

Electron spin resonance in single crystal yttria stabilized zirconia

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Electron spin resonance has been observed at 35 GHz in 8 and 12 mol% yttria stabilized zirconia single crystals before and after blackening by current passage. Measurements were made between 293 and 77K. In both as-grown and blackened crystals the spectra showed anisotropic lines (type A) characterized by $g_{||} = 2.003 \pm 0.002$ and $g_{\perp} = 1.880 \pm 0.002$ with respect to a [111] symmetry axis and a broader, slightly anisotropic line (type B) centred near $g = 1.993$. In current blackened crystals a weak isotropic line (type C) was also found near $g = 1.986$. The type A lines are attributed to a charged complex formed by an electron trapped at an oxygen vacancy and associated with an yttrium ion. Tentative models are suggested to explain the type-B and type-C lines.

1. Introduction

Yttria stabilized zirconia (YSZ) is zirconium oxide (ZrO_2) stabilized by the addition of more than about 7 mol% of yttrium oxide (Y_2O_3). Pure zirconia exhibits a phase change between a monoclinic and a tetragonal structure at about 1400K and therefore, due to the associated volume change, is unsatisfactory as a ceramic [1]. However, the addition of yttria enables the refractory properties of zirconia to be used since yttria stabilized zirconia adopts a cubic structure between room temperature and its melting point, about 2800K [2]. For yttria concentrations between about 7 and 50 mol% the fluorite structure is adopted [3]. The cation sites lie on a face centred cubic lattice and the oxygen sites lie at the centres of the small cubes formed by dividing the unit cell into eight (Fig. 1). There are two oxygen sites to one cation site. Thus the presence of the yttria implies that there must be defects, either oxygen vacancies or cation interstitials. The existence of oxygen vacancies in YSZ has been generally accepted since they were proposed by Wagner [4]; this has subsequently been substantiated by the correlation of X-ray and density measurements [5]. Since the vacancies are mobile at elevated temperatures, the material is valuable as a refractory conductor, e.g. in MHD electrode and fuel cell applications. (At 1400K the conductivity of $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ is about $1.2 \Omega^{-1} m^{-1}$). When an electric field is applied the vacancies migrate to the

cathode. However, if there is not sufficient oxygen to fill them as they arrive, a black zone starts to spread from the cathode and eventually the material crumbles. Preliminary electron spin resonance studies on single crystal YSZ have been reported previously [6] and the present work was undertaken in an attempt to examine the defect structure more closely.

2. Experimental details

Single crystals of $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ and $(Y_2O_3)_{0.12}(ZrO_2)_{0.88}$, made by electrofusing mixtures of the pure powdered oxides [7], were obtained from W. & C. Spicer Ltd. The as-received crystals varied in appearance from transparent amber to dark and almost opaque. Their orientation was determined by X-ray back reflection methods. They were robust and hard and were cut using a diamond wheel, without difficulties due to fragmentation or cracking. Samples treated in several ways were investigated. Some were studied in the as-received state; some were examined after current blackening; others after being heated in argon, air or oxygen, without having current passed through them. Current blackened samples were prepared by passing direct current through as-received material (using platinum paste contacts) in an argon atmosphere at 1070K. (This temperature was low enough to be reached easily yet high enough to make the material sufficiently conducting.) Currents between 10 and 250 mA were

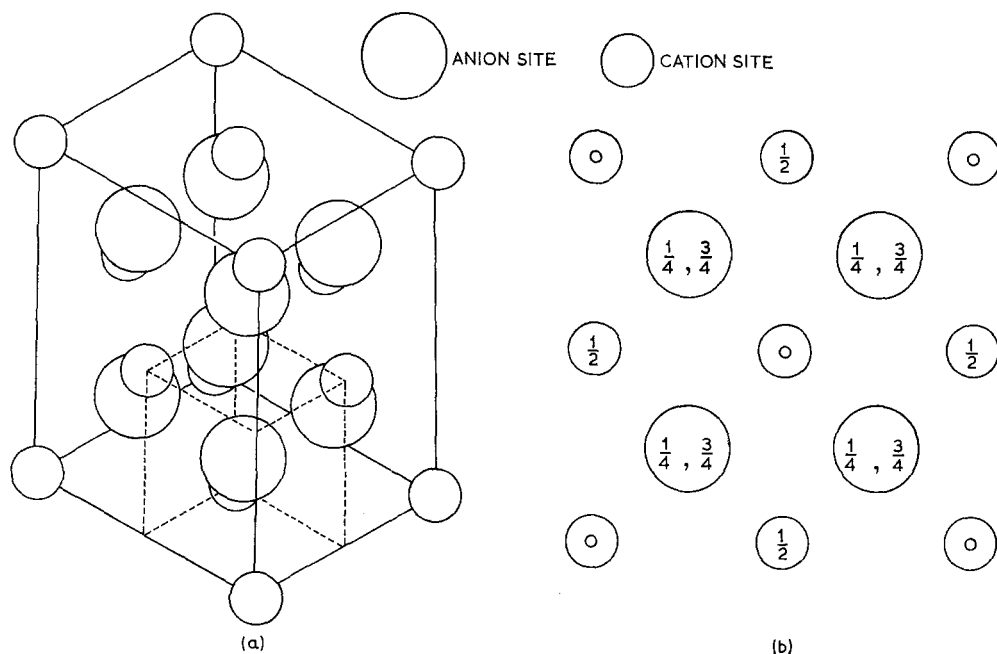


Figure 1 The unit cell of yttria stabilized zirconia; (a) general view, (b) plan view in which the numbers give the heights of the sites above the base in terms of the lattice parameter.

passed, for times ranging from 3 min to 1 h through rods of 1 mm² cross-section. Immediately after current passage the sample holder was withdrawn from the furnace allowing the sample to cool under argon to 670K in 2 min and subsequently to room temperature. This made the rods very friable. It also left them with a silvery, highly conducting surface layer. The occurrence of conducting surface layers has been reported previously [8, 9], and here they were thought to arise from impurities in the dried argon supply. The layer was easily removed by dipping the sample into hot phosphoric acid (typically for 5 sec at 200°C). The removal of the layer was indicated by appearance, by the high value of the surface resistance and especially by the reduced effect of the sample on the cavity damping. Etching was repeated until there was no further improvement. For comparison purposes some samples were prepared under the same conditions of atmosphere and temperature but without passing current; their colour became paler.

As-received material heated in air or oxygen turned white and translucent and showed signs of cracking. Treatments ranged from heating in air at 1020K for 6 h (which only whitened a

sample to a depth of a few mm) to heating in oxygen at 1275K for 50 h (which whitened a sample throughout). No change in weight greater than the experimental sensitivity (1 part in 10⁴) was observed.

To resolve the lines more clearly than had been possible in the previous study at 9.3 GHz, measurements were made at 35.5 GHz. A cavity spectrometer employing phase sensitive detection at 160 KHz was used. The coupling and tuning of the cavity were adjustable. A ruby sample (with which the cavity Q-factor was ≈ 2000) was used to estimate the spectrometer sensitivity. From this it was deduced that the spectrometer could detect 10¹² spins per millitesla linewidth at room temperature, working at a power level of 1 mW with a time constant of 1 sec. The introduction of yttria stabilized zirconia samples into the cavity affected the coupling. Furthermore, current blackened samples degraded the cavity Q-factor seriously making spectra difficult to observe. Accordingly the sample volume was chosen, at about 1 mm³, to give a sufficient number of spins in the sample while retaining an adequate Q-factor. With as-received samples $Q \approx 900$. Most measurements were made at 290K and some at 77K. The magnetic field was

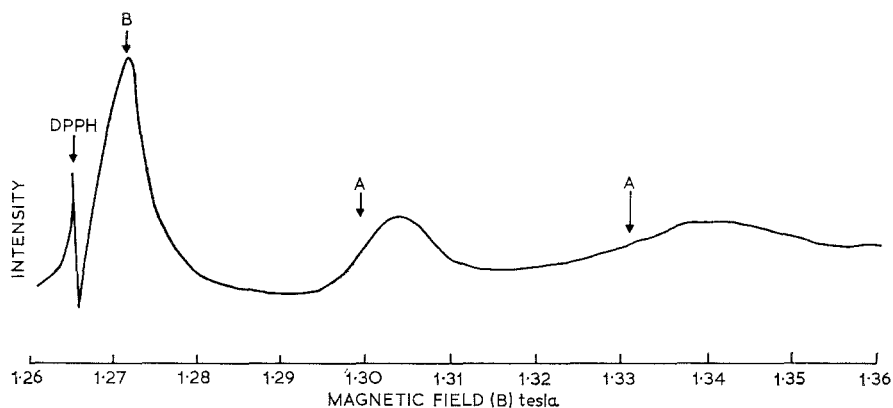


Figure 2 Spectra observed in as-received 8 mol % yttria stabilized zirconia. Magnetic field 16 degrees from $[100]$ direction in (001) plane; 35.5 GHz, 290K.

measured using a calibrated sweep and a DPPH marker. (1 millitesla \equiv 10 gauss.)

3. Results

Spectra were seen in all samples. They were characterized by three types of line of different shape, intensity and variation with polar angle.

In 8 mol % YSZ the lines from the as-received samples were deduced to be of two types, which will be referred to as type A and type B (Fig. 2). The two lines labelled "A" seen when the magnetic field lay in the (100) plane, were believed to be due to one type of site because of their similarity in shape and intensity and especially because of their g -value variation with polar angle (Fig. 3). The peak-to-peak width of an A-type line varied according to the field value at which it occurred from 20 mT at 1.32 T to 8 mT at 1.27 T in the (100) plane, reducing further to 5 mT at 1.26 T in the (111) plane. In the (111) plane three apparently symmetrical lines were clearly seen near this range of g -values, and a fourth was just detectable. Over a matter of months crystals kept at room temperature lost their type-A lines.

The single type-B line was asymmetrical and of higher intensity. Its slightly anisotropic behaviour and the change in the width with polar angle were observed. The width changed periodically between 10 ± 1 mT and 6 ± 1 mT corresponding to the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions of the unit cell. The g -values were 1.990 and 1.997 along the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions respectively.

In samples which were heat treated without current passage no type-A lines were observed,

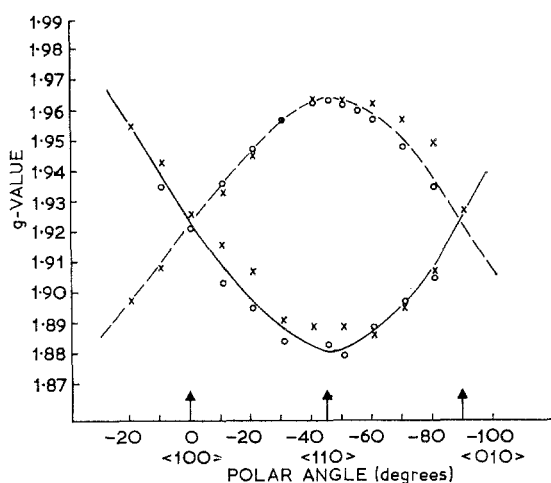


Figure 3 Variation of g -value for two A-type lines with polar angle. (Key: open circles, measured in (001) plane; crosses, measured in (100) plane.)

but the type-B line seemed unchanged. The room temperature ESR spectrum appeared to be independent of the atmosphere (air, oxygen or argon) used for the heat treatment. Current blackened samples exhibited both type-A and type-B lines and also an additional peak (designated type-C) close to the type-B line (Fig. 4). The type-C line was isotropic and so at some polar angles was obscured by the type-B line. The variations with polar angle of the resonance field values for the type-A, -B and -C lines are given in Fig. 5. There was some indication that the intensity of the type-C line increased with increased current density. The position of

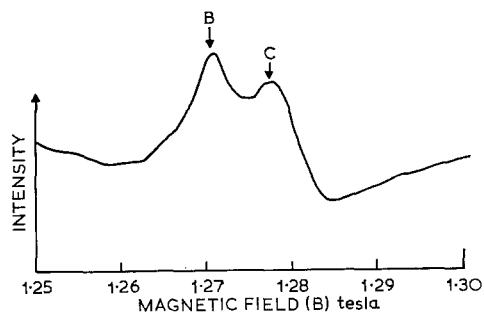


Figure 4 Spectra observed in current blackened 8 mol % yttria stabilized zirconia. Magnetic field 5 degrees from [100] direction in (001) plane; 35.5 GHz, 290K.

the peak of the type-C line corresponded to a *g*-value of 1.986.

The information is summarized in Table I. Only samples known to exhibit type-A lines before treatment were used.

Preliminary measurements have been made at lower temperatures. For as-received 8 mol % YSZ samples the spectra recorded at 77K were similar to those obtained at 290K and no extra lines were seen. With current blackened 8 mol % samples the type-C line was also present down

TABLE I

Description of sample	Type of line present (room temperature)	Result of treatment (compared with 1)
(1) As-received (new) A, B	A, B	Reference standard (type-A and type-B present)
(2) As-received (old) B	B	Type-A not present
(3) Heated in argon without current passage	B	Type-A not present
(4) Current blackened (while heating in argon)	A, B, C	Type-C is weak. (N.B. Type-A present)
(5) Heated in air or oxygen without current passage	B	Type-A not present
(6) As (5), subsequently heated in vacuum at 1100°C for 3.5 h	B	Faint trace of Type-A lines

to 148 K, the lowest temperature at which measurements were made. The relative intensities of the type-A, -B and -C lines were approximately

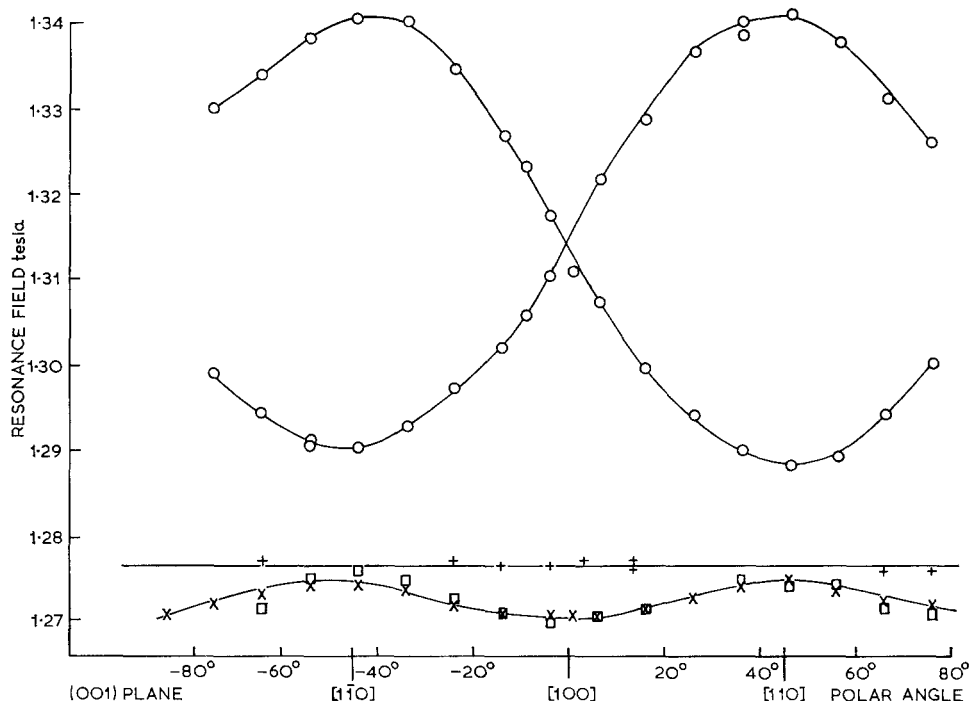


Figure 5 Variation with polar angle of line peak positions in as-received and current blackened YSZ. (Key: open circles, A-type line in as-received sample; crosses, B-type line in as-received sample; open square, B-type line in current blackened sample; addition signs, C-type line in current blackened sample.)

the same at room temperature and low temperature.

In as-received and current blackened 12 mol % YSZ similar results were obtained.

4. Discussion

4.1. Type-A lines

The results shown in Fig. 3 suggest that each type-A site must have a principal axis along one of the [111] directions. This would mean that there were four alternative A-type sites corresponding to the four three-fold axes. Thus, for certain orientations of the magnetic field four type-A lines should be seen. Observations in the (111) plane supported this postulate. The intensities of the lines indicated that all four sites were occupied by roughly equal populations. The g -value of a given site was a maximum, (2.003 ± 0.002), parallel to one of the [111] directions and a minimum (1.880 ± 0.002) perpendicular to it.

A model for this centre can be proposed on the basis of two associated point defects, the first containing a free spin and the second creating an additional component of crystal field. A trapped electron in an oxygen vacancy would provide a free spin on an oxygen site. This process is likely to occur in YSZ as it contains oxygen vacancies. The electron paramagnetic resonance properties of F-centres in alkali halides, reviewed by Markham [10] show g -values between 1.987 and 2.0029 with linewidths of more than 5 mT. The correspondence between these results and the behaviour of the type-A lines (coupled with their time and temperature dependence) supports the assignment of the line to a complex.

To explain the temperature variation of the conductivity of unblackened YSZ, Caillet [11] has proposed a model based on "free" and "trapped" oxygen vacancies. The vacancies were trapped by forming a complex with either one or two Y^{3+} ions. The model suggested here corresponds to Caillet's first "trapped" vacancy with the addition of an electron. With regard to blackened YSZ, Casselton [12] postulated that the onset of current blackening and an enhanced conductivity is accompanied by the injection of electrons from the cathode. Using the model suggested this would be consistent with the re-appearance of type-A lines after current blackening since the complexes would act as electron traps.

The required axial symmetry could be obtained if an yttrium ion was on a cation site with the

other three nearest cation sites occupied by zirconium ions.

4.2. Type-B line

The type-B line was seen in all samples irrespective of treatment. The symmetry of the variation of resonance field with polar angle showed that the most likely location for this defect centre would be a cation site. The normal occupants of these sites, Zr^{4+} and Y^{3+} , are diamagnetic and consequently would give no spin resonance spectra. The defect has not yet been positively identified.

A possible explanation may be valency changes of the cations. Ionization energy considerations indicate that the ions most likely to be formed would be Zr^{3+} and Y^{2+} . This may apply in the reducing conditions created during crystal growth by electrofusion. No resonance data on Zr^{3+} has been reported in the literature. However, O'Connor [13] has reported electron spin resonance of Y^{2+} in CaF_2 at 4.2K and quotes a g -value of 1.994 ± 0.005 . This is similar to the mean g -value, (1.993), found for the type-B line. The observed intensity of the type-B line corresponded to a spin density of about 10^{15} mm^{-3} . On the assumption that Y^{2+} was responsible this would indicate that about 1 in 10^4 yttrium ions had changed their valency state.

An alternative possibility, that the type-B line might be due to an impurity, cannot be excluded although optical spectrographic analysis showed that the only major impurities present were hafnium (about 2.2%), titanium (300 ppm), calcium (100 ppm), and tantalum (300 ppm).

4.3. Type-C lines

The type-C lines only appeared after current passage. The line was isotropic, with $g = 1.986$, and its intensity (like those of the type-A and type-B lines) was not strongly temperature dependent over the range studied.

A possible model for this site is an F-centre consisting of an oxygen vacancy with a trapped electron surrounded by a tetrahedron of zirconium ions. In as-received material the existence of such a site would be more unlikely than the complex used to explain the type-A lines. The oxygen vacancies occur because yttrium is substituted for zirconium (one vacancy is produced for two yttrium ions), and the cation tetrahedra in which yttrium is not substituted for zirconium would not be expected to have an associated vacancy. During current passage the applied

potential may cause migration of vacancies and the injection of electrons. These electrons may be trapped in vacancies having two different surroundings (i) a tetrahedron of four zirconium ions or, (ii) a tetrahedron of three zirconium ions and one yttrium ion as proposed for the type-A site. The isotropy of the type-C line may be explained because this tetrahedral arrangement of zirconium ions will produce balanced components of crystalline field. This model would be consistent with Caillet's postulate of "free" vacancies.

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