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HYDROTHERMAL SYNTHESIS OF ZIRCON, THORITE AND HUTTONITE*

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ABSTRACT

Zircon and thorite have been synthesized by heating admixed SiO_2 and ZrO_2 or ThO_2 gels in water over the range 150° C. and 4.8 bars to 700° and 3100 bars. Material synthesized at 150° shows strong absorption in the infra-red at 2.75 microns due to hydroxyl, and apparently contains $(OH)_4$ in substitution for (SiO_4). Zircon containing an undetermined but quite small amount of Th and of U in solid solution has been synthesized at 400° to 700° from charges containing Zr: Th or U=1:1; thorite or $(U, Zr)O_2$ are also formed. Thorite containing an undetermined amount of U in solid solution was obtained similarly. Huttonite has been synthesized hydrothermally at 300° and 700°. It is found that metamict natural thorite and zircon recrystallize when heated in water, at temperatures considerably below those needed when heated dry in air, and the presence of (OH) was verified by infra-red study in one such recrystallized sample.

ZIRCON

Historical

Zircon was first synthesized by Deville and Caron (1858) by the action at red heat of SiF_4 on ZrO_2 and of ZrF_4 on SiO_2. Hautefeuille and Perrey (1888) obtained crystals by the fusion of ZrO_2 and SiO_2 in lithium dimolybdate at 700°–1000°. Minute anhydrous crystals were obtained by Chrustschoff (1892) by heating a sealed bomb containing gelatinous ZrO_2 and SiO_2 to dull red heat over a Bunsen burner. Stott and Hilliard (1945) recrystallized zircon by heating zircon sand with KF at about 1525°. Crystalline zircon dissociates slowly at about 1540° and more rapidly with increasing temperature to ZrO_2 and SiO_2 or silica glass, and re-associates on slow cooling (Curtis and Sowman, 1953). Zircon also is formed by sintering ZrO_2 and SiO_2 in air at high temperatures, and this method has been employed in the preparation of $ZrSiO_4$ phosphors (Leverenz, 1950). We have found that co-precipitated ZrO_2 and SiO_2 gels do not react when heated for 24 hours in air at either 800° or 900° but that zircon is formed in the range 1000° to 1500°.

New Data

We have hydrothermally synthesized microcrystalline zircon over the range 150° to 700° by heating gelatinous ZrO_2 and SiO_2 with water in steel bombs (Table 1). The reaction is speeded by adding traces of ZrF_4. Our synthetic zircon formed at 400° and 700° gave sharp *x*-ray patterns

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with cell dimensions identical with those of dry-sintered $ZrSiO_4$. Material synthesized in the range 150° to 350°, however, gave rather diffuse patterns and the cell dimensions are different; with decreasing temperature the value of a_0 increases and the value for c_0 decreases slightly (Table 1). When these low temperature samples are heated in air the patterns become sharper and the cell dimensions increase to those of dry-sintered $ZrSiO_4$. The changed dimensions of the low temperature material are attributed to the presence of $(OH)_4$ in substitution for (SiO_4), for which we have additional evidence, and the change on heating to thermal decomposition:

$$Zr(SiO_4)_{1-x}(OH)_{4x} \rightarrow (1-x)ZrSiO_4 + xZrO_2 + 2xH_2O$$

TABLE 1. HYDROTHERMAL SYNTHESES OF ZIRCON

Temperature	Pressure in bars	Duration in hours	Reagents	Results	Zircon a_0	Zircon c_0
(1000° dry sinter)				Zircon	6.61 Å	5.98 Å
700°	1000	48	ZrO_2,SiO_2 mixed gels	Zircon	6.61	5.98
400°	1000	168	ZrO_2, SiO_2 gels	Zircon	6.61	5.98
350°	165	48	ZrO_2, SiO_2 gels	Zircon	6.62	5.97
325°	121	240	ZrO_2, SiO_2 gels	Zircon		
300°	86	120	ZrO_2, SiO_2 gels, NaCl	Zircon		
240°	34	72	ZrO_2, SiO_2 gels, ZrF_4	Zircon		
150°	4.8	500	ZrO_2, SiO_2 gels, ZrF_4	Zircon	6.64	5.96
700°	1000	48	Zr, U gel (1:1) SiO_2 gel	Zircon, $(Zr, U)O_2$	6.68	6.02
700°	1000	48	Zr, U gel (1:1) Na_2SiO_3	Zircon, $(U, Zr)O_2$		
600°	1000	24	Zr, U gel (1:1) SiO_2 gel	Zircon $(U, Zr)O_2$	6.67	6.02
500°	1000	48	Zr, U gel (1:1) SiO_2, Zr nitrate	Zircon, $(U, Zr)O_2$	6.66	6.01
400°	1000	48	Zr, U gel (1:1) SiO_2 gel	Zircon $(U, Zr)O_2$	6.68	6.00
700°	3100	48	Zr, Th gels (1:1) SiO_2 gel	Zircon, thorite		
700°	1000	48	Zr, Th gels (1:1) Na_2SiO_3	Zircon, thorite		

We also have synthesized zircon containing uranium and thorium in solid solution. The uranium runs were made with co-precipitated gelatinous ZrO_2 and UO_3, with Zr: U = 1:1, mixed with gelatinous silica. The products included zircon with relatively large cell dimensions (the only evidence of uranium content) and an isometric fluorite-type oxide, UO_{2+x}, with a_0 5.35 Å. The uranium content of the zircon from approximate measurements of the relative amounts of the two phases present must be very small, perhaps only a few atomic per cent. It proved impossible to isolate and separately analyze the zircon and the oxide.

The thorium runs were made from SiO_2 gel admixed with co-precipitated ZrO_2 and ThO_2 gels, with Zr: Th = 1:1. Zircon with slightly increased cell dimensions (the only evidence of thorium content) and thorite with essentially normal cell dimensions were formed in approximately equal amounts. The diffraction patterns were of very poor quality. The solubility of Th in zircon under these conditions apparently is small. It is interesting to note that in these zircon runs that the added Th crystallized as $ThSiO_4$ but that the added U crystallized as UO_2. All efforts to synthesize anhydrous $USiO_4$ have failed, although $U(SiO_4)_{1-x}(OH)_{4x}$ has been synthesized (Hoekstra and Fuchs, 1956). We have observed that natural coffinite remains stable when heated in water at 700° and 1000 bars.

Hydroxyl Content of Synthetic Zircon

The substitution of $(OH)_4$ for (SiO_4), analogous to the hydrogarnets, has been indicated in certain natural zircon and thorite (thorogummite) by Frondel (1953) and in thorogummite and the related mineral coffinite by infra-red study by Stieff *et al.* (1956). Infra-red measurements to determine the presence of (OH) were made on a number of our synthetic samples. The data were obtained on a Perkin-Elmer double-beam recording spectrophotometer, with a rock-salt prism, using mineral oil (Nujol) as the mounting medium. The region from 2 to 7 microns was scanned. Undoubted evidence of the presence of (OH) was obtained on only one sample, that of zircon synthesized at 150°. This material showed a strong absorption at 2.775 microns due to (OH), with also a weak absorption at 3.075 microns and a weak absorption of molecular water at about 6.0 microns (Fig. 1). The sample was dried at 110° before measurement. When the sample was dried at 300° the (OH) absorption at 2.775 microns remained unchanged. The unreacted SiO_2-ZrO_2 gel after drying at 110° did not show the (OH) absorption at 2.775 microns. Zircon synthesized at 400° and 500° did not show the 2.775 micron absorption, but showed weak absorption at 2.90 and 3.075 microns. The absorptions at 2.9–3.1 microns have been attributed to hydrogen bonding and to molecular water in part, but are not critical in the present work because they were observed on unreacted gels of both ZrO_2-SiO_2 and ThO_2-SiO_2 that had been dried at 110°.

THORITE

Historical

$ThSiO_4$ was first synthesized by Troost and Ouvrard (1887) by heating a mixture of ThO_2, SiO_2 and $CaCl_2$ to white heat in air. $ThSiO_4$ prepared by sintering of ThO_2 and SiO_2 at 1000°–1300° has been employed in investigations of phosphors (Leverenz, 1950). These preparations usually are referred to as tetragonal $ThSiO_4$ (thorite), but in the absence of critical evidence, they may have been the monoclinic polymorph huttonite, described in 1951, which can be synthesized similarly. Both tetragonal and monoclinic $ThSiO_4$ has been obtained by Pabst (1952), and others by heating metamict thorite in air to high temperatures. Duboin (1909) sought to synthesize $ThSiO_4$ by reaction of sodium silicate and thorium nitrate at room temperature in water but no significant results were obtained [a gel is obtained that does not give a diffraction pattern]. Britton (1927) made an electrometric titration of $ThCl_4$ solution with sodium silicate and found that the precipitate was deficient in silica for $ThSiO_4$.

New Data

We have synthesized thorite hydrothermally over the range 150° to 800° by heating gelatinous SiO_2 and ThO_2 with water in steel bombs

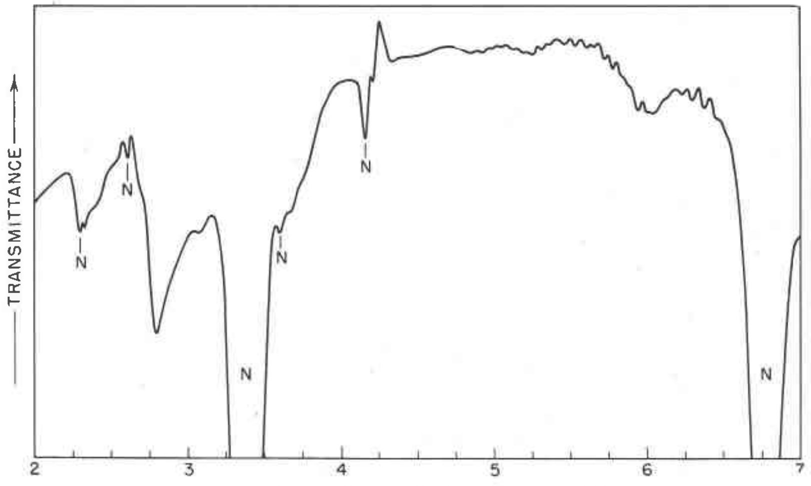

FIG. 1. Infra-red absorption curve of zircon synthesized at 150°. The chief absorptions due to the mounting medium (Nujol) are indicated by the letter N.

TABLE 2. HYDROTHERMAL SYNTHESES OF THORITE

Temperature	Pressure in bars	Duration in hours	Reagents	Products	Thorite	
					a_0	c_0
(1000° dry sinter)				$ThSiO_4$	7.08 Å	6.31 Å
800°	1000	24	Th:U=1:1 SiO_2 gel	Thorite, $(Th, U)O_2$ quartz, unident.		
700°	1000	24	Th nitrate, SiO_2 gel	Thorite	7.08	6.31
400°	1000	48	ThO_2, SiO_2 gels	Thorite	7.12	6.29
250°	40	72	ThO_2, SiO_2 gels	Thorite		
240°	34	96	ThO_2, SiO_2 gels	Thorite	7.14	6.29
150°	4.8	168	ThO_2, SiO_2 (ThF_4), SiO_2 gels	Thorite	7.18	6.28
700°	3100	24	Th:U=1:1 SiO_2 gels	Thorite, $(Th, U)O_2$ quartz, unident.	6.88	6.27
700°	1000	24	Th:U=4:1 SiO_2 gels	Thorite, $(Th, U)O_2$ quartz, unident.		
600°	1000	24	Th:U=4:1 SiO_2 gels	Thorite, $(Th, U)O_2$ quartz, unident.		
600°	3100	24	Th:U=1:1 SiO_2 gels	Thorite, $(Th, U)O_2$ quartz, unident.	7.00	6.30
400°	1000	48	Th:U=1:1 SiO_2 gels	Thorite, $(Th, U)O_2$, quartz	7.09	—

(Table 2). The products were very fine-grained. Thorite containing an unknown but considerable amount of uranium in solid solution, as evidenced by a variation in unit cell dimensions, was obtained at 400°–800° (Table 2). The solubility increases with temperature. The presence of U in solid solution decreases the cell size of $ThSiO_4$ and increases that of $ZrSiO_4$, as would be expected from the relative sizes of the ions involved. These runs were made with SiO_2 gel admixed with co-precipitated hydrous Th and U oxides, with Th:U=1:1. The products included uranoan thorite (which could not be separated for analysis), a fluorite-type oxide $(Th,U)O_2$ of variable cell size, and an unidentified phase.

The synthetic thorite showed the same features of infra-red absorption and variation in cell size as did the zircon. The material synthesized at 150° to 400° had changed cell dimensions; with decreasing temperature the value of a_0 increases and the value for c_0 decreases slightly (Table 2). On heating these samples to 1000° the patterns sharpened and the cell dimensions decreased to those of dry-sintered thorite. Infra-red absorption measurements obtained on material synthesized at 150° showed strong (OH) absorption at 2.75 microns in a sample dried at 110°. This absorption remained unchanged after the sample had been dried at 300° but disappeared when the sample had been heated to 1000°. Material synthesized at 700° did not show the (OH) absorption at 2.75 microns.

HUTTONITE

Huttonite is the monoclinic, monazite-type polymorph of $ThSiO_4$. It has been synthesized by Pabst (1952) by heating metamict thorite or a mixture of ThO_2 and SiO_2 in air to 900°–1000°, and higher. It also has been obtained by Karkhanavala (1956) by sintering ThO_2 and SiO_2 at 1500°. We have obtained huttonite by sintering poorly washed ThO_2 and SiO_2 gels at 1300°–1500°, and find that neither synthetic thorite nor crystalline thorogummite is converted to huttonite by heating for 24 hours at 1000°. We also have synthesized huttonite hydrothermally by heating very thoroughly washed ThO_2 and SiO_2 gels in water alone or in weakly alkaline water solutions at 700° and 1000 bars. If the gels are heated in dilute thorium nitrate or chloride solutions, or if uranium is present, thorite is produced. Huttonite also was obtained by heating the pure gels in water at 300° and 77 bars. Thorite is produced in this region if the gels are not thoroughly washed. The interplanar spacings of huttonite synthesized hydrothermally at 300° are distinctly smaller than those of material synthesized by sintering at 1400°.

HYDROTHERMAL RE-CRYSTALLIZATION OF METAMICT THORITE AND ZIRCON

Wholly metamict thorite and zircon can be recrystallized by heating in water at temperatures much lower than those required by heating dry in air. The metamict thorite from Hybla, Ontario, analyzed by Ellsworth (1927), does not give a diffraction pattern either when unheated or after heating in air at 600° for 24 hours; strong patterns of huttonite and ThO_2 appear only after heating to 1050° or higher. This is in general agreement with the work of Pabst (1952). The DTA measurements of Kulp, Volchok, and Holland (1952) indicate that metamict zircon recrystallizes at 890°–910°.

The Hybla thorite recrystallizes and gives a strong and sharp pattern of thorite—not huttonite—when very finely powdered and then heated with water alone for two days at 600° and 1000 bars or for seven days at 500° and 2000 bars. Lower temperatures were not investigated. Wholly metamict thorite from Arendal, Norway, and zircon from Brevik, Norway, also recrystallized in water at 600° and 1000 bars. Infra-red absorption measurements made on the unheated thorite did not show (OH) absorption at 2.75 microns but did show strong molecular water absorption at 6.0 microns and weak bands of hydrogen-bonded (?) and molecular water at 2.875–2.95 and 3.075–3.125 microns. The same material after heating in water showed a small but definite (OH) absorption at 2.75 microns. This recalls the natural alteration of metamict thorite to hydroxyl-containing thorogummite described by Frondel (1953).

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