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Colour centres in neutron irradiated aluminium oxy-nitride

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Abstract. Aluminium oxy-nitride ($9\text{Al}_2\text{O}_3 \cdot 5\text{AlN}$) has been neutron irradiated to fluences varying from 10^{18} – 10^{24} n m^{-2} ($E_n > 1$ MeV) at 60°C . The defect structures were studied by x-ray lattice parameter measurements and optical spectroscopy. The lowest neutron doses produced an anomalous volume expansion of 0.17% which was also reflected in a shift of the absorption edge to longer wavelengths. The exponential variation of the absorption edge with photon energy suggests that the 'edge' is the long wavelength side of an exciton band. The identification of two V bands with the intrinsic octahedral aluminium vacancy (2.225 eV) and the tetrahedral aluminium vacancy (3.15 eV), and their relative strengths after low neutron doses, suggested that the volume expansion may be associated with the octahedral aluminium vacancy centre. The oscillator strength of the two V bands was calculated to be 3×10^{-5} . At higher neutron fluences the increase in lattice parameter and anion vacancy concentration showed good agreement with those found for equivalent doses in Al_2O_3 . Comparison with the absorption spectrum of irradiated Al_2O_3 leads to the following assignment of anion vacancy centres to absorption bands in AlON: F^- —5.46 eV, F^+ —5.00 eV, F_A^- —4.6 eV, F_2^- —4.1 eV, F_2^+ —3.68 eV.

1. Introduction

Aluminium oxy-nitride with a composition of $\text{Al}_{23}\text{O}_{27}\text{N}_5 \equiv 9\text{Al}_2\text{O}_3 \cdot 5\text{AlN}$ has a cubic spinel structure with a solubility range of 27–40 mol% AlN [1]. For brevity the material will be referred to as AlON. Previous work by Pells and Gilbert [2] used luminescence and excitation spectroscopy to study colour centres produced in AlON by fast neutron irradiation. They found three luminescence bands and four excitation (absorption) bands. Only one luminescence band at 3.13 eV (397 nm) was found to increase in intensity with increasing neutron fluence which, with the mirror image excitation band at 3.68 eV (337 nm), was provisionally ascribed to an F_2^- -type centre. Inspection of the remaining excitation and luminescence bands placed an F-type centre at 5.45 eV (228 nm) and the relationships between the other bands allowed them to be tentatively ascribed to vacancy–impurity complexes. The present work will describe further optical absorption studies, the stability of the colour centres and x-ray lattice parameter measurements.

2. Experimental procedure

The polycrystalline AlON supplied by Raytheon Research Division, Lexington, MA was of 99.8% theoretical density and of high optical transparency. A chemical analysis is

Table 1. Chemical analysis of ALON. The value for aluminium is in wt.% and for the major impurities in ppm by weight.

Al	Ba	Ca	Cr	Fe	Mg	Si	Sr	Ti	Y
54.7	1.6	105	<0.5	4.8	51	<100	0.5	2.2	0.4

given in table 1. Details of the neutron irradiation and sample preparation were given by Pells and Gilbert [2]. The absorption spectra were measured at room temperature in a Perkin-Elmer, Lambda 9 spectrophotometer with the UV extended to 170 nm. In order to follow absorption below 205 nm samples were ground and polished to give thicknesses of <0.1 mm. Heat treatment was performed in controlled atmosphere furnaces having a temperature stability of ± 1 °C. The stability of various colour centres was followed as a function of ionisation by exposure to 90 kV peak x-rays from a Philips 3 kW, tungsten anode tube.

X-ray lattice parameter measurements were made using Cu $K\alpha$ radiation on a Siemens D500 automatic diffractometer incorporating pulse height discrimination and a curved graphite secondary monochromator. The absolute error in the lattice parameter measurements was 10^{-4} nm.

3. Experimental results

Optical absorption spectra are given in figure 1 for both unirradiated ALON and samples irradiated to a maximum neutron fluence of 10^{24} n m $^{-2}$ ($E_n > 1$ MeV). Unlike α -Al $_2$ O $_3$ there are no clearly defined absorption bands only points of inflection from a series of overlapping bands. The most obvious inflections can be seen at ~ 230 nm and ~ 350 nm although others could be seen when the spectra from samples of various thickness were examined in greater detail. The other notable feature is the high absorption below 200 nm. As the Lambda 9 spectrophotometer is not capable of determining whether the intense absorption below 200 nm is an absorption band or edge, samples were examined in the vacuum ultraviolet using a Hilger 1 m grating monochromator by kind permission of Dr G Freeman of the National Physical Laboratory, Teddington. The samples were all found to be completely opaque down to 140 nm (8.85 eV) even for those as thin as 0.08 mm.

3.1. The absorption edge

It can be clearly seen in figure 1 that the absorption edge had moved to lower energies after neutron irradiation. The largest shift occurred after a neutron fluence of only 10^{18} n m $^{-2}$ which is equivalent to an ionisation dose of $\sim 10^4$ Gy. Exposure of 'as-received' ALON to an equivalent, purely ionising dose of 90 kV x-rays did not produce any measurable change in the ultraviolet spectrum. The absorbance of the edge varied exponentially with the photon energy as shown in figure 2, which also emphasises the constant shift in the edge produced by neutron fluences of 10^{18} – 3×10^{19} n m $^{-2}$. Energy values for the absorption edge have been calculated for a natural logarithm of absorbance equal to

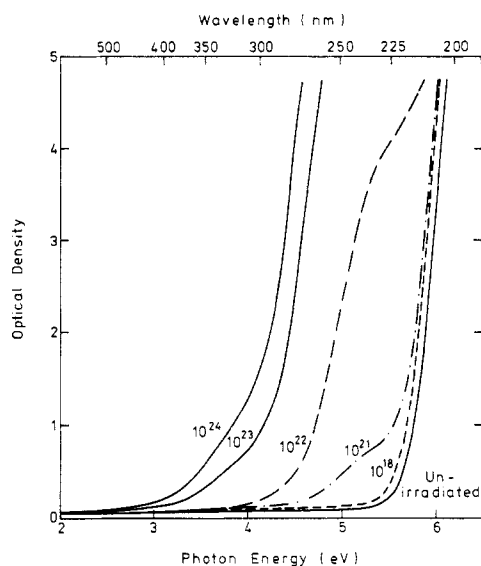


Figure 1. The absorption spectra for AlON irradiated in the HERALD light water reactor to the neutron fluences (n m^{-2} , $E_n > 1 \text{ MeV}$) given in the figure. The sample thickness was 0.09 mm.

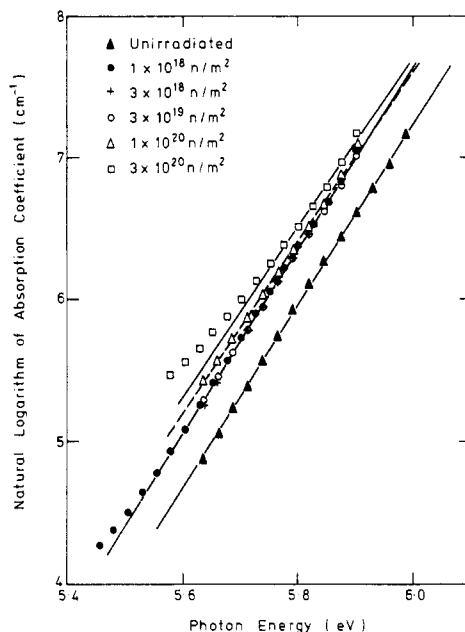


Figure 2. The logarithmic variation of the absorption coefficient at the absorption edge as a function of photon energy.

one and the results are presented in figure 3. A discontinuity was also apparent in the x-ray lattice parameter values obtained for irradiated and unirradiated AlON also shown in figure 3.

Unirradiated AlON annealed for 14 hours at 867 °C in flowing oxygen showed a slight shift of the absorption edge to higher energies but this may have reflected a change in composition as anneals at higher temperatures clearly began to oxidise the sample.

3.2. Absorption bands

In the overview of the effects of neutron irradiation on the AlON absorption spectrum presented in figure 1, the main feature is clearly the large shoulder to the absorption edge which increased progressively with increasing neutron dose. There is also a small inflection in the spectra for the two highest doses at about $\sim 3.7 \text{ eV}$. More detailed examination of samples of varying thickness showed that the shoulder may be resolved into three overlapping bands centred on 4.6 eV (270 nm), 5.00 eV (248 nm) and 5.46 eV (227 nm). The 4.6 eV band became apparent at the lowest neutron dose of 10^{18} n m^{-2} but did not grow significantly with increasing dose. The 5.46 eV and 5.00 eV bands appeared after irradiation to $3 \times 10^{19} \text{ n m}^{-2}$ and increased with neutron fluence as shown in figure 4 on a log/log plot. Two other bands occurred at 3.68 eV (337 nm) and 4.1 eV (302 nm). The 3.68 eV band appeared as a weak inflection in the spectral envelope at a neutron dose of 10^{20} n m^{-2} and remained constant over a decade of neutron fluence. After 10^{21} n m^{-2} the 4.1 eV band became apparent and at higher doses both the 4.1 eV and 3.68 eV bands increased in intensity with increasing neutron fluence. The details of

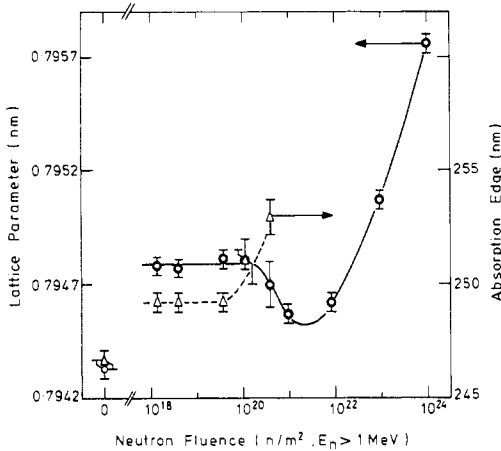


Figure 3. The variation of lattice parameter and absorption edge as a function of fast neutron dose. The absorption edge is defined as the wavelength at which $\ln A = 1$.

Table 2. The peak positions and full width at half maximum of absorption bands in neutron irradiated ALON compared with the excitation spectra obtained by Pells and Gilbert.

Peak positions		Full width at half maximum (eV)	Pells and Gilbert [2]	
(nm)	(eV)		Peak (eV)	Half- width (eV)
557	2.25 ± 0.005	0.98 ± 0.04	2.22	0.93
393	3.15 ± 0.05	0.94 ± 0.05	—	—
337	3.68 ± 0.03	0.45 ± 0.03	3.68	0.38
302	4.1 ± 0.1	0.55 ± 0.1	4.1	0.9
270	4.6 ± 0.1	0.65 ± 0.1	4.65	0.8
248	5.00 ± 0.02	0.46 ± 0.02	5.02	0.66
227	5.46 ± 0.02	0.46 ± 0.02	5.45	0.60

the absorption bands are given in table 2 which also lists the absorption bands identified through excitation spectroscopy by Pells and Gilbert [2].

Pells and Gilbert also reported that a broad band peaking at 2.22 eV (558 nm) could be produced by x-irradiation of both neutron irradiated and unirradiated samples. However, figure 5 shows that, although reactor irradiation initially increased the strength of the band, a maximum was obtained after $\sim 10^{21} \text{ n m}^{-2}$ with no trace of the band remaining for neutron fluences $> 10^{23} \text{ n m}^{-2}$. It should be noted that no changes in peak position or half-width of the band were observed. X-irradiation also increased the strength of the ultraviolet bands to some extent and a new band was observed at 3.15 eV (393 nm) which could only be found after x-irradiation. There were no traces of the band to be found in the sample irradiated to 10^{24} n m^{-2} . The growth of the 2.22 eV band with 90 kV x-ray dose and its subsequent decay as a function of time after x-irradiation have been measured. The results are given in figure 6 where it can be seen that the decay has an unusual linear dependence on the logarithm of time.

3.3. Annealing effects

Two samples of ALON (0.09 mm and 1.0 mm thick) which had been neutron irradiated to 10^{24} n m^{-2} at 60 °C, were given one-hour anneals in flowing nitrogen at progressively

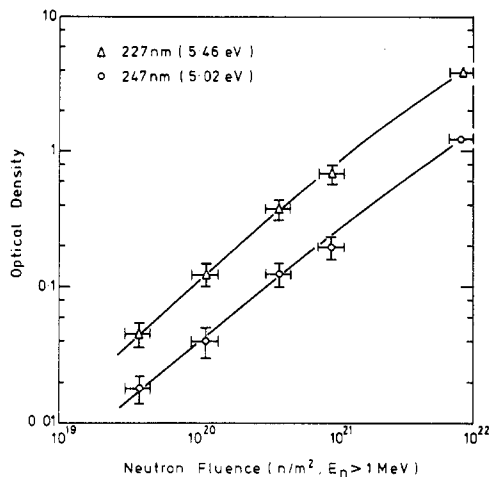


Figure 4. The variation of the resolved F²⁺ (Δ) and F⁻ (○) bands with fast neutron fluence. The sample thickness was 0.09 mm.

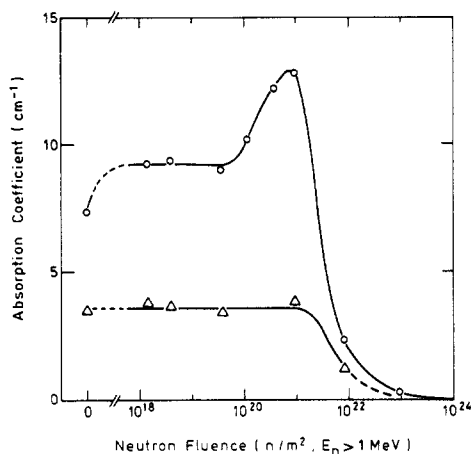


Figure 5. The variation of the resolved 2.22 eV (○) and 3.15 eV (Δ) absorption bands as a function of fast neutron fluence following 90 kV peak x-irradiation to saturation as shown in figure 6.

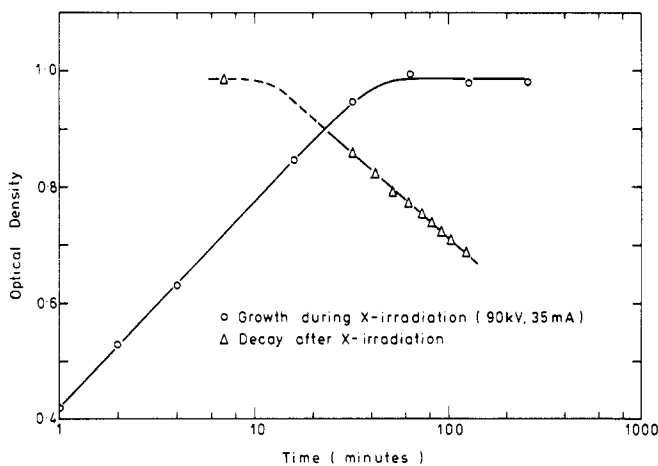


Figure 6. The logarithmic time dependence of the x-ray induced growth of the 2.22 eV absorption band and its subsequent decay.

higher temperatures. Selected spectra are shown in figure 7 to indicate the changes produced by the heat treatment. The intensity of the absorption bands made it impractical to follow the changes in each band at the lower annealing temperatures, although from figure 7 the progressive shift of the absorption spectra suggests that all of the bands annealed continuously from 100 °C upwards. At low temperatures no bands were observed that had not been present in the 'as-irradiated' samples but annealing at 700 °C

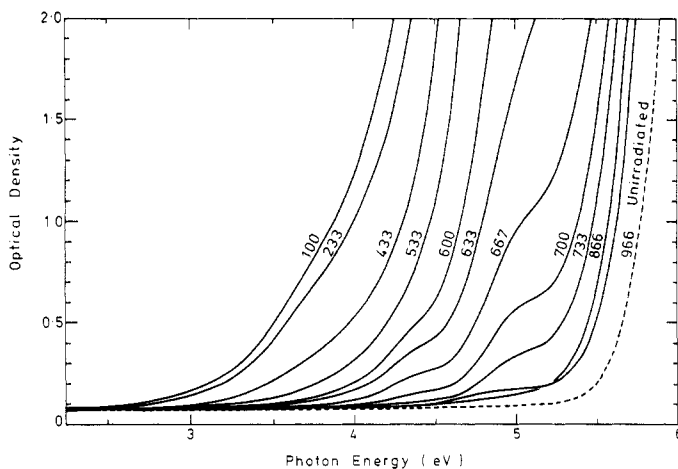


Figure 7. Optical absorption spectra after one hour anneals at the indicated temperatures ($^{\circ}\text{C}$) for AlON irradiated to 10^{24} n m^{-2} ($E_n > 1 \text{ MeV}$) at 60°C . The thickness of the sample was 0.09 mm .

did present the overlapping bands more clearly and hence allow the spectra to be deconvoluted into their respective bands with greater precision. The majority of the colour centres had annealed out by 900°C although the most intense band at 5.46 eV still persisted at 1000°C . At temperatures above 866°C a new band appeared at 4.87 eV (255 nm) with a half-width of $\sim 0.53 \text{ eV}$. The x-ray-induced 2.22 eV band, which had been completely suppressed by irradiation to 10^{24} n m^{-2} , did not fully recover its pre-irradiation value even after annealing at 1000°C . Anneals at temperatures above 1000°C produced thermal etching of the sample surface and unacceptable light scattering.

4. Discussion

The effects of neutron irradiation upon the optical absorption spectrum of AlON are similar in many respects to those experienced in other oxide systems where point defects produced by displacement damage can become optically active colour centres. However, AlON has two distinguished features: the first being that all of the absorption bands have significant overlap which makes the identification of individual bands difficult and secondly very low neutron doses appear to produce changes in both the lattice parameter and some optical features.

AlON has a centrosymmetric $Fd\bar{3}m$ space group based on a face centred cubic lattice of oxygen ions with cations occupying some of the interstitial positions. McCauley [3] has argued that a constant anion model is most appropriate to AlON giving a total of 32 anions in the unit cell of which 5 out of the 32 anion sites will be occupied by N^{3-} ions with the remainder being O^{2-} ions. Both number and electrical charge balance would be satisfied if the nitrogen ions occupied the cube corners, face centres and body centre lattice positions. However, Knight [4] has used x-ray diffraction to search for superlattice lines and found none, therefore the symmetry of the spinel structure is not violated in AlON and the nitrogen ions must occupy random sites. Given the ratio of O^{2-} to N^{3-}

ions in AlON it is not possible to maintain charge balance if all of the sites are occupied by Al^{3+} ions and McCauley concluded that there must be one missing aluminium atom per unit cell. Of the 24 interstitial sites occupied by the aluminium ions 8 are on tetrahedral sites and 16 on octahedral sites. The vacant aluminium site must be distributed randomly.

The defects produced by reactor irradiation of AlON clearly fall into two régimes, that of low and high dose. However, the colour centres in the visible part of the spectrum are common to both régimes and will be discussed first.

4.1. The 2.22 eV and 3.15 eV absorption bands

The absorption bands centred at 2.22 eV and 3.15 eV had half-widths of 0.98 and 0.94 eV respectively. They show strong similarities to absorption bands in other refractory oxides such as MgAl_2O_4 , Al_2O_3 and MgO which have been ascribed to V centres. White, Jones and Crawford [5] showed that the broad absorption band produced by gamma irradiation of MgAl_2O_4 could be deconvoluted into three or possibly four overlapping bands by suitable heat treatment and optical bleaching experiments. The absorption bands centred on 2.8, 3.1, 3.6 and possibly 3.9 eV had half-widths of ~ 1 eV. It was suggested that the bands arose from aluminium and magnesium site mixing which produces $[\text{Mg}]_{\text{Al}}^-$ and $[\text{Al}]_{\text{Mg}}^+$ hole and electron traps and from an excess of Al_2O_3 producing Mg^{2+} vacancies. The aluminium vacancy centres in sapphire have been discussed by Crawford [6] who concluded that the O^- ions adjacent to sites of positive charge deficiency absorb in a broad band of photon energies centred near 3.1 eV. The absorption band at 2.3 eV in MgO is the only one to have been ascribed unambiguously to a V centre where parallel optical and ESR measurements by Wertz *et al* [7], Tohver *et al* [8] and Chen and Sibley [9] established that the optical band was a complex of closely overlapping V^- , V_{OH} , V_{Al} and V_{F} centres with a half-width of 1.09 eV at room temperature. The properties of V centres and other defects in alkaline earth oxides have been extensively reviewed by Henderson and Wertz [10].

Optical absorption at a cation vacancy centre is due to electron transitions in a nearest neighbour oxygen ion between the p_z ground state and the p_x , p_y orbitals although strictly speaking these are forbidden by the Laporte selection rules as they involve a redistribution of electrons within the same type of orbital in a single quantum shell. Experimentally the oscillator strength for the 2.3 eV band in MgO has been found [9] to vary between 0.1–0.2. No matter what the change in environment due to impurities the optical transition starts out from a well-localised p_z orbital on the O^- ion and Henderson and Wertz [10] have calculated that changes in the peak position of 0.07–0.3 eV could be expected. Hughes and Henderson [11] have shown that, for a hole state in the $2p_z$ orbital pointing into the cation vacancy, optical absorption should occur at a photon energy of

$$\Delta = \frac{8}{9}(e^2/R^3)\langle r^2 \rangle \quad (1)$$

where R is the anion cation separation and $\langle r^2 \rangle$ denotes the integral for the radial part of the O^- 2p function.

An alternative description of the V^- centre has been given by Schirmer *et al* [12] in which the optical transition is best regarded as a small-polaron transition. The main V^- transition results from hole transfer from one 'axial' oxygen to one of four equivalent 'equatorial' oxygen neighbours of the vacancy in a time so short that the lattice does not

relax to a new equilibrium position. Thus the transition energy is determined by the self-trapping distortion produced by the hole. Calculation of the optical absorption energy for the V^- centre in MgO by Norgett *et al* [13] gave good agreement with the experimental value of 2.3 eV. The oscillator strength was estimated to be 0.09.

In the case of AlON the 2.22 and 3.15 eV bands occur in both neutron irradiated and unirradiated material with similar intensities which suggests that the bands are initially due to intrinsic aluminium vacancies on both tetrahedral and octahedral cation sites. This proposition is supported by the fact that in the unirradiated material the relative intensity of the 2.22 eV and 3.15 eV bands is 2.1:1, a value very close to that of 2:1 expected for random occupation of octahedral and tetrahedral cation sites by the one missing aluminium ion per unit cell proposed by McCauley. Therefore one may tentatively ascribe the 2.22 eV band to a V centre at an octahedral cation vacancy and the 3.15 eV band to a V centre at a tetrahedral cation vacancy. The charge state of either centre is not known. Further evidence for the proposed assignment of the two bands may be obtained by reference to equation (1), where it can be seen that the ratio of the peak energies of the two bands should be inversely proportional to the ratio of the cubes of the cation–anion separation for the octahedral and tetrahedral sites. The cation–anion separations in AlON are 0.199 nm for the octahedral site and 0.172 nm for the tetrahedral site, which gives $R^3(\text{tetrahedral})/R^3(\text{octahedral}) = 0.65$ in comparison with the ratio of the proposed octahedral/tetrahedral band energies of 0.70. The two ratios are in good agreement considering the simplicity of the model.

More indirect evidence for the two absorption bands being V centres is obtained from the ‘anomalous’ decay of the bands in which the band intensity varied linearly with the logarithm of time. Similar behaviour had been observed for the V centre in sapphire and a theoretical model has been presented by Wood *et al* [14] in terms of electron–hole migration by either a common excited state or a quantum mechanical tunnelling mechanism.

Finally, if the intrinsic cation vacancies are responsible for the 2.22 eV and 3.15 eV bands then the oscillator strength for the transitions may be calculated from Smakula’s equation for a Gaussian band shape

$$Nf = 0.87 \times 10^{17} [n/(2 + n^2)^2] \alpha W \text{ cm}^{-3} \quad (2)$$

where N is the volume concentration of defects, n is the refractive index, α the absorption coefficient and W (eV) the full band width at half peak height. Then for the 2.22 eV band of half width 0.98 eV and $n = 1.785$ [15] the oscillator strength is 3×10^{-5} which is entirely consistent with a non-allowed p–p transition but orders of magnitude less than that found for the V centre in MgO. With the high number of intrinsic aluminium vacancies and the low impurity content the low oscillator strength is probably a true value. Higher oscillator strengths may be obtained when the simple V centre is perturbed by neighbouring impurities or other defects.

4.2. Low neutron dose effects

Reference to figures 3 and 5 will show that there is a distinct change in both lattice parameter and optical properties after a neutron fluence of only 10^{18} n m^{-2} which then persists unchanged up to fluences of $\sim 5 \times 10^{19} \text{ n m}^{-2}$. The change in lattice parameter, which is equivalent to a volume increase of 0.17%, is remarkably persistent as 6-hour anneals at temperatures up to 1000 °C produced no change. This should be compared with the annealing curves in figure 7 for a sample which had been neutron irradiated to

10^{24} n m^{-2} where it can be seen that some annealing of defects begins at temperatures as low as 200°C and proceeds rapidly above 600°C . Although figure 7 shows that after the highest annealing temperature of 1000°C the absorption edge did not return to the original value of the unirradiated sample.

The lattice expansion cannot be explained by the production of displacement damage by neutrons alone as a simple Kinchin and Pease type of calculation (using a displacement threshold energy $E_d = 50 \text{ eV}$ and a damage efficiency of 0.1 (Pells [16])) shows that 10^{18} n m^{-2} would only produce $\sim 10^{-8}$ displacements per atom (DPA). In fact figure 3 shows that the swelling maintained a constant value up to 10^{20} n m^{-2} above which the lattice parameter decreased towards the unirradiated value before increasing again at fluences $> 10^{22} \text{ n m}^{-2}$. The latter expansion is similar to that experienced in other neutron irradiated oxides (see Wilks [17]) where the swelling was believed to result from the production of interstitial atoms by displacement damage processes following neutron collisions with the lattice atoms. So how could the low dose reactor irradiations produce the observed lattice expansion in AlON? The thermal neutron flux at the irradiation position was approximately equal to the fast neutron flux and with the known capture cross-sections for AlON could not produce sufficient transmutation products to have any effect. The fast neutrons, of average energy 1 MeV, when colliding with lattice atoms will produce a primary knock-on atom (PKA) of $\sim 100 \text{ keV}$ average energy. The PKA will produce ~ 200 further displacements of which ~ 20 will survive as stable defects. An estimate of the volume containing a displacement cascade was calculated using the TRIM code and was found to approximate to a cylinder of 140 nm length and of 20 nm diameter or $\sim 2 \times 10^{-22} \text{ m}^3$. Therefore, a neutron fluence of 10^{18} n m^{-2} with an average collision cross-section of $3 \times 10^{-28} \text{ m}^2$ gives a total damage volume of $\sim 6 \times 10^{-3} \text{ m}^3$. Such a small volume fraction of disturbed material would not be readily detectable by x-ray lattice parameter measurements and is consistent with the expanded lattice remaining constant up to neutron fluences of $1\text{--}3 \times 10^{20} \text{ n m}^{-2}$ at which dose cascade overlap may become significant. Therefore, as fast neutron damage does not appear to be capable of promoting the change in lattice parameter there only remains the simultaneous gamma-irradiation that occurs during reactor irradiation. An x-ray dose equivalent to the energy deposited by 10^{18} n m^{-2} did not produce any measurable change. However, the gamma dose rate in the HERALD reactor of $\sim 3000 \text{ Gy s}^{-1}$ is ~ 500 times greater than the maximum dose rate available from the x-ray tube. Even so a simple calculation shows that such high ionising dose rates are not capable of simultaneously ionising sufficient nearest neighbour atoms for a new configuration to be adopted. Therefore, the mechanism by which low dose reactor irradiation increased the lattice parameter of AlON remains a mystery.

The intensity changes of the resolved V bands following reactor irradiation (see figure 5) suggest that the shift in lattice parameter is associated with the octahedral aluminium vacancies as the 2.22 eV absorption band is increased by $\sim 26\%$ whereas the 3.15 eV band did not change at all. It is unlikely that the increase in the 2.22 eV band is due to a proportionate increase in octahedral vacancies as this would involve the displacement of a further $5 \times 10^{26} \text{ m}^{-3}$ aluminium ions over and above the intrinsic octahedral aluminium vacancy concentration of $1.3 \times 10^{27} \text{ m}^{-3}$. The change is more likely to be associated with some shift in the electronic configuration on the oxygen ions surrounding the aluminium vacancy leading to some mixing of electronic states and hence a relaxation of the selection rules and an increase in the oscillator strength.

The absorption 'edge' in the far ultraviolet has been shown to increase exponentially with photon energy. In pure alkali halides it has been demonstrated that such behaviour

is due to the long wavelength side of the first exciton absorption band. To demonstrate that the AlON absorption edge is due to an exciton band would require very much thinner samples than it is possible to prepare from such large-grain-sized material. However, future work will follow the temperature dependence of the edge to see if it obeys Urbach's empirical equation [7] which predicts a thermally activated shift in the absorption edge due to exciton–lattice interactions. The equation also suggests that the edge wavelength should shift with the lattice constant as is observed in the low irradiation dose samples.

4.3. High neutron dose effects

The most noticeable feature of the absorption bands as they increased in intensity with increasing neutron dose was the large degree of band overlap such that at no stage did any one band stand out clearly from its neighbours. The bands could only be identified clearly by subtracting one spectrum from another after incremental changes in either neutron fluence, annealing temperature or x-irradiation. Nevertheless, this procedure allowed a total of seven absorption bands to be identified as listed in table 2. The majority of them show good agreement with the peak positions of those identified by Pells and Gilbert [2] using excitation spectroscopy although most of the ultraviolet bands had narrower widths at half maximum. All of the bands increased to some extent after x-irradiation in a manner similar to that observed in sapphire by Turner and Crawford [18] who concluded that the ultraviolet absorption bands were electron trapping centres.

4.4. Electron trapping centres

The present measurements are not capable of positively identifying the colour centres responsible for each absorption band but reasonable assignments may be made by reference to previous work and by analogy with known defects in sapphire and spinel. The 5.46 eV band was discussed by Pells and Gilbert [2] who ascribed it to an F centre on the basis of the large Stokes shift in the luminescence band associated with the 5.46 eV absorption. The F centre concentration may be calculated from the growth curve given in figure 4 using Smakula's equation. The oscillator strength is unknown but if the value of $f = 1.33$ quoted by Evans and Stapelbroek [19] for the F centre in sapphire is used then almost exact agreement is obtained with the number of F centres they give for an equivalent dose at a similar temperature in sapphire: in fact the agreement was far better than the neutron dosimetry which was probably not better than $\pm 20\%$. Nevertheless, the numerical agreement lends support to the assignment of the 5.46 eV band to an F centre. Figure 4 shows that the 5.00 eV band also grows with increasing neutron dose in a similar manner to the 5.46 eV band although it is only about one third as intense. Pells and Gilbert found that an excitation band at 5.02 eV (half-width 0.66 eV) was associated with a luminescence band at 2.5 eV which was present in all samples and did not increase with neutron dose. They suggested that the absorption and luminescence bands may be due to an F_A centre. It is unlikely that the 5.00 eV absorption band of half-width 0.46 eV identified in the present work is due to an F_A centre as the defect concentration calculated from the data in figure 4 exceeds the magnesium or calcium content after a neutron dose of 10^{22} n m^{-2} . Therefore there would appear to be two closely overlapping bands with the 5.00 eV band being ascribed to an F^+ centre by analogy with that in MgAl_2O_4 (4.75 eV) given by Summers *et al* [20]. The 4.6 eV absorption band which did not increase with neutron dose was also noted by Pells and Gilbert and ascribed to an F_A centre. It is

interesting to note that Knight [4] has shown, by EDX studies of ALON TEM samples, that the magnesium and calcium impurities are uniformly distributed throughout the grains rather than being segregated at grain boundaries or precipitates.

Both the 4.1 eV and 3.68 eV absorption bands increased in intensity with neutron dose above 10^{21} n m^{-2} although the 3.68 eV band was just detectable after 10^{20} n m^{-2} . Pells and Gilbert assigned the latter band to an F_2 -type centre by analogy with the F_2 centre at 3.46 eV in sapphire [21]. More recently Pogatshnik *et al* [22] on the basis of photo-bleaching experiments have identified various charge states of single and paired anion vacancies. They assign the 4.1 eV absorption band in sapphire to a charge neutral F_2 -centre (four trapped electrons) whose excited state lies very close to the conduction band. This would be consistent with the observation by Pells and Gilbert that the 4.1 eV excitation band in ALON contributed to all three luminescence bands. The 3.68 eV absorption band with its mirror image luminescence band [2] could then be equated with the F_2^+ centre at 3.46 eV in sapphire whose excited state lies at an energy much greater than kT below the conduction band.

4.5. Hole trapping centres

As was discussed earlier the 3.15 eV and 2.22 eV absorption bands are most probably due to V centres at the tetrahedral and octahedral cation sites respectively; in other words cation vacancies with optical activity being provided by electron transitions at next nearest neighbour oxygen ions. With such a large number of intrinsic defects (1.33×10^{21} octahedral vacancies cm^{-3} and 0.66×10^{21} tetrahedral vacancies cm^{-3}) it is to be expected that high neutron doses would be required to make any significant change in the V centre concentration. A simple estimate shows that a neutron fluence of $\sim 6 \times 10^{24} \text{ n m}^{-2}$ would be required to create aluminium Frenkel pairs equal to the intrinsic aluminium vacancy concentration. Figure 5 shows that the 2.22 eV band doubles after only 10^{21} n m^{-2} which suggests that the increase in V band strength at neutron fluences $>10^{20} \text{ n m}^{-2}$ is probably due to an increase in oscillator strength. The decrease in the intensity of both V band for neutron fluences $>10^{21} \text{ n m}^{-2}$ is difficult to account for but may result from changes in the population of oxygen ions surrounding the aluminium vacancy following the work of Halliburton and Kappers [23]. They deduced from electron spin resonance measurements on MgO neutron irradiated to $\sim 10^{21} \text{ n m}^{-2}$ that the spectra were best explained by an O_2^- molecule located at a single anion site which is stabilized by a cation vacancy. The presence of the cation vacancy allows the O_2^- molecule to tilt towards the vacancy. It was proposed that the O_2^- molecule was formed as the result of an oxygen interstitial combining with the O^- component of a V centre.

5. Conclusions

The effect of neutron irradiation on aluminium oxy-nitride is to create defects which show strong similarities to those identified in sapphire and the iso-structural MgAl_2O_4 spinel. Examination of spectral differences produced by varying neutron dose, annealing temperature and x-irradiation have allowed seven absorption bands to be isolated from the absorption spectra. The bands have been provisionally associated with the following defects:

2.225 eV (557 nm)—a V^- centre at an octahedral anion vacancy

- 3.15 eV (393 nm)—a V^- centre at a tetrahedral anion vacancy
- 3.68 eV (337 nm)—an F_2^+ centre
- 4.10 eV (302 nm)—an F_2 centre
- 4.60 eV (270 nm)—an F_A centre
- 5.00 eV (248 nm)—an F^+ centre
- 5.46 eV (227 nm)—an F centre.

The lattice expansion and F centre production rate in AlON obtained by exposure to a thermal reactor neutron spectrum closely matched that found in sapphire although an anomalous increase in lattice parameter occurred at very low neutron doses. There were also anomalies in the variation of the V bands intensities with neutron dose which require further study.

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