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Study of metamict Ceylon zircons

E. R. VANCE
Chemistry Department, University College, London

B. W. ANDERSON
The Laboratory of the London Chamber of Commerce, 15 Hatton Garden, London

SUMMARY. X-ray, density, refractive index, and optical absorption measurements have been made on metamict Ceylon zircons. The appearance of a previously reported anomalous optical absorption spectrum in low Ceylon zircons has been associated with small particles of cubic or tetragonal zirconium dioxide in a radiation-damaged zircon lattice, in both heated and unheated stones. No evidence of a previously reported second phase was detected in intermediate Ceylon zircons.

ZIRCON often contains significant quantities of uranium and thorium. The amount by which the density and refractive index of a zircon are lower than that of non-metamict zircon provides a measure of the lattice breakdown due to α-particles emanating from the uranium and thorium impurites (see e.g. Blumenthal, 1958, pp. 201–29; Deer *et al.*, 1962; Anderson, 1962, 1963).

Holland and Gottfried (1955) reported that intermediate zircons having densities between about 4·6 and 4·1 gm cm^{-3} (cf. ~4·7 gm cm^{-3} for non-metamict zircon) showed an extra X-ray reflection near the 112 zircon reflection, with the intensity of the extra reflection depending on the degree of lattice breakdown. However, their X-ray work was confined to powders and their data were reported only in the immediate vicinity of the 112 zircon reflection.

Anderson (1962, 1963) reported that low Ceylon zircons, with densities of about 4·0 gm cm^{-3}, were apparently composed of two classes. One group, the *minority*, showed an anomalous (A) optical absorption spectrum, with strong bands at 6910, 6855, 6690, 6525, 4730, and 4510 Å, whereas the major group showed a nearly-absent spectrum, with only a weak, diffuse band near 6560 Å and sometimes with a fairly sharp, weak band at 5200 Å. This major group, however, showed the A spectrum after heating at 800 to 1000 °C, the change being accompanied by a slight decrease in density and refractive index. However, two of these stones showed some development of the normal (N) absorption spectrum, the strong lines of which occur at 6535, 4830, and 4315 Å, as well as the A spectrum, after being heated for 2 hr at 1100 °C. A density measurement on one of these stones showed an increase from 4·00 to 4·21 gm cm^{-3}. One of the unheated stones showing the A spectrum was reported by Stott and Hilliard (1946) to give an X-ray powder pattern of monoclinic ZrO_2. However, Claringbull (private communication) found that a single-crystal chip from an unheated stone showing the A spectrum gave a slightly diffuse powder pattern that was indexable as cubic ZrO_2. Claringbull also found that chips of other low zircons showed

The X-ray work on intermediate Ceylon zircons was carried out on fragments of three yellow–green stones, of densities 4·48, 4·29, and 4·18 gm cm^{-3}.

Results and discussion

Low zircons: stones X and Y. The X-ray results on heated chips of X and Y are shown in table II and some photographs are shown in figs. 1–3. Several specimens of X and Y were annealed later at a temperature lower than that of a previous anneal; the results were characteristic of the higher annealing temperature.

The largest piece of each of X and Y was successively annealed for 1 hr at 850 °C, 950 °C, 1100 °C, and 1225 °C. The results of the optical and density measurements are given in table III; the X-ray results were consistent with those in table II except that no trace of the powder pattern of tetragonal ZrO_2 was observed from the largest piece of Y after it was annealed for 1 hr at 1225 °C. The normal (N) and anomalous (A) optical absorption spectra are shown in fig. 4.

A second piece of X was vacuum-annealed at 850 °C and 950 °C and the results were essentially similar to those obtained for the largest piece of X. The second piece of X and a second piece of Y were successively annealed, for 1 hr at 1150° and 1350 °C. The results are included in table III; the X-ray results were consistent with those in table II. For each piece of X and Y no refractive index values could be obtained after annealing at temperatures of 1150 °C and above.

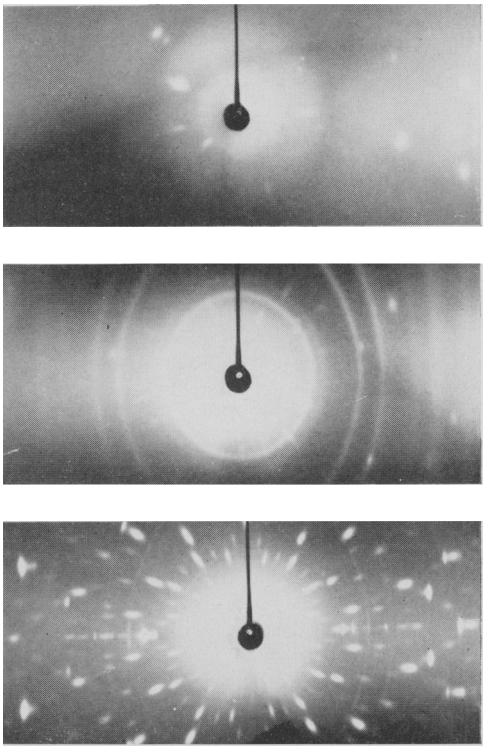

FIG. 1. Chips from stone X. Laue photographs. *Top.* Heated 1 hr at 700 °C, random orientation, not filtered. *Centre.* Heated 1 hr at 850 °C, random orientation, filtered. *Bottom.* Heated 1 hr at 1150 °C, *c* axis along beam, *a* axis vertical, unfiltered.

For annealing temperatures $\leqslant$1000 °C, the optical and X-ray results in tables I, II, and III show that the slightly diffuse powder pattern indexable as cubic ZrO_2 appears to be characteristic of stones showing the A spectrum, i.e. of Y-type stones after heating to $\leqslant$1000 °C and X-type stones after heating at 800 to 1000 °C. Though the pattern was indexable as cubic ZrO_2, the X-ray lines were too broad to decide whether the ZrO_2 was cubic or tetragonal; the c/a ratio of tetragonal ZrO_2 is about 1·02 (quite close to unity). However, since the ZrO_2 was definitely tetragonal after

TABLE II. *X-ray results on low zircons*

Annealing temp. (1 hr)	Chips from X		Chips from Y	
	Quality of Laue pattern	Powder pattern	Quality of Laue pattern	Powder pattern
< 800 °C	Faint, diffuse	—	Faint, diffuse	Slightly diffuse, indexable as cubic ZrO_2
800 °C	,, ,,	Very weak, diffuse, indexable as cubic ZrO_2	,, ,,	,, ,,
850 °C	,, ,,	Slightly diffuse, indexable as cubic ZrO_2	,, ,,	,, ,,
950 °C	,, ,,	,, ,,	,, ,,	,, ,,
1000 °C	Fairly well-defined, diffuse	,, ,,	Fairly well-defined, diffuse	,, ,,
1100 °C	Well-defined, diffuse	Sharp, tetragonal ZrO_2	Well-defined, diffuse	Sharp, tetragonal ZrO_2
1150 °C	As above + diffuse streaks	Very weak, sharp, tetragonal ZrO_2	As above + diffuse streaks	,, ,,
1225 °C	,, ,,	—	,, ,,	Very weak, sharp, tetragonal ZrO_2
1350 °C	,, ,,	—	,, ,,	—

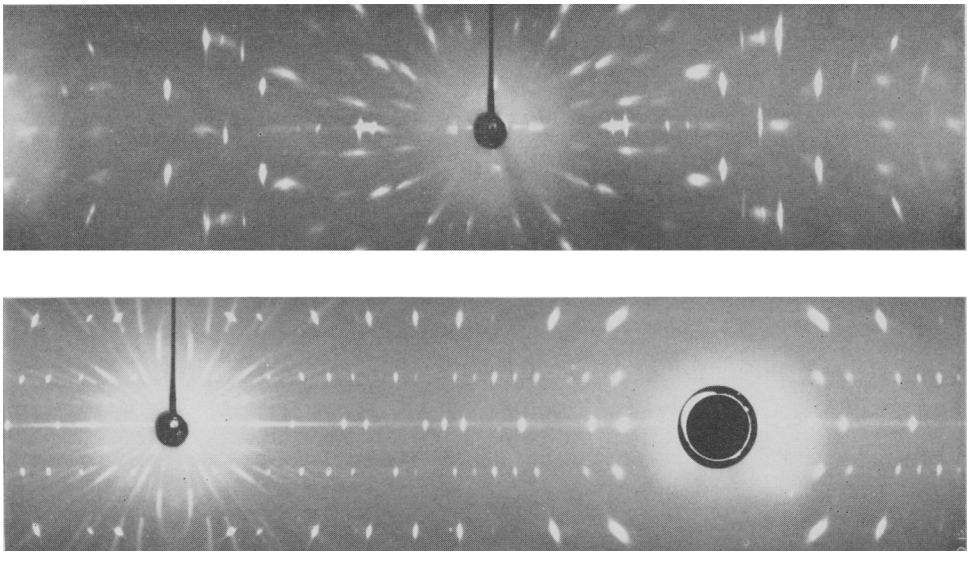

FIG. 2. Chip from stone X, heated 1 hr at 1350 °C, *c* axis vertical. *Top.* Laue photograph, unfiltered, *a* axis along beam. *Bottom.* Rotation photograph, filtered: note streaks associated with zircon reflections.

annealing at 1100 °C, when the stones showed the A spectrum only, the ZrO_2 observed after annealing at lower temperatures might well have been tetragonal. The problem of distinguishing cubic and tetragonal ZrO_2 has also been discussed by Wittels *et al.* (1962). It was of interest that a lower annealing temperature (1225 °C) was required to remove the X-ray evidence of tetragonal ZrO_2 than that required to remove the A spectrum (1350 °C); the reason for this behaviour is not clear but it should be noted that whereas the optical spectrum is derived from the bulk of the specimen, an X-ray pattern is derived from a thin surface layer only.

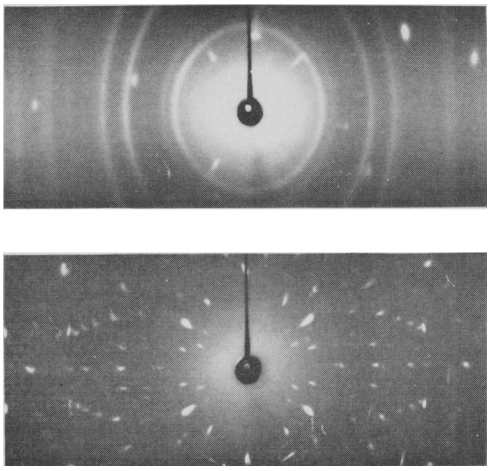

FIG. 3. Chips from stone Y. Laue photographs. *Top.* Not heated. Random orientation. Filtered. *Bottom.* Heated 1 hr at 1350 °C. *c* axis along beam, *a* axis vertical.

Since monoclinic ZrO_2 was not detected in any stone showing the A spectrum, the conclusion of Stott and Hilliard (1946; see above) was not confirmed. However, it should be mentioned that both figs. 1 and 2 in the paper of Stott and Hilliard (1946) resemble powder patterns of cubic (or tetragonal) ZrO_2 rather than those of monoclinic ZrO_2—see powder patterns of both species in Wittels and Sherrill (1956).

TABLE III. *Optical and density results on heated zircons*

Annealing temp. (1 hr)	Density		Refractive index		Absorption spectrum	
	X	Y	X	Y	X	Y
—	3·99	3·96	1·823	1·793	Weak, diffuse band near 6560 Å	A
850 °C	3·94	3·93	1·796	1·795	A	A
950 °C	3·94	3·97	1·795–9†	1·794–8†	A	A
1100 °C	4·02	4·05	1·790–3†	1·796	A	A
1150 °C*	4·12	4·12	—	—	A+N‡	A+N‡
1225 °C	4·45	4·44	—	—	A+N‡	A+N‡
1350 °C*	4·37	4·41	—	—	N	N

* Data obtained on separate pieces of X and Y (see text).
† Specimens showed birefringence.
‡ Both spectra had roughly equal intensities.

As noted by Stott and Hilliard (1946), the transparence of stones showing only the A spectrum means that the ZrO_2 particles must be smaller than about 1000 Å. Assuming only particle-size contributes to the widths of the ZrO_2 powder lines, application of the Scherrer equation (James, 1948) leads to a particle-size of ~100 Å for X annealed

at 850 to 950 °C and Y annealed below 950 °C, ~200 Å for both X and Y annealed at 1000 °C, and >500 Å for both X and Y annealed at 1100 °C (the ZrO_2 is clearly recognizable as tetragonal after annealing at this temperature).

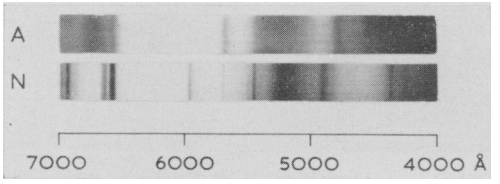

FIG. 4. Normal (N) and anomalous (A) absorption spectra for Ceylon zircons.

The diffuse streaks observed after annealing at 1150 °C and above (fig. 2) had the symmetry of the zircon lattice and were not due to oriented platelets of ZrO_2. The nature of the defect structure (which must be coherent with the zircon matrix) giving rise to the diffuse streaks is unknown but may be connected with the increasing opacity of the stones when annealed at 1150 °C and above.

As has been mentioned by other workers, the presence of ZrO_2 in low metamict zircons implies the presence of SiO_2. The absence of any characteristic SiO_2 X-ray lines means that the SiO_2 is amorphous. Taking 2·21 gm cm^{-3} for the density of amorphous silica and 6·2 gm cm^{-3} for that of cubic or tetragonal ZrO_2 (Blumenthal, 1958, p. 159), the calculated density of a mixture would be about 3·9 gm cm^{-3}, in reasonable agreement with the density of low zircons showing the X-ray powder pattern indexable as cubic ZrO_2. However, it should be noted that a 'skeleton' zircon lattice is still present and that impurities, notably Hf, could well be present also.

The simplest explanation of the differences between the two groups of low zircons (see above) is that, after reaching the low metamict state (X-type), some stones have been heated sufficiently to convert them to Y-type stones. However, another possibility is that Y-type stones have suffered more radiation damage than X-type stones. Neutron irradiation experiments and neutron activation analyses for U and Th are in progress to test this possibility.

Low zircons showing the 5200 Å band. The X-ray results on stone Z, showing the 5200 Å absorption band, suggest that the stone was inhomogeneous. However, the X-ray results also suggested that the stone was intermediate between X-type and Y-type. Since the X-type → Y-type transformation can be effected by heating, it was thought that the 5200 Å absorption band might be produced in an X-type zircon (not showing the 5200 Å band) by heating at temperatures somewhat lower than those required to produce the A spectrum. The remaining piece of X was annealed for various periods in the 700 to 850 °C range and the optical and X-ray results are shown in table IV. No density measurements were made. Though the results confirmed the association of the A spectrum and X-ray evidence of small particles of cubic or tetragonal ZrO_2, it seems clear that the 5200 Å band does not represent an intermediate state between X-type and Y-type zircons.

Stone Z was heated for 1 hr at 900 °C. After heating the density had increased from 3·96 to 3·99 gm cm^{-3}, but the refractive index decreased from 1·806 to 1·789. Since the stone showed the A spectrum after heating, the results were consistent with those

reported by Anderson (1963) on stones showing the 5200 Å band, except for the slight increase of density. However, a somewhat lower annealing temperature might well have resulted in a density decrease. Each of several edge X-ray photographs showed the characteristic diffuse powder pattern indexable as cubic ZrO_2.

TABLE IV. *Annealing behaviour of piece of stone X (heat treatments are successive)*

Heat treatment	Refractive index	X-ray powder pattern indexable as cubic ZrO_2	Estimated ZrO_2 particle size	Absorption spectrum
—	1·823	—	—	Faint, diffuse band near 6560 Å
1 hr at 700 °C	1·816	—	—	,, ,,
+4 hr at 700 °C	1·811	—	—	As above and edge at 6500 Å and very faint line at 5820 Å
+10 hr at 700 °C	1·810	—	—	Faint, diffuse band near 6560 Å and fairly sharp band at 6535 Å
+1 hr at 750 °C	*	—	—	As above and possible beginnings of A spectrum
+4 hr at 750 °C	*	Faint, very diffuse	10–15 Å	Very faint A spectrum
+10 hr at 750 °C	~1·788	,, ,,	15 Å	Fairly well-developed A spectrum
+1 hr at 800 °C	~1·788	,, ,,	20 Å	Well-developed A spectrum
+1 hr at 850 °C	1·790	Well-defined, slightly diffuse	100 Å	Full A spectrum

* No refractive index values could be obtained, possibly because of the stone being in a 'transition' state.

X-ray photographs were taken of eight different regions of another low metamict Ceylon zircon showing a clear 5200 Å band. The stone, designated Z1, weighed 1·044 gm and had a refractive index of 1·815 and a density of 3·98 gm cm^{-3}. No photograph exhibited any powder diffraction lines and it is concluded that the 5200 Å band is not characteristic of any definite crystalline phase. It should be noted that no traces of Laue spots were observed on any of the (stationary crystal) photographs. Since, as mentioned previously, the Laue spots on the photographs obtained from stone Z, showing the 5200 Å band, were very weak, there may be some correlation between the absence or near-absence of Laue spots and the 5200 Å band.

Intermediate zircons. Some X-ray photographs of intermediate Ceylon zircons are shown in figs. 5 and 6. No evidence of a second phase was detected and it would appear that the extra X-ray reflection observed by Holland and Gottfried (1955)

may have been due to impurities introduced by crushing in a steel mortar, although magnetic separation was used, or in the elaborate procedures involved in the subsequent preparation of their X-ray samples (Holland *et al.*, 1955).

The zircon of density 4·48 gm cm^{-3} with a density decrease ($\Delta\rho/\rho$) of about 5 % due to radiation damage showed sharp spots on Laue photographs with patches of

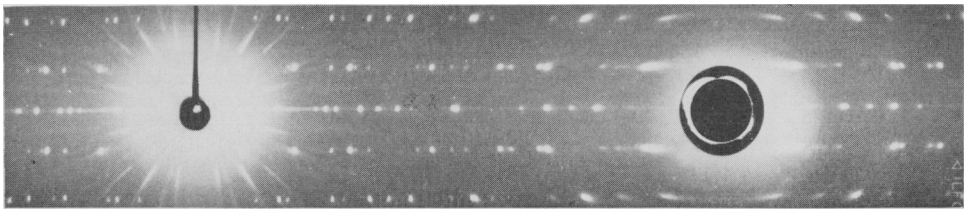

FIG. 5. Chip from intermediate zircon of density 4·48 gm cm^{-3}, *a* axis vertical. Rotation photograph, filtered.

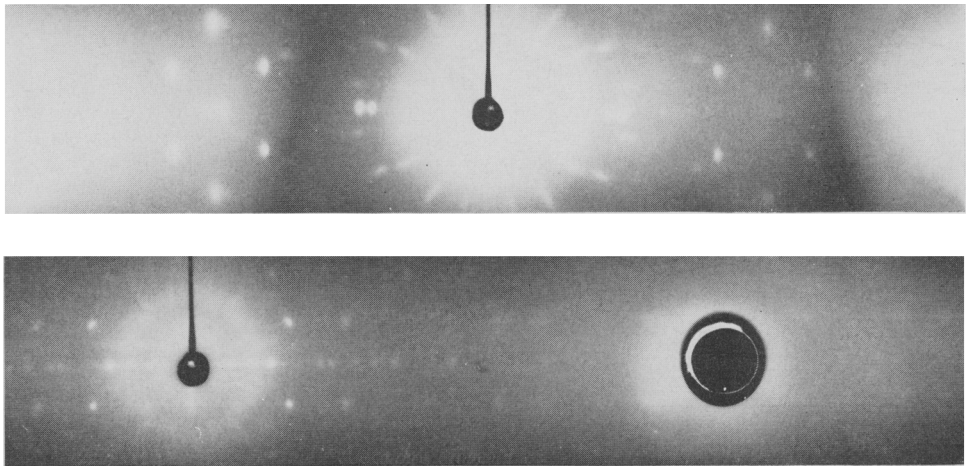

FIG. 6. Chip from intermediate zircon of density 4·18 gm cm^{-3}, *a* axis vertical. *Top.* Laue photograph. *c* axis along beam, not filtered. *Bottom.* Rotation photograph, filtered.

diffuse scattering due to the *K* component of the beam. The diffuse scattering on rotation photographs lay on the high-angle side of the Bragg reflections, with the diffuse maxima lying closer to the Bragg positions of the metamict crystal than those of the non-metamict crystal. These results are qualitatively similar to those obtained on neutron-irradiated diamonds having $\Delta\rho/\rho \simeq 6$ % (Vance, 1971; see also Keating, 1963, 1968). Zircons of densities 4·29 and 4·18 gm cm^{-3} showed diffuse spots on both Laue and rotation photographs, as is the case for neutron-irradiated diamonds having comparable values of $\Delta\rho/\rho$ (Vance, 1971).

Annealing of the intermediate zircons resulted in increases of density, with no appearance of a second phase, except in the case of the zircon of initial density

4·18 gm cm^{-3}, which showed very faint powder lines indexable as cubic ZrO_2 when annealed at 900 °C but not at 1100 °C or higher.

Conclusions

Cubic or tetragonal ZrO_2 appears to be a sufficient condition for the appearance of the anomalous (A) absorption spectrum in both heated and unheated stones.

For low zircons not showing the A spectrum before heating, the decrease of density and refractive index after annealing is associated with the formation of small particles of cubic (or tetragonal) ZrO_2 and the A spectrum.

The densities of low zircons increase after annealing at temperatures insufficient to remove the A spectrum and the X-ray evidence of tetragonal ZrO_2.

A previous report of the presence of a second phase, due to radiation damage, in intermediate zircons is not confirmed.

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