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Chemical Vapor Transport of Layer Structured Crystal β-ZrNCl

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A layer structured compound β-ZrNCl is transported to a higher temperature zone with the aid of ammonium chloride as the transporting agent in the temperature range of 823–1173 K. The transport mechanism can be explained by the formation of a volatile compound $(NH_4)_2ZrCl_6$:

$$\beta\text{-}ZrNCl + 5NH_4Cl \rightarrow (NH_4)_2ZrCl_6 + 4NH_3.$$

The measurements of the vapor pressure and the mass spectrum revealed that $(NH_4)_2ZrCl_6$ decomposed congruently according to the equation:

$$(NH_4)_2ZrCl_6(s) \rightarrow ZrCl_4(g) + 2NH_3(g) + 2HCl(g).$$

The enthalpy change for the decomposition was determined to be 533 kJ/mol. By combining the above two equations, a simplified transport equation is derived:

$$\beta\text{-}ZrNCl(s) + 3HCl(g) \rightleftharpoons ZrCl_4(g) + NH_3(g).$$

Introduction

In a previous study (*1*), we reported on a novel synthesis of layer structured compound β-ZrNCl by the direct reaction of zirconium or zirconium hydride with ammonium chloride at elevated temperatures. The as-prepared powder sample could be chemically transported and purified into a highly crystalline form having a 3*R* stacking structure. The transport was much accelerated by adding ammonium chloride. In this paper, the mechanism of the transport was studied by identifying the gaseous species involved in the reactions. Some thermodynamic properties have also been determined through the measurement of the vapor pressures of the system.

Experimental

Materials. β-ZrNCl was prepared from ZrH_2 and NH_4Cl by the procedure reported previously (*1*). ZrH_2 was subjected to reaction with gaseous NH_4Cl in a stream of NH_3 at 923 K, and directly converted to β-ZrNCl in high yields (>70%) via the reaction:

$$ZrH_2 + NH_4Cl \rightarrow \beta\text{-}ZrNCl + 3H_2.$$

Ammonium hexachlorozirconate $(NH_4)_2ZrCl_6$ was synthesized by the direct reaction of $ZrCl_4$ and NH_4Cl in a sealed glass tube, and purified by sublimation according to the method reported elsewhere (*2*). Found: Zr, 27.3; N, 8.22; Cl, 62.6%. Calcd. for $(NH_4)_2ZrCl_6$: Zr, 26.8; N, 8.24; Cl, 62.6%.

Vapor pressure measurement. The subli-

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mation vapor pressure of $(NH_4)_2ZrCl_6$ was measured to 773 K. A Pyrex glass Bourdon gauge with a spoon-shaped membrane was used, which was designed after the gauge used by Saeki (*3*). A quartz Bourdon gauge was also used, but the Pyrex one was found to be satisfactory for the measurements in the temperature range below 773 K. A schematic drawing of the gauge is shown in Fig. 1. Under a dry argon atmosphere, a weighed amount of $(NH_4)_2ZrCl_6$ (about 20 mg) was loaded into the gauge (about 40 cm^3), and then the entire system was evacuated to a pressure of about 10^{-1} Pa and sealed off at point A. The sealed apparatus was heated in a vertical furnace at a heating rate of 1 K/min. In the course of raising the temperature, the gauge was intermittently kept at constant temperatures at several measurement points in order to check the equilibrium of the system. The vapor pressure in the spoon was balanced with the same pressure of air introduced to chamber C through valve D. The balancing air pressure was measured by a digital pressure transducer (Tokyo Kokukeiki, Model DG-630) within an accuracy of 1.3×10^2 Pa. The imbalance of the pressures was detected from the deflections of a fiber B attached to the top end of the spoon using a cathetometer.

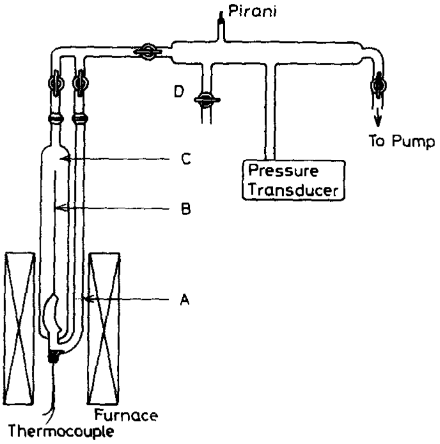

FIG. 1. Bourdon gauge for the measurement of vapor pressures of $(NH_4)_2ZrCl_6$.

Mass spectra. The mass spectrometer used was a double-focusing type with a sample holder heatable to 873 K (Denshi-Kagaku, Model EMD-05SH). $(NH_4)_2ZrCl_6$ was heated at a heating rate of 20 K/min, and the volatile species were analyzed as a function of temperature in the sweep range 1–500 *m/z* for the ionization energy of 70 eV.

Results and Discussion

Chemical transport. The as-prepared β-ZrNCl powder sample was vacuum-sealed in a quartz tube (8 mm in diameter and 150 mm in length) and placed in a furnace with a temperature gradient of 1023–1123 K. The sample (about 0.5 g) was loaded in the lower temperature zone. The β-ZrNCl was transported to the higher temperature zone in a few days as a highly crystalline form. The transported crystals were taken out and vacuum sealed again; no transport, however, was observed. If the transported crystals were sealed with a small amount of NH_4Cl (about 30 mg), the crystals could be transported to the higher temperature zone like the as-prepared sample. If the as-prepared sample was sealed after evacuation at 773 K for 3 hr, the rate of transport was much reduced even in the same temperature gradient. It is very likely that the as-prepared β-ZrNCl was contaminated with a small amount of NH_4Cl used in the preparation of the β-ZrNCl, which can be removed by prolonged evacuation at 773 K. It is apparent that NH_4Cl is a transporting agent for β-ZrNCl.

The as-prepared β-ZrNCl was mixed with NH_4Cl in a ratio of 1/5 and vacuum-sealed in a Pyrex glass tube, which was placed in a furnace with a temperature gradient of 698–653 K. The mixture was loaded in the higher temperature zone this time. After 3 days, white crystals of

$(NH_4)_2ZrCl_6$ were deposited at the lower temperature end of the sealed glass tube. The reaction can be written by the equation

$$\beta\text{-}ZrNCl(s) + 5NH_4Cl \rightarrow (NH_4)_2ZrCl_6(s) + 4NH_3(g), \quad (1)$$

where NH_4Cl dissociates into $NH_3(g)$ and $HCl(g)$. In the temperature range 823–1173 K, $(NH_4)_2ZrCl_6$ was decomposed to β-ZrNCl, whereas at temperatures above 1323 K, it was decomposed to ZrN. Although optimal transport conditions to obtain large single crystals have not been determined, pretty large crystals were obtained from the as-prepared β-ZrNCl in a temperature gradient of 1023–1123 K. A typical scanning electron micrograph of the obtained crystals is shown in Fig. 2.

Vapor pressure of $(NH_4)_2ZrCl_6$. $(NH_4)_2ZrCl_6$ is a face-centered cubic crystal with the K_2PtCl_6-type structure and easily sublimed at elevated temperatures (*2*). In previous studies (*1, 2*), this was prepared through several reaction routes:

$$\text{(i)}\quad ZrCl_4 + 2NH_4Cl \rightarrow (NH_4)_2ZrCl_6;$$

$$\text{(ii)}\quad Zr + 6NH_4Cl \rightarrow (NH_4)_2ZrCl_6 + 4NH_3 + 2H_2;$$

$$\text{(iii)}\quad ZrH_2 + 6NH_4Cl \rightarrow (NH_4)_2ZrCl_6 + 4NH_3 + 3H_2.$$

In this study, $(NH_4)_2ZrCl_6$ was prepared by reaction (i), and in order to understand the gaseous species involved in the sublimation vapors, the vapor pressure was measured as a function of temperature by using a glass Bourdon gauge. The pressure vs temperature curve is shown in Fig. 3. The sublimation vapor pressure increases rapidly from about 600 K. The curve exhibits an inflection point at 730 K, where all the solid was sublimed to vapors. An ideal gas law was assumed, and the total pressures after the inflection point were extrapolated to the origin by a dashed line (Fig. 3). The slope of the line indicates that 1 mole of $(NH_4)_2ZrCl_6$ is sublimed to 4.9 moles of gaseous molecules.

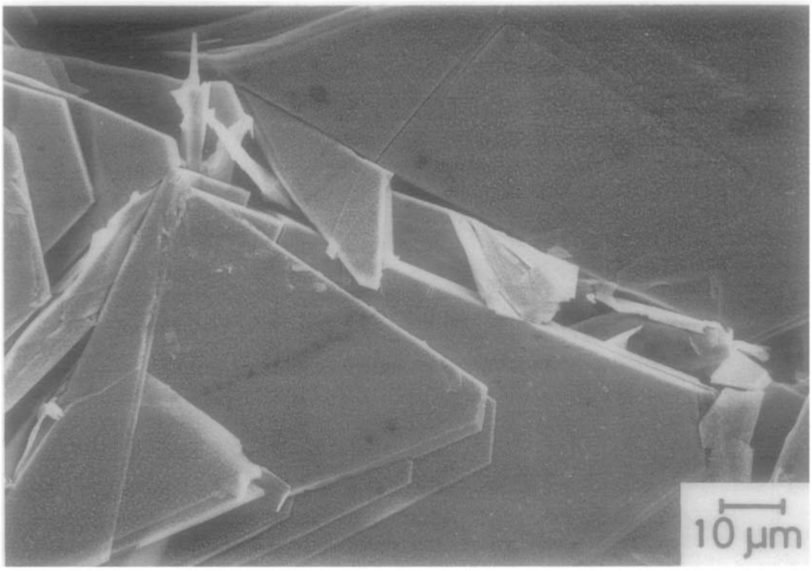

FIG. 2. Scanning electron micrograph of the crystals β-ZrNCl transported in a temperature gradient of 1023–1123 K.

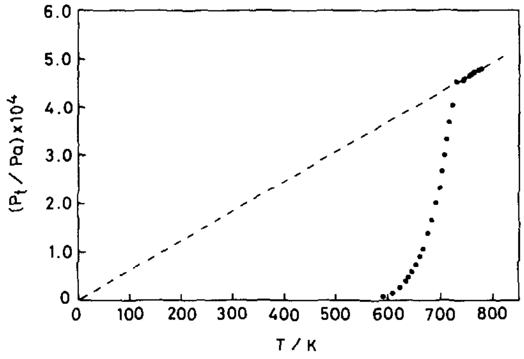

FIG. 3. Temperature dependence of vapor pressure of $(NH_4)_2ZrCl_6$.

Thermal decomposition of a similar series of compounds M_2ZrCl_6 (M = Na, K, and Cs) have been studied by Morozov and In'-Chzhu (*4*) and Lister and Flengas (*5*). These compounds decompose in the following equation:

$$M_2ZrCl_6(s) \rightarrow ZrCl_4(g) + 2MCl(s).$$

It is reasonable to assume that $(NH_4)_2ZrCl_6$ decomposes in a similar way.

$$(NH_4)_2ZrCl_6(s) \rightarrow ZrCl_4(g) + 2NH_3(g) + 2HCl(g), \quad (2)$$

where NH_3 and HCl come from the decomposition of NH_4Cl. This equation shows that 1 mole of $(NH_4)_2ZrCl_6$ is sublimed to 5 moles of gaseous molecules. The number of gaseous molecules estimated from the vapor pressure measurement of $(NH_4)_2ZrCl_6$ is in good agreement with this value.

When solid $(NH_4)_2ZrCl_6$ coexists with the vapors, the equilibrium constant (K_p) for reaction (2) is given by the following equation.

$$K_p = (P_{ZrCl_4}/P_0)(P_{NH_3}/P_0)^2(P_{HCl}/P_0)^2,$$

where P_{ZrCl_4}, P_{NH_3}, and P_{HCl} represent the partial pressures of $ZrCl_4$, NH_3, and HCl, respectively, and P_0 is the standard pressure. Since all the partial vapor pressures of the components are known, if the total pressure (P_t) of the system is measured, K_p is related to P_t by

$$K_p = (P_t/5P_0)(2P_t/5P_0)^2(2P_t/P_0)^2 = C(P_t/P_0)^5,$$

where C is a constant.

Figure 4 shows a plot of $\ln(P_t)$ against $1/T$. From the slope of the linear plot and the Gibbs–Helmholtz equation

$$\frac{d(\ln K_p)}{d(1/T)} = -\frac{\Delta H}{R},$$

where R is the gas constant, the enthalpy change for Eq. (2), ΔH, is calculated to be 533 kJ/mole.

Since the enthalpy change for the vaporization of NH_4Cl,

$$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g) \quad (3)$$

is 161 kJ/mole at 700 K (*6*). The enthalpy change for the reaction,

$$(NH_4)_2ZrCl_6(s) \rightarrow ZrCl_4(g) + 2NH_4Cl(s), \quad (4)$$

is calculated to be 211 kJ/mole. The heat of formation for $(NH_4)_2ZrCl_6(s)$ is also calculated to be $\Delta H^\circ_{f700} = -1693$ kJ/mole on the basis of the heats of formations of $ZrCl_4(g)$,

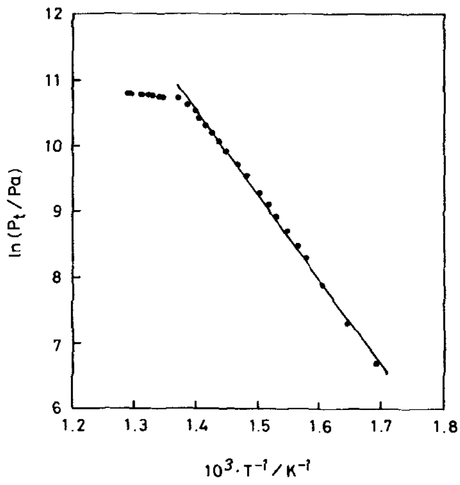

FIG. 4. Plots of $\ln(P_t/Pa)$ against $1/T$.

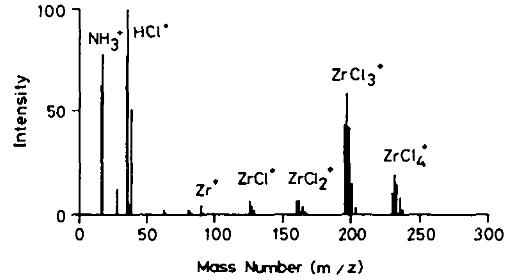

FIG. 5. Mass spectrum of $(NH_4)_2ZrCl_6$ vaporized at 673 K.

NH_3(g), and HCl(g) at 700 K: −868, −52.6, and −93.6 kJ/mole, respectively (*6*). As for K_2ZrCl_6, which is isostructural with $(NH_4)_2ZrCl_6$, the enthalpy change for the following decomposition was measured by Morozov and In'Chzhu (*4*) and Lister and Flengas (*5*).

$$K_2ZrCl_6(s) \rightarrow ZrCl_4(g) + 2KCl(s).$$

The former group obtained 218 kJ/mole by the transpiration method, whereas the latter group obtained 354 kJ/mole by a Bourdon gauge measurement. Although there is large discrepancy between the values from the two groups, the value (218 kJ/mole) by Morozov and In'-Chzhu is comparable with the value (211 kJ/mole) obtained in this study for reaction (4).

Mass spectrometry. Figure 5 shows a mass spectrum of the volatile components of $(NH_4)_2ZrCl_6$ at 673 K. The amount of volatile components began to increase from about 570 K, and the mass spectra obtained were essentially unchanged in the temperature range 573–823 K. The peak at 232 m/z is attributed to $ZrCl_4^+$. Some fragments of $ZrCl_4^+$ were observed in the m/z range 90–203. The spectrum also shows intense peaks at $m/z = 17$ and 36 due to NH_3^+ and HCl^+, respectively. These findings are in accordance with the conclusion made on the decomposition of $(NH_4)_2ZrCl_6$ from the pressure measurement.

Mechanism of chemical transport of β-ZrNCl. β-ZrNCl reacts with NH_4Cl as a transporting agent and forms $(NH_4)_2ZrCl_6$, which is congruently decomposed to $ZrCl_4$, NH_3, and HCl at elevated temperatures. The vapor phases are transported to the higher temperature zone and form β-ZrNCl. The transport Eq. (1) can be simplified into the following equation by using Eqs. (2) and (3):

$$\beta\text{-}ZrNCl(s) + 3HCl(g) \rightleftharpoons ZrCl_4(g) + NH_3(g).$$

This equation suggests that HCl gas could also be a transporting agent of β-ZrNCl. As a matter of fact, when the transported β-ZrNCl was sealed with HCl gas of a pressure of 2.7×10^4 Pa and placed in a temperature gradient 1023–1123 K, β-ZrNCl was transported to the higher temperature zone. The transport reaction must be exothermic because the transport occurs to the higher temperature zone.

In the preparation of β-ZrNCl, gaseous NH_4Cl is flowed over ZrH_2 or Zr. Since the NH_4Cl acts as the transporting agent as well as the reactant, the NH_4Cl supply must be stopped as soon as the reaction is finished. The prolonged flowing of NH_4Cl vapor would remove the β-ZrNCl formed in the form of volatile $(NH_4)_2ZrCl_6$ and result in a low yield of β-ZrNCl.

Acknowledgments

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