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Color centers in vitreous and crystalline $\text{Na}_2\text{B}_4\text{O}_7$

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Chimica. — *Color centers in vitreous and crystalline* $\text{Na}_2\text{B}_4\text{O}_7$ (*).
Nota di CARLO BETTINALI (**) e PAOLO GRANATI (**), presentata (***)
dal Corrisp. G. SARTORI.

RIASSUNTO. — Si sono discusse le reazioni proposte in letteratura per spiegare la formazione di centri di colore nel borace fuso irradiato. Si è studiata la differenza provocata nella formazione dei centri di colore dallo stato, cristallino, amorfo o vetroso del $\text{Na}_2\text{B}_4\text{O}_7$.

I centri formati in seguito ad irradiazioni con gamma sono stati investigati mediante assorbimento Ottico, risonanza di spin di elettrone, termoluminescenza, spettri di termoluminescenza.

L'assorbimento ottico indotto da radiazioni mostra: nel cristallo rispetto al vetro un aumento della banda a 3,8 ed una diminuzione di quella a 5-6 eV. L'intensità della banda a 2,8 eV resta immutata.

L'assorbimento di risonanza di spin di elettrone (*esr*) mostra nel cristallo la presenza di uno spettro ad 8-10 bande di cui 7 apparentemente ad eguale intervallo invece del solito spettro a 5 bande del vetro. L'intensità dell'assorbimento, a parità di dose di irradiazione, è 20 volte minore nel cristallo. Si è discusso se l'assorbimento nel cristallo sia dovuto ad un buco su ossigeno che interagisce con due atomi di boro tetracoordinato equivalenti oppure, come avviene nei vetri, ad una interazione con un solo atomo di boro in un centro a simmetria assiale. Ulteriori esperienze sono necessarie. Le glow curves di termoluminescenza effettuate nell'intervallo fra 100 e 600 K. su $\text{Na}_2\text{B}_4\text{O}_7 \cdot \text{N}_2\text{IO H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7$ amorfo $\text{Na}_2\text{B}_4\text{O}_7$ tetragonale, $\text{Na}_2\text{B}_4\text{O}_7$ vetro mostrano: a bassa temperatura - (100-250 K) la presenza di un'unica banda nei composti non cristallini che si risolve in due o tre picchi nei cristallini. I dati sono consistenti con il modello delle trappole strutturali nei vetri.

Il borace amorfo mostra un comportamento fra quello dei vetri e quello dei cristalli. Le intensità di TL a parità di dose di irradiazione sono più elevate nel cristallo anidro che nel vetro e nel cristallo amorfo.

A temperatura elevata (300-600 K) di TL del $\text{Na}_2\text{B}_4\text{O}_7$ amorfo cristallino e vetroso presenta due bande con massimo fra 300 e 350 K e 450-500.

L'intensità di TL nel vetro è circa 20 volte maggiore che negli altri composti. Si è discussa la correlazione fra i dati di TL e quelli ottenuti con altri metodi. Resta confermata la particolare sensibilità della TL alle variazioni di struttura.

INTRODUCTION.

The concept of " structural units " has been suggested [1, 2] to explain the formation of irradiation centers in inorganic solids having a complex composition.

The radiation interacts with a defined chemical group giving rise at first to an electron and a hole. Subsequently, a bond can be broken to give inorganic radicals. Often the formation of irradiation centers requires the diffusion of anions and cations and this process is obviously influenced by the structure of the solids.

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In the present note we present the results obtained by comparing the radiation induced centers in fused borax and crystalline anhydrous borax. Optical absorption, electron spin resonance, thermoluminescence glow curves and thermoluminescence spectra have been studied.

EXPERIMENTAL.

The materials studied were prepared from reagent grade $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Anydrous amorphous $\text{Na}_2\text{B}_4\text{O}_7$ was prepared by prolonged heating of borax [5]. Crystalline tetragonal $\text{Na}_2\text{B}_4\text{O}_7$ was prepared by heating at 475°C the borax [3]. Fused borax was prepared by melting anhydrous borax in a Pt crucible at 1000°C . Irradiation was performed with a Co^{60} gamma cell emitting $2 \times 10^5 \text{ r/h}$. For low temperature glow curves the irradiation was performed with an X-ray source. The optical absorption was measured by means of diffuse refractance with a Beckmann DK spectrophotometer. The irradiated sample was measured against an unirradiated sample. The *esr* was performed at ambient temperature with an Hilger and Watt spectrometer. The resonating frequency employed was 94 KMc. Thermoluminescence glow curves were obtained with a previously described apparatus using an EMI 6255 B f.m. (ref.).

Thermoluminescence spectra were studied both by means of filters and by a rapid scanning technique according to previously described methods [4, 5].

RESULTS.

Fig. 1 shows the optical absorption of fused borax (solid line) and crystalline anydrous tetraborate (dotted line), irradiated with a dose of 10^7 . In both samples an absorption maximum is present at 2.3 eV, having the

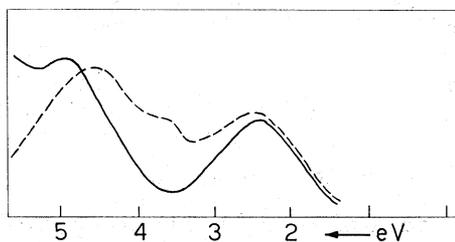


Fig. 1. - Optical absorption from diffuse refractivity of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10^7 \text{ r}$ gamma irradiated.

Full line: glass; shaded line: crystal.

same intensity in both cases. Crystalline samples show an increased absorption at 3.8 eV and a well resolved maximum at 4.5 eV. In vitreous samples the 4.5 eV peak is shifted to 5 eV and a more prominent absorption occurs in the high energy region of the spectrum.

Fig. 2 shows the derivative *esr* curve of fused borax irradiated with 10^7 r of gamma rays. In the fused borax-curve the well known five line resonance spectrum appears with a mean *g* value of 2.0014 [6, 7, 8, 9].

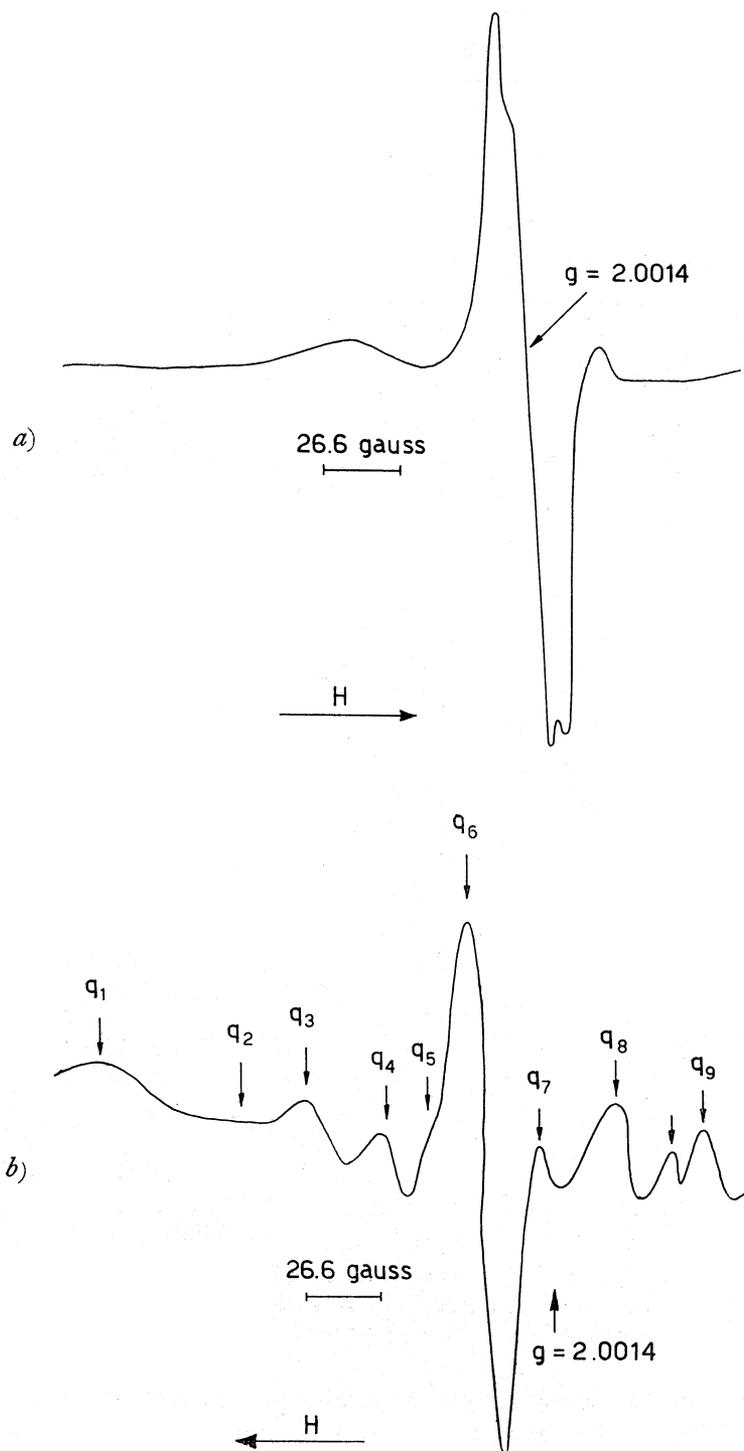


Fig. 2. - Electron spin derivative absorption of $10^7 r$ gamma irradiated $\text{Na}_2\text{B}_4\text{O}_7$.

a) Glass; b) Crystal.

In curve B the esr derivative curve of crystalline anhydrous borax is shown: the intensity at $10^7 r$ doses irradiation is about 50 times less. Curve 2 shows the esr derivative spectrum of crystalline $Na_4B_4O_7$. Seven lines spaced about 25 gauss apart appear. One of these lines is more intense and has a mean g value of about $g = 2.0004$.

Another line appears at $g = 1.9954$. The resonance line at about $g = 2.0034$ seems to be a composite of two lines. The esr resonance absorption intensity is about 20 times less than that of the fused borax.

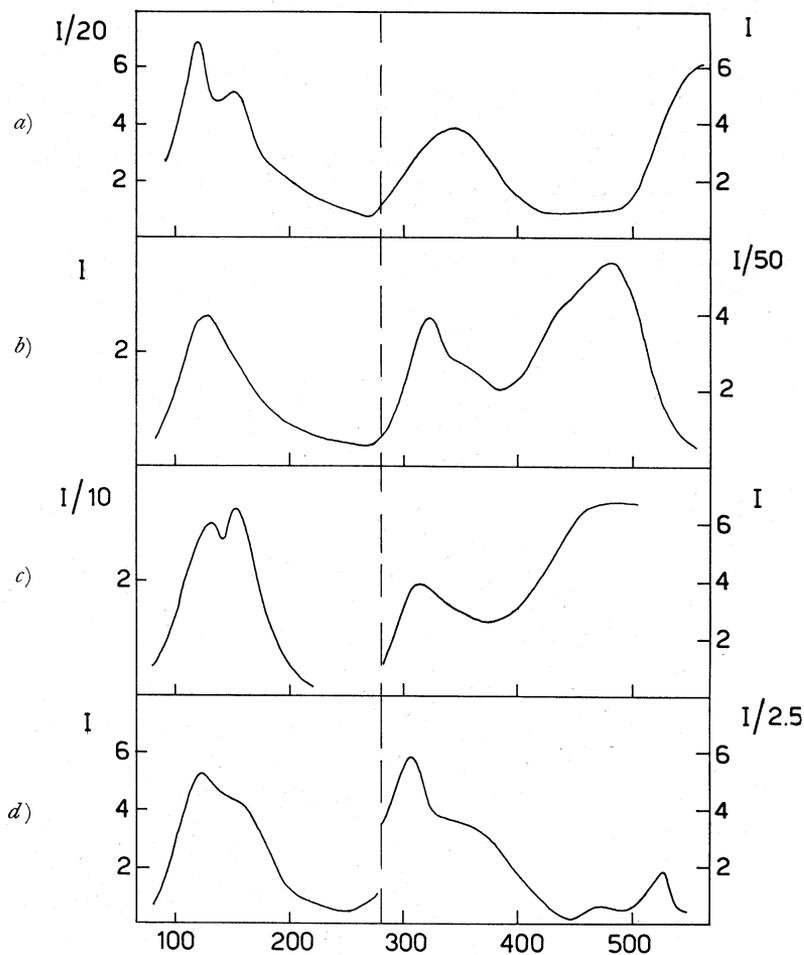


Fig. 3. - Thermoluminescence glow curves.

a) $Na_2B_4O_7 \cdot 10 H_2O$; *b)* $Na_2B_4O_7$, prepared by heating sample *a* at 100° ;
c) $Na_2B_4O_7$, prepared by heating sample *a* at 475° ; *d)* Glassy $Na_2B_4O_7$.

Fig. 3 shows the glow curves of compounds studied. Curve *a* refers to $Na_2B_4O_7 \cdot 10H_2O$. The glow curve shows maxima at 120, 140 and 195 K.

A continuous light emission starts from about $350^\circ K$, which is the decomposition temperature. Curve *b* shows the $Na_2B_4O_7$ prepared by heating the borax at $100^\circ C$. This compound is amorphous to X-rays [3].

Thermoluminescence peaks are present at 120 and there is a shoulder at 147° K. A wide band is present between 290 and 410° K. A sharp peak is present at 560° K. Curve *c* shows $\text{Na}_2\text{B}_4\text{O}_7$ prepared by heating the borax at 475° C. The compound is crystalline [3].

Thermoluminescence peaks are present at 120, 140, 190, 210, 293, and 560° K. Curve *d* shows the $\text{Na}_2\text{B}_4\text{O}_7$ prepared by melting the anhydrous borax. Thermoluminescence peaks are present at 123 and there are also shoulders at 355 and 430 and a peak at 455° K. The TL intensities of the samples are related respectively to the curves *a*, *b*, *c*, and *d* 1, 20, 200, 20 for the emission below zero and 1, 1, 1 and 50 for the emission above zero.

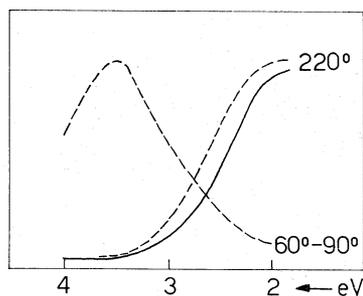


Fig. 4. - Thermoluminescence spectra.

full line: 220° and 90° TL peaks of glassy $\text{Na}_2\text{B}_4\text{O}_7$;
broken line: crystalline $\text{Na}_2\text{B}_4\text{O}_7$.

Fig. 4 shows (solid line) the TL spectra related to the low and high temperature peaks of the fused borax. The broken line shows the spectra of the high and low temperature peaks of crystalline $\text{Na}_2\text{B}_4\text{O}_7$. One can see that the emission of the low temperature peaks is shifted toward higher energy in crystalline compounds.

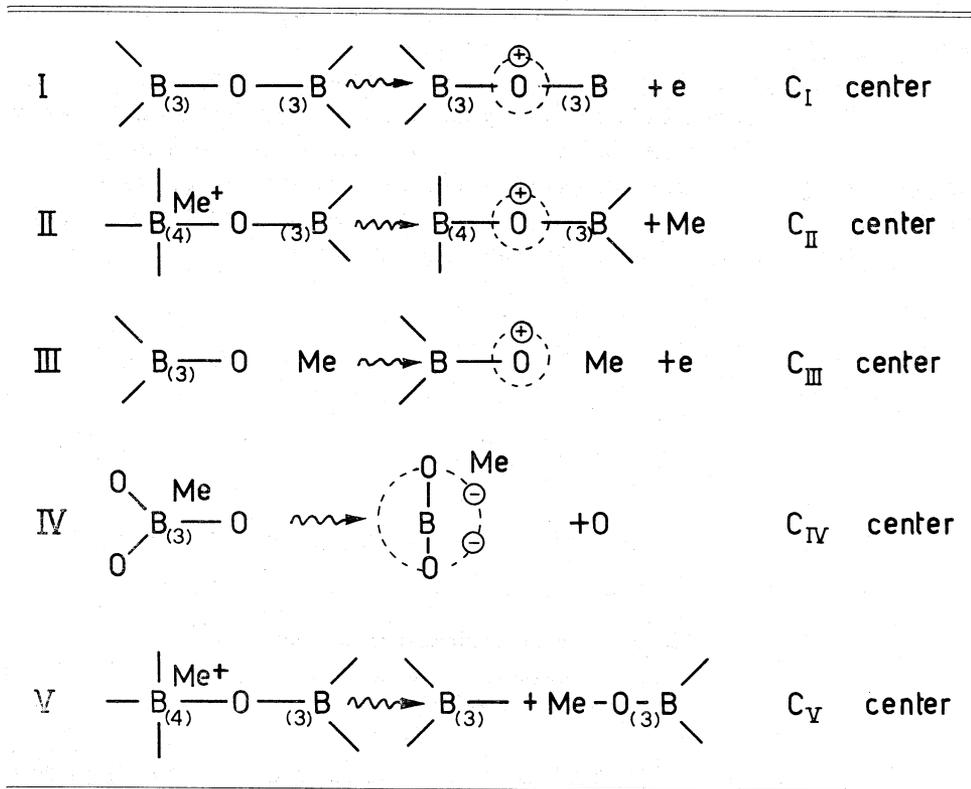
DISCUSSION.

In the case of the glassy and crystalline borates the boron can assume both coordination 3 and 4 with respect to oxygen. The reactions which have been suggested to explain the formation of color centers in borate glasses are therefore (Table I).

The first four reactions can give rise to color centers and the last to the formation of tricoordinated boron atoms in the place of 4 coordinated. We shall now discuss the characteristics of the different types of centers.

These centers must be paramagnetic. If a hole interacts with two boron atoms having a nuclear spin of $3/2$ a hyperfine spectrum must occur: if an isotropic symmetry is postulated, a 7 line band must arise and will be discussed further, if an axial symmetry is postulated a 14 line band must result. Of course a lesser number of bands may be seen because of the overlapping of the two sets of bands.

TABLE I.



The type I center has not been recognized in glasses.

The C_{II} center consists of a hole on an oxygen which is situated between two boron atoms having different coordination.

In this case, owing to the excess of negative charges shown by the 4-coordinated boron atom, the hole will interact with this atom. In the case of a symmetric crystalline field the *esr* spectrum will show 4 bands, or, in the case of an axial symmetric crystalline field, 8 bands. In the case of lower symmetry there will be 12 bands. Of course, again, a lesser number of bands may be seen because of overlapping. According to the literature a 4 band spectrum occurs in alkali borates when they have a low alkali content [7]. In borate glasses having a high alkali content a 5 line spectrum has been found which is related to a type of center which has an axial symmetric field [8].

It has been demonstrated that the presence of a 5 line spectrum instead of an 8 line spectrum, results from the overlapping of two sets of peaks. This center probably gives rise to an optical absorption at 5 eV which prevails in glasses which have a medium alkali content. In borate glasses having a high alkali content a paramagnetic center which has different structure has been found.

In this case the *esr* spectrum consists of a singlet having $g = 2.0023$.

This type of center has been related to the 3.8 eV absorption in irradiated borate glasses.

The C_{III} type of centers will give a hole interacting with a 3-coordinated boron atom. This type of interaction has not been studied and differences between this type and C_{II} types of centers have not been evaluated.

The C_{IV} type of center is not paramagnetic: the absorption at 2.4 eV has not been related to this type of center in the borate glasses. Besides these centers, $O^- [10]$, $MeO^- [11]$ and $O_2^- [12]$ centers can occur in these compounds [12].

Furthermore, in glasses, irradiation can give rise to a series of reactions with impurities. A list of the reactions which have been seen to occur are illustrated in Table II.

Many of the ions listed in Table II exhibit *esr* absorption both before and after irradiation [13].

When irradiation interacts with impurities it can give rise to both acceptor and donor centers. Observing Table II we can see that if some of these reactions are reserved they can give rise to luminous emission because the atoms involved are known to form luminescent centers. As an example see equations 5, 4 and 6, Table II.

TABLE II.

1) $Fe^{3+} + e Fe^{2+}$	5) $Mn^{++} Mn^{+++} + e$
2) $Pb^{++} + e Pb^+$	6) $Ce^{4+} Ce^{3+} + e$
3) $Pb^+ + e Pb^0$	7) $Pb^{++} Pb^{+++} + e$
4) $Cu^{++} + e Cu^+$	8) $Pb^{+++} Pb^{++++} + e$

Optical absorption. The results obtained using fused borax are in accordance with the literature data [2, 7, 8, 9].

The results of crystalline sodium tetraborate are quite different from those of fused borax. The optical absorption shows an increase of the 3.8 eV. Reaction II seems, therefore, more probable in crystalline compounds. This reaction requires metal diffusion which has also been found in the $NaPO_3$ glass- $NaPO_3$ crystal system (II). Other types of centers, which are formed with lower efficiency, are related to the 6 eV absorption. These types of centers are composed of four equivalent oxygen atoms which surround a boron atom but different centers having different properties can occur according to different types of interactions. Some authors suggest that the asymmetry of the *esr* quadruplet which occurs at medium alkali content may be related to an axial symmetry of this center. The 6 eV optical absorption has been related to this kind of center. Other authors show that in the case of axial symmetry a 5 line spectrum must occur and this happens at high alkali content.

These facts suggest that the assignment of an axial symmetry to the 6 eV centers is not certain. The intensity of optical absorption is comparable in glassy and crystalline borax irradiated with the same dosage of gamma rays.

Electron spin resonance absorption. Our results on fused borax are practically the same as those of the literature and will not be discussed. The *esr* of crystalline borate, on the contrary, is quite different. The intensity at the same radiation dose is much lower. A spectrum having 8 or 9 lines was observed. Seven of these lines seem equally spaced with a 25 gauss spacing. However the line at lower H value is separated by about 50 gauss.

The absorption strength of the *esr* signal as a function of t and magnetic field is a first order approximation given by the expression [15]

$$dN = (N_0/2) (4 H_0^2/H^3) \times \{(g_p^2 - g_n^2) [(2H/H)^2 - g_n^2]\}^{1/2} dH$$

where N_0 is the number of absorbing paramagnetic centers

$$H_0 = h\nu_0/2m \quad \text{where } h = \text{the Planck Constant; } \nu_0 = \text{frequency of microwawe radiation applied perpendicular to the magnetic field, and } m = \text{Bohr Magnetron.}$$

g_n = effective $g^{(1)}$ factor normal to symmetry axis

g_p = effective $g^{(1)}$ factor perpendicular to symmetry axis

$$H = (I/gm)(h_{00} - KM/g) \quad \text{where } K = (g_p^2 A^2 \cos^2 O + g_n^2 B^2 \cos O)^{1/2}$$

A = Hyperfine splitting tensor parallel to the axis of symmetry

B = Hyperfine splitting tensor normal to the axis of symmetry

O = angle between the symmetry axis and the direction of the applied magnetic field.

In the case of spherical symmetry $g = g_p = g_n$; A = B and so $K = (A^2 g^2)^{1/2}$

M = magnetic quantum number of a nucleus with spin I.

The values of M can be, in the case of the interaction of an electron having a spin 1/2 with a B¹¹ nucleus having a spin 3/2 as a first approximation:

a) If an interaction of the electron with a single boron atom in a spherical symmetry field is postulated $2(3/2 + 1) = 4$ lines.

b) If an interaction with two boron atoms and a spherical symmetry field is postulated $2(3/2 + 3/2) + 1 = 7$ lines.

c) If axial symmetry and interaction with a single boron atom is postulated $2(3/2 + 1) = 8$ lines.

d) If axial symmetry and interaction with two equivalent boron atoms is postulated $2[2(3/2 + 3/2) + 1] = 14$ lines.

(1) g effective derives from the incorporation in the spectroscopic splitting factor of the free electron = 2.0023 from the effects related to interaction of the surrounding local magnetic and electric field.

It is possible however that the observed lines are much less. In fact [8], the spacing of one set of $2I + 1$ equally spaced peaks is given by $A/g_p m$ and that of the other set of $2I + 1$ equally spaced peaks by $B/g_p m$.

If one denotes H_p and H_n as the centers of the $2I + 1$ equally spaced peaks by $H_p(M)$ and $H_n(M)$ respectively, the separation between H_n and H_p is given by $H = H_n - H_p = hv_0/m (1/g_n - 1/g_p)$. This expression indicates that H is linearly proportional to the operating frequency v_0 . Furthermore, if the spacing $H_n(M = -I) - H_p(M = +I)$ between the peaks at $H_n(M = -I)$ and $H_p(M = +I)$ is denoted $H(I)$ the following relation holds:

$$I(A/g_n m) - H + I(B/g_p m) = H(I)$$

If $A/g_p m = B/g_n m$ some peaks of the two $2(2I + 1)$ sets overlap. The *esr* spectra of crystalline $\text{Na}_2\text{B}_4\text{O}_7$ give rise to 7 equally spaced lines. One can assign the observed *esr* to a center of type I. Owing to the fact that other peaks are present and that the values of g_n and g_p and A and B for a crystal are not well known, further work is needed to obtain a more reliable assignment.

Measurements at higher dosage (to improve the resolution of the *esr* spectra) and measurements at different v_0 are needed to determine whether or not the resulting spectrum is influenced by the overlap of many sets of lines.

Thermoluminescence. The thermoluminescence in irradiated glasses arises obviously from the recombination of irradiation-formed trapped electrons or holes with luminescent centers [5].

At the present state of knowledge it is difficult to assign with certainty the reaction which gives rise to thermoluminescence to the recombination of a given type of centers.

It is known that, in fused borax the maxima at 90° and 240° are related to the annealing of centers giving rise to 1.8 — 2.3 eV optical absorption [10], which are probably related to oxygen vacancies having two electrons trapped.

The *esr* anisotropic quadruplet which is present in fused borax is related to the thermoluminescence maxima which appear at high dosages [17].

The thermoluminescence spectra of fused borax, fig. 4, is composed of a 4 eV emission related to the low temperature peak and a red one related to high temperature peak.

The photoluminescence of fused borax containing 1% and 10% lead shows both an u.v. component 3.9 eV and a visible one at 2.8 eV. A shift toward the red of the 2.8 component at low concentration of lead is also possible.

The behavior of the doped compound can be related to the different lead emissions in different crystalline fields [18, 19].

Another possibility is that luminous transitions arise from Mn^{++} impurities. In glasses Mn^{++} gives rise to red and green emission according to the coordination ($20'$). Cerium too can be considered to behave similarly to Mn^{++}

as activating impurity. In glasses cerium gives rise to an emission at about 3.8 eV [].

The presence of the red emission can be justified assuming an energy transfer from Ce to Mn. In crystalline compounds Mn emission is prevalent from transfer processes in the crystal; all the energy of the cerium is transferred to the Mn^{++} [21].

At least emission can arise from recombination of electrons and holes. Thus we can have $C_{IV} + C_I \rightarrow \text{light}$ or $C_{IV} + C_{III} \rightarrow \text{light}$. The luminescence will come from the annealing of both electron and hole centers.

This emission has not yet been proved in glasses but in crystalline compounds is known to give rise to a line emission [22].

In conclusion, it is very likely that both the presence of impurities and radiation-produced structural centers must be considered to explain the thermoluminescence emission of glasses.

It is well known that the TL of glasses shows a different behavior of the peaks occurring at temperatures lower than ambient temperature and those above it [4, 5].

Low temperature thermoluminescence in glasses is made from a single peak; this peak has been related to the traps produced by the fluctuations of bonds between structural units [23].

The peaks at high temperature, on the contrary, are probably related to traps formed and not filled by radiation. In the set of borate compounds examined a maximum at 123 K is present in all cases. In the two crystalline compounds two more maxima are present at 143 and 190 K.

The different behaviour of crystalline compounds is here clearly evident. At higher temperature all the compounds examined show, at the irradiation doses employed, a band having peaks at about 290–350 K and 450–560 K.

The temperature of the TL maximum is dependent on the crystallinity of the materials. These data suggest that the TL peaks at high temperature arise from the same type of centers but having a different thermal stability. The different origin of the low and high temperature TL peaks seem confirmed from the study of their intensities.

Crystalline $Na_2B_4O_7$ has an intensity much higher than amorphous and vitreous samples, however the high temperature thermoluminescence is 50 times greater in the glass.

The fact that hydrated sample has a TL intensity much lower than anhydrous samples corresponds to the behaviour observed in a series of hydrogen phosphates, where the presence of hydrogen atoms decreases the thermoluminescence intensity [24].

The amorphous sample shows a behaviour which is intermediate between glassy and crystalline samples.

The lower thermoluminescence intensity found at high temperature in crystalline compounds can be related to the decreased efficiency of formation of paramagnetic centers or to a greater efficiency of quenchers which decreases the efficiency of the luminous recombination.

CONCLUSIONS.

The formation of color centers in materials prepared by heating a unique sample (i.e. having the same number of impurities) is very different according to the data; amorphous, glassy or crystalline. Differences are both qualitative (different types or formed centers) and quantitative (lesser efficiency of center formation). The formation of defects stable at room temperature is more efficient in glasses. This fact seems to confirm the presence of diffusion mechanisms in the color centers formation in glasses.

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