As is shown in Fig. 6, the crystals of K_3VF_6 were fine at the molar ratios of 1 : 6—1 : 7 and coarse at 1 : 8—1 : 12. The growth feature observed at 1 : 8—1 : 12 indicates that the grain of K_3VF_6 somewhat dissolves in the KHF_2 melt.

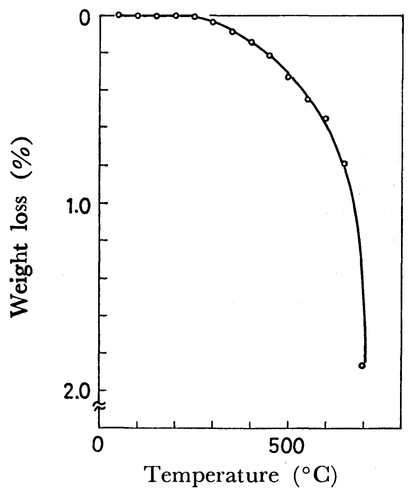

Fig. 7. Oxidation curve of K_3VF_6 in air.

Oxidation-resistance of K_3VF_6. A knowledge of the oxidation-resistance of K_3VF_6 is important for the synthesis of K_3VF_6 and also for the preparation of the electrolytic bath for the electroextraction of vanadium. One gram of K_3VF_6, the crystal sizes of which are shown in Fig. 6b, was heated at a given temperature for 30 min in air; then the product was weighed and analysed by means of an X-ray diffraction technique. The thermogravimetric analysis curve thus obtained is shown in Fig. 7. It may be seen that K_3VF_6 is

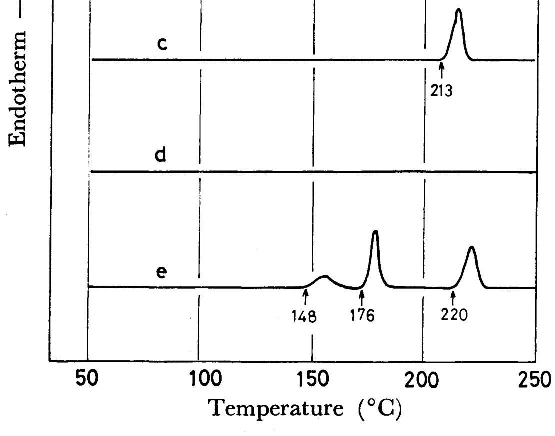

Fig. 8. DTA curves of K_3VF_6.
Curve a: K_3VF_6 prepared by using KHF_2 of a special reagent grade, curve b, c, d, e: K_3VF_6 prepared by using KHF_2 with the addition of a small amount of $NaHF_2$ or LiF.
b: $NaHF_2/KHF_2=1/999$, c: $NaHF_2/KHF_2=1/99$, d: $NaHF_2/KHF_2=5/95$, e: $LiF/KHF_2=1/999$.
Heating rate: 5 °C/min.

stable in air up to about 300 °C and is oxidized at temperatures higher than 300 °C. Therefore, when a mixture of V_2O_3 and KHF_2 is heated at temperatures higher than 300 °C in order to decompose the excess KHF_2, heating must be done in a stream of an inert gas. The decomposition of excess KHF_2 to KF and HF makes the subsequent water-leaching easy. The product oxidized at 700 °C was yellowish green and was readily soluble in water. Its X-ray diffraction pattern was quite different from that of α-K_3VF_6, but was similar to that of γ-K_3VF_6, which will be shown below. This product is suspected to be tetrafluorodioxovanadate(V), $K_3VO_2F_4$.

Transition of K_3VF_6. The transition of K_3VF_6 was examined by differential thermal analysis and X-ray diffraction analysis. Curve a in Fig. 8. is the differential thermal analysis curve of the K_3VF_6 obtained by using KHF_2 of a special reagent grade. From curve a it may be seen that K_3VF_6 has four polymorphic forms and that the transition points are 158, 200, and 218 °C. These polymorphic forms will be called α, β, γ, and δ respectively as follows:

$$\alpha \overset{158}{\rightleftharpoons} \beta \overset{200}{\rightleftharpoons} \gamma \overset{218}{\rightleftharpoons} \delta$$

These transitions are all reversible. Figure 9 shows the X-ray diffraction patterns of α, β, γ, and δ. δ was found to be cubic with a lattice parameter of $a=8.722$Å at 235 °C. Cretenet⁷⁾ has found two polymorphic forms for K_3VF_6 and reported that the high-temperature form is cubic, with a lattice parameter of $a=8.7$ Å at 250 °C.

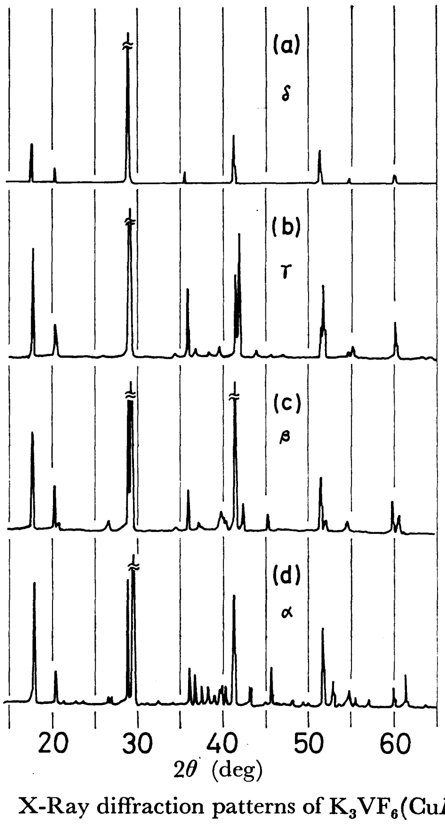

Fig. 9. X-Ray diffraction patterns of K_3VF_6(Cu$K\alpha$, Ni-filter). (a): 230 °C, (b): 210 °C, (c): 180 °C, (d): room temperature.

Table 2. The influence of sodium ion on the crystal transition of K_3VF_6

Molar ratio of $NaHF_2$ to KHF_2	1/999—3/997	8/992—20/980	30/970	50/950
Type of K_3VF_6	α γ	γ	γ δ K_2NaVF_6	δ K_2NaVF_6

K_3VF_6 was synthesized by heating a mixture of KHF_2 (with the addition of a small amount of $NaHF_2$) and V_2O_3 in a molar ratio 1 : 8 at 450 °C in a stream of argon.

When KHF_2 of a reagent grade was used in the synthesis of K_3VF_6, the X-ray diffraction pattern of the product showed some peaks of γ besides the peaks of α, or only the peaks of γ at room temperature. This was considered to be due to some impurity in the reagent used. Thus, $NaHF_2$ or LiF was deliberately added to KHF_2 of a special reagent grade in the synthesis of K_3VF_6. The K_3VF_6 thus obtained was examined by X-ray diffraction analysis and differential thermal analysis. Table 2 shows the relationship between the ratio of $NaHF_2$ to KHF_2 and the form of K_3VF_6. It may be seen that, on the addition of a small amount of Na^+, γ and δ remain stable, even at room temperature. Curve b, c, d, and e in Fig. 8 are the differential thermal analysis curves of the K_3VF_6 prepared by using the KHF_2 reagent with the addition of Na^+ or Li^+. With an increase in the amount of Na^+, first the β-γ transition temperature decreased, then the β-γ transition disappeared, and finally the γ-δ transition disappeared. These results show that a small amount of Na^+ stabilizes the high-temperature forms, γ and δ, at room temperature. This effect may be explained by the idea that Na^+, which has a smaller ionic radius than K^+, cancels the distortion of the lattice contraction caused by a lowering of the temperature. On the addition of a minute amount of Li^+, the β-γ transition temperature decreased, as in the case of Na^+. Lithium fluoride was almost insoluble in KHF_2, so the addition of more than 1/999 of LiF was not attempted.

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