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Electron spin resonance of gamma irradiated borogermanate glasses

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Chimica. — *Electron spin resonance of gamma irradiated borogermanate glasses.* Nota(*) di CARLO BETTINALI(**), PAOLO GRANATI(*) e GIUSEPPE VIRTUOSO(*), presentata(***) dal Corrisp. G. SARTORI.

RIASSUNTO. — È stata studiata la risonanza paramagnetica di elettrone di due campioni di vetro borogermanato irradiato con raggi gamma in confronto a quella del $Na_2B_4O_7$ e del Na_2O—GeO_2.

La composizione dei campioni in mol è: Campione A Na_2O (13,9), B_2O_3 (75,7) GeO_2(12,7). Campione B Na_2O (14,6), B_2O_3 (18,7), GeO_2 (67,2). Nel campione A compaiono 5 massimi nella derivata di esr. Di questi 4 hanno una separazione di 12,4 ± 1 gauss ed il quinto di 24,5 ± 1 gauss. Il valore medio di g relativo ai 4 massimi è 1,993, relativo ai 5 massimi 2,003, del 5° picco 2,018. I centri paragnetici osservati sono stabili fino a 250° C. Per riscaldamento di 20 h a 280° si ha una diminuzione di intensità di 5 volte ma il rapporto fra i picchi non muta. Assumendo che i 5 picchi derivino da un centro a simmetria assiale che interagisce con un atomo di B^{11}, come avviene nei borati di sodio, abbiamo calcolato il valore del tensore iperfine B relativo ad una simmetria assiale. Il valore ottenuto è $2{,}01 \cdot 10^{-3}\ cm^{-1}$ maggiore che nel vetro Na_2O—B_2O_3 con un contenuto in Na_2O inferiore al 25%.

Nel campione B lo spettro sembra la sovrapposizione dello spettro del germanato sodico con quello del campione A. È quindi probabile la formazione di un vetro polifasico.

INTRODUCTION.

The study of radiation induced centers gives useful information concerning the structure of glasses; the borate glasses have been the object of very intense study [1–13]. The germanate glasses have been studied also and a correlation was found between radiation induced centers and coordination of germanium [14–16]. In this note we give some preliminary results on the electron spin resonance (e.s.r.) absorption of gamma irradiated borogermanate glasses.

EXPERIMENTAL.

The samples were prepared by melting reagent grade oxides in a P*t* crucible and then rapidly quenching to avoid devitrification. The samples studied were the following: 1) Na_0O (13.9 mol %), B_2O_3 (75.7 mol %), GeO_2 (12.7 mol %); 2) Na_2O (14.6 mol %), B_2O_3 (18.7 mol %), GeO_2 (67.2 mol %); 3) $Na_2B_4O_7$ and 4) Na_2O—GeO_2. Electron spin resonance measurements were taken at ambient temperature at 9.5 Kmc by means of an Hilger and

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Watts spectrometer. Thermoluminescence glow curves were obtained with a previously described apparatus [17]. The irradiation was done in a Co^{60} gamma cell giving 2.10^5 r/h.

RESULTS.

The e.s.r. derivative spectrum of borogermanate glass A irradiated 24 hours at ambient temperatures is shown in fig. 1, curve 1. A five line spectrum is observed and the peaks are indicated P_1, P_2, P_3, P_4 and P_5. The first four peaks are equally spaced and are separated by about 12.4 ± 1 gauss. The P_1—P_2 separation is 24.5 ± 1 gauss. The mean g value of P_1—P_5 peaks is 2.0030. The g value of the P_1 line is 2.0180 and the g value between P_2—P_5 lines is $g = 1.993$. Curve 2 shows same sample as curve A heated 20 hours at 260°. The intensity is ten times less then that of curve A. The e.s.r. spectrum of sample 2 is shown in curve 3. Two main lines and an absorption bond are present. The g value of the two peaks are respectively 2.021 and 2.008.

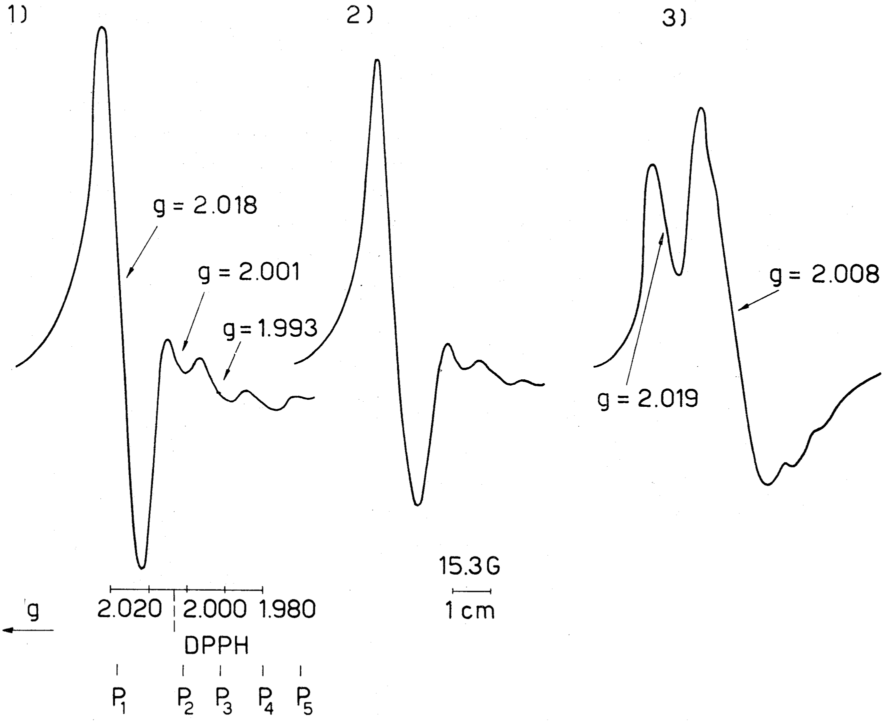

Fig. 1. – ESR derivative absorption of

curve 1) Na_2O (13.9) B_2O_3 (75.7) GeO_2 (12.7)
curve 2) Na_2O (13.9) B_2O_3 (75.7) GeO_2 (12.7) heated 20 h at 260°
curve 3) Na_2O (14.6) B_2O_3 (18.7) GeO_2 (67.2).

Fig. 2, curve 4 shows the e.s.r. spectrum of sample 3, sodium tetraborate glass, which had received a 2 Mr dose. The well known four line spectrum is present. The separation between the P1, P3, P4 lines is about 14 gauss.

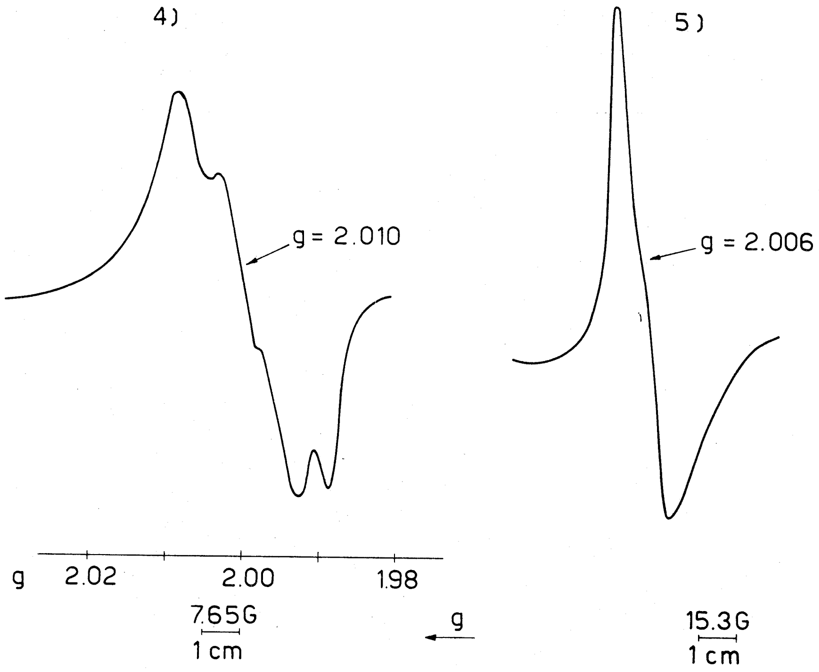

Fig. 2. – ESR derivative absorption of

curve 4) $Na_2B_4O_7$
curve 5) Na_2O–GeO_2 .

The mean *g* value is 2.010. The e.s.r. spectrum of sample 4, sodium germanate glass, is shown in curve 5. A single peak resonance spectrum is present having a mean *g* value of 2.006.

Fig. 3 shows the thermoluminescence glow curves of samples 1 and 2. A single maximum is present at about 50°.

DISCUSSION.

The spectrum of sample I displays a five line structure. Two interpretations are possible taking into account the results published on e.s.r. of irradiated borates [4, 7, 9] and germanates [13, 14].

A five line structure arising from an axyal symmetric center related to an unpaired electron interacting with a B^{11} atom having a nuclear spin of 3/2 fig. 4 A or C.

A four line structure arising from an unpaired electron interacting with the B^{11} nucleus in a isotropic center plus a single line related to an unpaired electron on a sp^2 orbital of an esacoordinated Ge atom giving rise to the low field absorption line having $g = 2.018$ [14, 15] fig. 4 B. According to some authors the five line spectrum can be derived by making the following assumptions: for axial symmetry of the crystalline field g (parallel) $= g_z$ and g (normal) $= g_x$; $A = K_z$ and $B = K_x = K_y$ where $g_x, g_y, g_z =$ main values of the spectroscopic splitting factor g and $K_x, K_y, K_z =$ hyperfine tensor of the splitting constant when z is the symmetry axis.

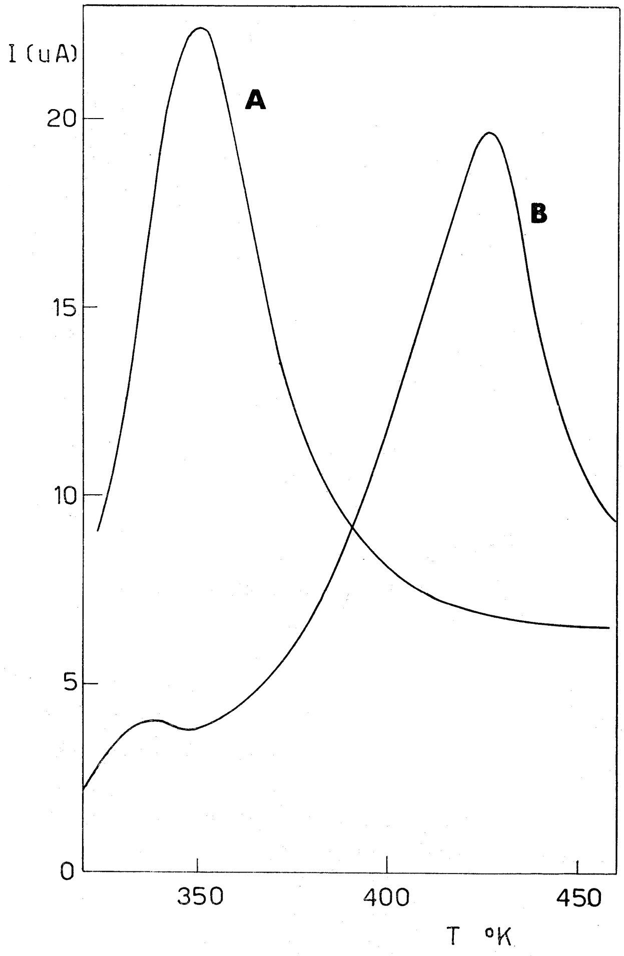

Fig. 3. – Thermoluminescence of gamma irradiated samples.

curve A) Na_2O (13.9) B_2O_3 (75.7) GeO_2 (12.7)
curve B) Na_2O (14.6) B_2O_3 (18.7) GeO_2 (67.2).

The first order hyperfine resonance condition in single crystals is given by [18] $H = (I/gb)(hv - KM) = (hv/b)(g_p^2 \cos^2\theta + g_n^2 \operatorname{sen}^2\theta)^{-1/2} - (M/b) \cdot \cdot (A^2 g_p^2 \cos^2\theta + B^2 g_n^2 \operatorname{sen}^2\theta)^{+2/1} \times (g_p^2 \cos^2 O + g_n \operatorname{sen}^2 O)^{-1/2}$ where $O =$ the angle between the symmetry axis and the direction of the applied magnetic field and $b =$ Bohr Magneton. The principal axes are the same for both g, and the hyperfine tensor g_p and g_n are both positive. The components A and B of the hyperfine tensor may have either sign. In the case of glassy or powdered substances having random values of O, two sets of $2\,I + 1$ equally spaced e.s.r. absorption peaks must arise [19]. When $I = 3/2$, $g_p > g_n$ and $A > B > 0$, 8 peaks must arise. If $A/g_p \cdot b = B/g_n \cdot b = \Delta \cdot H$ there is an overlapping of the peaks and five lines are observed.

According to these assumptions the observed derivative peaks can be tentatively related to some of the energy levels. It is possible that the P1 peak in the derivative curve arises from $H_n (M = 3/2)$ while the peaks P2, P3, P4 and P5 arise from $H_p (M = 3/2)$, $H_p (M = -1/2)$, $H_p (M = 1/2)$ and $H_p (M = -3/2)$ respectively. In our case the $H_p (M = 1/2)$ and $H_n (M = 1/2)$ peaks coincide, thus obeying equation [1].

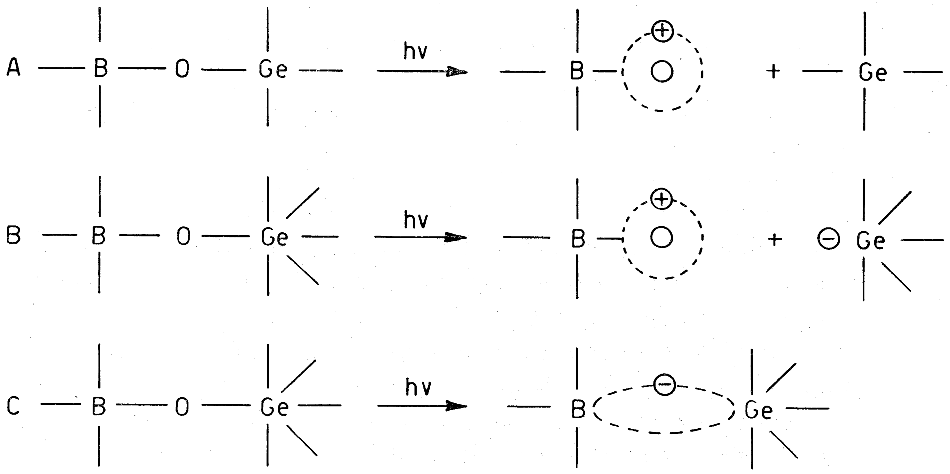

Fig. 4. – A) Formation of a couple of centers by breaking of the O—Ge bond. Ge thetracoordinated. B) Idem with Ge six coordinated. C) Centers formed following the formation of an oxygen vacancy.

As a result of the validity of this hypothesis the values of B and g_p can be determined. In fact, $B/g_n\ b$ is the separation between the four equally spaced peaks P2, P3, P4 and P5. The value of DH from fig. 1 is about 21,4 gauss. The values of g related to the four peaks of borates is 1.093 (fig. 1).

This value is related to g_n. According to the resonance condition $hv = bgH\ g_n bH_n = g_p bH_p$ and $H = H_p = H_n = H_n (g_p - g_n)/g_n = H_0\ G/2 = = 1675\ g = 1675\ (g_p - g_n) \cdot H_0$ is the intensity of the magnetic field at the resonance peak with the X band and free electron. Being the value $g_p \cong g_n \cong g_0 \cong 2$ and $H_p \cong H_n \cong H_0 \cong 3350$ gauss

Therefore $g_p = g_n + H/1675 = 1.993 + 21.4/1675 = 2.0057$. The value of $B = g_n bH = 1.993 \times 21.4 \times 4;\ 67 \cdot 10^{-5} = 2.01 \cdot 10^{-3}$. Experimental determination of A require measurements with a K band spectrometer.

The center observed in the borogermanate glass-sample I is like that of borate glasses at low sodium content [4] having a $4 + I$ line spectrum.

Some differences can be observed: the value of g_n is lower than the free electron value, on the contrary in borate glasses both g_n and g_p are higher than 2,0023. The assignment of the observed center (fig. 3, A and B) to an hole center (fig. 3 A) related to an hole on an oxygen atom experiencing a axyal symmetric field is not quite sure owing to differences between g_n and g_p whose values are respectively higher and lower than free electron values. A center related to an unpaired electron on a bridging oxygen vacancy situated between a Ge and B atom is not quite absurd (fig. 3 C). The electron could be situated on a sp^2 orbital of the Ge atom [14]. The value of the hyperfine tensor B which is higher than that found in borate glasses displaying a five line spectrum indicates a more strong axial field acting on the unpaired electron than occurs in borate glasses [4].

The other hypothesis is that of two independent centers: a four line center plus a single line center. The four line center arises from independent BO_4^+ centers and the single line from GeO_6^- units. This hypothesis can suggest the presence of demixed phases, a borate phase and a germanate phase. Unfortunately some objections must be overcomed.

The 4 line is related to an electron center having the g value shifted to the trapped electron value with respect to the borate centers.

The single line g value is higher than the value found in Na germanate glasses (see fig. 5). The thermal quenching experiments show a constant decrease of the e.s.r. lines of sample I (see fig. 1, curve 2).

In the case of the sample 2 a new line seems superimposed on the spectra of the sample 1. The g value of this line seems to correspond rather well to the sodium germanate line. Thermal quenching experiments show that the annealing rate of this line is different. It seem likely that an increasing germanium content leads to the formation of germanate glass phases. Further work on a larger number of compositions may help to clarify these points.

Thermoluminescence occurs in both samples at a temperature at which the e.s.r. centers are thermally stable. Therefore no relation seems to exist between T.L. and the annealing of e.s.r. color centers.

CONCLUSIONS.

The borogermanate glasses having a low Ge content and a high B/Na ratio give rise to a five line resonance spectrum.

They are probably related to an unpaired electron interacting with a B^{11} atom in an axially symmetric center. The g value related to the normal component seems related to a trapped electron center, the g value related to the parallel component to an hole center. So the attribution of the center remain doubtful. Borogermanate glass having high Ge content and a low B/Na ratio shows a five line resonance structure superimposed on a single line having the same g value as the sodium germanate glass. It is therefore probable that the Ge presence gives rise to sodium germanate phases.

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