The Electron Spin Resonance of Sodium Polyphosphate Glass Irradiated with γ-Rays

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Phosphate glass is easily colored upon irradiation with γ-rays. Krapetyan and Yudin have reported that the red color of phosphate glass induced by the irradiation of γ-rays is to be attributed to the electron trapped by phosphorus atoms.[1] By taking the *g* values and the coupling constant into account, however, it has recently been concluded that the color is caused by the hole trapped by the oxygen atom rather than by the electron trapped by the phosphorus atom.[2]

These authors have used phosphate glasses, but the degrees of polymerization were not determined. No relationship between the effect of γ-rays on the glass and its degree of polymerization, $\bar{n}$, has yet been established. The purpose of the present work is to investigate this relationship by using sodium polyphosphate, which is so-called Graham's salt. Samples of sodium polyphosphate glass with various values of $\bar{n}$ were prepared and irradiated with γ-rays from a ^{60}Co source at room temperature. The ESR and optical-absorption measurements were then carried out on these glasses.

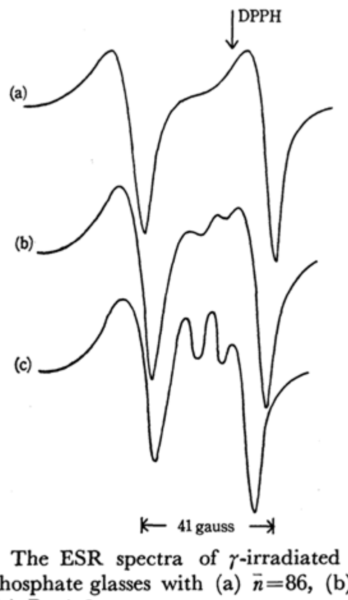

Fig. 1. The ESR spectra of γ-irradiated sodium polyphosphate glasses with (a) $\bar{n}$=86, (b) $\bar{n}$=11 and (c) $\bar{n}$=4.8.

The glass with a higher value of $\bar{n}$, as is shown in Fig. 1a, gave two asymmetric ESR absorptions which are hyperfine structures originating from the interaction between the ^{31}P nucleus and the hole trapped in the non-bonding orbital of the oxygen atom. The coupling constant between these two absorptions became smaller and, at the same time, a new doublet appeared more definitely with a decrease in the $\bar{n}$ value (Figs. 1b and 1c). The latter doublet may be attributed to the hole trapped in the oxygen ion of the end group, PO_4^{2-}, because it has a much smaller coupling constant than that of the former doublet and becomes more evident with an increase in the content of the end groups.

After the irradiation of 5×10^5 r., the ESR measurement on each glass was carried out at room temperature. The intensity of the larger doublet decreases rapidly as the value of $\bar{n}$ decreases.

Each transparent sheet of these glasses showed an intrinsic absorption band in the ultraviolet region. After the irradiation with γ-rays, however, each gave two additional bands, one in the visible, and the other in the ultraviolet region. The wavelengths of the maximum absorption of these bands depend upon the value of $\bar{n}$. The visible absorption band may be due to the electronic transition between the excited level of the non-bonding orbital, where the trapped hole is mainly localized, and the lower levels of the bonding orbital. On the other hand, the ultraviolet absorption may be caused by the charge transfer of the trapped electron to the neighbors.

Thus, from the ESR spectra of γ-irradiated sodium polyphosphate glasses, two doublets were found; the larger doublet is due to the hole trapped by the main chain of polyphosphate, while the smaller doublet is due to the hole trapped by the end group. The ESR of the larger doublet and the optical absorption of the glass may be modified by the change in the distortion of the P-O-P bond caused by the variation in the degree of polymerization.

1) G. O. Krapetyan and D. M. Yudin, *Fiz. Tverd. Tela*, **3**, 2827 (1961).
2) Y. Nakai, This Bulletin, **38**, 1308 (1965).