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Neutron irradiation of sapphire for compressive strengthening. II. Physical properties changes

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Abstract

Irradiation of sapphire with fast neutrons (0.8–10 MeV) at a fluence of $10^{22}/m^2$ increased the *c*-axis compressive strength and the *c*-plane biaxial flexure strength at 600 °C by a factor of ~2.5. Both effects are attributed to inhibition of *r*-plane twin propagation by damage clusters resulting from neutron impact. The *a*-plane biaxial flexure strength and four-point flexure strength in the *c*- and *m*-directions decreased by 10–23% at 600 °C after neutron irradiation. Neutron irradiation had little or no effect on thermal conductivity, infrared absorption, elastic constants, hardness, and fracture toughness. A featureless electron paramagnetic resonance signal at $g = 2.02$ was correlated with the strength increase: This signal grew in amplitude with increasing neutron irradiation, which also increased the compressive strength. Annealing conditions that reversed the strengthening also annihilated the $g = 2.02$ signal. A signal associated with a paramagnetic center containing two Al nuclei was not correlated with strength. Ultraviolet and visible color centers also were not correlated with strength in that they could be removed by annealing at temperatures that were too low to reverse the compressive strengthening effect of neutron irradiation. Published by Elsevier Science B.V.

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1. Introduction

The previous paper described neutron irradiation conditions to increase the *c*-axis compressive strength of sapphire at 600 °C by a factor of ~3 [1]. The present paper documents mechanical, optical, thermal, and spectroscopic properties of the irradiated material.

2. Experimental procedure

Most test coupons were Hemlite-grade sapphire from Crystal Systems, Inc. (Salem, MA, USA) polished at Insaco (Quakertown, PA, USA) to a nominal 60/40

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scratch/dig [1] finish and then annealed at 1200 °C in air for 24 h (while supported on sapphire fixtures) with heating and cooling rates of ~5 °C/min. Specimens were then exposed at the University of Massachusetts, Lowell, for ~70 h to a fast neutron dose of 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy) [1]. Thermal neutrons were limited by employing shields of borated aluminum (4.2 mg ^{10}B/cm^2 dispersed in 1-mm-thick 6061 aluminum, from Eagle-Picher, Tulsa, OK, USA) and Cd metal (1-mm-thick) around the irradiation basket. Following irradiation, the material was washed with 8 M HNO_3, 48% HF, and water, and then heated at 600 °C in air for 10 min (while supported on alumina or polished, fused silica fixtures) with heating and cooling rates of 10 °C/min. The 600 °C heating, which we refer to as 'decolorization', eliminates most of the yellow brown color produced in sapphire by neutron irradiation. After decolorization, the material is pale yellow.

Mechanical testing was done at the University of Dayton Research Institute (Dayton, OH, USA) with Instron testing machines at a crosshead speed of 0.508 mm/min. Specimens were heated at 10 °C/min and equilibrated at the final temperature for 10 min before testing. Tests were performed with and without 0.13-mm-thick Garlock 900 Grafoil® between the sapphire and the silicon carbide test fixture [2,3]. Biaxial flexure disks (38 mm diameter × 2 mm thick, cut within 1° of the stated plane) were tested with a load ring diameter of 15.88 mm and an outer support diameter of 31.75 mm. Rectangular four-point flexure specimens ($3 \times 4 \times 45$ mm^3) were tested with an inner load span of 10 mm and an outer span of 40 mm. Load was applied parallel to the 3 mm direction.

Compression test cylinders (3.17 mm diameter × 6.35 mm long) were optically polished to a nominal scratch/dig specification of 80/50 on all surfaces. The cylinder axis was parallel to the *c*-axis within 1° and ends were parallel to within 12 arc min. Edges were not chamfered. Rectangular flexure Bars were cut to within 1° of the stated crystal directions and optically polished to a 60/40 scratch/dig specification. Edges were not chamfered. For some experiments, flexure Bars were prepared from Czochralski-grown sapphire (Crystar, Victoria, British Columbia, Canada) fabricated at Meller Optics (Providence, RI, USA). The four long edges of Crystar/Meller Bars had a 45° chamfer beginning 0.1 mm from the original edges. For ring-on-ring testing, unchamfered *c*- or *a*-plane disks were fine ground on the sides and chemo-mechanically polished on the faces to an optical finish with a nominal scratch/dig specification of 60/40.

Elastic moduli were calculated from the measured speed of longitudinal and shear waves [4]. Optically polished disks (38 mm diameter × 9.5 mm thick) with *c*, *a*, *m* or *r* crystal axes normal to the disk were annealed at 1200 °C for 24 h in air and irradiated with 1×10^{22} fast neutrons/m^2 using Cd and ^{10}B shielding. Specimens were not decolorized at 600 °C. One side of the disk was irradiated with a 60 ns pulse from a CO_2 laser (10.6 μm) to generate an acoustic wave. The speed of the wave was measured by observing deflection at the back side of the disk with a path-stabilized 532 nm laser interferometer.

Thermal conductivity was measured by the laser flash method at Holometrix (Bedford, MA, USA). One surface of a 1-mm-thick *c*-plane sapphire disk was coated with 100 nm of gold and overcoated with graphite. To measure thermal diffusivity, the coated surface was irradiated with a 1.06 μm laser while the temperature of the uncoated surface was monitored with an infrared pyrometer. Conductivity is calculated from diffusivity × density × specific heat.

For electron paramagnetic resonance experiments, two *c*-axis sapphire prisms ($3 \times 3 \times 15$ mm^3) were annealed at 1450 °C for 24 h in air. They were then wrapped in aluminum foil and irradiated with 0.5 or 1.0×10^{22} fast neutrons/m^2. A week after irradiation, each sample was decolorized by heating in air at 600 °C for 10 min. Samples were washed with 8 M HNO_3, 48% HF, and water to remove surface contamination. Spectra were recorded on a Brüker ESP300 spectrometer at 9.5 GHz. Initial spectra were similar at 80 and 300 K, so subsequent spectra were recorded at 300 K. The magnetic field was perpendicular to the *c*-axis of the crystal. Rotation about the *c*-axis had little effect on the spectra.

Ultraviolet–visible spectra of irradiated, 1-mm-thick sapphire were recorded on a Hitachi 330 spectrometer using unirradiated sapphire as a reference. Annealing experiments were performed in an air atmosphere by placing the sapphire disk in a preheated furnace for 30 min and then cooling to room temperature.

3. Results and discussion

3.1. c-Axis compressive strength

Fig. 1 and Table 1 show that the *c*-axis compressive strength of neutron-irradiated sapphire is greater than that of unirradiated material in the temperature range 300–700 °C. The previous paper [1] suggests that the mechanism of compressive strength enhancement is the

[1] The first number of the scratch/dig specification is the scratch number, which is the width of the maximum allowable scratch in 0.1 μm units. The second number is the dig number, which is the maximum allowable diameter of a pit, bubble, pinhole or inclusion in 10 μm units. A scratch/dig specification of 60/40 permits no scratch wider than 6 μm and no dig wider than 400 μm. A more complete description is found in Military Specification MIL-0-13830A; American National Standard PH3-617, American National Standards Institute, New York (1980).

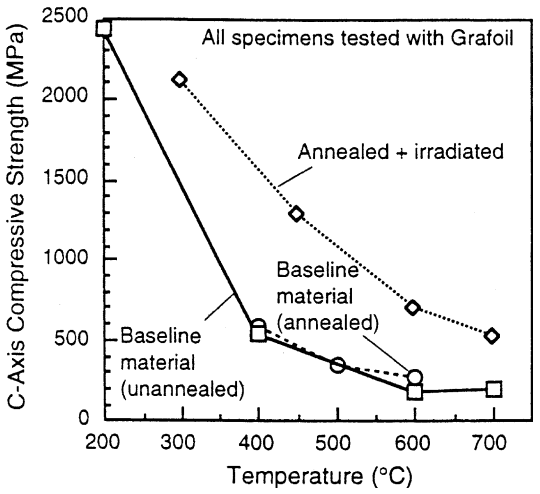

Fig. 1. *c*-Axis compressive strength of sapphire cylinders (3.18 mm diameter × 6.35 mm long).

inhibition of *r*-plane twin propagation by neutron damage sites that are 5–25 nm in diameter. For unirradiated sapphire, there was little difference in strength between annealed and unannealed material.

All of the tests in Table 1 were done with a thin sheet of Grafoil between the sapphire and the silicon carbide load plate [2,3]. It is believed that Grafoil distributes the load more uniformly on the specimen and reduces friction that would prevent lateral spreading of the ends of the sapphire when it is compressed. The compressive strength of unirradiated *c*-axis sapphire at 600 °C increased from ~55 MPa without Grafoil to ~230 MPa with Grafoil.

In contrast to the behavior of unirradiated sapphire, neutron-irradiated sapphire has the same apparent *c*-axis compressive strength at 600 °C whether or not it is tested with Grafoil. Sapphire cylinders irradiated without filtering of thermal neutrons for 50 h had the following *c*-axis compressive strengths (± standard deviation) at 600 °C:

Tested without Grafoil: 614 ± 36 MPa (four specimens)

Tested with Grafoil: 653 ± 96 MPa (six specimens).

Neutron irradiation has little effect on the *a*-axis compressive strength of sapphire at 600 °C. In previous work, the *a*-axis compressive strength was much higher than that of *c*-axis sapphire at elevated temperature [5,6]. In the present work, five neutron-irradiated *a*-axis specimens (tested with Grafoil) had a mean strength of 2002 ± 381 MPa at 600 °C, which can be compared to the 712 MPa *c*-axis strength of irradiated sapphire in Table 1. In previous work, the *a*-axis compressive strength of unirradiated sapphire tested without Grafoil was 2002 ± 293 MPa (five specimens) at 20 °C and 1581 ± 92 MPa (five specimens) at 800 °C [6].

3.2. Biaxial flexure strength

Table 2 shows that unirradiated *c*-plane disks lose two thirds of their room temperature strength at 600 °C. By contrast, neutron-irradiated disks do not have a significant change in flexure strength between 20 and 600 °C. Unirradiated *a*-plane disks lose 18% of their room temperature strength at 600 °C. Irradiated *a*-plane disks are 10% weaker than unirradiated disks at 600 °C.

Grafoil has a large effect on the biaxial flexure strength of neutron-irradiated sapphire at 600 °C. Table 3 shows that the strength of *c*-plane disks drops by a factor of 4 when tested without Grafoil. The strength of *a*-plane disks decreases by a factor of 2 when Grafoil is not used. These results are in contrast to *c*-axis compression of irradiated sapphire cylinders in which Grafoil had no effect on the strength at 600 °C. Material in Table 3 was all from one lot. The strengths of disks

Table 1
c-Axis compressive strength of sapphire[a]

Test temperature (°C)	Strength (MPa) ± standard deviation (number of specimens)		
	Baseline material (not annealed)	Baseline material (annealed[c])	Irradiated material[b] (annealed[c])
200	2434 ± 101 (5)		
300			2104 ± 421 (23)
400	550 ± 169 (5)	598 ± 135 (28)	
450			1280 ± 290 (10)
500		359 ± 64 (27)	
600	192 ± 82 (5), 203 ± 46 (30)	274 ± 85 (55)	712 ± 85 (30)
700	205 ± 61 (5)		532 ± 89 (30)

[a] All tests were done with Grafoil between the sapphire and the silicon carbide load plate.
[b] Irradiated material received 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy).
[c] Sapphire was annealed at 1200 °C for 24 h in air after polishing (before neutron irradiation).

Table 2
Biaxial flexure strength of sapphire disks tested with Grafoil

Test temperature (°C)	Strength (MPa) ± standard deviation (number of specimens)			
	c-Plane not irradiated	*c*-Plane irradiated[a]	*a*-Plane not irradiated	*a*-Plane irradiated[a]
20	1593 ± 396 (8)	1330 ± 659 (7)	924 ± 197 (10)	984 ± 231 (20)
600	536 ± 119 (11)	1285 ± 244 (13)	760 ± 146 (10)	683 ± 262 (25)

[a] Irradiated material received 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy).

Table 3
Effect of Grafoil on biaxial flexure strength of neutron-irradiated sapphire at 600 °C[a]

	Strength (MPa) ± standard deviation (number of specimens)	
	No Grafoil	Grafoil
c-Plane	349 ± 63 (5)	1370 ± 184 (5)
a-Plane	363 ± 105 (5)	640 ± 134 (5)

[a] Irradiated material received 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy).

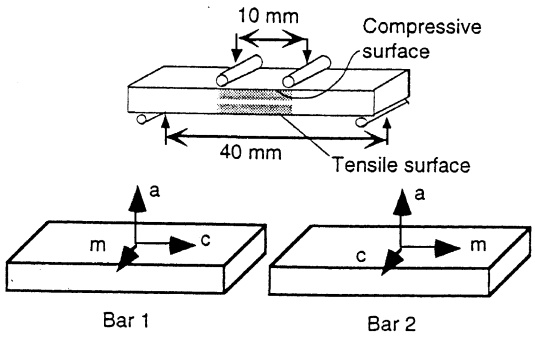

Fig. 2. Crystal orientations of four-point flexure specimens.

tested with Grafoil in Table 3 lie within one standard deviation of comparable disks on the bottom line of Table 2.

In previous studies [7–9] summarized by Pells [10], neutron fluences were 10^2–10^4 times greater than the fluence of ~10^{22}/m^2 used in our work. Pells concluded that for doses up to 10^{26}/m^2, there was no change in the flexure strength of sapphire. In the present work, the principal mechanical effect of fast neutron irradiation at a fluence of ~10^{22}/m^2 is to increase the *c*-axis compressive strength at elevated temperature. We attribute the increased flexure strength of *c*-plane sapphire disks to the same factor that increases *c*-axis compressive strength. Contact compression in the *c*-direction during the biaxial flexure test would induce *r*-plane twinning in the absence of neutron irradiation. In irradiated material, *r*-plane twinning is retarded, so a higher load is needed to take the specimen to failure.

3.3. Four point flexure strength

Two crystal orientations were chosen to explore a range of response. Bar 1 in Fig. 2 has tension in the *c* direction on one surface and compression in the *c* direction on the opposite surface. It is expected to fail in tension at 20 °C and in compression at 600 °C [6]. Bar 2 has no significant stress in the *c* direction. It is expected to fail in tension at 20 and 600 °C. The first line of Table 4 shows that neutron irradiation has no significant effect on the strength of these Bars at 20 °C. The second line shows that both Bars 1 and 2 lose 20–23% of their strength at 600 °C after irradiation.

Czochralski-grown flexure bars shown on the bottom line of Table 4 were also tested [11]. These bars were annealed at 1200 °C for 24 h in air prior to neutron irradiation, but Grafoil was *not* employed in the strength

Table 4
Four-point flexure strength of sapphire bars

Test temperature (°C)	Strength (MPa) ± standard deviation (number of specimens)			
	Bar 1 not irradiated	Bar 1 irradiated[a]	Bar 2 not irradiated	Bar 2 irradiated[a]
Crystal Systems/Insaco sapphire tested with Grafoil				
20	1331 ± 534 (10)	1321 ± 253 (10)	685 ± 180 (4)	651 ± 186 (6)
600	647 ± 135 (10)	520 ± 169 (10)	670 ± 236 (5)	515 ± 65 (6)
Crystar/Meller Optics sapphire tested without Grafoil				
600	230 ± 28 (18)	612 ± 82 (20)	513 ± 110 (24)	559 ± 92 (20)

[a] Irradiated material received 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy).

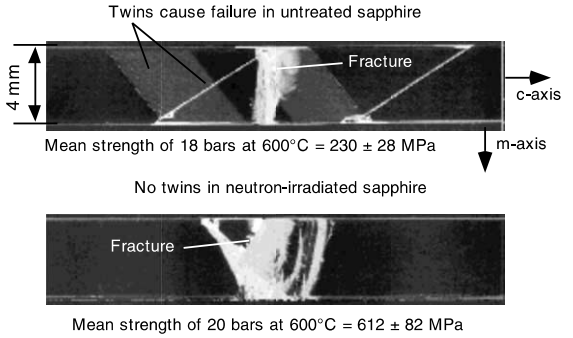

Fig. 3. Top view of four-point flexure Bar 1 (Fig. 2) showing effect of neutron irradiation on morphology of failure. These specimens of Czochralski-grown material [11] were tested without Grafoil.

tests. When tested at 600 °C without Grafoil, unirradiated Bar 1 is much weaker than when it is tested with Grafoil (230 vs. 647 MPa). This is a direct effect of Grafoil in the testing of Bar 1 [2]. The increase in strength of Bar 1 after irradiation (612 vs. 230 MPa) is attributed to the increase in *c*-axis compressive strength induced by neutron irradiation. For Bar 2, which fails in tension, irradiation had little effect on strength (559 vs 513 MPa).

Fig. 3 shows that neutron irradiation changes the mechanism of failure of Bar 1 tested at 600 °C without Grafoil. Unirradiated Bar 1 specimens tested at 600 °C were extensively twinned and there was a twin–twin intersection at each failure origin. Irradiated material did not have twins and appeared to fail in tension.

3.4. Attempt to reduce damage in sapphire from grinding and polishing after neutron irradiation

We sought to use neutron irradiation to reduce damage caused by grinding and polishing – and thereby increase the tensile strength of sapphire – by the following procedure: oversized sapphire cylinders removed from a boule by a core drill were irradiated with neutrons prior to slicing blanks for 38-mm-diameter × 2-mm-thick disk test specimens from the cylinder. Our hypothesis was that compressive strengthening induced by irradiation would make the sapphire less susceptible to damage during the slicing, grinding, and polishing of disks. After polishing, the disks were annealed at 1200 °C in air for 24 h to heal the neutron damage. The purpose of this anneal was to reverse all neutron damage so any change in mechanical strength could be attributed to reduction of grinding and polishing damage – not to neutron-induced defects. It is also possible that annealing would cause aggregation of defects and could affect strength.

Table 5 shows that sapphire irradiated prior to machining was not significantly stronger than untreated

Table 5
Attempt to increase biaxial flexure strength of sapphire at 600 °C by irradiating prior to machining

Disk orientation	Strength (MPa) ± standard deviation (number of specimens)		
	Not irradiated[a]	Irradiated before machining disks[b]	Standard irradiation after machining disks[c]
c-Plane	536 ± 119 (11)	590 ± 80 (12)	1285 ± 244 (13)
a-Plane	760 ± 146 (10)	783 ± 130 (10)	683 ± 262 (25)

[a] Unirradiated disks were annealed at 1200 °C/24 h/air after polishing.

[b] Irradiation with 1×10^{22} fast neutrons/m^2 was performed prior to slicing, grinding, and polishing. Finished disks were then annealed at 1200 °C/24 h/air to remove neutron damage.

[c] Disks were annealed at 1200 °C/24 h/air after polishing and then irradiated to a level of 1×10^{22} fast neutrons/m^2. Following irradiation, disks were decolorized at 600 °C for 10 min.

disks. By comparison, the last column of Table 5, repeated from Table 2, shows that irradiation after polishing doubles the flexure strength of *c*-plane sapphire and lowers the flexure strength of *a*-plane sapphire. These results indicate that irradiation prior to machining does not reduce the susceptibility of sapphire to damage during machining, and that annealing at 1200 °C in air for 24 h does reverse the mechanical effects of neutron irradiation.

Doubling of the flexure strength of *c*-plane sapphire is thought to be a direct result of *c*-axis compressive strengthening. The flexure strength of *c*-plane sapphire drops from 1050 to 140 MPa when the temperature is raised from 20 to 800 °C [6]. By contrast, the flexure strength of *a*-plane material only decreases from 610 to 370 MPa over the same temperature range [6]. In flexure tests, it is thought that contact compressive stress on *c*-plane disks at the load rings induces twinning which contributes to mechanical failure at elevated temperature. In *c*-plane flexure tests, contact compressive stress is directed along the *c*-axis of the crystal, which is the axis susceptible to twinning. In *a*-plane disks, contact compression is directed along the *a*-axis, which is not as susceptible to twinning.

3.5. Hardness, fracture toughness, and elastic modulus

Hardness and apparent fracture toughness were measured with a Vickers indentor on the *c*-plane of sapphire with fractures oriented in the *a*- and *m*- directions. The hardness in Table 6 is essentially the same for irradiated and unirradiated sapphire. Since the conventional equations to compute fracture toughness from crack lengths are inappropriate for anisotropic single crystals, only a qualitative estimate of differences in

Table 6
Vickers hardness and fracture toughness of sapphire at 20 °C[a]

Treatment	Hardness (GPa)		Fracture toughness (MPa$\sqrt{m}$)	
	a-Plane	*m*-Plane	*a*-Plane	*m*-Plane
Unirradiated	12.4 ± 0.3	12.7 ± 0.1	1.7 ± 0.1	2.2 ± 0.2
Irradiated[b]	12.7 ± 0.1	12.6 ± 0.1	1.72 ± 0.09	1.80 ± 0.02

[a] Hardness was computed from the equation $H = P/2a^2$, where P is the indentation load (4.9 N for 10 s) and the indentation diagonal length is $2a$. Fracture toughness (K_{Ic}) was computed from the equation $K_{Ic} = (0.016 \pm 0.004)\ \sqrt{E/H}(P/c^{3/2})$, where E is Young's modulus (425 GPa) and $2c$ is the radial crack length from the indentation.
[b] Irradiated material received 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy).

fracture resistance was made based on observed differences in crack length. The fracture resistance was the same for irradiated and unirradiated material on the *a*-plane, but was reduced ~20% on the *m*-plane for irradiated material.

The fracture toughness on the *a*-plane in Table 6 can be compared to a value of 1.9 (MPa$\sqrt{m}$) reported previously from indentation studies [12]. In that previous work, fractures would not propagate along the *m*-plane so no toughness was reported for that plane. In other work based on three-point flexure strength of pre-indented sapphire, the fracture toughness was reported to be 2.4 (MPa$\sqrt{m}$) on the *a*-plane and 3.1 (MPa$\sqrt{m}$) on the *m*-plane [13].

The trigonal symmetry of the sapphire crystal gives rise to six distinct elastic constants that can be computed from the speed of sonic waves in different crystal directions [4]. Table 7 compares elastic constants in untreated and irradiated sapphire to those reported by Goto et al. [14]. We find that c_{11}, c_{33} and c_{44} are nearly unchanged by irradiation. Small differences in c_{12}, c_{13} and c_{14} might partially be from the larger error in determining these off-diagonal moduli, which are based on both a specific wave arrival time and on previously determined moduli.

Table 7
Elastic constants of sapphire (GPa)[a]

Test temperature (K)	c_{11}			c_{33}		
	Goto et al. [14]	Untreated	Irradiated	Goto et al. [14]	Untreated	Irradiated
296	497.3 (±1.5)	493.0	489.4	500.9 ± (1.8)	495.9	494.5
400	494.7	492.3	488.0	497.2	494.7	493.0
500	490.6	489.7	485.5	493.6	492.6	490.7
600	486.0 (±1.3)	486.0	481.8	489.2 (±1.6)	489.5	487.7
700	481.5	481.5	477.1	484.9	485.8	484.0
800	476.8	476.6	472.8	480.4	481.5	480.0
	c_{44}			c_{12}		
296	146.8 (±0.2)	145.3	145.2	162.8 (±1.7)	176.8	168.0
400	144.4	144.4	144.4	163.8	178.5	168.4
500	141.8	142.7	142.7	163.7	180.4	168.8
600	139.2 (±0.2)	140.7	140.5	163.1 (±1.5)	182.0	169.0
700	136.5	138.2	137.8	162.9	183.8	169.3
800	133.9	135.1	135.3	162.4	185.6	169.5
	c_{13}			c_{14}		
296	116.0 (±1.8)	106.0	96.5	−21.9 (±0.2)	−29.6	−26.9
400	115.3	106.6	95.9	−22.7	−30.2	−27.2
500	114.4	107.0	95.5	−23.0	−30.8	−27.5
600	113.0 (±1.6)	107.5	95.0	−23.3 (±0.2)	−31.4	−27.7
700	111.9	107.9	94.5	−23.4	−32.0	−28.0
800	110.6	108.4	94.1	−23.7	−32.6	−28.3

[a] Sapphire investigated by Goto was not irradiated. Material for the present study was either unirradiated or it received 1.0×10^{22} neutrons/m^2 (~0.8–10 MeV neutron energy).

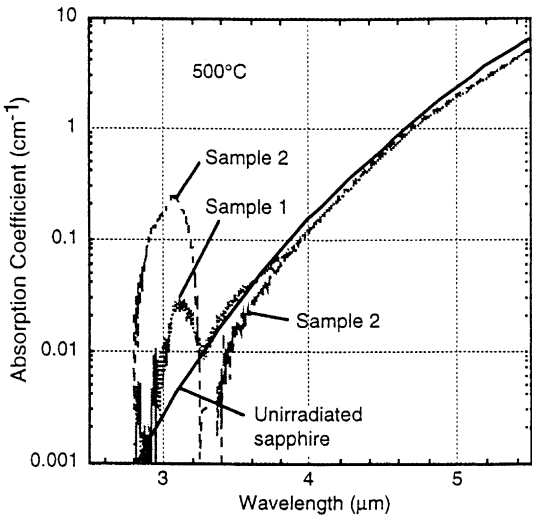

Fig. 4. Infrared absorption coefficient of irradiated sapphire disks and reference curve for unirradiated sapphire. Samples 1 and 2, both 6.0 mm thick, received 1×10^{22} fast neutrons/m^2 with Cd and ^{10}B filtering of thermal neutrons. Neither sample was annealed at 1200 °C prior to irradiation nor decolorized at 600 °C after irradiation.

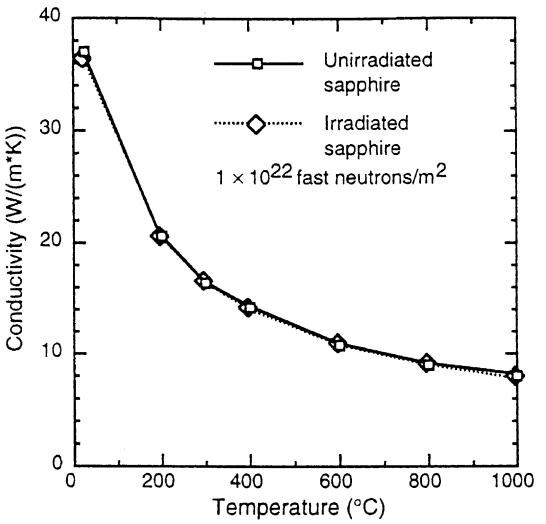

Fig. 5. Thermal conductivity of sapphire in c direction. Each data point is the mean value for two different specimens.

3.6. Infrared absorption

Infrared transmittance was measured on sapphire that was *not* decolorized after neutron irradiation. The absorption coefficient was computed from the transmittance and the known refractive index. In the region 3.2–5 μm in Fig. 4, there is no significant difference between irradiated and unirradiated material. Weak absorption near 3.1 μm is probably OH stretching from H^+ introduced into the crystal by (n,p) nuclear processes such as $^{27}Al + {}^1n \rightarrow {}^1H + {}^{27}Mg$. This absorption band was not present prior to irradiation and disappeared one month after the infrared measurements were made.

3.7. Thermal conductivity

Fig. 5 shows that the thermal conductivity of sapphire is unaffected by neutron irradiation at a level of 1.0×10^{22}/m^2. In previous work with much higher neutron fluence, the thermal conductivity decreased significantly near 25 °C, as indicated in Table 8 [15]. The conductivities of unirradiated and irradiated sapphire approach each other at elevated temperature.

3.8. X-ray diffraction and topography

No differences between irradiated and unirradiated sapphire were observed by single- and double-crystal X-ray diffractometry. Irradiation did not change the peak positions or line shapes of (0 0 0 6) and (0 0 0 12) reflections or rocking curves from (1 1 0 5) and (1 1 0 8) reflections. There is no evidence for any change in lattice parameters or for the presence of a second phase.

Table 8
Thermal conductivity of neutron-irradiated sapphire in c direction

Irradiation (neutrons/m^2)	Conductivity (W/m K)	
	25 °C	1000 °C
None (present work)	36.8	7.9
None [15]	33.8	8.0
1×10^{22} (present work)	36.2	7.7
5×10^{24} [15]	26.7	7.3
2×10^{25} [15]	10.9	6.4
4×10^{25} [15]	9.3	6.4

Attempts to observe differences by X-ray topography [16] also gave negative results (Fig. 6). Many features such as dislocations and scratches were readily observed, but they were not changed by irradiation. Neutron-induced damage is below the resolution of X-ray topography.

3.9. Electron paramagnetic resonance

Electron paramagnetic resonance spectroscopy identified two kinds of defects in irradiated sapphire that had been decolorized at 600 °C. The strong, nearly featureless signal at $g = 2.02$ in Fig. 7 has been attributed previously to an electron trapped at an anion vacancy and a hole trapped at either a cation vacancy or a charge-deficient cation site [17,18]. It was reported [19]

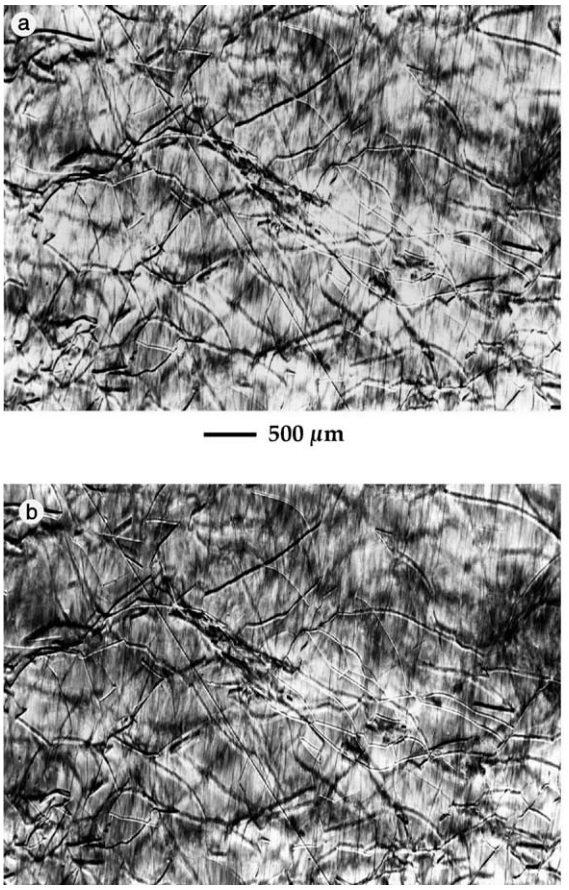

Fig. 6. X-ray topographs ((3 0 $\bar{3}$ 0) symmetric transmission at 10 keV) of polished *c*-plane crystal systems sapphire before (a) and after (b) receiving 1×10^{22} fast neutrons/m^2.

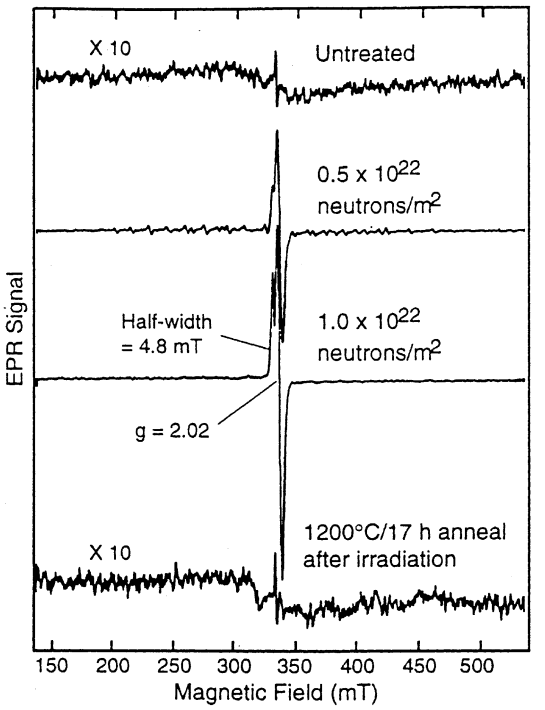

Fig. 7. Electron paramagnetic resonance spectra of sapphire before and after neutron irradiation. The lowest trace shows that the signal nearly disappears after annealing for 17 h at 1200 °C in air.

that the vacancies reach a concentration of $\sim 5 \times 10^{18}$/cm^3 for a neutron dose of $\sim 4 \times 10^{21}$/m^2 (>10 keV), which is similar to what we observe ($\sim 10^{19}$/cm^3 for a dose of 1×10^{22}/m^2). However, the signal reported previously disappeared after annealing at 500 °C for 1 h. The signal in Fig. 7 was observed after decolorization at 600 °C for 10 min, but disappeared after annealing at 1200 °C for 17 h. The signal in Fig. 7 is correlated with compressive strengthening, which increases with increasing neutron fluence (in the range $0.5–1.0 \times 10^{22}$/m^2) and which is lost after annealing at 1200 °C for 17 h, but not after decolorizing at 600 °C. It is possible that the $g = 2.02$ signal is associated with unpaired spins present in the defect clusters observed by transmission electron microscopy in Fig. 5 of the previous paper [1].

A second paramagnetic defect is not correlated with sapphire strengthening. The multi-line spectrum in Fig. 8 centered at $g = 2.07$ exhibits coupling to two ^{27}Al ($I = 5/2$) nuclei with coupling constants of 1050 and 460 MHz (37.4 and 16.4 mT). The signal is absent in unirradiated sapphire. It is strong after a fast neutron fluence of 0.5×10^{22}/m^2, but *decreases* at a neutron fluence of 1×10^{22}/m^2. In contrast, compressive strengthening increases with increasing fluence. The paramagnetic resonance signal disappears after annealing the irradiated sapphire at 1200 °C for 17 h. A similar spectrum was assigned to a paramagnetic center consisting of two neighboring aluminum ions [20,21]. One resides at a normal lattice site and the other occupies a site that would be vacant in an ideal sapphire lattice.

3.10. Ultraviolet and visible spectroscopy

Absorption spectra (200–800 nm) of sapphire irradiated with 0.5 or 1.0×10^{22} fast neutrons/m^2 were recorded without decolorizing the specimens at 600 °C after irradiation. The strongest band near 210 nm in Fig. 9 has previously been assigned to an F center – an oxygen vacancy occupied by two electrons [22–24]. Weaker bands observed near 230, 260 and 300 nm have been assigned to an F^+ center – an oxygen vacancy occupied by one electron [24]. (A band at 230 nm was observed in *c*-plane sapphire, but not in *a*-plane sapphire.) Another study assigned bands near 202, 256 and 229 nm to the

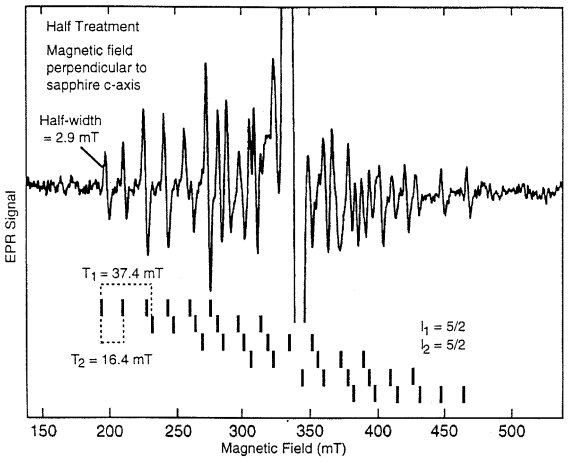

Fig. 8. Expanded scale showing electron paramagnetic resonance spectrum arising from Al–Al pairs in sapphire irradiated at a level of 0.5×10^{22} fast neutrons/m^2. Stick figures interpret the spectrum as six groups of six lines arising from a strong hyperfine interaction of the unpaired electron with one ^{27}Al nucleus and a weaker interaction with a second ^{27}Al nucleus.

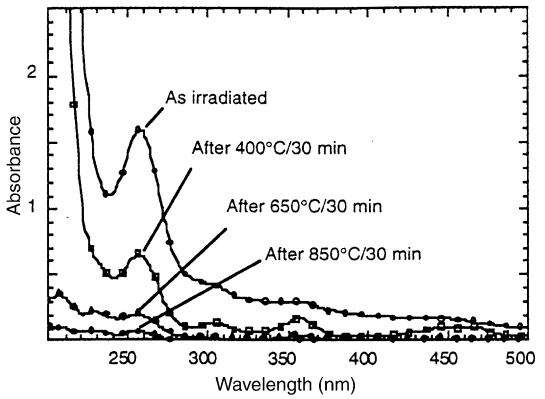

Fig. 9. Effect of heating on ultraviolet-visible absorption of *a*-plane sapphire (1-mm-thick) that had been irradiated with 0.5×10^{22} fast neutrons/m^2.

F^+ center, but did not observe a band near 300 nm [25]. The band near 300 nm has also been attributed to a V center (a singly ionized aluminum vacancy) [21,26]. We observed at least 10 weak bands between 360 and 750 nm which have been noted before and suggested to arise from electrons in oxygen vacancies and clusters of oxygen vacancies [27].

Bands associated with the F and F^+ centers lose intensity upon heating (Fig. 9). The 260 nm band is reduced by 90% after heating at 650 °C for 30 min and by 99% after 850 °C for 30 min. Since neutron-irradiated sapphire annealed under these conditions does not lose its *c*-axis compressive strength, the F and F^+ centers cannot be responsible for strength enhancement. Weak visible absorptions do not lose intensity at 400 °C, but are almost gone after heating to 650 °C for 30 min.

Photon illumination of neutron-irradiated sapphire induces electrical conductivity [24]. We examined photo-induced birefringence of neutron-irradiated sapphire. A linearly polarized 325 nm laser source was used to create a variation in refractive index, which was detected by optical birefringence using an orthogonal polarized 800 nm laser. The refractive index variation is associated with the generation and migration of photocarriers. Birefringence saturates after a few minutes of ultraviolet illumination and relaxes at the conclusion of illumination. No birefringence was detected after heating at 850 °C for 30 min. The birefringence response supports the results from optical absorption: viz., moderate heating quenches the neutron-generated defects.

4. Summary

Fast neutron (0.8–10 MeV) irradiation at a fluence of 10^{22}/m^2 had the following effects on sapphire:

- The *c*-axis compressive strength at 600 °C increased by a factor of ~2.5. The strength increase is attributed to retardation of *r*-plane twin propagation by neutron damage sites. The *a*-axis compressive strength of sapphire is high (~2000 MPa) with or without irradiation.
- The biaxial flexure strength of *c*-plane disks was increased by a factor of ~2.5 at 600 °C, presumably because the disks were less susceptible to twinning failure.
- The biaxial flexure strength of *a*-plane disks and the four-point flexure strength of bars with two different crystal orientations was decreased by 10–23% at 600 °C.
- Hardness, toughness, and elastic constants of sapphire were not changed very much.
- The 3–5 μm infrared absorption coefficient of sapphire at 500 °C was essentially unchanged. A weak, broad absorption band near 3.1 μm attributed to O–H stretching disappeared several months after irradiation.
- The thermal conductivity of sapphire from 20–1000 °C was unchanged.
- No changes could be discerned by X-ray diffraction or X-ray topography.
- A strong, featureless signal in the electron paramagnetic resonance spectrum near $g = 2.02$ is correlated with mechanical strength. It increases with neutron dose and was lost by annealing at temperatures that also affect mechanical strength.
- Ultraviolet and visible absorption features (color centers) do not appear to be correlated with mechanical strength.

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