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Abstract

Full Text

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PHYSICS

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THE NATURE OF TRAPPING CENTERS IN QUARTZ GLASSES

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As was noted earlier ([1–3]), quartz glasses fused in the flame of an oxyhydrogen burner are more resistant to the action of ionizing radiation than glasses fused from the same raw material in electric resistance furnaces. Electrically fused glasses are colored in the visible region (the 550 mμ band) and in the ultraviolet (the 300 and 220 mμ bands) regions of the spectrum much more strongly than gas-fused ones. Gas-fused glasses contain a large amount ($3 \div 5 \cdot 10^{-2}$ wt.%) of so-called structural water, i.e., hydroxyl groups OH^- bonded to the glass network.

Most investigators agree that the presence of OH^- groups accounts for the higher radiation resistance of gas-fused glasses. It has been established ([4]) that, with increasing concentration of OH^- groups in quartz glass, the intensity of the induced 210-220 mμ absorption band decreases proportionally. Since the 210-220 mμ band is associated with an electron captured at Si—O lattice defects, the authors of ([4]) propose a model according to which OH^- groups block the aforementioned defects.

Fig. 1. EPR spectra of γ-irradiated gas-fused quartz glasses: *a* —dose 10^5 r; *b* —10^6 r; *c* —10^7 r; *d* —10^8 r.

We employed the EPR method for further investigation of the role of OH^- groups in radiation processes in quartz glasses.

Quartz glasses containing Al^{3+} ions ($\sim 10^{-3} \div 10^{-2}$ wt.%) as a contaminating impurity and glasses doped with small additions of Eu (from 0.001 to 0.1 wt.%) were investigated.

Figure 2

Figure 2: Figure 2

Glass samples were irradiated with γ-rays from a Co^{60} source at room temperature. EPR spectra were recorded at 77 and 300°K on a JES-3BS radiospectrometer at a frequency $\nu = 9440$ MHz. Optical spectra were recorded on a Hilger spectrophotometer in the wavelength range 200–700 mμ.

In the EPR spectra of irradiated quartz glasses, a narrow signal with $\Delta H = 2.4$ Oe and $g_{\parallel} = 2.002$ and $g_{\perp} = 2.000$ was observed; two doublet signals with $A/g\beta = 71$ Oe and $g_{\text{eff}} = 2.002$ (center H') and with $A/g\beta = 116$ Oe and $g_{\text{eff}} = 2.000$ (center H''); and also a signal with six hfs lines with $g_{\text{eff}} = 2.009$ and $A/g\beta = 8.2$ Oe, due to the natural impurity Al^{3+} ($I = 5/2$) in the samples (Figs. 1 and 2). This signal correlates with coloration in the visible spectral region near $\lambda = 540$ mμ. Comparing with the data of works ([5,6]) and taking into account the value of the g-factor and $A/g\beta$, it may be concluded that this signal is due to complexes of six-coordinated aluminum.

Fig. 2. EPR spectra of γ-irradiated quartz glasses: **a** –especially pure synthetic quartz glass, dose 10^7 r; **b** –synthetic quartz glass doped with Al^{3+}, dose 10^7 r; **c** –gas-melted quartz glass, dose 10^7 r.

The study of quartz glasses doped with Eu_2O_3 was carried out in order to determine the nature of the trapping centers in them. We have shown experimentally that the signal with $\Delta H = 2.4$ Oe and $g_{\text{eff}} = 2.0013$, associated with the 220 mμ absorption band ([7]), is electronic in nature, while the signal with $g_{\text{eff}} = 2.009$ and $A/g\beta = 8.2$ Oe is hole-like in nature, since the former is weakened in glasses doped with Eu^{3+}, and the latter in glasses with Eu^{2+}. The valence state of europium was determined from luminescence spectra.

It was further established that the doublets H' and H'' are observed only in samples of quartz glasses in whose IR spectrum there is an absorption band at 2.75 μ, caused by hydroxyl groups. This band is weakened under γ-irradiation.

In work ([4]) it was shown that the intensity of the doublet signal with $A/g\beta = 71$ Oe is proportional to the content of OH groups in quartz glasses; however, the nature of this center was not discussed. We found that the intensity of the doublet with $A/g\beta = 116$ Oe is also proportional to the content of OH groups. It was established that the doublet H'' is observed in samples containing natural impurities, and its intensity proved proportional to the content of Al^{3+}. The doublet H' is observed in samples of especially pure synthetic vitreous silica (Fig. 2) and in samples containing Al^{3+} impurities, but at γ-ray doses of 10^7 r and higher, when the doublet H'' becomes saturated (Fig. 1).

In synthetic vitreous silica doped with aluminum oxide, after γ-irradiation with a dose of $5 \cdot 10^6$ r, both doublet signals H' and H'' were detected (Fig. 2).

In samples of irradiated quartz glasses containing OH groups in their struc-

ture, the EPR signal with $g_{\text{eff}} = 2.009$ and $A/g\beta = 8.2$ Oe and an absorption band near 540 mμ appear after the doublet signals H' and H'' (Fig. 1), which indicates the hole nature of the centers H' and H''.

Analyzing the experimental data obtained, one may propose

propose for the H'' centers a model according to which the hole is localized on the oxygen of a hydroxyl group and interacts with a neighboring proton and an aluminum–oxygen complex:

$$\begin{array}{c} \\ -\mathrm{Al}\ldots\mathrm{O}\ldots\mathrm{H}. \\ \end{array}$$

For H' centers not associated with aluminum impurities, by analogy with the preceding we obtain

$$\begin{array}{c} \\ -\mathrm{Si}\ldots\mathrm{O}\ldots\mathrm{H}, \\ \end{array}$$

i.e., the hole is localized on the oxygen of a hydroxyl group associated with a silicon–oxygen complex.

In the case of complete localization of the unpaired spin on the proton, the magnitude of the h.f. splitting would be 508 oersted ([8]). In addition, only electron capture can take place directly on protons.

In the present case splittings of 71 and 116 oersted are observed, which makes it possible to estimate the spin density of the trapped hole on the proton ([8])

$$|\psi_0|^2 = A/21.2\, g_I,$$

where A is the measured h.f.s. value in oersteds, g_I is the nuclear g-factor, and $|\psi_0|^2$ is the spin density at the nucleus in $(\text{Å})^{-3}$.

For the H' center we obtain $|\psi_0(\mathrm{H}^+)|^2 = 0.60$ $(\text{Å})^{-3}$, and for the H'' center $|\psi_0(\mathrm{H}^+)|^2 = 0.98$ $(\text{Å})^{-3}$. In the case of free hydrogen, however, $|\psi_0(\mathrm{H}^+)|^2 = 4.3$ $(\text{Å})^{-3}$.

It follows from this that the silicon–oxygen complex polarizes the trapped hole more strongly than the aluminum–oxygen complex.

In view of the fact that the Si^{28} nuclei have no magnetic moment, the lines of the H' doublet are narrower (9 oersted) than the lines of the H'' doublet (13 oersted). In the latter case the doublet lines are broadened because of an additional h.f. interaction of the hole with the spin of the Al^{27} nucleus ($I = 5/2$).

The presence of h.f. splitting, its dependence on the position of OH groups in the lattice of vitreous silica, and also the different linewidths of the doublet lines show that the unpaired spin is spatially distributed over the proton, the oxygen ligands of the complex, and the central ion.

Conclusions. 1. It has been established that in vitreous silica holes are localized at impurity centers, and electrons at intrinsic defects of the lattice.

2. Two possible positions of hydroxyl groups in vitreous silica have been determined: near silicon-oxygen (the H' centers) and aluminum-oxygen complexes (the H'' centers).

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References

1. V. Garino-Canina, Rev. theor. instrum. opt., Paris, **3**, No. 5 (1956).
2. R. Jocota, Phys. Rev., **95**, 1145 (1954).
3. O. K. Botvinkin, A. I. Zaporozhskii, *Quartz Glass*, Moscow, 1965, p. 68.
4. R. A. Weeks, E. Lell, J. Appl. Phys., **35**, No. 6 (1964).
5. G. O. Karapetyan, S. A. Stepanov, D. M. Yudin, FTT, **6**, 5, 1531 (1964).
6. J. H. E. Griffiths, J. Owen, I. M. Ward, Nature, **173**, 439 (1954).
7. R. A. Weeks, J. Appl. Phys., **27**, 10, 1376 (1956).
8. R. V. Rempel, in: *Collection: NMR and EPR Spectroscopy*, Moscow, 1964, p. 205.

Note: Figure translations are in progress. See original paper for figures.