Electron Paramagnetic Resonance Spectra of Phosphate Glasses Irradiated with Gamma-rays

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The electron spin resonance (ESR) of irradiated glasses has been reported on several times in the past five years,[1] since the paramagnetic centers have been expected to contain localized electrons and holes.

ESR study of the defect centers in irradiated glasses containing phosphorus was first reported on by Karapetyan and Yudin.[2] They observed an ESR spectrum consisting of two lines at $g=2.0038$. This two-line structure was attributed to hyperfine interaction with a P nucleus. In the present investigation, it was found that there are three distinct types of defect centers in irradiated phosphate glasses.

Phosphate glass samples with the composition of (RPO_3) [R=Li, Na, Ca, Ba,], where R/P=1, were irradiated at room temperature with Co^{60} gamma-rays ($5\sim6\times10^6$r.). The derivative curve was obtained with a Varian 4501 ESR spectrometer at room temperature, employing a modulation frequency of 100 kc./sec.

The irradiated lithium phosphate glasses ($LiPO_3$) exhibit the ESR spectra of two strong lines (P_1 and P_2) and of the other two weak absorption lines (Fig. 1). One of the weak

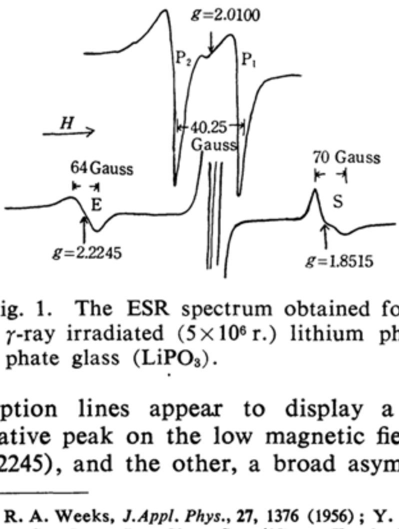

Fig. 1. The ESR spectrum obtained for a γ-ray irradiated (5×10^6 r.) lithium phosphate glass ($LiPO_3$).

absorption lines appear to display a broad derivative peak on the low magnetic field side (g=2.2245), and the other, a broad asymmetric derivative peak on the high magnetic field side (g=1.8575). The former is denoted by E, and the latter, by S.

The intensity of the two-line structure can easily be reduced by heating at 100°C. The fading speed by the thermal treatment is dependent on the kinds of alkali or alkaline earth modifiers. The derivative peaks denoted by P_1 and P_2 are spaced with a spacing of 40.25 gauss, and the g value at the center of these two peaks is observed to be g=2.0100. This two-line structure has the same response to both the thermal annealing and the optical bleach, and it is independent of the type of alkali or alkaline earth modifiers.

The observed g value of the two-line structure is larger than that of the free electron. This suggests that the paramagnetic center is a hole trapped on a singly bonded oxygen. The hyperfine structure arises from the overlap of the hole orbital on a phosphorus atom with a spin of 1/2. The principal values of g in the axial field are given by $g_{\parallel}=2.0243$ and $g_{\perp}=2.0100$.

The process of this creation can perhaps be interpreted as follows. An electron in the π-orbital of oxygen associated with the P=O link is thrown out because of the action of γ-rays. Thus, migrating through the valence zone, the formed hole goes to the nucleus of a four coordinate phosphorus ion.

Karapetyan and Yudin have interpreted the magnetic centers of phosphate glasses as arising from electron capture in the (PO_4) groups, not as oxygen vacancies in the vicinity of the alkali or alkaline earth ions. In this present work, however, we found that the shapes of the other weak resonance lines (E and S) were dependent on the kinds of alkali or alkaline earth ions. The resonance spectra in irradiated phosphate glasses containing a calcium or barium modifier appear as is shown in Fig. 2. In the case of a sodium or potassium modifier, the spectra disappear on both the low and the high magnetic field sides. The sample of (KPO_3), however, is not in the state of glass but is a highly polymerized crystal.

In phosphate glasses modified with such ions

1) R. A. Weeks, *J. Appl. Phys.*, **27**, 1376 (1956); Y. Nakai, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **82**, 1629 (1961); S. Lee and P. J. Bray, *Phys. Chem. Glasses*, **3**, 37 (1962); S. Lee and P. J. Bray, *J. Chem. Phys.*, **39**, 2863 (1963).

2) G. O. Karapetyan and D. M. Yudin, *Fiz. Tverd. Tela*, **4**, 2647 (1962).

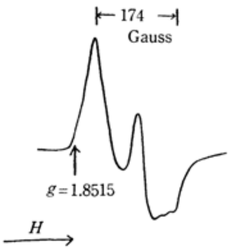

Fig. 2. The ESR spectrum (S band) obtained for a γ-ray irradiated ($\sim 10^5$ r.) calcium phosphate glass ($CaPO_3$).

as calcium, barium or lithium, that can coordinate with the tetrahedral oxygen atom in the glass network, the two weak resonance lines seem to appear just as well as with a low dosage of γ-rays irradiation.

The g value of the E band is far larger than that of the free electron, and yet it depends upon the kinds of alkaline earth ions. Consequently, it is possible that it has something to do with new valence zone of alkali ions coordinated with the oxygen atom in the glass network.

The intensity of the S band is hardly reduced at all by heat treatment at 200°C for 5 hr. This suggests that the S band may arise from electrons trapped at oxygen vacancies in the vicinity of the alkali ions, as has been assumed previously.[3]

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3) R. A. Weeks, *J. Appl. Phys.*, **27**, 1376 (1956).