Variation in the structure of zircon.

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IN the course of an investigation on refractory materials, in which the identification of minerals by their X-ray diffraction patterns had a prominent place, an interesting observation was made on a zircon of gem quality which was lent to us by the courtesy of Mr. B. W. Anderson.

It may be recalled that the existence of three allotropes has been postulated in order to explain the considerable variations of physical properties which are found when comparing different specimens of zircon. In particular, densities ranging from 3·95 to 4·86 have been observed, the density of zirconium silicate, calculated from X-ray measurements, being 4·71. The difference between 4·71 and 4·86 may be assumed to be due to the presence in solid solution of metals heavier than zirconium, amongst which hafnium is usually present to an appreciable extent. On the other hand, the discrepancy between 4·71 and 3·95 is too large to be due to the influence of impurities of low density. The work of Anderson and Payne, of Chudoba, and of others,[1] has discredited the alternative hypothesis of allotropes of zircon, and the view is generally accepted that natural zircon of low density contains decomposition products of the original mineral. Thus, whilst zircon having a density of about 4·7 may be expected to exhibit a normal X-ray diffraction pattern, the characteristic spots or lines (according to the method of obtaining the pattern) produced by zircon of low density are diffuse to an extent depending on the deviation from the standard density. The diffuse pattern, however, is still that of zirconium silicate, although in one instance Chudoba observed in addition a pattern corresponding with a cubic form of zirconia, which is known to exist in the presence of a small quantity of magnesia. The liberated silica appears to form a glassy phase.

It would appear that the lattice of zircon of low density contains a vast number of imperfections which are equivalent to localized decomposition, the products of which are very commonly amorphous in the case of material of gem quality. The degradation of the lattice is associated with changes in optical properties, and zircon gems of very low density are usually green.

The specimen[2] lent to us by Mr. Anderson is a typical, almost clear green stone from Ceylon, and has the very low density of 3·965. For X-ray examination the pear-shaped specimen was mounted so that molybdenum radiation could be passed through its tip, the specimen being rotated during exposure. Contrary to expectations, the diffraction pattern, instead of being that of a single crystal, is a sharp pattern of the 'powder' type showing no appreciable preferred orientation, or in other words, the gem contains a large number of minute crystals with

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[1] Mineralogical Abstracts, 7–130, 131, 522, 523; 8–123, 377.

[2] B. W. Anderson and C. J. Payne, Gemmologist, London, 1939, vol. 9, p. 4. [M.A. 7–522.]

their axes arranged at random. The pattern (fig. 1) is that of monoclinic zirconia (fig. 2), no trace of the silicate or of crystalline silica being evident. If we assume the gem to contain the theoretical proportions of zirconia and silica (67·23:32·77), and take the density of monoclinic zirconia to be 5·70, and that of amorphous silica to be 2·21, the calculated density of the mixture is 3·76. This is somewhat lower than the measured density of 3·965, but the difference may be reasonably ascribed to the presence of hafnium and other impurities, and perhaps partly to a slight excess of zirconia in the gem, for analyses of various stones have shown such variation to be possible.

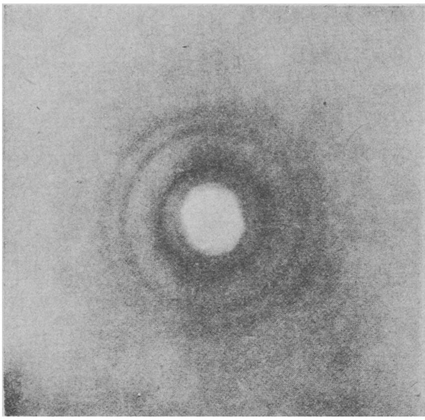
FIG. 1. Low-density gem zircon.

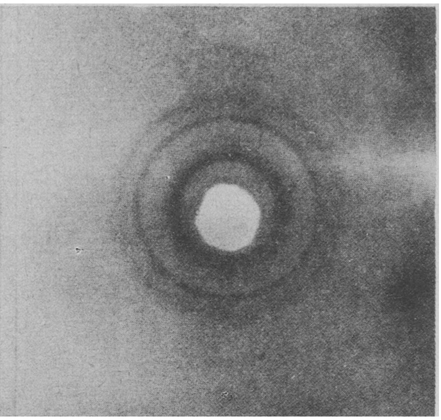
FIG. 2. Monoclinic zirconia.

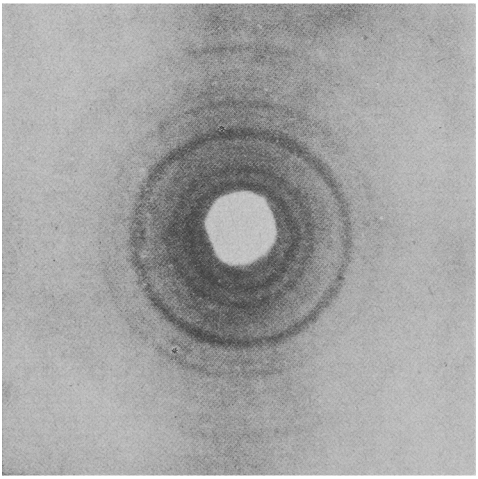
FIG. 3. Zirconium silicate (normal zircon).

That there is little or no preferred orientation of the zirconia crystallites in the gem is indicated by the close approach to uniformity of density in each circle appearing in fig. 1. In fact, each separate crystallite yields a pattern consisting of one or more groups of spots, each group consisting of spots falling on one of a number of imaginary circles through the common centre of which passes the axis of the original X-ray beam. The combination of such patterns produced by a large number of randomly oriented crystallites results in a number of rings of almost uniform density.

Whilst it is easy to understand that decomposed zircon consisting of amorphous material should be transparent, it is surprising to find that a material consisting of a large number of crystallites embedded in a glass of high silica content is almost clear, for there is a large difference between the refractive indices of monoclinic zirconia and that of amorphous silica. The crystallites in the almost clear gem are presumably too small to scatter much light, and for this reason their linear dimensions cannot be much greater than 10^{-5} cm. The X-ray pattern shows, however, that they cannot be much smaller than this, for if they were, the diffraction rings would be more diffuse. The range of possible size of the crystallites is therefore fairly small. The value of 10^{-5} cm. is to be regarded merely as an estimate which roughly satisfies the conditions.

We have recently had occasion to carry out various heat-treatments on zircon of normal density and constitution, and on certain related materials. By means of X-ray analysis estimates have been made of the proportions of zirconium silicate and zirconia in the crystalline part of the products. Zirconium silicate is tetragonal, and in all our experiments the zirconia has been found to be monoclinic, whilst the silica was always present in a glassy state. Probably the presence of impurities and the comparatively rapid rate of cooling were hindrances to the crystallization of the silica. As thermal decomposition proceeds, the X-ray pattern due to zirconium silicate naturally becomes fainter, but in our experience these patterns remain sharp, unlike the pattern given by Chudoba's gems. On the other hand, the zirconia pattern, although it becomes stronger with increasing decomposition of the silicate, becomes at the same time more diffuse. Such diffuseness suggests the presence of very fine particles or of lattice distortion, or of both. With regard to the first possibility, zirconia crystallites can be seen with the microscope in specimens of zircon which have undergone considerable decomposition, and these crystallites appear larger the further decomposition has proceeded. They may, however, be accompanied by crystallites which are too small to see, and which may thus be responsible for the broadening of the lines of the X-ray diffraction pattern.

Some of the results which may be relevant in connexion with any theory devised to explain the formation of a gem specimen such as described above are given in table I.

With regard to the additions shown in table I, the metals added to specimens 14 to 25 and to specimens 28 and 29 are chemically equivalent to the potassium contained in an addition of 2 % KF. In the case of specimens 30 and 31 the fluorine addition is equivalent to an addition of 2 % KF.

Considering specimens 1 to 6 it will be noticed that heating for an hour at 1,650° C. effects some decomposition. It is possible, however, that the amount of decomposition occurring at a high temperature is greater than that found after cooling, since recombination may occur if cooling be slow enough. The series of specimens 7 to 10 shows that zircon which has decomposed to a considerable extent can be reconstituted by firing to Cone 20 (about 1,500° C.). Similarly, experiments 32 and 33 show that zirconium silicate may be synthesized.

Heatings and coolings described as slow were carried out in a recuperative kiln in which heating occupied about a week, and cooling about three days. Those described as quick were carried out in a smaller furnace which was taken to the maximum temperature in a few hours, and cooled in about 24 hours. It seems unlikely that much recombination took place during the cooling of this furnace, for specimens 16, 21, and 27 contained no zirconium silicate after firing. Specimen 34 was heated in a recuperative kiln which was better lagged than that used for other slow firings. Unlike the cases just quoted, specimen 34 contained no addition. The estimated degree of decomposition is in line with the corresponding values for specimens 1 to 6.

TABLE I. Heating experiments.

No.	Specimen.	Addition to zircon wt. %.	*Heating and cooling rate.*	Firing schedule. (*Cone 20, about* 1,500° C.)	Estimated composition of crystalline part after cooling. $ZrSiO_4$ (tetragonal).	ZrO_2 (monoclinic).
1.	Zircon compact	0	slow	Cone 20	100	0
2.	No. 1 re-fired	0	slow	1,500° C. for 6 days	100	0
3.	No. 1 re-fired	0	quick	1,600° C. for 1 hour	100	0
4.	No. 1 re-fired	0	quick	1,650° C. for 1 hour	90	10
5.	No. 2 re-fired	0	quick	1,700° C. for 1 hour	60	40
6.	No. 1 re-fired	0	quick	1,750° C. for 1 hour	60	40
7.	Zircon sand	0	—	Unfired	100	0
8.	Zircon sand	0	quick	1,750° C. for 1 hour	30	70
9.	No. 8 crushed, compacted, and re-fired	0	slow	Cone 20	100	0
10.	No. 9 re-fired	0	quick	1,700° C. for 1 hour	50	50
11.	Zircon gem from Ceylon	0	—	Unfired	100	0
12.	Green zircon gem from Ceylon (fig. 1)	0	—	Unfired	0	100
13.	Zircon sand	5% KF	quick	1,700° C. for 1 hour	5	95
14.	Zircon compact	3% BaF_2	slow	Cone 20	70	30
15.	No. 14 re-fired	ditto	slow	1,500° C. for 6 days	70	30
16.	No. 15 re-fired	ditto	quick	1,700° C. for 1 hour	0	100
17.	Zircon compact	1·1% MgF_2	slow	Cone 20	95	5
18.	No. 17 re-fired	ditto	slow	1,500° C. for 6 days	95	5
19.	Zircon compact	1·9% AlF_3	slow	Cone 20	100	0
20.	No. 19 crushed, compacted, and re-fired,	ditto	slow	Cone 20	100	0
21.	No. 20 re-fired	ditto	quick	1,700° C. for 1 hour	0	100
22.	Zircon compact	1·3% Li_2CO_3	slow	1,500° C. for 6 days	100	0
23.	No. 22 re-fired	ditto	quick	1,700° C. for 1 hour	60	40
24.	Zircon compact	3·9% Pb_3O_4	slow	Twice to Cone 20	100	0
25.	No. 24 re-fired	ditto	quick	1,700° C. for 1 hour	75	25
26.	Zircon compact	3% China-clay	slow	Cone 20	100	0
27.	No. 26 re-fired	ditto	quick	1,700° C. for 1 hour	0	100
28.	Zircon compact	2·4% K_2CO_3 added as frit	slow	Cone 20	100	0
29.	No. 28 re-fired	ditto	quick	1,700° C. for 1 hour	30	70
30.	Zircon compact	2·5% $ZrOF_2$	slow	1,500° C. for 6 days	95	5
31.	No. 30 re-fired	ditto	quick	1,700° C. for 1 hour	40	60
32.	72·3 parts $ZrOF_2$ + 30 parts SiO_2 (pptd.)		slow	1,500° C. for 6 days	60	40
33.	142 parts K_2ZrF_6 + 30 parts SiO_2 (pptd.)		slow	1,500° C. for 6 days	70	30
34.	Zircon compact	0	specially slow	1,690° C.	70	30

From consideration of the phase rule it would be expected that equilibrium would be possible between zirconium silicate, zirconium oxide, and the amorphous phase at a fixed temperature, or more exactly at a temperature varying to an unimportant extent with ordinary variations of pressure. In the presence of impurities, instead of an equilibrium temperature, a small range of temperatures would be expected. The experiments quoted above, based on X-ray diffraction data, indicate that the decomposition temperature of zirconium silicate probably lies between 1,500° and 1,650° C.

TABLE II. Chemical analyses of zircon sand from Travancore, before and after heating.

	Natural zircon sand as received.	After firing to 1,700° C. for 1 hour.
SiO_2	29·41	31·62
ZrO_2+HfO_2	61·82	63·01
TiO_2	2·33	2·24
Al_2O_3+rare-earths+P_2O_5	5·61	2·60
Fe_2O_3	0·45	0·48
Mn_3O_4	0·27	0·11
MgO	0·10	nil
CaO	nil	nil
Na_2O	0·12	0·36
	100·11	100·42

At an early stage of the present work, there was some reason to suspect that the addition of a small quantity of potassium fluoride to zircon, followed by suitable heat-treatment, might result in vigorous crystal growth. Figs. 4 and 5 show respectively raw zircon sand, and a compact of the same with addition of 4 % of potassium fluoride. The compact was maintained for 4 hours in a gas furnace at a temperature between 1,500° and 1,550° C. The well-developed crystal with sharp edges shown in fig. 5 is typical of many others, and has probably been formed by growth from the original material. The average difference in size, however, between the new and the old crystals is small, and owing to difficulties of sampling a sure choice cannot be made between the alternative hypotheses of crystal growth and of slow etching of the sand grains by the glassy matrix. In attempting to form a judgement, it must be remembered that fig. 5 shows prominently the pyramid faces of zircon, but the greater part of the crystal is hidden by these faces.

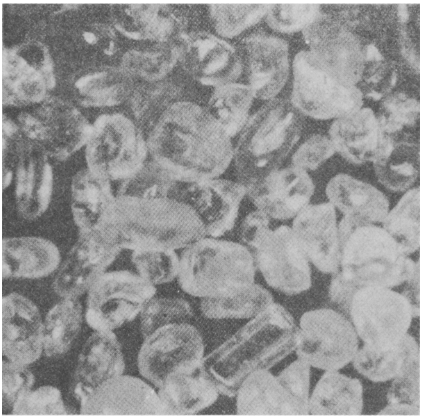

FIG. 4. Natural zircon sand. × 60.

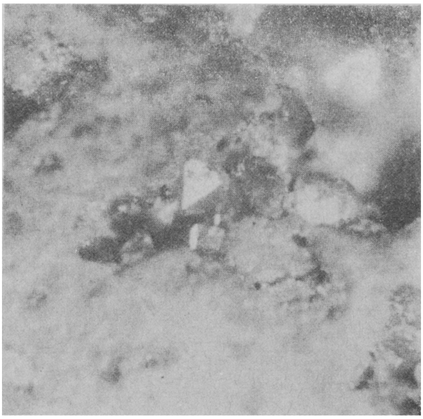

FIG. 5. Recrystallized zircon. × 60.

It is hoped that the information obtained, especially the establishment of the decomposition temperature in the neighbourhood of 1,580° C., may prove of assistance to mineralogists.

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