PHASE STABILITY IN THE ThGeO₄ SYSTEM IN THE RANGE 750–1450°C AT 1 ATM[1]

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ABSTRACT

The relative stability of the two tetragonal polymorphs of ThGeO₄ (scheelite– and zircon–type) was studied in air at 750–1450°C and 1 atm. Crystallization of zircon–type ThGeO₄ from $Li_2O \cdot 2MoO_3$ or $Li_2O \cdot 2WO_3$ flux without evidence of the scheelite modification suggested that the former is thermodynamically the more stable form in the range studied. This was substantiated by conversion of separately prepared scheelite–type samples to zircon type in presence of a mineralizer at 750°C or above. At $1420 \pm 20°C$, zircon–type ThGeO₄ melted incongruently into ThO₂ + liquid.

INTRODUCTION

Finch *et al.* (1964) previously used a crystal–growth technique to determine the temperature of the phase transformation between the thorite (tetragonal, zircon–type) and huttonite (monoclinic, monazite– type) forms of ThSiO₄. They found the transition temperature to be $1225 \pm 10°C$ by bracketing the nucleation and growth of the preferred polymorph from $Li_2O \cdot 2MoO_3$ or $Li_2O \cdot 2WO_3$ flux in this temperature vicinity. The results of this study, which were later confirmed by Chase and Osmer (1966), suggested that crystal growth might serve as a powerful tool in delineating regions of polymorphic phase stability.

To test the above technique, we decided to apply it to another polymorphic system and compare the results with those obtained by other methods of phase study. We were attracted to the related polymorphic compound ThGeO₄, in which a low-temperature scheelite phase reportedly transforms to a high–temperature zircon form at 1100–1250°C (Bertaut and Durif, 1954; Perez y Jorba *et al.*, 1961; Keller, 1963). We chose this system because study of germanates often provides a better understanding of the corresponding silicates. This would appear particularly so in this case, where the zircon modifications of ThGeO₄ and ThSiO₄ form a complete series of solid solutions (Keller, 1963). Another consideration was that the reported transformation was in a temperature range convenient for applica-

tion of the same crystal–growth solvents and techniques used in the thorite–huttonite study.

Synthesis by Flux Crystal Growth

ThGeO$_4$ crystals were grown in a near isothermal system in air from molten solvents of either Li$_2$O·2MoO$_3$ (750–1100°C) or Li$_2$O·2WO$_3$ (1000–1400°C). The experimental procedure was briefly as follows.

A 20-ml platinum crucible was charged with the above solvents, either of which had been previously melted (saturated) with ~20 wt percent ThO$_2$ at 1250°C. After thermal equilibrium at a desired test temperature, a 2-g lump of fused 99.9 percent pure GeO$_2$, secured at the end of a 1-mm platinum wire, was immersed into the upper, liquid portion of the crucible contents. On subsequent reaction of the GeO$_2$ lump with the ThO$_2$-saturated solvent, nucleation of ThGeO$_4$ occurred on the wire within several hours. At desired intervals the progress of nucleation and growth was checked by removing the wire and inspecting it microscopically.

This procedure was carried out at 100°C intervals between 750 and 1250°C, and at 1400°C. A fresh charge of ThO$_2$-saturated solvent (free of GeO$_2$) was used with a clean platinum crucible and wire for each test. The experiments were prolonged for several days at a given nucleation temperature to produce sufficient sample for characterization.

Synthesis by Solid–State Reaction

Equimolar quantities of 99.99 percent pure ThO$_2$ and 99.9 percent pure GeO$_2$ powders were mixed and pelletized. The samples were heated in air at temperatures up to 1250°C, using a 60 percent Pt–40 percent Rh–wound horizontal-tube furnace. The temperature was controlled to within ±10°C, and the sample temperature was read by a Pt–Pt 10 percent Rh thermocouple located at the sample. The samples were cooled to room temperature within one minute.

Synthesis by Coprecipitate Ignition

An amorphous coprecipitate of the approximate composition ThO$_2$·GeO$_2$ was obtained by the method of Stöcker and Collongues (1957), which consists of adding NH$_4$OH to an equimolar aqueous solution of GeO$_2$ and Th(NO$_3$)$_4$·4H$_2$O. The resulting material was dried at 150°C, ignited 24 hr in air at 800°C, and cooled to room temperature within one minute. It should be noted that a strong exothermic reaction accompanied the ignition, which initially raised the reaction temperature to about 1100°C for several seconds.

Optical and X–ray Methods

The polarizing microscope, X–ray diffractometer, and X–ray powder camera were used to identify the phases present, as well as to determine previously unreported properties of these phases. Cu$K\alpha$ ($\lambda = 1.5418$ Å) radiation was used in all the X–ray analyses.

High-Temperature X–ray Methods

A high temperature X–ray attachment was used in conjunction with the Norelco high–angle goniometer. The samples were heated by a resistance strip

heater which also acted as a sample holder. The strip heater was formed from 5-ml-thick platinum foil. All experiments were carried out in air.

RESULTS AND DISCUSSION

The ThGeO$_4$ crystals grown by the flux method over the entire temperature range from 750° to 1400°C were exclusively the zircon polymorph. However, the solid–state synthesis at 1050°C gave the scheelite form, and about two weeks and several regrindings were required for near complete reaction; solid–state synthesis at 1250°C gave the zircon phase. The product obtained from ignition of the coprecipitate at 800°C was also the scheelite phase, which contained traces of the zircon form (possibly due to the increased temperature during the previously noted brief exothermic reaction). The lattice parameters of both phases were consistent with those reported in the literature (Keller, 1963). Previously unreported optical data for the zircon polymorph are: uniaxial positive with refractive indices $\omega = 1.874 \pm 0.002$ and $\epsilon = 1.954 \pm 0.002$. (The refractive indices of the scheelite form could not be accurately determined due to fine crystallite size.) All of the samples were judged to be >99.9 percent pure on the basis of spectrochemical analysis and reagent purity.

The above results were surprising in that the scheelite polymorph did not appear in any of the crystal–growth experiments, while it readily formed in the solid–state and coprecipitate synthesis at 1050° and 800°C, respectively. Either crystal growth was not a valid criterion of phase equilibrium, or there was in fact no enantiotropic phase transformation in the range studied. To resolve this question, we conducted a series of heat–treatment experiments in which samples of scheelite–type ThGeO$_4$ were heated for prolonged periods at various temperatures below 1180°C (the reported scheelite–zircon phase transition temperature for ThGeO$_4$). The heat–treatment apparatus and technique was identical to that described for the solid–state synthesis.

After 6 days at 1130°C, the sample from the solid–state synthesis showed appreciable conversion to the zircon form. The coprecipitate sample held at 1130°C for 12 days resulted in the zircon polymorph being the primary phase in the mixture. However, further heat–treatment experiments at still lower temperatures indicated that the transformation was too sluggish to produce observable changes within a convenient length of time.

To offset this sluggishness, we conducted several heat–treatment experiments in the presence of a catalyzing flux or mineralizer (Verma and Krishna, 1966). A mineralizer of the composition LiCl–40 wt

percent KCl was chosen on the basis of its successful application in determining the GeO_2 (rutile) $\rightarrow$ GeO_2 (α-quartz) transformation (Laubengayer and Morton, 1932). It had the advantage of being water soluble, permitting easy removal from $ThGeO_4$ at the end of a test. The results of heat–treatments of powdered $ThGeO_4$ samples, mixed with 10 wt percent of the mineralizer are given for the range 400–900°C in Table 1. The mineralizer did not appear to be effective much below 750°C, since several mineralized heat treatments of predominantly scheelite– and of pure zircon–type samples at 400° and 650°C resulted in no structural changes in either. However, it is significant that a complete conversion of scheelite– to zircon–type occurred at 750°C within 5 days.

The high–temperature X–ray diffraction experiments indicated that zircon–type $ThGeO_4$ melts incongruently into ThO_2 + melt. The temperature was established as $1420 \pm 20°C$ which is considerably higher than the 1280°C cited by Keller (1963). However, it is compatible with our growth of zircon–type $ThGeO_4$ crystals from $Li_2O \cdot 2WO_3$ at ~1400°C.

Conclusions

If an enantiotropic phase transformation exists in $ThGeO_4$, it would appear to be at lower temperatures and higher pressures than studied here. The scheelite phase which forms at 1050°C in solid state or coprecipitate ignition syntheses may be understood as a trapped metastable form requiring a high activation energy for conversion to the thermodynamically more stable zircon phase (Ostwald, 1897). Considerable superheating occurs before the scheelite $\rightarrow$ zircon transformation occurs at a vigorous rate. This would explain the high temperature range previously observed for the transformation.

Table 1. Heat Treatment of Scheelite- and Zircon-Type $ThGeO_4$ Powders

with 10 wt % LiCl–40 wt % KCl Mineralizer

Test No.	Sample Origin*	Phase Composition†	Heat Treatment		Phase Composition after Heat Treatment
			Temp. (±10°C)	Duration (days)	
1	B	S + Z (trace)	400	5	S + Z (trace)
2	B	S + Z (trace)	650	3	S + Z (trace)
3	A	Z	650	3	Z
4	B	S + Z (trace)	750	5	Z + T (trace)
5	B	S + Z (trace)	900	1	Z + T (trace)
6	A	S + T + G	900	1	Z

*A: synthesis from 1:1 mole ThO_2:GeO_2 pellet.

B: synthesis from coprecipitate according to method of Stöcker and Collongues (1961).

†T = ThO_2 (fcc); S = scheelite-type $ThGeO_4$; Z = zircon-type $ThGeO_4$; G = GeO_2 (hcp).

A temperature in the 1100–1250°C range as previously reported has been rejected as an enantiotropic phase transition point in $ThGeO_4$ for the following reasons:

1) growth of exclusively zircon–type crystals from fluxes at 750–1250°C;

2) conversion of scheelite– to zircon–type in presence of a mineralizer at 750°C and above;

3) absence of any inversion of the zircon phase to the scheelite on prolonged heating at 750–1250°C;

4) formation of the zircon modification during hydrothermal synthesis at 300°C (Keller, 1963) (increased pressure would even more favor the denser scheelite form).

Our original goal of determining the enantiotropic phase transformation temperature in $ThGeO_4$ at 1 atm was not achieved due to apparent absence of such a transition in the range studied. However, the investigation confirmed that crystal growth is a useful criterion of polymorphic phase stability. The crystal–growth results in the thorite–huttonite work were essentially validated.

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