Analele Universităţii de Vest din Timişoara
Vol. XLVII, 2005
Seria Fizică

EPR SPECTRA OF RADIATION-DEFECT CENTRES IN $B_2O_3Li_2OAl_2O_3ZnO$ GLASSES

Lavinia Cociu[1], Ioan V. Nicula[2]

[1]*Faculty of Physics, "Babes-Bolyai" University, 400084, Cluj-Napoca, Romania*
[2]*Liceul "Tiberiu Popoviciu" , Cluj-Napoca, Romania*

Abstract
Computer line-shape simulations were carried out of the electron paramagnetic resonance (EPR) spectra of several $B_2O_3Li_2OAl_2O_3ZnO$ glass samples following exposure to gamma and subsequent UV radiation at room temperature. Three paramagnetic centers were identified : boron oxygen hole centre (BOHC), peroxy radical and Zn^+ (ns^1) electron centre.
Keywords: computer simulation, EPR line-shape, radiation-induced defects

1. Introduction

A radiation-induced defect state is defined as any electronic configuration differing from those typical of the unirradiated material [1]. EPR technique is suitable for identifying those states which include unpaired electrons/holes. Recent achievements in the study of radiation defects in vitreous B_2O_3 and alkali borate glasses are reviewed in the [2] paper. Finding a good UV transmission of an aluminium-lithium borate glass [3] ,we have investigated by cw-EPR technique both gamma and UV irradiated $B_2O_3Li_2OAl_2O_3ZnO$ glass system ; the results are shown in the present paper.

2. Methods and samples

The samples were prepared by fusing reagent grade substances [$B(OH)_3$, Li_2CO_3 , Al_2O_3, ZnO] in corundum crucibles. The melt of oxides was maintained for 1 hour at 1100^{o}C and then supercooled at room temperature. No EPR spectrum was detected before gamma irradiation. The γ-irradiation of the samples and the record of the EPR (X band) spectra were done at room temperature.. The EPR spectra of the γ-irradiated glasses are complex , so we tried to reveal component spectra by both a subsequent UV-irradiation and/or thermal

treatments of γ-irradiated samples. After an isochronal thermic treatment of the γ-irradiated samples at 380 ^{o}C , for 15 minutes, the EPR spectrum consists of a single asymmetrical derivative line associated with Zn cations. Figure 1 shows an experimental EPR spectrum of a γ- and subsequent UV-irradiated sample; it remains a complex one and computer simulation of the EPR spectra were performed in order to establish its components.

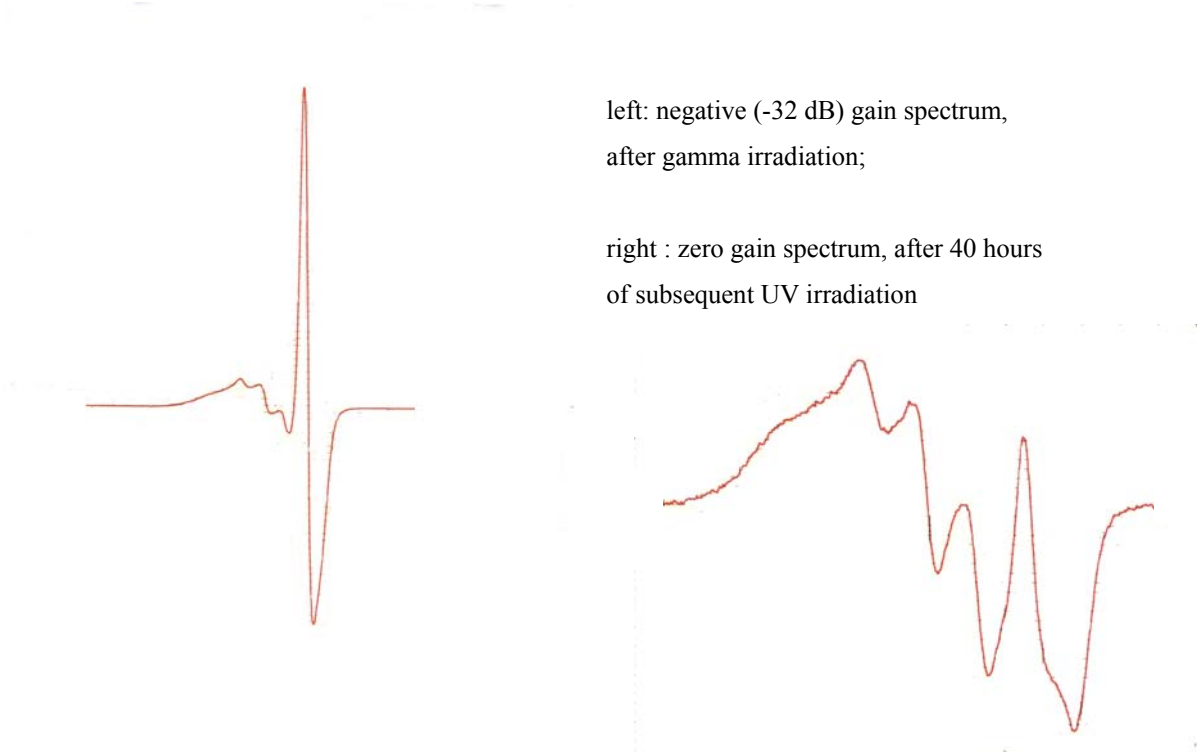

Fig.1 Room temperature experimental X band EPR spectra of γ- (left) and subsequent UV- (right) irradiated $0.8B_2O_3 0.07Li_2O 0.05Al_2O_3 0.08ZnO$ glass sample.

3. Results and Discussions

Results of the computer simulations are shown in Figs. 2-5. The resonance field values are calculated in the second order perturbation (SOP) theory. Figure 2 shows an example of calculated spectrum as superposition of 3 components with weighting factors in parentheses.

The essential aspects of all the EPR spectra of the defects in glasses are determined by the Zeeman and hyperfine interactions because S = 1/2. The first component spectrum is from boron-oxygen-hole centre (BOHC) [4], [5]; it is known like a "five-line-plus-a-shoulder" one [1]. In simulation, we have used the spin-Hamiltonian (H) parameters shown in fig. 3 caption.

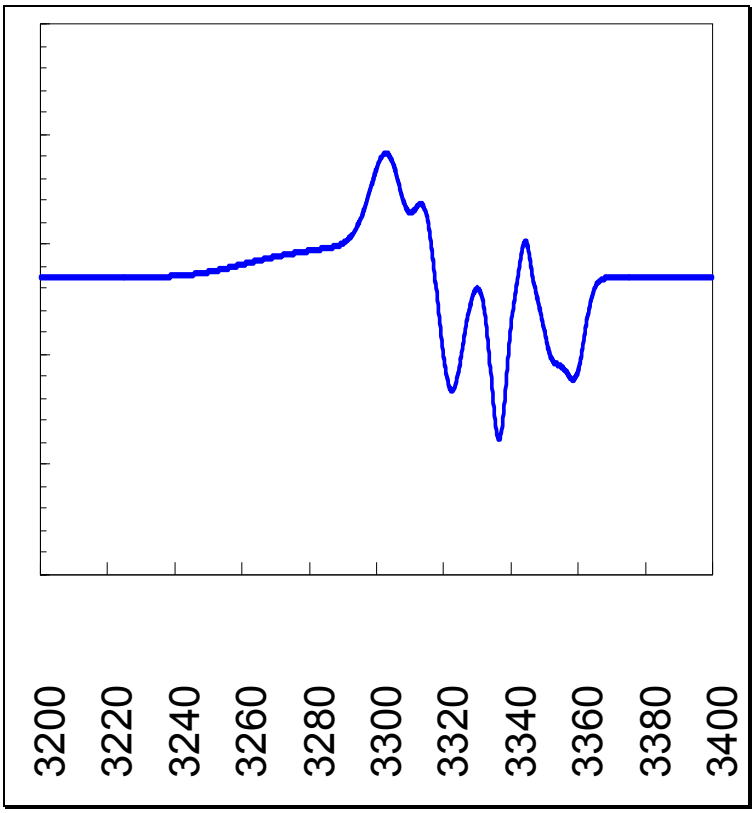

Fig. 2 Calculated EPR spectrum as superposition of three simulated spectra of the radiation defects: a) BOHC (35%): b) peroxy radical (40%); c) Zn^{+} centre (25%)

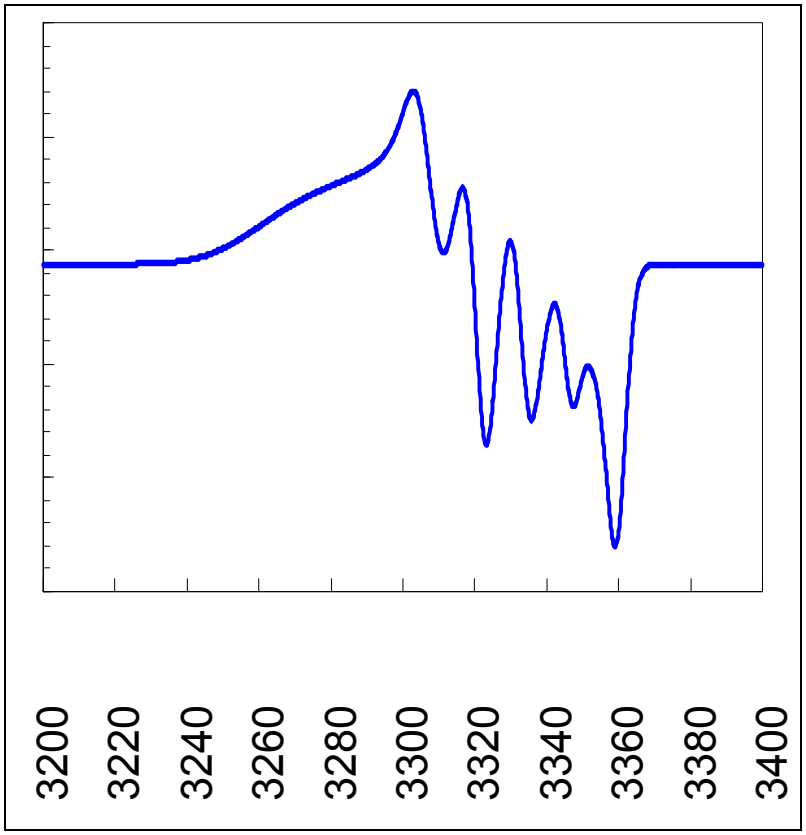

Fig.3. Simulated RPE spectrum of BOHC. S=1/2; I=3/2.

ν =9.3635 GHz.. H parameters are :

$g_1 = 2.00250$; $g_2 = 2.01000$;

$g_3 = 2.03870$; $A_1 = 11.5*10^{-4}$ cm^{-1} ;

$A_2 = 13.32*10^{-4}$ cm^{-1} ;

$A_3 = 11.26*10^{-4}$ cm^{-1}.

A Gaussian line shape was used, with anisotropic peak to peak line width values (in gauss) : 5;7;25. The values (in gauss) of the static magnetic field are given in abscissa.

The calculated resonance field values (4 divergences and 8 shoulders) , in gauss , are:

3359.28	3349.66	3299.26
3346.93	3335.43	3287.38
3334.63	3321.23	3275.55
3322.39	3307.09	3263.77

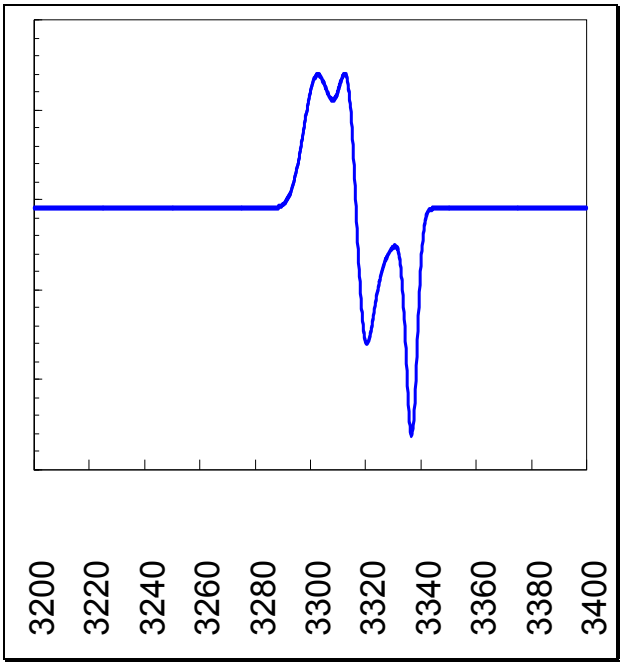

Fig.4. Simulated RPE spectrum of the peroxy radical. ν = 9.3635 GHz. S=1/2.
H parameters are: $g_x = 2.00480$; $g_y = 2.01700$; $g_z = 2.02610$. A Gaussian line shape was used, with anisotropic peak to peak line width values (in gauss) : 4; 6; 9.

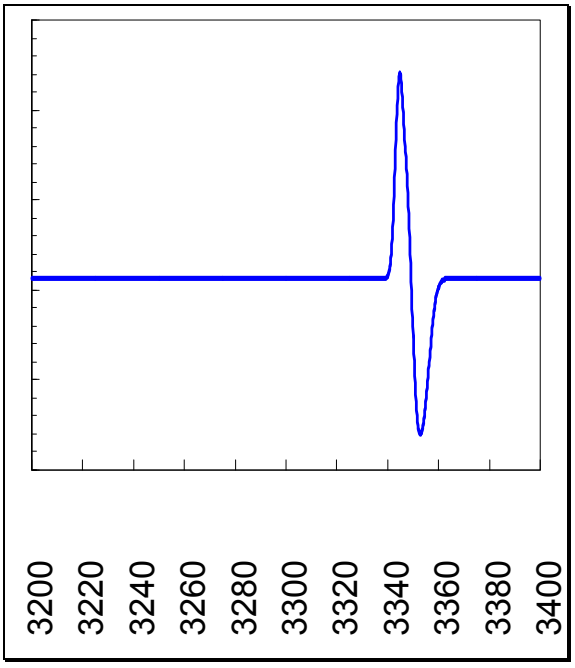

Fig.5. Simulated RPE spectrum of the Zn^+ centre. ν =9.3635 GHz. S=1/2. H parameters are $g_x = 2.0000$; $g_y = 1.9970$; $g_z = 1.9940$. A Gaussian line shape was used, with anisotropic peak to peak line width values (in gauss) : 3; 4; 5

BOHC EPR spectrum was enhanced by the subsequent UV irradiation of the samples. The second component of calculated EPR spectrum is that of the peroxy radical (POR) , shown in Fig. 4 . POR is an O_2^- molecular ion which is bonded at one end to another molecular structure [1]. Upon γ-irradiation, the peroxy linkages B-O-B-O trap holes and form POR. H parameters (**g**-tensor components) for O_2^- molecular ions have various values [6]. The computer simulation imposed us the shown **g**-tensor components (Fig. 4 caption) in agreement with Känzig and Cohen work [7].

POR EPR spectrum also disappeared after a 380 ^{o}C isochronal (15 min) annealing, but Zn^{+} centre was preserved**.** The interstitial cations in glasses may serve as electron traps; ns^{1} centre is the result of such a capture. We have simulated Zn^{+} ($4s^{1}$) spectrum (Fig. 5) with orthorhombic **g-**tensor; the component values prove that the unpaired electron of this centre is not captured in a pure s orbital because of the action of ligand oxygens. UV radiation has diminished Zn^{+} EPR line.

No aluminium-related defect EPR spectrum was detected in irradiated glasses.

4. Conclusions

Computer simulations of the EPR spectra allowed us to distinguish three paramagnetic defect centres in irradiated glasses, their spin-Hamiltonian parameters as well as the proper weighting factors at various stages of the irradition processes.

Acknowledgements

We are very grateful to Professor P. J. Bray who sent us the Lineshape Program Manual.

References

[1] E. J. Friebele and D. L. Griscom, "Radiation Effects in Glass", in *Treatise on Materials Science and Technology,* Vol 17, Glass II, edited by M. Tomozawa and R. H. Doremus, Academic Press, New York, (1979) p.257

[2] I. A. Shkrob, B. M. Tadjikov and A. D. Trifunac, J. Non-Crystalline Solids, 262, (2000) 6

[3] I. Nicula, Lavinia Cociu, I. Milea, Al. Nicula, Studia Univ. Babes-Bolyai, Physica, XXIII (1978) 32

[4] S. Lee and P. J. Bray, J. Chem. Phys., 39, (1963) 2863

[5] D. L. Griscom, P. C. Taylor, D. A. Ware and P. J. Bray, J. Chem. Phys., 48, (1968) 5158

[6] D. L. Griscom and E. J. Friebele, *Fluoride Glass Fiber Optics*, ISBN 0-12-044505, Ch. 8.

[7] W. Känzig and M. H. Cohen, Phys. Rev. Letters, 3, (1959) 509