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Luminescence in lead borate glasses

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Luminescence in lead borate glasses*. Nota di Carlo Bettinali e Gastone Ferraresso [*], presentata [**] dal Corrisp. G. Sartori.

Riassunto. — È stata studiata l'emissione di luminescenza a 130°K circa di alcuni vetri del sistema Na_2O—B_2O_3 contenenti dall'1 al 33% di PbO, eccitati con luce UV (Riga a 2537 Å del Hg). Le caratteristiche di emissione sono state confrontate con quelle di composti cristallini del sistema $BaCl_2$—$PbCl_2$: tutti i composti studiati presentano un massimo di emissione tra 2.50 e 2.88 eV ed altri due massimi tra 3.30 e 3.90 eV. Il $PbCl_2$ presenta solo il massimo nel visibile. I massimi hanno forma gaussiana.

Sono stati discussi i vari meccanismi possibili per spiegare l'emissione osservata: modello a bande, modello molecolare, modello atomico. Pur non escludendo il modello molecolare, i dati sperimentali sembrano meglio spiegati attribuendo l'emissione osservata nell'UV alle transizioni $^3P_1 \rightarrow {}^1S_0$ e $^1P_1 \rightarrow {}^1S_0$ dello ione Pb^{++}. L'emissione nel visibile è stata attribuita, come ipotesi, alla transizione $^3P_0 \rightarrow {}^1S_0$, tenendo conto: che i centri emittenti interagiscono tra loro; che si trovano in posizione associata a difetti; che pertanto le regole di selezione non sono applicabili.

È stata pure studiata la dipendenza termica della luminescenza nei vari composti. I valori della energia di attivazione della transizione non radiattiva e della costante preesponenziale relativi ai due massimi di due campioni rappresentativi sono state determinate. Tali valori risultano caratteristici per ogni massimo di emissione e per ogni composto. Concordano, come ordine di grandezza, con quell riportati in letteratura per gli ioni isoelettronici col Hg.

INTRODUCTION.

By prosecuting the researches on the nature of lead centres in glasses [1], we expose the results obtained by studying the luminescence spectra and the thermal dependence of luminescence of lead borate glasses. The emission of the glasses has been compared to the emission of crystalline compounds of $BaCl_2$—$PbCl_2$ system.

EXPERIMENTAL.

The apparatus and methods have been previously described [1, 2, 3]. In this work we give some basic data: the luminescence spectra was detected by means of an EMI 6256 B photomultiplier fixed to an automatically driven

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quartz monocromator; the exciting light was produced by means of a Mineralight type lamp, and was filtered with Wood and Backstrom filters. The filtered light was composed mainly of the 2537 Å Hg line. The relative quantum efficiency was measured in comparison with a standard MgO sample [4]. The glasses were prepared by melting reagent grade products in Pt crucible, using an electric furnace.   The $BaCl_2$—$PbCl_2$ samples were also prepared by fusion.

The studied compounds were:

Glasses: 1) B_2O_3—PbO 1 % mol.; 2) B_2O_3—PbO 10 % mol.; 3) B_2O_3——PbO 33 % mol.; 4) Fused borax–PbO 1 % mol.; 5) Fused borax–Pb O 10 % mol.;

Crystals: 6) $BaCl_2$—$PbCl_2$ 0.1 % mol.; 7) $BaCl_2$—$PbCl_2$ 10 % mol.; 8) $PbCl_2$.

RESULTS.

The luminescence spectra reported here were performed at about 130° K. The peaks have been identified by means of a gaussian decomposition. This assumption is proved to be valid by the plot of $[ln\ I_0/I]^{1/2}$ vs. the wavelength expressed in eV (fig. 4).
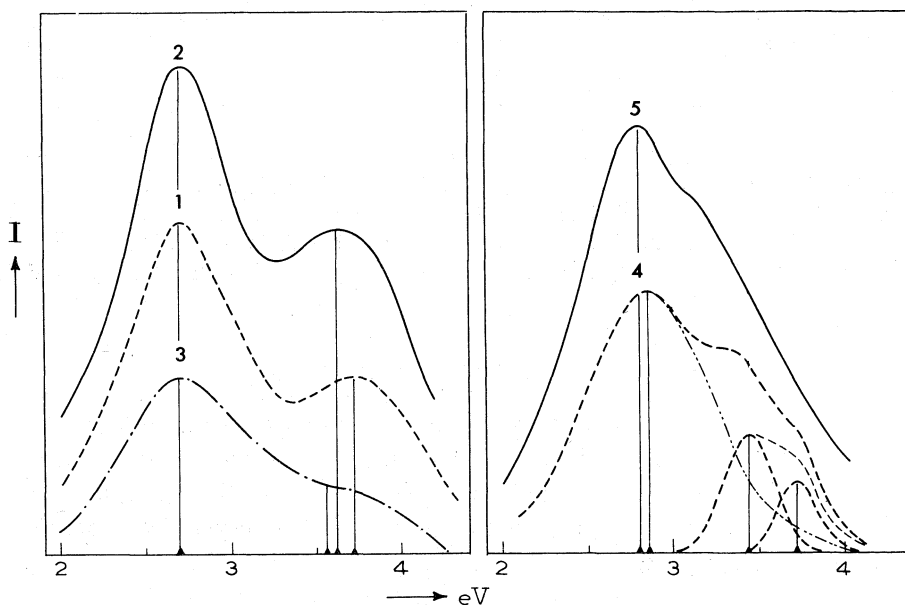

Fig. 1. – Luminescence spectra at 130°K of B_2O_3—PbO glasses Curve 1: B_2O_3—PbO1% mol.; Curve 2: BO—PbO 10% mol.; Curve 3: B_2O_3—PbO 33% mol. (Curve 1 is drawn to 1/2 scale).

Fig. 2. – Luminescence spectra at 130° K of fused Borax—PbO glasses: Curve 4: Fused Borax—PbO 1% mol.; Curve 5: Fused Borax—PbO 10% mol.

Fig. 1 shows the luminescence spectra of samples 1, 2 and 3. These spectra are composed of two peaks having a width of about 0.7 eV at half of their intensity. The first peak, at 2,65 eV, is present in all the samples.

The second occurs at 3.74 eV in sample 1, at 3.64 eV in sample 2 and at 3.56 eV in sample 3. It is noted that the intensities decrease as a function of the lead content.

Fig. 2 shows the spectra of samples 4 and 5 related to fused borax having 1 % and 10 % mol. of PbO respectively. The intensities observed are about 10 times greater than the samples of fig. 1. A maximum at 2.86 eV is present in both samples and at higher energies, two other maxima are present; the first is at about 3.44 eV, the second is at 3,70 and 3.90 eV.
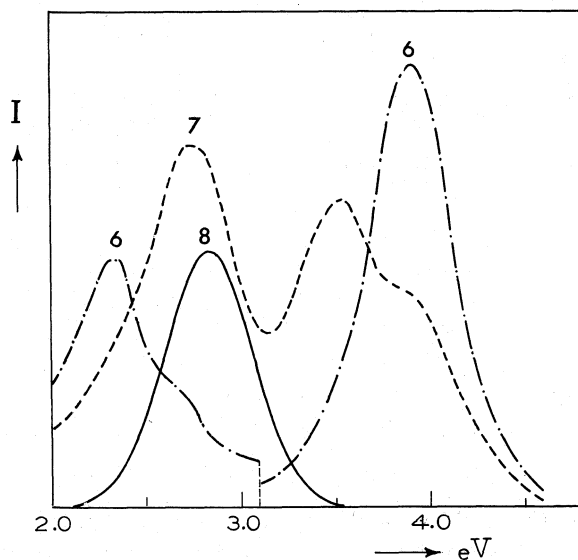

Fig. 3. – Luminescence spectra at 130°K of $BaCl_2$—$PbCl_2$ crystals Curve 6: $BaCl_2$—$PbCl_2$ 0.1 % mol.; Curve 7: $BaCl_2$—$PbCl_2$ 10 % mol.; Curve 8: $PbCl_2$.

Fig. 3 shows the spectra of samples 6, 7 and 8 related to crystalline compounds of the $BaCl_2$—$PbCl_2$ system. In $BaCl_2$—$PbCl_2$ 0.1 % mol. (curve 6) two maxima are present; the first is at 2,32 eV and the second at 3.90 eV, is four times more intense. This latter maximum has also been found in KCl(Pb) [7]. In $BaCl_2$—$PbCl_2$ 10 % mol. (curve 7) three maxima are present as in sample 4 (glass), at 2.74, 3.54 and 3.90 eV. $PbCl_2$ presents only a single maxima at 2.82 eV. The intensities of this set of crystalline compounds are about 5 times greater than those of the fused borax of samples 4 and 5. The low energy maximum shifts towards higher energy as the lead content increases.

Fig. 5 shows the thermal dependence of luminescence intensities at the main luminescence maximum of each of the samples. The intensities of the samples 1, 2 and 3 at 130° K are about 10 times larger than those which occur at ambient temperature. The luminous intensities of samples 4 and 5 are reduced about 2/5 and sample 8 does not present luminescence at 220° K.

In order that we could calculate the thermal activation energies from the thermal quenching curves it was necessary to include a correction for
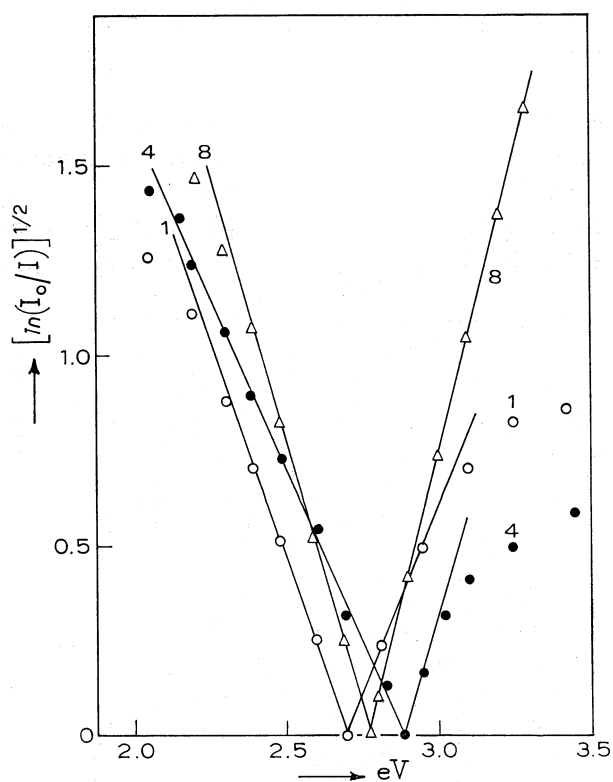
Fig. 4. – Plot $[\ln I_0/I]^{1/2}$ vs. wavelength (eV): Curve 1: B_2O_3—PbO 1 % mol.; Curve 4: Fused Borax—PbO 1 % mol.; Curve 8: $PbCl_2$.
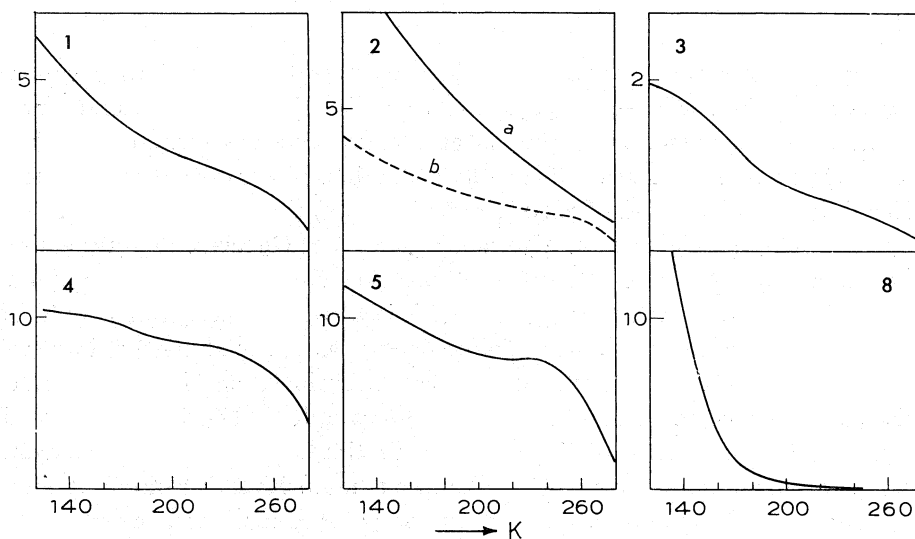
Fig. 5. – Thermal dependence of relative quantum efficiency at the maximum of the spectra. The number of the curves is related to the samples. Curve b of sample 2 is related to UV emission.

the absorption of the exciting light, which very often is not constant in the experimental range. As an example, fig. 6 shows thermal dependence of the 2.76 and 3.45 eV peaks of samples 7 (curves e and *d*). The thermal dependence of reflected light as a function of the temperature and the correct-
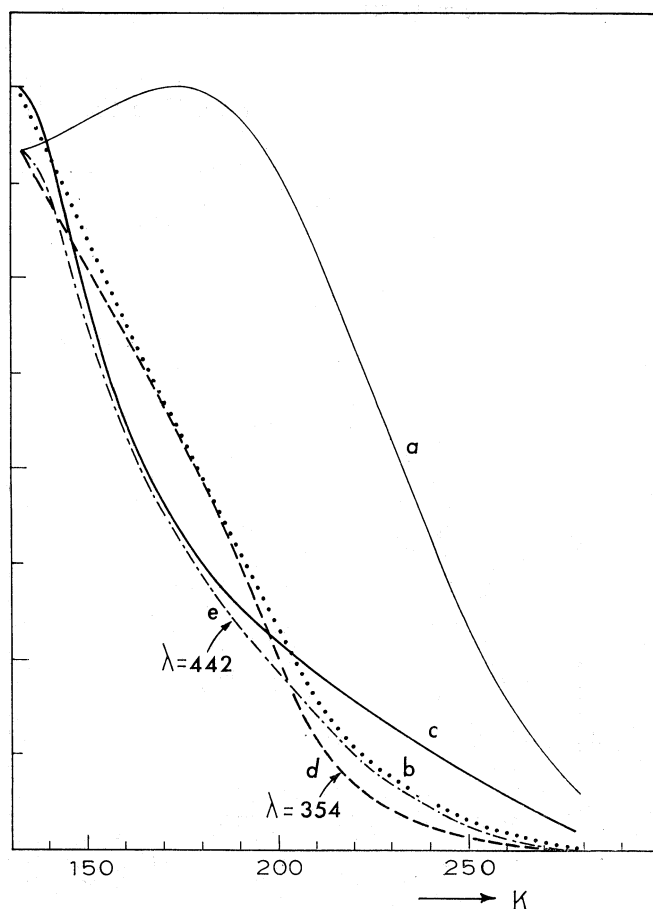
Fig. 6. – Thermal dependence of relative quantum efficiency BaCl$_2$—PbCl$_2$ 10% mol.: Curve *a*: Reflection of the 2537 Å Hg line; Curve *b*: uncorrected emission at 3.5 eV; Curve *c*: uncorrected emission at 2.8 eV; Curve *d*: corrected emission at 3.5 eV; Curve e: corrected emission at 2.8 eV.

ed thermal dependence curve of the 2.76 and 3.55 eV peaks can be seen in fig. 6. To calculate the activation energies of thermal quenching we had to consider the well known relation derived from the Mott and Seitz theory [5, 6], that is

(1)
$$\eta = \frac{P_r}{P_r + P_{nr}}$$

where η is the efficiency of the process, P_r is the probability of radiative transition and P_{nr} is the probability of a radiationless transition. As a first approximation, one can assume that P_r is not temperature dependent and therefore is a constant. In this case we have

$$(2) \qquad \eta = (1 + C\, e^{-E/kT})^{-1}$$

where $C = s/p$, s is the probability of a radiationless transition at the break point temperature, p is the photon emission rate, E is the activation energy

Fig. 7. – Activation energies of thermal quenching related to B_2O_3—PbO 10% mol. The intersections of lines with the ordinate axis represent the values of C.; full line: 2.65 eV peak; dotted line: 3.5 eV peak.

of the thermal quenching, k is the Boltzman constant and T the temperature in °K degree. From eqt. (2) we obtain

$$(3) \qquad ln\,(1/\eta - 1) = -E/kT + ln\,C.$$

Plotting $ln\,(1/\eta - 1)$ against $1/T$, it is possible to calculate E from the slope of the first portion of the curve and, by extrapolation, to obtain the values of C. Fig. 7, curve a and b, shows the plot related to the peaks at 2.76

and 3.65 eV of the $BaCl_2$—$PbCl_2$ 10 % mol. (sample 7).   Fig. 8, curve *c* and *d*, shows the plot related to peaks at 2.65 and 3.70 eV of the B_2O_3—PbO 10 % mol.   In Table I we summarized the values obtained.
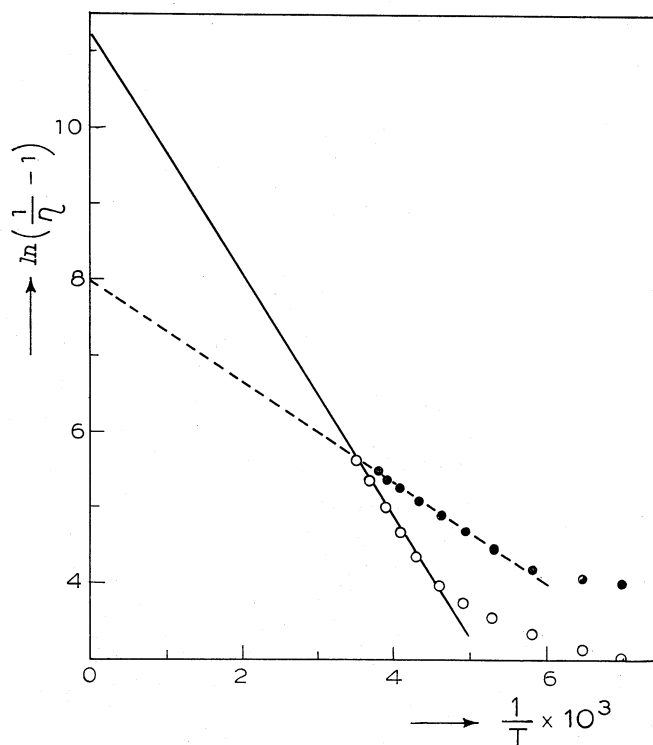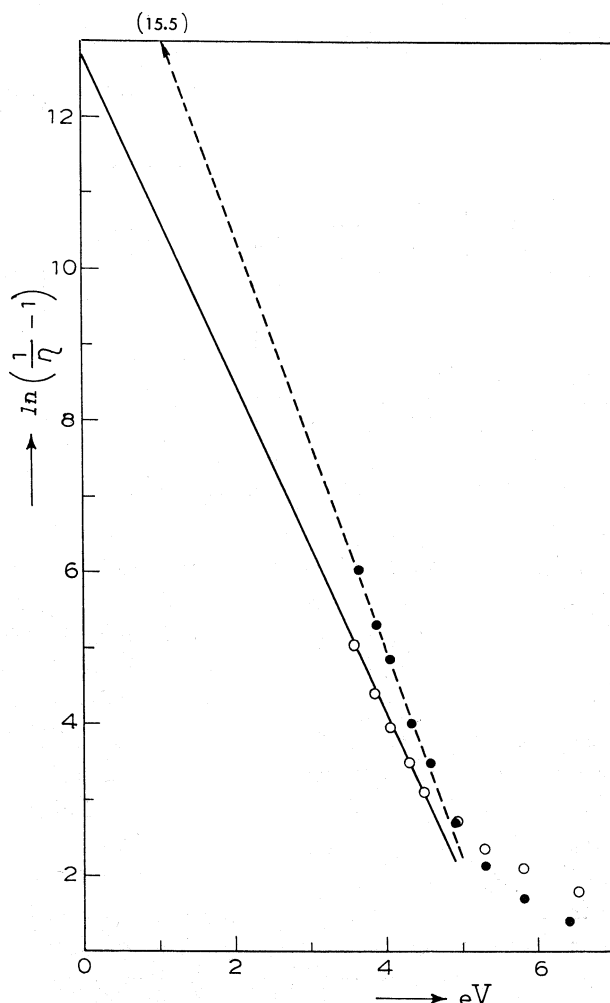

Fig. 8. – Activation energies of thermal quenching related to $BaCl_2$—$PbCl_2$ 10% mol.; The intersections of lines with the ordinate axis represent the values of C; full line: 2.76 eV peak; dotted line: 3.65 eV peak.

DISCUSSION.

Observing experimental results the following facts must be underlined: *a*) A luminescence maximum from 2.30 to 2.88 eV is present in all the examined compounds; *b*) Two maxima are present from 3.30 to 3.90 eV except in $PbCl_2$; *c*) Thermal quenching curves are in accordance with the

Mott and Seitz theoretical model. The values of E are different for the different peaks of the same compounds and different for the different compounds. The values of C varies as E and in the same direction.

TABLE I.

Sample	Peak (eV)	E(eV)	C
B_2O_3—PbO 10%	2.65	0.14	8×10^4
	3.70	0.06	3×10^3
BaCl—$PbCl_2$ 10%	2.76	0.17	3.5×10^5
	3.65	0.20	5×10^6
KCl(Tl) (*)	4.00	0.53	9.2×10^4

* see reference 5.

The Pb in luminescent compounds can act as sensitizer of foreign impurities [10], as sensitizer of the host crystal [11] and, at least, as an activator itself. Although the samples studied were very different both in composition and in solid type, the luminescence was, on the contrary, very similar. It is therefore probable that Pb acts as an activator, that is to say, the luminous emission arises from Pb centers. The luminous emission of Pb centers can be explained according to different models: 1) The emission is related to atomic levels of Pb^{++} (the so called Hg–like emission). This model has been widely used to explain the spectroscopic properties of alkali halide phosphors activated Hg–like ions such as Tl^+, Pb^{++} and Sb^{+++} [12]. 2) The luminous emission arises from a coordinated bond between Pb and other atoms. In this case the transitions occur between the fundamental and the excited state of the bond. The following explanation is also possible: an unshared electron coming from another atom rises to the empty orbital of the heavy metal. These suggestions have been made to explain the luminous emission from $NaNO_2(Pb)$ [13] and can be valid to explain radiative transitions from a $PbCl_n^{-(n-2)}$ complex [9]. 3) There exists the formation of permitted levels in the forbidden band of the host solid by consequence of the introduction of Pb^{++} atoms [14].

We can see by which of these models one can explain the experimental data:

Band model: This hypothesis implies, in our case, the reliability of a band model to explain the electronic phenomena in glasses. This is a very debated question. If we excite our samples with an X–ray source, we can see that the glasses (samples 1 to 5) are not luminescent and that the crystal-

line materials (samples 6 to 8) present luminescence whose intensity is comparable to the photoluminescence intensity. This fact indicates that no indirect excitation of luminogen centers occurs in our glasses. This model therefore does not seem to be very probable.

Molecular model: To discuss this model qualitatively we assume that: *a*) the energy of the excited state of Pb—Cl and Pb—O bond is proportional to the dissociation energy; *b*) The Stokes shift must not be more than 2 eV. The summation of the Stokes shift and emission maximum energy yields the energy of the excited state, that to say, about $2.6 + 2 = 4.6$ eV for the low energy emission. The energy of dissociation of the Pb—O and Pb—Cl bonds in the gas state are 4.3 and 3.17 eV [15]. These data are not contradictory if one takes into account that the dissociation energy is higher than that for the gases. We conclude that this model is not unreliable.

Atomic model: The problem is to which of the allowed Pb^{++} transitions can the observed emission maxima be related. Selection rules for Hg–like atoms in cubic symmetry indicate that the transitions from the $^3P_1$ and $^1P_1$ levels are allowed and that those from the $^3P_0$ and $^3P_2$ levels are forbidden [12]. These rules seem valid for the alkali halides doped with Tl^+ of low concentration but have not been confirmed for Pb^{++} doped compounds. Incidently, the fact that Pb interacts more strongly with surrounding atoms [17] seems to indicate that emission and absorption in Pb doped compounds only occur when Pb^{++} ions are in defective positions [18]. Furthermore the selection rules for cubic symmetry are not strictly valid in lead compounds. It is reasonable therefore to take into account the emission of $^3P_0$ level as suggested by some authors [8].

The UV emission of our samples can be easily related to the $^3P_1 \rightarrow {}^1S_0$ transition. It is more difficult, however, to explain the visible emission. This type of emission has been found to be very weak in KCl(Pb) [7] and prominent in KCl(Tl) [19]. The emission of KCl(Tl) has been related by some authors to the $^1P_1 \rightarrow {}^1S_0$ transition. Other authors relate it to Tl^+ ions in very disturbed positions [20], as happens in TlCl [21]. To explain the visible emission of our compounds we suggest taking into account the $^3P_0 \rightarrow {}^1S_0$ transition, owing to the fact that the $^1P_1 \rightarrow {}^1S_0$ transition implies, for low energy emissions, a very high Stokes shift [22].

The fact that E and C are different in a single emission peak and different in different compounds implies that these values are typical of the luminous transitions of the studied compounds. In fact, C is the ratio between s, the probability of a radiationless transition, and p, the photon emission rate. The s parameter is related to the transition, that to say to the crossing point between the configuration coordinate of the fundamental and excited state; p is related to the number of emitting centers. The interpretation of these data is obviously related to whatever model we use to explain the luminescence. In the case of Hg–like emission, as in the case of the Pb^{++} emission, p is probably constant for the same compound, since different peaks are related to different levels of the same emitting ion: then C will depend on s. In the

case of the molecular model if different luminescence peaks arise from different energy levels of the bond of the same molecule, C will depend, as in the above mentioned case, on s. If the different emissions are related to different molecular groups, the C value of each compound will depend both on s and p.

CONCLUSIONS.

The luminescence of lead borate glasses is similar to that of crystalline compounds of the system $BaCl_2$—$PbCl_2$. Three maxima of emission have been found in each of the compounds studied except $PbCl_2$. The most probable model which could explain the observed facts is one in which there occur radiative transitions between the levels of the Pb^{++} ion. The emission in the visible region can be tentatively related to the $^3P_0 \rightarrow {}^1S_0$ transition. Thermal dependence of the relative luminous efficiency is characteristic of peaks of single compounds as well as of each compound itself.

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