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Optical absorption in current-blackened yttria-stabilized zirconia

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The nature of the blackening caused by high-temperature electrolysis of 8 and 12 mol % yttria-stabilized zirconia single crystals has been investigated by studying the optical absorption between 260 and 700 nm. In the early stages the band edge remained at 271 nm, the crystal became red and the transmission showed a broad minimum centred at 480 nm; in the later stages the crystal became black and the transmission was reduced drastically over the whole visible range. The low transmission was shown, by integrating sphere measurements, to be due to absorbing centres. These were attributed to the formation of vacancy aggregates which ultimately produced colloidal metallic particles.

1. Introduction

Single crystal yttria-stabilized zirconia (YSZ) is typically, in the as-grown state, a transparent pale yellow or light brown material which does not absorb strongly in the visible region of the spectrum. In its polycrystalline form, which is more widely used for applications [1], the freshly prepared material is white. Electrical conduction is almost entirely due to oxygen ion transport in a lattice where anion vacancies (approximately 4 %) have been created by the substitution of yttrium for some of the zirconium. However, during current passage in reducing atmospheres a reduction process occurs which leads, in both single crystal and polycrystalline material, to blackening and may cause disintegration of the sample. In the initial stages the blackening is not uniform over the sample. Previous studies [2, 3] have shown that blackening originates at the cathode and progresses through the sample towards the anode. The blackened zone has a tongue shape, Fig. 1, and the position reached by the front of the blackened zone is determined, for given current density and oxygen partial-pressure conditions, by the time for which current is passed. As regards optical behaviour, the earlier work [3] established that for as-grown 8 mol % YSZ single crystals with low colouration, the transmission was high and almost uniform throughout most of the visible range, falling only at the band edge near 285 nm. The work also showed that, in contrast, blackening was accompanied by a marked decrease in transmission at all wavelengths from 300 to 700 nm. It was suggested that this might be due to the formation of colloidal particles, possibly of metallic zirconium. More extensive optical measurements have now been made to test the validity of this interpretation; these are reported here.

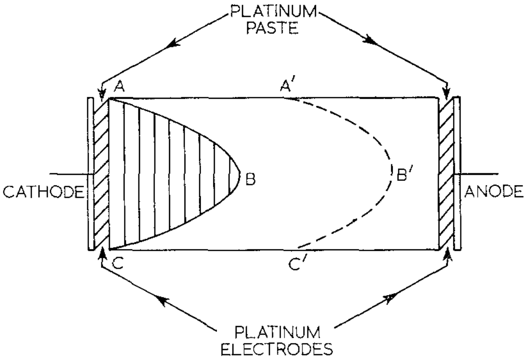

Figure 1 Formation of blackened zone during current passage.

2. Techniques

The experiments have been made on 8 and 12 mol% yttria-stabilized zirconia grown by electrofusion. Single crystals were supplied by W. and C. Spicer Ltd (Cheltenham). The as-grown crystals could be cut with a diamond wheel without undue difficulty and thin slices (typically 0.01 cm thick) were polished to a 0.25 μm diamond

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finish. Current blackening was carried out in dry argon atmospheres at 800°C by mounting a crystal slice between platinum electrodes as shown in Fig. 1. Two features emerged from initial trials. Firstly, the effective absorption in the visible was extremely high; for example, the beam from a 69 nm helium-neon laser was reduced to less than 10^{-7} of its initial value in traversing a lightly-blackened sample 0.01 cm thick. Secondly, the blackened samples were very fragile; cracking occurred at current densities exceeding about 5 A cm^{-2} and the friable nature of the blackened material led to considerable difficulty in producing thin polished slices. For these reasons the method adopted to study absorption behaviour was to measure separately the surface reflection coefficient R, for a thick sample with one polished face and the transmission T, through a thin polished slice blackened under identical conditions. To eliminate the effects of surface layer formation [4] all samples were etched in phosphoric acid before examination. The reflection coefficients were measured directly between 300 and 2500 nm using monochromators as sources and photomultipliers as detectors. Transmission spectra were obtained at room temperature using an Optica CF4-DR spectrophotometer in the wavelength range 250 to 2500 nm. For as-grown material refractive indices were also measured in the visible wavelength range by the minimum deviation method, using a prism cut from a large single crystal.

The derivation of the absorption coefficient K, was based on the standard expression [5] for transmission T, through a layer of thickness d, namely,

$$T = \frac{I_T}{I_0} = \frac{(1-R)^2 \exp(-Kd)\left(1+\frac{k^2}{n^2}\right)}{1 - R^2 \exp(-2Kd)} \quad (1)$$

in which R is the surface coefficient of reflection, k the attentuation index $(K = (4\pi/\lambda)k)$ and n the refractive index of the layer. Refractive index data showed that over the visible wavelength range $n \approx 2.1$. The preliminary transmission experiments showed that in the thinnest samples we could prepare, absorption was complete for values of K greater than 700 cm^{-1}. Thus in all results recorded, $K < 700$ so that $k^2 << n^2$. Consequently, Equation 1 could be simplified and K derived from the relation

$$K = \frac{1}{\mathrm{d}}$$

$$ln = \frac{2\,TR^2}{-(1-R)^2 + \sqrt{[(1-R)^4 + 4T^2R^2]}}\,. \quad (2)$$

This gave an overall accuracy in the determination of K of ± 2%.

To estimate the relative contributions of genuine absorption and of scattering in the transmission spectra further measurements were made with an integrating sphere. Here the method developed by Bastin *et al* [6] was adopted, using a magnesia-coated sphere of internal diameter 15.0 cm; following their notation σ has been used to represent the scattering coefficient, μ the genuine absorption coefficient and Σ (equal to the sum of μ and σ) the effective absorption coefficient. The accuracy in measuring Σ and μ was ± 5%.

Density measurements were also made by determining the change in weight on immersing in water.

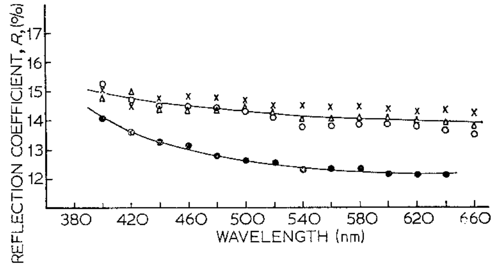

Figure 2 Reflectivities of as-grown and current-blackened 8 mol % yttria-stabilized zirconia (visible region). Full circles, as-grown; open circles, 0.1 cm^{-2}; triangles, 1.0 A cm^{-2}; crosses, 5.0 A cm^{-2}.

3. Results

3.1. Transmission measurements

The reflection coefficient–wavelength results for as-grown and current-blackened crystals in the visible region are compared in Fig. 2. A small increase in reflectivity was observed on blackening but the reflection coefficient remains at about 15% throughout the visible range. There was no significant difference in reflection coefficient between samples blackened at low and high current densities.

The general features of the optical absorption are shown in Fig. 3. At current densities below 80 mA cm^{-2} no blackening was produced; transmission began near 300 nm (corresponding to the band edge) and the absorption

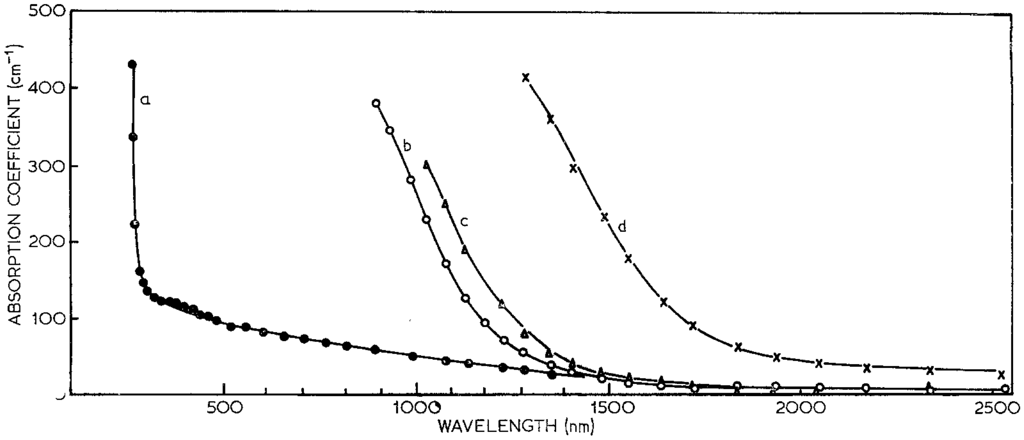

Figure 3 General features of optical absorption in current-blackened 8.0 mol % yttria-stabilized zirconia. Curve a, as-grown single crystal; curves b, c and d, current blackened at 0.1, 1.0 and 5.0 A cm^{-2} respectively.

coefficient–wavelength variations were exactly the same as that for an as-grown crystal, depicted by curve a. Above this threshold a sudden change occurred. At 0.1 A cm^{-2}, curve b, no transmission was recorded below about 900 nm; the transmission rose with further increase in wavelength giving a value of absorption coefficient of 5 cm^{-1} at about 1500 nm. Curves c and d, corresponding to samples blackened at 1.0 and 5.0 A cm^{-2} were of the same form but showed a progressive shift of the transmission cutoff to longer wavelengths as the current density was increased. Similar behaviour was observed for current-blackened 12 mol % YSZ, Fig. 4; here however it was noticeable that, for a given current density, the transmission cutoff occurred at a longer wavelength for crystals having 12 mol % yttria than for those with 8 mol % yttria.

Two auxiliary experiments were made to ascertain whether the observed shift might be due to a change in lattice parameter. In the first the band edge positions for 8 and 12 mol % YSZ as-grown crystals were compared. The room temperature absorption-coefficient data given in Fig 5, shows that the band edge occurs at 271 nm for 8 mol % YSZ and at 278 nm for 12 mol % YSZ. In the second experiment, complementary X-ray diffraction studies were made to establish lattice parameters. Yttria

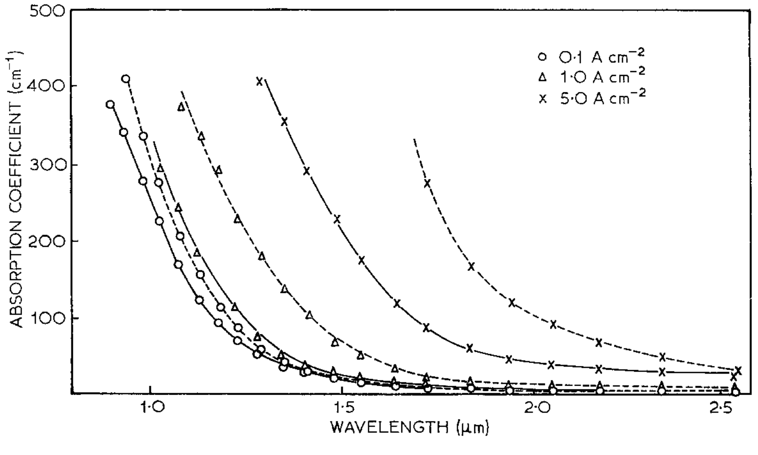

Figure 4 Comparison of near infra-red absorption of 8 and 12 mol % current-blackened yttria-stabilized zirconia. (Full lines 8 mol % dotted lines 12 mol %.)

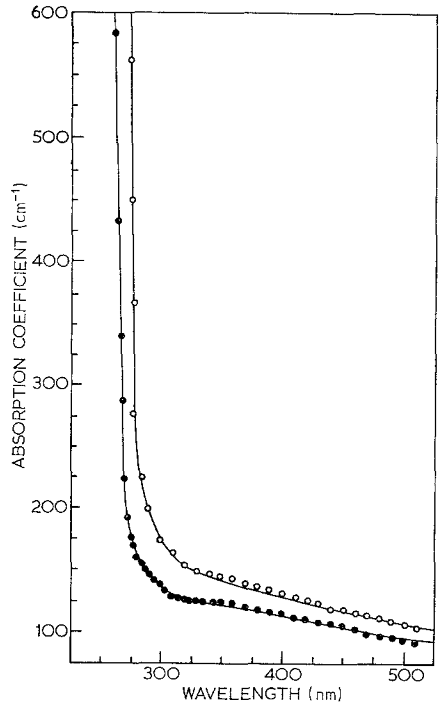

Figure 5 Dependence of position of band edge on composition. (Open circles, 8 mol % yttria; full circles, 12 mol % yttria).

stabilized zirconia has a cubic structure with a fluorite type of lattice. The lattice parameters were found to be 5.138 ± 0.001 Å and 5.149 ± 0.001 Å respectively for the 8 and 12 mol % compositions. These observations suggested that unrealistically large changes in lattice parameter would have been necessary to account for the shifts in transmission cut-off revealed by Fig. 3. Furthermore, extensive X-ray measurements confirmed the previous finding [3] that the lattice parameter was unaltered on blackening, a result also corroborated by recent studies of the effect of current blackening on the elastic constants of YSZ [7].

From these results, it appeared most likely that the very low transmission in the visible range observed in the blackened samples was due to increased absorption, or to increased scattering or to a combination of both effects. Consequently, a further attempt was made to observe the form of the transmission curve. A thin crystal slice was prepared, under low current-density conditions, in which the blackened tongue (Fig. 1) did not quite reach the anode end. With a well-collimated beam it was then possible to probe regions near the anode and successively nearer the cathode end. The form of the transmission curves obtained is shown in Fig. 6. Near the edge of the tongue the crystal was in fact red in transmitted light, becoming grey to black slightly nearer the cathode. In the red region the band edge remained at 271 nm, but a broad absorption band, centred near 480 nm occupied much of the visible range. At a position nearer the cathode, curve 2, the absorption band had increased in width to occupy the whole range from the band edge to 620 nm, and no transmission could be detected at less than this wavelength.

The transmission through the red region was measured at liquid air temperature. The absorption peak was unchanged in width, but shifted 10 nm to shorter wavelength, compared with room temperature.

No structure was observable in either the red or black regions using optical microscopy and magnifications up to x1250. It has not been possible so far to examine specimens by electron microscopy.

3.2. Integrating sphere measurements

Integrating sphere measurements were made on a number of as-grown crystals, on crystals heat-treated in oxygen or argon and on current blackened crystals. For pale yellow as-grown crystals, e.g. Fig. 7, the genuine absorption (μ), falls steadily with increasing wavelength though there is a significant contribution from scattering (σ), to the overall effective absorption ($\sum$). Heat-treatment in oxygen turned the initially clear yellow crystals white and opaque; after such treatment μ is decreased and almost the whole of the substantially increased effective absorption is due to scattering.

Since the current-blackening technique involved heating the crystals in argon at 800°C, the effect of this heat-treatment alone was investigated. The initially yellow crystals again turned progressively white and opaque though much more slowly than during the oxygen heat-treatment. Fig. 8 shows that here again the major factor contributing to the increase in $\sum$ is scattering.

In contrast, the integrating sphere results for current-blackened samples, Fig. 9, show definitely that the major part of the high effective absorption is in fact due to genuine absorption. Since σ is obtained by subtraction of the two large quantities μ and $\sum$ the σ curves are

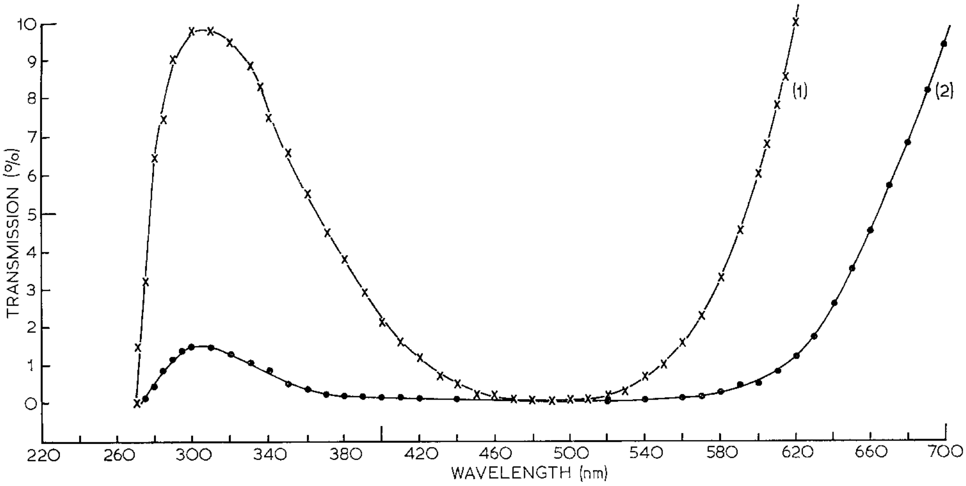

Figure 6 Transmission in visible through current-blackened 8 mol % yttria-stabilized zirconia. Curve 1, region near anode; curve 2, region nearer cathode.

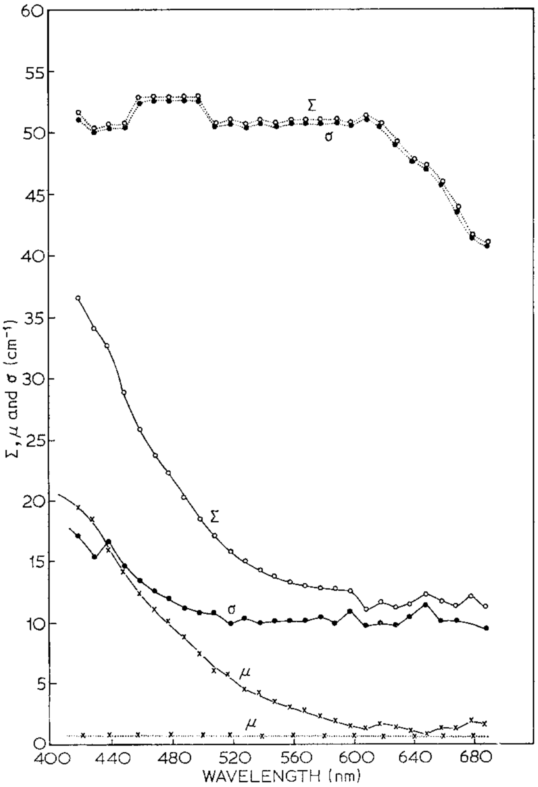

Figure 7 Absorption and scattering (a) in as-grown 8 mol % YSZ (full lines) and (b) after heating in oxygen at 1100°C for 2.5 h, (dotted lines). Symbols: open circles, Σ; closed circles, σ; crosses, μ.

not very reliable; there are indications however that at some wavelengths the scattering is larger than would be expected purely from the effect of the heat-treatment during electrolysis, and that there is a significant amount of scattering of yellow and red light.

3.3. Density measurements

With 8% molecular yttria, fluorite structure, lattice parameter 5.138 Å, one can calculate from the structure a theoretical density of 5.95 Mg m^{-3}, corresponding to an oxygen vacancy of $2.3 \times 10^{27}\,m^{-3}$. The measured density is 6.01 ± 0.01, which corresponds with $1.7 \times 10^{27}\,m^{-3}$ vacancies.

For 12% yttria, the theoretical density is 5.89 Mg m^{-3}, indicating $3.2 \times 10^{27}\,m^{-3}$ vacancies. The measured density is 5.94 ± 0.01, corresponding with $2.6 \times 10^{27}\,m^{-3}$ vacancies.

Within experimental error the densities in both compositions are unchanged after blackening. Thus the change in vacancy density, if any, is less than $10^{26}\,m^{-3}$.

4. Conclusions

The main conclusion is that passage of current above a critical current density produces centres which absorb strongly in the visible wavelength range, and which spread from the cathode to the anode. The first consequence we have detected is a red colouration and an absorption band peaking at 480 to 500 nm, followed rapidly by darkening and blackening, and absorption throughout the visible range. Blackening produces no detectable change in the position of

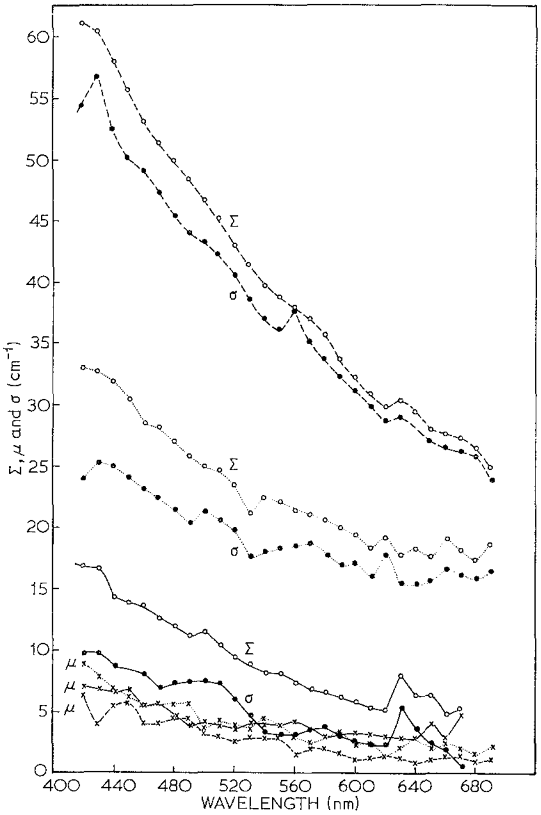

Figure 8 Absorption and scattering in crystals heated at 800°C in argon; (a) 1 h, (full lines); (b) 5 h, (dotted lines); (c) 15 h, (dashed lines).

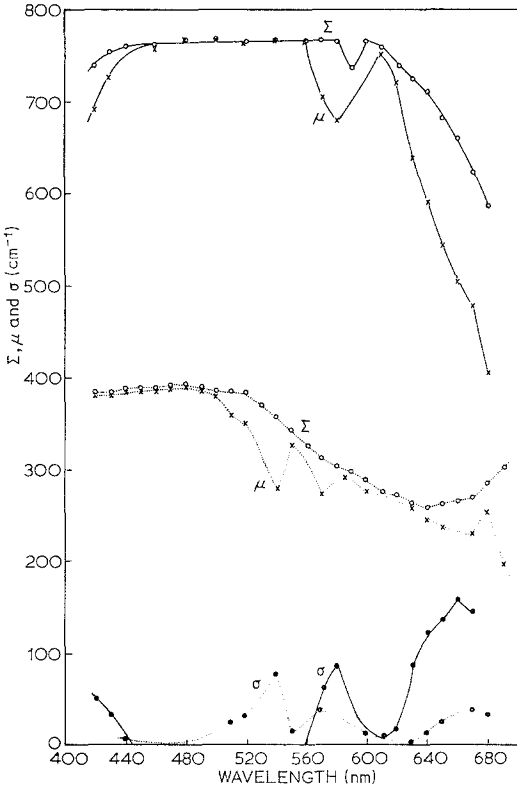

Figure 9 Absorption and scattering in current-blackened crystals; (a) current density 1 A cm^{-2}, 30 min, argon 800°C (full lines); (b) current density 0.1 A cm^{-2}, (dotted lines). Symbols: open circles, $\sum$; closed circles, σ; crosses, μ.

the band edge, in density, in lattice parameter [3] or in elastic constants [7]. The centres are stable in air at room temperature, but can be removed by heat-treatment in oxygen. They cannot be detected by optical microscopy. The esr spectrum has been studied [4], and shows no marked change as a result of blackening. Defects with unpaired spins are present in material as-grown, but there is no detectable change in their density with blackening. A very weak new signal appears due to unpaired spins, but is too weak to correlate with the severe darkening. Thus the centres causing darkening are not singly-charged vacancies. The temperature variation reported above for the 480 nm band does not correspond with that established for singly charged vacancies (F centres) in alkali halides.

Evidence in earlier papers [1, 2] indicates that electrons are injected into the crystal from the cathode, forming the centres which produce the darkened region, which has lower resistivity than the remainder, so that a virtual cathode moves across the crystal, B B′ in Fig. 1. The first stage is probably trapping of electrons at vacancies, which later aggregate, but the evidence is not clear as to the stage at which this aggregation occurs. It would lead to deposition of colloidal "particles", possibly of zirconium metal. Such particles occur for example following the high-temperature electrolysis of silica [8] which leads to precipitation of finely-divided metal from the electrodes, and of sodalime glass [9], in which brown colouration is due to colloidal sodium metal.

When the crystal is red, with the 480 nm absorption peak, the question is whether a low density of very fine colloidal particles has already been formed, or whether the centres are atomically dispersed, e.g. of the F′ type. In the later stages of electrolysis when the crystal is black, larger particles appear to have formed with sizes in the 30 to 100 nm range, as indicated by the scattering of red light. Mie's theory [10] as applied by Savostianova [11] to NaCl shows that when there is an increase in average particle size, range of size and variety of shapes, the absorption band will widen and scattering of red light will occur. It seems very unlikely the absorption over the whole range 300 to 1800 nm could occur because of centres which are still atomically dispersed.

On the question of the identification of the centres producing the 480 nm band, the following points arise. Application of the Ivey-Mollwo relation [12] as modified by Turner [13] for the alkaline earth oxides and fluorides (fluorite structure), to 8 mol % yttria in zirconia, predicts the F centre peak at 325 nm ($6.4a^{2.4}$ with $a = 5.138$ Å) and the F′ centre (less confidently) at 400 nm ($2.65\ (6.4/8.0)a^{3.2}$). This does not agree with the observed peak at 480 nm, so that there is no support for the F′-centre model from this calculation. However, the calculation is not sufficiently reliable to be conclusive. The position of the absorption band agrees better with that of the X-band in the alkali halides [14], and moreover its behaviour agrees with that of the X-band in that the half-width is the same at 77 and 290 K, and the peak is shifted by only 10 nm. Several writers attribute the X-band to finely divided colloidal meal [14] (particles less than 5 nm in diameter, too small to produce scattering) but Shatalov [15] disagrees and attributes it to atomically dispersed centres. It is clearly impossible at this stage to be certain of the situation in ZrO_2, when controversy continues on the extensively studied alkali halides.

In the alkali halides the formation either of F centres or of colloidal particles leads to an increase in hardness, elastic limit and breaking strength [16]. The changes in both cases are attributed to the pinning of dislocations. In ZrO_2, however, there is a decrease in strength and the crystals crack and crumble on handling after 5 A cm^{-2} has been passed. The ready cracking may result from strain produced by the presence of colloidal particles (or vacancy aggregates), but this is not yet proven. It is possible that the structure changes in a complex manner as in reduced TiO_2 [17], but this remains to be investigated.

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