Gamma-ray induced oxygen diffusion in germanium dioxide

Ionizing radiation on glassy and hexagonal GeO_2 yields an almost axially symmetric ESR signal of $g_{\parallel} = 2.002$ and $g_{\perp} = 1.994$ which was assigned to singly charged oxygen vacancies [1, 2]. In a previous paper [3] it was reported that these paramagnetic centres disappear after step annealing for 10 min to at least 500° C. If the disappearance of the ESR signal means the recovery of trapped electrons on oxygen vacancies to the pre-irradiated states, then the change of the signal intensity of identical radiation doses would reflect the change of the concentration of oxygen vacancies. The purpose of the present work was to know whether γ-rays can generate oxygen vacancies in glassy and hexagonal GeO_2, with repeated cycles of γ-irradiation, ESR measurement, and removal of the signal by heat-treatment. The effect of ambient oxygen on the ESR signal intensity was also studied.

Raw materials used in the present study were hexagonal GeO_2 of nominally 3N purity. No metallic impurities were detected by flame spectrometry. Glass samples A and A′ were obtained by melting raw materials in Pt foils at 1350° C for 3 h in air, quenching in liquid nitrogen, and crushing to $<44\,\mu m$ in particle size. Samples B and B′ were hexagonal powders dried at 800° C for 48 h in air. Sintered hexagonal powders C and C′ were obtained by heating the raw material at 1070° C for 48 h in air. Samples A, B and C were sealed in silica tubes evacuated by a diffusion pump having liquid nitrogen traps, while samples A′, B′ and C′ were sealed in air-filled silica tubes. γ-irradiations were made from a ^{60}Co source at a dose rate of $\sim 1.5 \times 10^5\,\text{rad}\,h^{-1}$. In order to monitor γ-ray doses, a glass powder of dimension $<44\,\mu m$ was co-irradiated as a control sample. The ESR measurements were made with an X-band spectrometer at room temperature. After each measurement of ESR, the signal was removed by heating a sample at 500° C for 30 min.

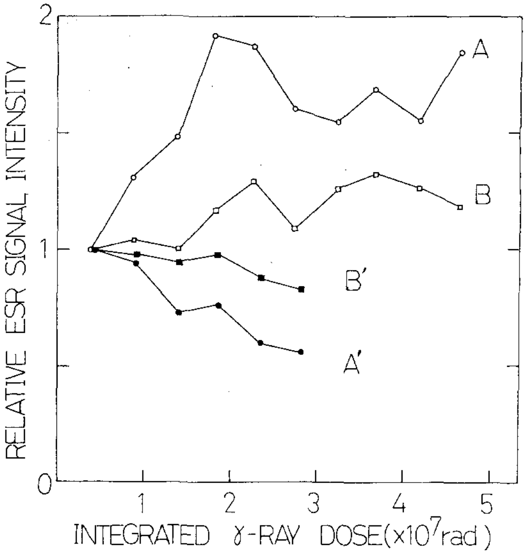

Figure 1 The ESR signal intensity relative to that at the first cycle as a function of integrated γ-ray dose for the samples A, A′, B and B′.

Fig. 1 shows the ESR signal intensity relative to that at the first cycle as a function of integrated γ-ray dose for the samples A, A′, B and B′. For small γ-ray doses ($<1 \times 10^4$ rad) where no radiation-induced effects were observed, the signal intensity ratio A/B = 1.1 ± 0.1 was almost independent of the dose. It is suggested therefore that the signal intensity is proportional to the concentration of oxygen vacancies or, in other words, that the hypothesis [4] that the fraction of oxygen vacancies occupied by electrons is constant for an identical dose irrespective of samples is substantiated. Furthermore, since under such a small γ-ray dose the observed signal intensity was the same for repeated cycles of γ-irradiation followed by thermal erasure of the signal, the disappearance of the ESR signal on heat-treatments at 500° C for 30 min would mean the recovery of trapped electrons on oxygen vacancies to the pre-irradiated state. Therefore, the signal intensity can follow the change of the concentration of oxygen vacancies with γ-ray dose.

An increase in the signal intensity with dose for A and B implies the generation of oxygen vacancies by γ-rays. Since Compton recoils of ~0.5 MeV from ^{60}Co γ-rays are sufficient to displace oxygen atoms from their lattice sites [5], it is quite likely that extrinsic oxygen vacancies are generated by γ-irradiation. The generation rate of oxygen vacancies in glass A was about three times larger than the rate in crystal B. It may be due to the fact that the open structure of the glass can provide many spaces available for γ-ray induced interstitial oxygens, while in the crystal only the vacancy

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clusters, dislocations or other imperfections can be the sites for interstitial oxygens.

A decrease of the signal intensity of A′ and B′ with dose would reflect a change in number of oxygen vacancies by the diffusion of oxygen from ambient atmosphere. Since the sample B′ was dried before the experiments at 800° C for 48 h, the heating process at 500° C for 30 min each in repeated cycles would provide a negligible contribution to the observed decrease. Although the diffusivity of oxygen is large in glass, the overall heating time of 3 h at 500° C was too short to lead to ~ x 0.55 of the original concentration of oxygen vacancies, especially when the effect of γ-ray induced generation of oxygen vacancies is considered. Fig. 1 suggests therefore the presence of γ-ray induced oxygen diffusion through the bulk. A possible mechanism for the process is as follows: (i) ambient oxygen is dissociated by γ-irradiation, adsorbed on the surface of powder particles, and diffused into the bulk on subsequent heating. (ii) Adsorbed oxygen molecules are dissociated by irradiation and diffused into the bulk on subsequent heating. (iii) Even if adsorbed oxygen in the dissociated state plays the major role in the observed vacancy annihilation, it must be freed from the trap site, and thermal spikes on γ-irradiation can provide sufficient energy for overcoming this constraint [6]. Alternatively there is a possibility that the MKM theory [7] holds for experimental observations. The theory states that as ions approach an insulator surface, ion neutralization by Auger or resonance processes [8] can lead to impurity migration in insulators even at room temperature. Here we assume that ions approaching the surface are some ionized species in air generated by irradiation, and impurities thus oxidated and moved away from the surface are adsorbed oxygens.

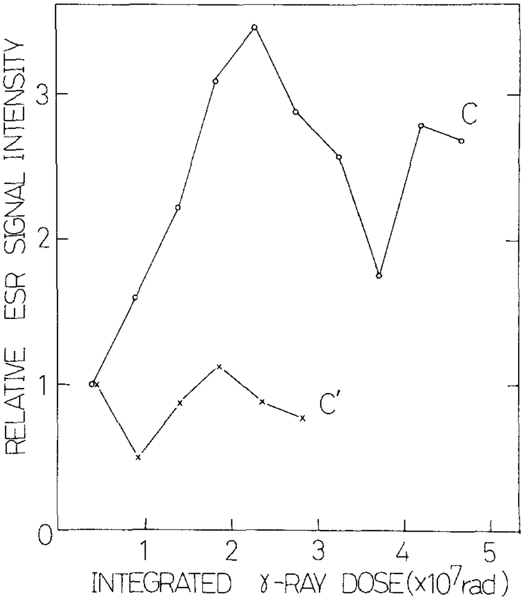

Figure 2 The ESR signal intensity relative to that at the first cycle as a function of integrated γ-ray dose for the samples C and C′.

Fig. 2 shows the ESR signal intensity relative to that at the first cycle as a function of integrated γ-ray dose for sintered hexagonal powders C and C′. Scanning electron micrographs of the hexagonal powder B and sintered powder C are illustrated in Fig. 3. A powder particle of B was found to be the

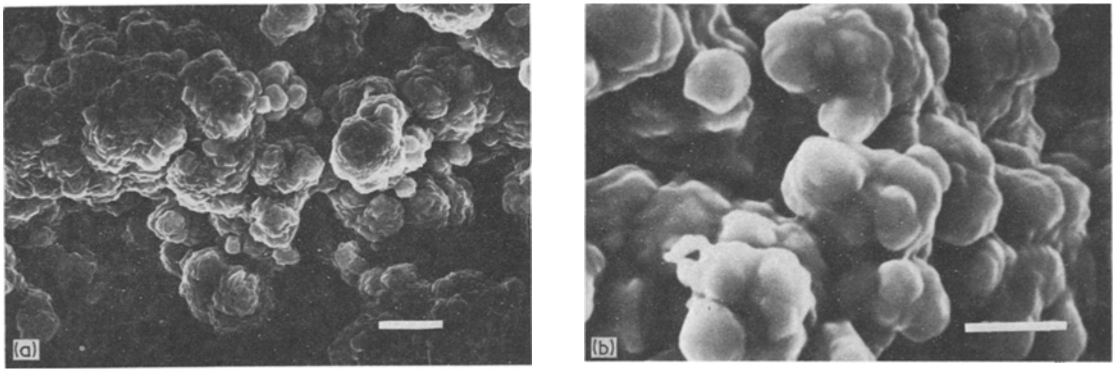

Figure 3 Scanning electron micrographs of (a) the hexagonal powder B and (b) the sintered powder, C. The white bar represents 4 μm.

aggregate of small lamellar crystallites and so would contain imperfections. Although the signal intensity was reduced to ~ x 0.03 on sintering, the relative generation rate of oxygen vacancies in C′ was large, so it is expected that sintering or crystalline growth from the surface [9] may move various imperfections into the centre of powder particles and the accumulated defects formed would provide ample space for interstitial oxygen.

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Co-polymer impregnation of gypsum casts

In a previous communication [1], it was reported that the properties of gypsum casts could be vastly improved by the incorporation of a polymer, poly(methylmethacrylate), into the inorganic matrix. The reported method involved the infiltration of an activated monomer system into the porous matrix, which would polymerize under ambient conditions in under 3 h.

Further work on the production of polymer impregnated gypsum (PIG) has produced gypsum casts with superior mechanical properties to those obtained on impregnation with the monomer alone [2]. It has been found that the incorporation of a co-monomer, namely ethylene glycol methacrylate, enhances the properties of PIG over those of the methyl methacrylate system [3]. This co-monomer when added to the methyl methacrylate activated system reduced the polymerization period to less than 1.5 h and it is also believed that the introduction of the ethylene gylcol dimethacrylate not only improves the immediate strength characteristics of the composite material, but also the durability of the material due to its secondary cross-linking.

Some work [4–6] has been carried out on the co-monomer ethylene gylcol dimethacrylate, but the concentration of the co-monomer appears to have been arbitarily chosen. In the present work it has been demonstrated that there is a critical maximum concentration of co-monomer, of the order of 2 to 3 per cent, necessary for the beneficial improvements.

In dental applications it is a prime requirement for the cast material to show both dimensional accuracy and stability, and it is believed that this present treatment could find application to such materials. The gypsum casts were prepared from unmodified industrial plaster of Paris, so as to contain a variable water–powder ratio (Table I). After allowing the samples to hydrate within the moulds, they were dried at 100° C for 24 h, allowed to cool to room temperature and stored over silica in a vacuum desiccator prior to impregnation. The samples were then immersed in an impregnation bath containing the activated system, which comprised methyl methacrylate (100 parts), lauroyl peroxide (4 parts), N,N′-dimethyl-*p*-toluidine (4 parts) and ethylene gylcol dimethacrylate (1 to 10 parts, wt/wt). In order to aid the solubility of the initiator and the promotor in the co-monomer solution, these constituents were dissolved in the methyl methacrylate prior to the addition of the dimethacrylate. After about 30 min the temperature was observed to rise and after about 45 min the samples were removed and polymerization allowed to continue at ambient temperature for approximately 30 min.

Some mechanical properties of the impregnated

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