Hydrothermal Synthesis of Some Varieties of Zircon

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Some varieties of zircon which contain yttrium, niobium, and phosphorus in solid solution have been synthesized at temperatures 500—550 °C and under pressures 700—1000 kg/cm^2. In zircon containing yttrium, the unit cell constants a and c increase with increase in yttrium content up to 70 mol%. From IR and TGA studies, a valence compensation accompanying the substitution of yttrium is assumed to be effected by a concomitant substitution of OH for O sites, and the variety is represented by a formula $(Zr,Y)Si(O,OH)_4$. On the other hand, the substitution of Nb^{5+} for Zr^{4+} is followed by a decrease in the cell constants. Zircon phase did not form from starting materials with more than 20 mol% of niobium content. From the syntheses of zircon containing both yttrium and niobium, the formula $(Zr,Y,Nb)\ Si(O,OH)_4$ is found to be appropriate for naegite. An attempt was made to synthesize some solid solutions between zircon and xenotime. The unit cell constant c of the products is found to decrease with the substitution of PO_4 for SiO_4.

Zircon, $ZrSiO_4$, a widely distributed accessory mineral in igneous rocks, is known to have many varieties such as cyrtolite (water, yttrium rich zircon), naegite (yttrium, niobium rich zircon) and yamaguchilite (yttrium, phosphorus rich zircon).$^{1)}$ Since the varieties of zircon usually occur in metamict state due to radioactive elements such as uranium and thorium, the properties of the varieties and the mechanisms of the substitutions are not well-known. In zircon, each silicon atom is surrounded by a tetrahedral group of four oxygen atoms at a distance of 1.61 Å, while each zirconium atom lies between four oxygen atoms at 2.15 Å and a further four at 2.29 Å. These Zr–O distances lie between the limits of 8- and 6-fold coordination.$^{2)}$ We have studied the isomorphous substitutions of Y^{3+}, Nb^{5+}, and P^{5+} for Zr^{4+} and Si^{4+} sites in zircon. From the relative sizes of the ions involved, it is expected that Zr^{4+} is substituted by Y^{3+} and Nb^{5+}, and Si^{4+} by P^{5+}. This is found to be true in the present work.

Frondel and Collette carried out the hydrothermal synthesis of zircon over the range 150 °C and 4.8 bars to 700 °C and 3100 bars by heating admixed ZrO_2 and SiO_2 gels with water in steel bombs.$^{3)}$ Single crystal of zircon was also obtained by hydrothermal method.$^{4,5)}$ In our study, the syntheses of some varieties were carried out by the hydrothermal crystallization of precipitated gels of stoichiometric composition, and the mechanisms of the substitutions and the variations of cell constants were studied.

Experimental

The reagents employed were dilute HNO_3 solutions of $ZrO(NO_3)_2 \cdot 2H_2O$ (EP-grade) and Y_2O_3 (99.99% pure), dilute H_2SO_4 solution of Nb_2O_5(99.9% pure) and aqueous solutions of Na_2SiO_3 (CP-grade, standardized by gravimetric analysis) and $(NH_4)_2HPO_4$ (EP-grade). The starting gels were prepared by mixing each solution to the desired composition. The mixed solutions were adjusted to pH 10 with dilute ammonia. The resulting precipitates were centrifuged, washed with dilute ammonia, dried at 130 °C in an oven and finely ground. The gels were sealed with 0.05 ml water in Ag capsules, inner diameter 3 mm and length 35 mm. The hydrothermal synthesis was carried out in a 150 ml cold seal rene bomb.

All the products were examined by the X-ray powder diffraction method using CuK_α radiation and internal silicon standard. The composition of synthesized zircon is assumed to have a composition corresponding to the initial gel when it appears in a single phase in the product. Unit cell constants were calculated according to the known space group. Some of the products were examined by infrared spectroscopy by the KBr disk method and TGA.

Results and Discussion

Isomorphous Substitution of Yttrium in Zircon. Syntheses of zircon which contains various amounts of yttrium were carried out with gels which have the composition $ZrO_2 : Y_2O_3 : SiO_2 = 1-x : x/2 : 1$, where x varied from 0 to 1. The runs were made under the conditions 530 °C, and 700 kg/cm^2 for 55 h. The products were white and microcrystalline. The calculated unit cell constants plotted against the initial gel composition are given in Fig. 1. The cell constants a and c increase linearly as a function of the composition up to about 70 mol% of yttrium content. The significant increase in the cell constants seems to indicate the continuous substitution of large Y^{3+} ion for Zr^{4+} ion. The limit of the substitution is about 70 mol% under our experimental conditions. The product is no longer present in a single phase beyond 70 mol% of yttrium content, and β-yttrialite $Y_2Si_2O_7$ phase and a small amount of an unidentified phase appear besides the zircon phase. Therefore, zircon with high yttrium content (more than 70 mol%) is presumed to be unstable and stabilized by forming

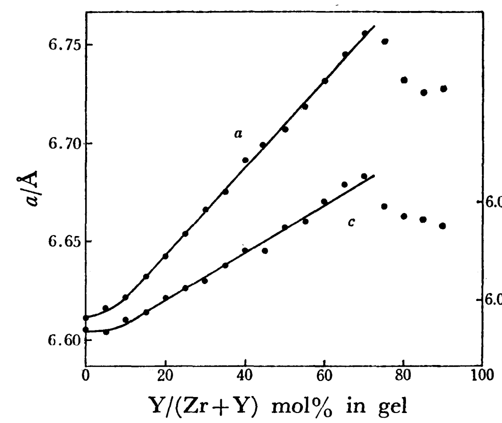

Fig. 1. Unit cell constants a and c of zircon containing Y.

β-yttrialite and zircon with low yttrium content.

The substitution of trivalent yttrium for quadrivalent zirconium requires some valence compensations in the zircon structure. From an EPR study of natural zircon, Bershov found that when two Y^{3+} ions enter simultaneously into two neighboring zirconium sites the structure is stabilized by the formation of O^- center.[6] The valence compensation of this type, however, seems to be possible only when yttrium is present in zircon in a low concentration less than a few per cent. It should be noted that some varieties of zircon often contain significant amount of water up to 10%. Frondel postulated that some of the water characteristically present in metamict zircon should be regarded as essential and required for the valence compensation in the structure.[7] He suggested a substitution of OH for O in SiO_4 tetrahedra as the valence compensation on the basis of the chemical analysis and thermal study of a natural sample by Kostyleva.[8] This mechanism is adopted here to explain the valence compensation in synthesized zircon. In order to determine the presence of OH, infrared measurements were made on a number of the products which had been dried at 130 °C before measurements. Figure 2 shows IR spectra of pure zircon and zircons containing niobium (16 mol%), yttrium (34 mol%) and yttrium (32 mol%) which was heated at 350 °C for 40 min in advance. Figure 3 shows IR spectra in the 2500—4000 cm^{-1} region of zircon with 5, 25, 45, and 65 mol% yttrium content and zircon with 60 mol% yttrium content which was heated at 1100 °C for 2 h in advance. Zircon containing yttrium gives weak infrared OH absorptions at about 3400, 3200, and 1600 cm^{-1}. Since the absorption at about 3200 cm^{-1} remained after the sample had been dried at 350 °C but disappeared when it had been heated to 1100 °C, the absorption is assumed to be due to OH substituting for O in the SiO_4 tetrahedra. The absorptions at about 3400 and 1600 cm^{-1} disappeared when the sample had been dried at 350 °C. These absorptions are assigned to molecular water and OH in the hydrogen bond. The relative intensity of the peak at about 3200 cm^{-1} increases with an increase in yttrium content (Fig. 3). The result seems to support the view that the absorption is due to OH substituting for O in the SiO_4 tetrahedra. The doublet absorption band centered at about 1000 cm^{-1} has been assigned to the Si–O bonds. We see from Fig. 2 that the doublet structure of the absorption band is very indistinct in zircon containing yttrium as compared with that of the band in pure zircon and zircon containing niobium. The indistinctness for the former is probably due to the non-uniformity of the strength of the Si–O bonds in zircon containing yttrium because it has two kinds of Si–O bond, *viz.* Si–O and Si–OH.

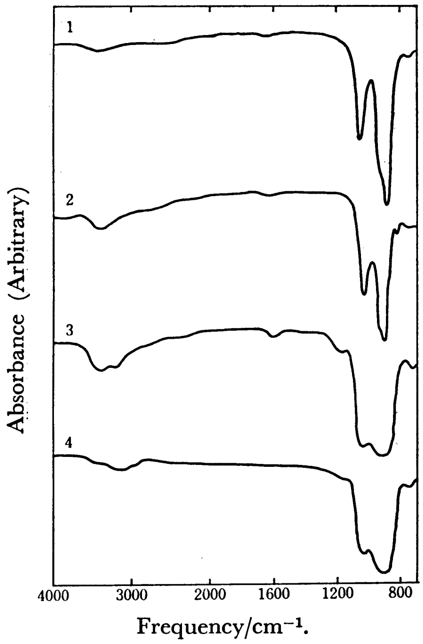

Fig. 2. IR spectra of zircon.
1: Pure, 2: containing 16 mol% Nb, 3: containing 34 mol% Y, 4: containing 32 mol% Y, heated at 350 °C for 40 min.

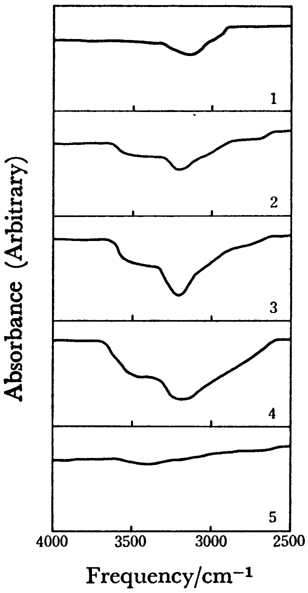

Fig. 3. IR spectra of zircon with Y content of 1 : 5 mol%, 2 : 25 mol%, 3 : 45 mol%, 4 : 65 mol%, 5 : 60 mol%, heated at 1100 °C for 2 h.

TGA study was carried out for the sample containing 40 mol% of yttrium. The result is given in Fig. 4. The TGA curve shows a gradual loss of H_2O up to 0.85% at 350 °C, and a gradual loss of 2.0% H_2O

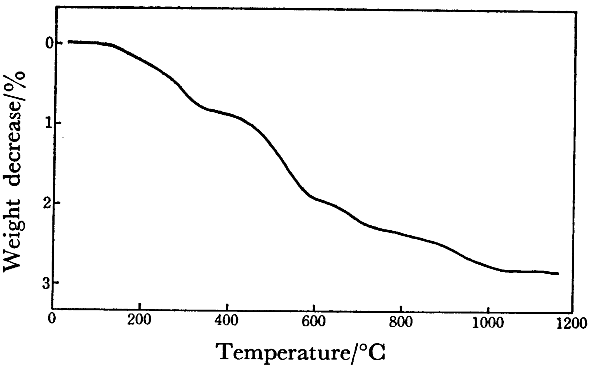

Fig. 4. TGA cuive for zircon containing 40 mol% Y.

from 350 to 1000 °C. The former seems to be caused by the dehydration of molecular water and the latter by that of OH substituting for the O sites. The latter 2.0% loss agrees with the calculated value 1.97% evaluated by assuming that the concentration of OH substituting for the O sites in zircon is equal to that of yttrium. The above observations suggest that the following formula is appropriate for the synthesized zircon : $(Zr,Y)Si(O,OH)_4$.

X-Ray diffraction powder pattern for the product heated at 1100 °C for 2 h shows the presence of β-yttrialite as well as zircon. This indicates that $(Zr,Y)Si(O,OH)_4$ decomposes to $ZrSiO_4$, $Y_2Si_2O_7$, and H_2O.

Study on Naegite by Means of Synthesis. One variety of zircon which mainly contains yttrium and niobium is called naegite* and usually written as $(Zr,Y)(Si,Nb)O_4$. The site occupancy of niobium in zircon is of interest. In order to confirm the assumption that Nb^{5+} does not substitute for Si^{4+}, attempts were made to obtain zircon containing niobium from gels having the composition $ZrO_2 : Nb_2O_5 : SiO_2 = 1-x : x/2 : 1$, where x varies from 0 to 1. The syntheses were carried out under the conditions 530 °C and 700 kg/cm^2 for 55 h. Attempts to prepare zircon containing over 20 mol% niobium were not successful, resulting in mixed phases of ZrO_2, SiO_2 and unknown substances which gave very diffuse X-ray powder patterns. The zircon phase is found to form only when niobium is less than about 15 mol% in the gel composition. A plot of the unit cell constants of the synthesized zircon *versus* the composition is given in Fig. 5. The cell constants decrease slightly with increase in niobium content up to 10 mol% but remain nearly constant above 10 mol%. In view of the relative size of ions, it seems reasonable to consider that the observed decrease in the cell constants results from the substitution of Nb^{5+} for Zr^{4+} and not for Si^{4+}. The substitution of Nb^{5+} for Zr^{4+} requires valence compensation. There are two explanations: (1) It is achieved by cation deficiency. When the concentration of the deficiency is high, cation deficient zircon becomes unstable. This corresponds to the fact that zircon with high niobium content is not obtained in our syntheses. (2) Niobium exists in zircon in the quadrivalent state but not in the quinquevalent state. The possibility of its presence was reported by Matkovich and Corbett.[9] They heated equimolar amounts of ZrO_2 and SiO_2 in the presence of Nb_2O_5 at 1000 °C in an electric furnace and obtained zircon with cell constants slightly smaller than that of pure zircon. They also heated equimolar amounts of ZrO_2 and SiO_2 in the presence of V_2O_5 and obtained light blue zircon. The color implies the presence of quadrivalent vanadium in zircon. By analogy with vanadium in zircon, they inferred the presence of quadrivalent niobium in zircon. There is, however, no direct evidence of quadrivalent niobium and its presence remains to be clarified.

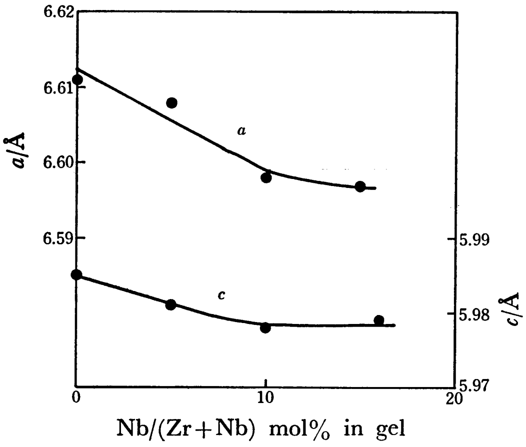

Fig. 5. Unit cell constants *a* and *c* of zircon containing Nb.

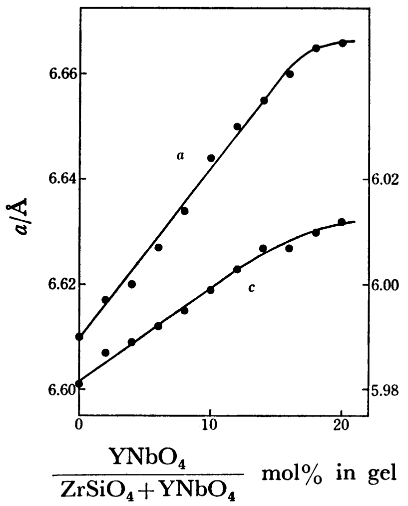

Fig. 6. Unit cell constants *a* and *c* of zircon containing Y and Nb.

The syntheses of naegite were carried out under the conditions 530 °C, and 1000 kg/cm^2 for 81 h. The initial gels had the composition $(Zr_{1-x},Y_x)(Si_{1-x},Nb_x)O_4$, x varying from 0 to 0.2. A plot of the cell constants of the products against the composition is shown in Fig. 6. If we compare the curves in Fig. 1

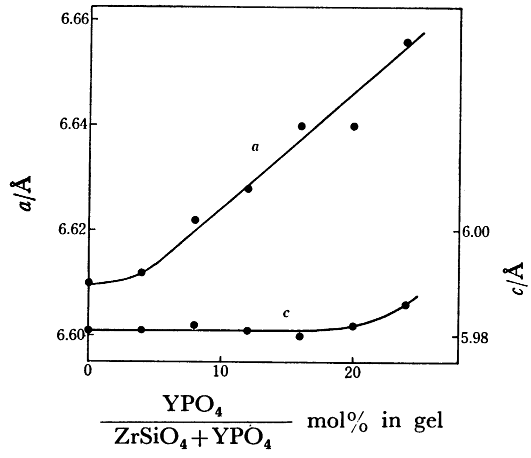

Fig. 7. Unit cell constants *a* and *c* of zircon containing Y and P.

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* A name proposed by T. Wada (1904).

and Fig. 6, we see that their shapes resemble each other. Since zircon does not contain niobium in high concentration, the variation in the cell constants seems to be mainly due to the yttrium concentration in synthesized naegite. This corresponds to the fact that yttrium is present in much higher concentration than niobium in natural naegite. Substitution of OH for O sites seems to occur in naegite for valence compensation. Thus the formula $(Zr, Y, Nb)Si(O, OH)_4$ might be appropriate for naegite. The phase $(Zr, Y, Nb)Si(O, OH)_4$ was no longer present in a single phase under the hydrothermal conditions 700 °C and 1000 kg/cm^2, decomposing into fergusonite $YNbO_4$ and zircon phases.

An Attempt to Synthesize Yamaguchilite $(Zr,Y)(Si,P)O_4$. The syntheses of yamaguchilite,* solid solutions oi zircon and xenotime (YPO_4), were carried out under the conditions 530 °C and 1000 kg/cm^2 for 81 h. The cell constants of synthesized $(Zr,Y)(Si,P)O_4$ *versus* initial gel composition are plotted in Fig. 7. Although there is no direct evidence of the $ZrSiO_4 : YPO_4$ ratio in the products, there is a significant difference in the variation of the cell constant c between the curves in Figs. 1 and 7: in $(Zr,Y)(Si,P)O_4$, c remains nearly constant up to 20 mol% of the yttrium content. Therefore the substitution of PO_4 for SiO_4 is found to cause a relative decrease in c dimension, not a dimension.

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* A name proposed by K. Kimura and Y. Hironaka¹⁾ (1936).