ATTI ACCADEMIA NAZIONALE DEI LINCEI

CLASSE SCIENZE FISICHE MATEMATICHE NATURALI

RENDICONTI

CARLO BETTINALI, GASTONE FERRARESSO, GIUSEPPE VIRTUOSO

Luminescence of glasses of system PbO-SiO_2-K_2O

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **43** (1967), n.6, p. 545–557.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1967_8_43_6_545_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1967.

Chimica. — *Luminescence of glasses of system* $PbO—SiO_2—K_2O$.

Nota di CARLO BETTINALI (*), GASTONE FERRARESSO (*) e GIUSEPPE VIRTUOSO, presentata (**) dal Corrisp. G. SARTORI.

RIASSUNTO. — È stata studiata l'emissione di luminescenza a 120° K di vetri del sistema $PbO–SiO_2–K_2O$, eccitata con U. V. corto (2537 Å). Tutti i campioni studiati presentano una banda di emissione, senza struttura fine, con un massimo tra 440 e 520 mμ. La lunghezza d'onda del massimo di luminescenza varia in modo discontinuo spostandosi verso energie minori nei campioni più ricchi in Pb. L'intensità dell'emissione luminosa è funzione sia del contenuto in Pb che del contenuto in K. Le curve di dipendenza termica dell'intensità luminosa hanno mostrato l'esistenza di tre tipi di andamenti a seconda dal contenuto in Pb. In base ai dati sperimentali sono state fatte ipotesi sulla natura dei centri di luminescenza.

INTRODUCTION.

Luminescence of lead-containing glasses has been previously studied by several authors [1, 2]. These same authors have seen that some types of silicate glasses, when excited at room temperature with short UV rays, present a blue luminescence. However, when the lead content by weight surpasses 5 per cent, the luminescence emissions decrease. This decrease seems to be due to concentration quenching and the spectral emission displaces itself to longer wavelengths. However, the role of lead in glass luminescence has not been well defined. Lead, in fact, can behave in different ways in different types of phosphors: *a*) as a Pb^{++} emitting ion, isoelectronic with Tl^{+} [3]; *b*) as an emitting complex group such as $PbCl_6^{-4}$, as seems to happen in KCl: Pb [4]; *c*) or as the oxyanionic group such as in the MeO : Pb oxides [5]. Lead, besides being an activator, can act as a sensitizer of other emitting ions such as Mn^{++} as in the case of $CaSiO_3$: Mn : Pb [6] or can be the sensitizer of the emission of the host crystal as in the case of $CaWO_4$: Pb [7]. In some of its compounds lead can act as the emitting radical [7].

The $PbO—SiO_2K_2O$ system studied by the authors of this note consents to obtain glasses of a high lead content. Primary experiments carried out by the authors at room temperature on the glasses of this system showed that the luminous intensity was strongly dependent on temperature and was much more intense at temperatures below 230° K. It was for this reason that all experiments were conducted at 120° K.

(*) CNEN, Lab. Chimica delle Radiazioni e Chimica Nucleare Istituto di Chimica, Generale ed Inorganica dell'Università di Roma.

(**) Nella seduta del 9 dicembre 1967.

EXPERIMENTAL.

All samples were prepared with materials having a high degree of purity (Merck, C. Erba, Fluka). In order to evaluate the influence of the probable impurities in silica, several samples were prepared with silica of very high degree of purity. No differences were found between the samples prepared with the two types of SiO_2. The samples prepared with materials of different origins all gave the same results with an error in the range of 10 per cent, probably due to the inevitable differences of thermal history. The samples were prepared by melting the oxides in platinum-rodhium (40 %) crucible in an electric furnace in an atmosphere of inert gasses. To eliminate phenomena of devetrification, the melts were cooled quickly in a metal cup lined with a thin layer of platinum and held at dry-ice temperature.

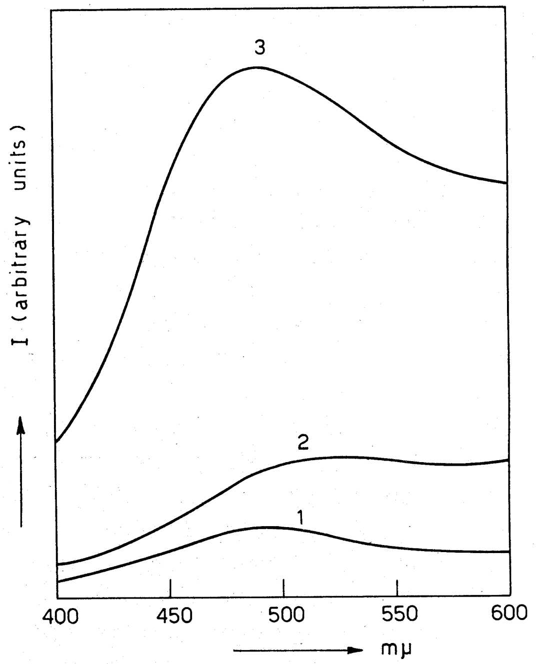


Fig. 1. – Luminescence spectra of samples of the $PbO–SiO_2$ system at 120° K.

Curve 1: $2\,PbO—SiO_2$; spectral maximum at 490 mμ. *Curve 2*: $PbO—SiO_2$; spectral maximum at about 510 mμ. *Curve 3*: $PbO—2\,SiO_2$; spectral maximum at about 485 mμ. The exciting radiation were the 2537 and 3130 Å mercury lines.

The fluorescence measurements were effectuated by a spectrophotofluorimeter for solids, described in previous papers [9]. A cryostat was built in which the sample reaches 120° K and can be tested at this temperature. The pressure within the cryostat was lowered slightly to avoid the formation of ice on the surface of the sample. The temperature dependence of luminous intensity was obtained using the same cryostat whose thermal rod had a calibrated electrical resistance. The luminous source consisted of a 9 watt low pressure "Mineralight" mercury lamp, supplied with a highly stabilized current. The light was filtered by Wood and Backstrom filters [10]. In this way the wavelength of light consisted of 2537 and 3130 Å mercury lines.

The detection of the luminescence was carried out by an EMI 6256 B photomultiplier with a photocathode having a diameter of 1 cm. The aperture of the slits of the monocromator was kept at a low value (10/100 mm) to permit viewing of an eventual fine structure.

The spectra obtained were corrected according to the spectral response of the photomultiplier.

RESULTS.

Fig. 1 shows the luminescence spectra conducted at 120° K of a series of compounds of the $PbO-SiO_2-K_2O$ system. The spectra of glasses of composition $2\,PbO-SiO_2$, $PbO-SiO_2$ and $PbO-2\,SiO_2$ present maxima at 490, 510 and 485 mn respectively.

Fig. 2 presents the luminescence spectra conducted at 120° K of some glasses having a constant SiO_2/K_2O ratio = 6 but with increasing quantities

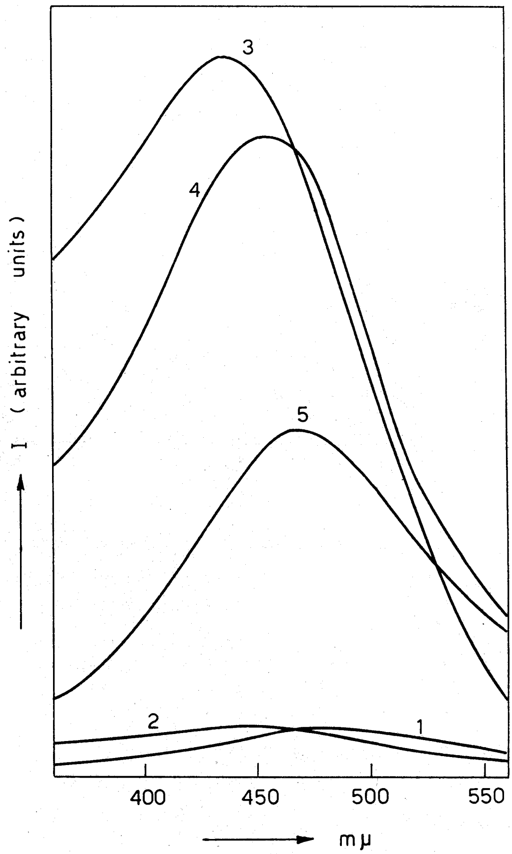


Fig. 2. – Luminescence spectra of samples of the $PbO-SiO_2-K_2O$ system having a constant SiO_2/K_2O ratio (= 6) and having variable quantities of PbO.

Curve 1: K_2O-SiO_2; spectral maximum at 474 mμ. *Curve 2*: $K_2O-SiO_2-0.16\%$ mol PbO; spectral maximum a; 442 mμ. *Curve 3*: $K_2O-SiO_2-1.5\%$ mol PbO; spectral maximum 442 mμ. *Curve 4*: $K_2O-SiO_2-10.7$ mol PbO; spectral maximum at 451 mμ. *Curve 5*: $K_2O-SiO_2-20\%$ mol PbO; spectral maximum at 467 mμ.

of PbO. The maxima of these emissions vary between 474 mn for the K_2O—SiO_2 sample and 442 mμ for the compounds containing 0.16 and 1.5 mol of PbO. In the samples having a PbO content of 12 and 22 per cent, the maxima of spectral emissions occurred at 451 and 467 mμ respectively.

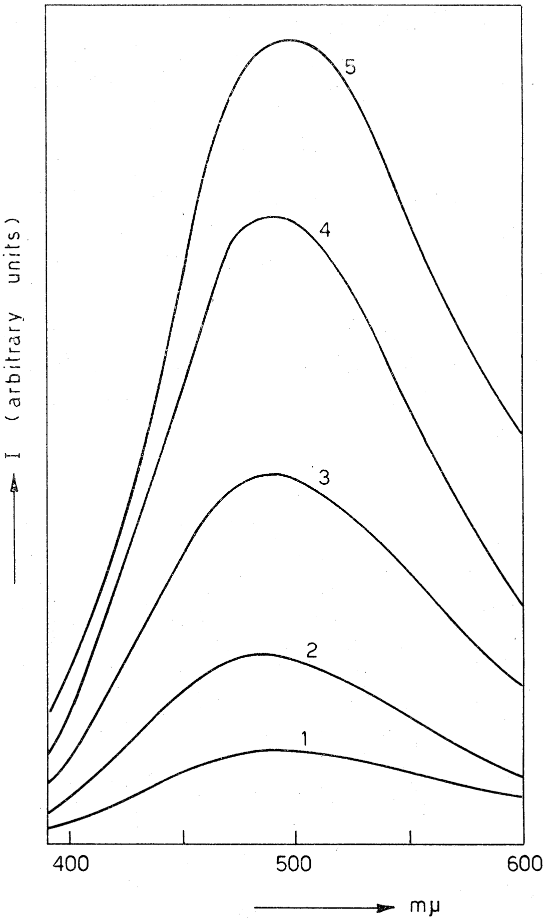


Fig. 3. – Luminescence spectra of samples of the system PbO—SiO_2—K_2O system having a constant SiO_2/PbO ratio (= 2) and having variable quantities of K_2O. The spectral maximum is quasi-constant for the examined samples.

Curve 1: 2 SiO_2—PbO; *Curve 2*: 2 SiO_2—PbO—5.3% mol K_2O; *Curve 3*: 2 SiO_2—PbO—10.7% mol K_2O; *Curve 4*: 2 SiO_2—PbO—14.5% mol K_2O; *Curve 5*: 2 SiO_2—PbO—25% mol K_2O.

One should note that these glasses present spectra whose maxima occur at higher wavelengths when the PbO content is increased.

The spectra of luminescence of the samples having a constant SiO_2/PbO ratio = 2 are shown in fig. 3. These samples have increasing contents of K_2O. The samples reported contain O, 0.16, 0.33, 0.50 and 1.0 per cent mol of K_2O: the wavelength maxima are respectively 485, 480, 484 and 498 mμ.

Fig. 4 shows the luminous intensities of the samples of the PbO–SiO_2 system. One can see an increase of luminous intensity when the SiO_2/PbO ratio increases.

Fig. 5 shows the behaviour of the luminous intensity of the samples having a SiO_2/K_2O ratio = 6 and an increasing PbO content. The luminous intensity in these cases increases rapidly for compounds containing 0.16 and 1.5 mol of PbO and decreases for all samples of greater content than 1.5 mol.

Fig. 6 shows the behaviour of the luminous intensity of samples having a constant ratio of SiO_2/PbO and increasing K_2O content. The increase in intensity appears in this case to be a function of the K_2O content.

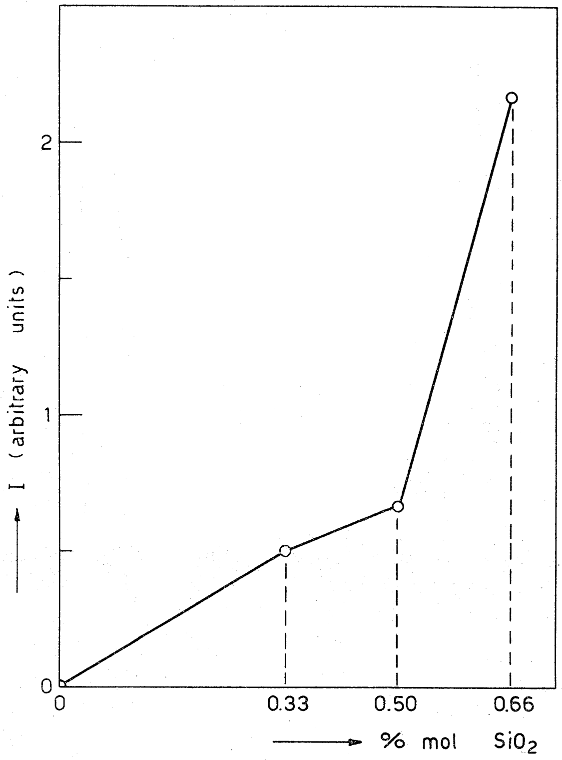


Fig. 4. – Luminous intensities of the spectral maximum of the individual samples of the PbO—SiO_2 system (see fig. 1) in function of the SiO_2 content.

Fig. 7 shows the temperature dependence of luminous intensity at the wavelength of the maxima of the spectra. The binary glasses of the PbO—SiO_2 system have such a weak luminous emission that it was impossible to obtain a sufficiently significant curve, except for the PbO—SiO_2 sample whose curve is shown. Observing the figure it is possible to see that three distinct types of behaviour exist: the A type consists of a primary path which is almost constant, a pronounced maximum at about 230° K followed by a rapid decrease between that maximum and 300° K. The B type presents a pronounced bend at about 230° K and decreases constantly between 120 and 300° K. The C type presents decreasing behaviour between 120 and 300° K without showing any outline of a possible maximum. One can thus observe a gradual variation from the type A to the type C in function of the increasing amount of PbO.

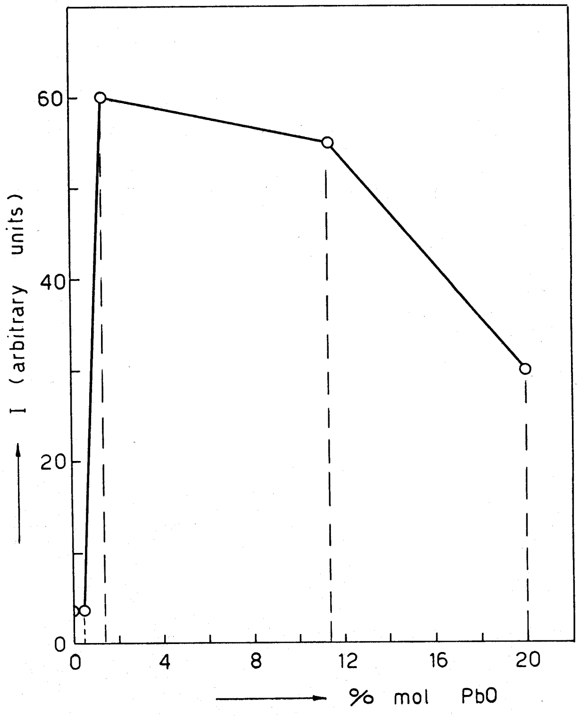


Fig. 5. – Luminous intensities of the spectral maximum of the individual samples of the Pbo—SiO_2—K_2O having a SiO_2/K_2O ratio = 6 (see fig. 2) in function of the PbO content.

DISCUSSION.

All the compounds that were studied were found to be luminous if excited by short UV rays at low temperatures. The individual emission spectra consist of a large band between 650 and 300 mμ. It was found that both the maximum of the band and its width are dependant on the composition of the samples. The maximum of the spectrum varies, as can be seen from figs. 1, 2, and 3 from a minimum of 440 mμ for the sample with a PbO content less than 10 per cent to a maximum of 510 mn for samples rich in PbO. Values have been found quite close to the above values for samples activated with Pb, as BaO : Pb and ZnS : Pb [5, 11].

In order to establish whether luminous emission is due to center containing lead, to anionic centers, or to impurities sensitized by lead, let us consider the spectra of K_2O—SiO_2 and K_2O—SiO_2—0.5 PbO shown in fig. 2. As one can see, the typical maximum of the spectral emission of K_2O—SiO_2 [12] is displaced from 470 to 440 mμ by the introduction of 0.16 per cent of PbO, while the intensity does not seem to have been modified. This fact permits one to speculate that the emitting group contains Pb but this does not permit one to establish whether the luminous emission is due to the transition $^3P_1 \rightarrow {}^1S_0$ of the Pb^{++} ion [1] or to a complex group of the type PbO_6 or PbO_4 which are known to exist in glasses [13, 14]. Since concentration quenchgin appears only for amounts of PbO which are much elevated (20 %) it seems only slightly probable that the luminous emission of the compounds having fractions of PbO which are slightly less than 20 per cent be due to isolated centers. In the case of Tl^+ (isolated center), the concentration quenching appears in fact for concentration in the range of 10^{-3} mol per cent [15].

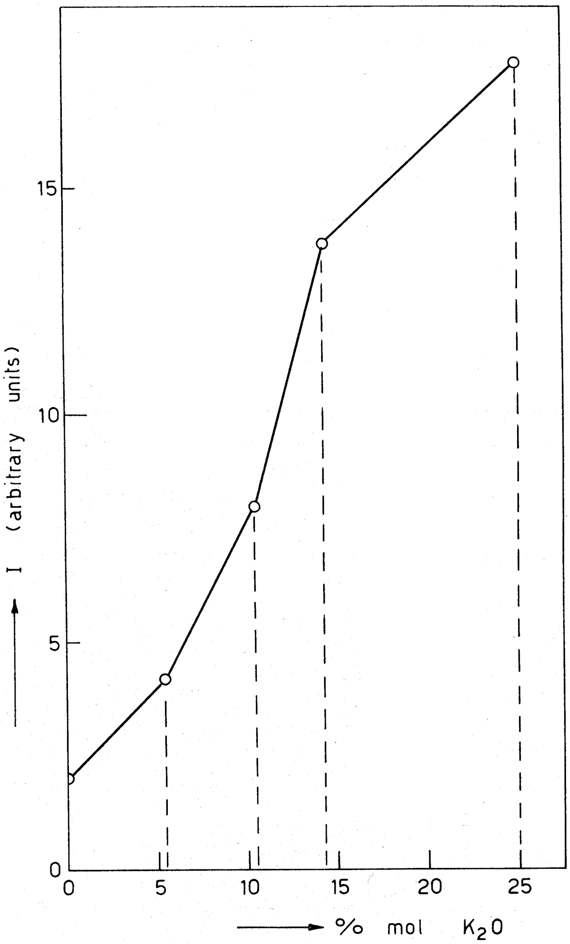
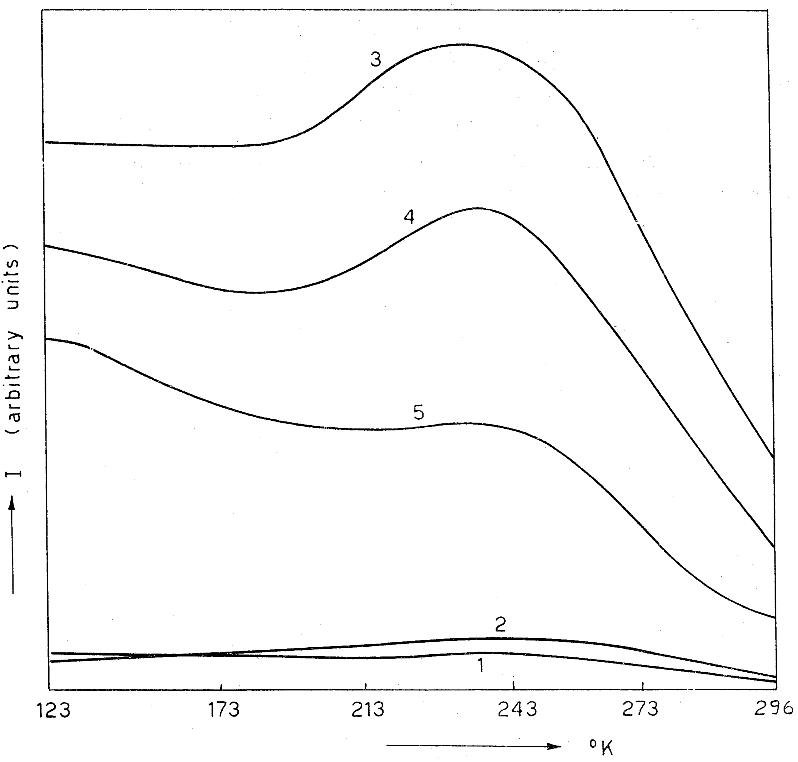
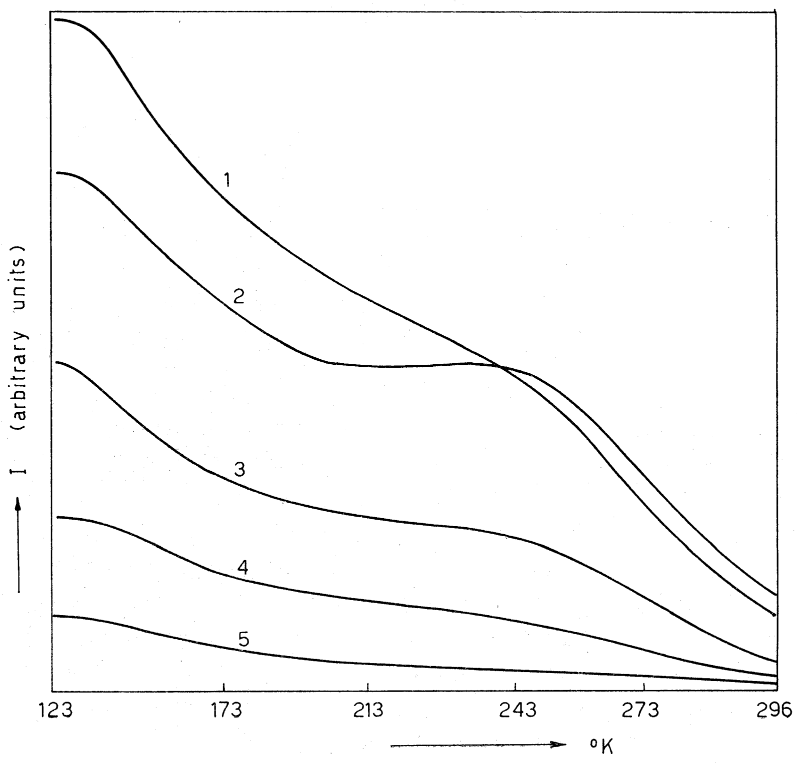


Fig. 6. – Luminous intensities of the individual samples of the PbO—SiO_2—K_2O system having a constant SiO_2/PbO ratio and a variable K_2O content (see fig. 3). The light emission increases with increasing K_2O content.


I (arbitrary units)
3
4
5
2
1
123
173
213
243
273
296
°K

7 *a*


I (arbitrary units)
1
2
3
4
5
123
173
213
243
273
296
°K

7 *b*

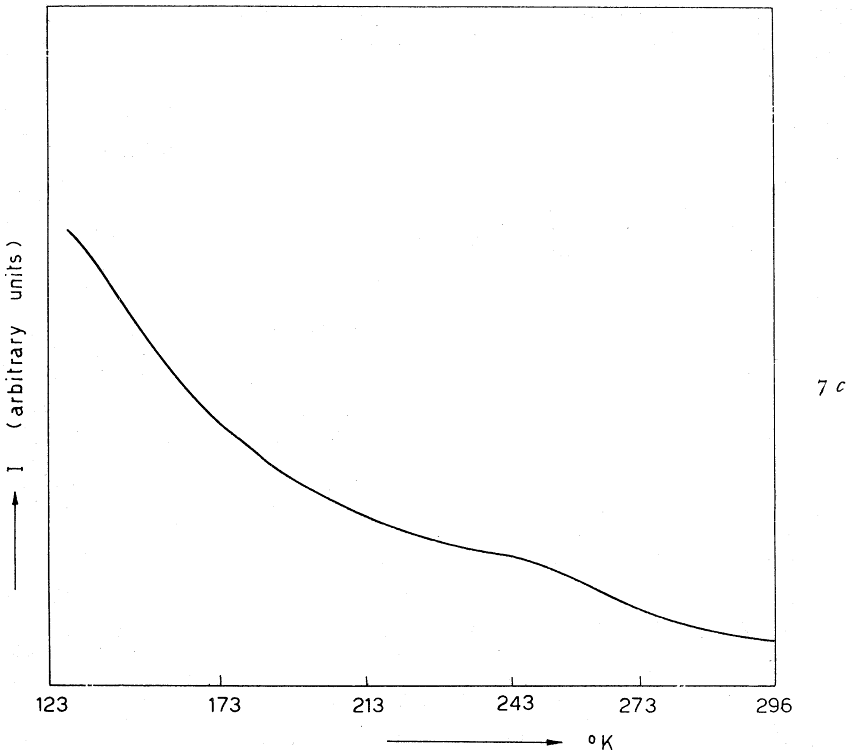


Fig. 7. – Thermal quenching of the luminous intensity of the three types of samples:

7 *a*: In this figure are reported the thermal quencing curves related to the samples of fig. 2. The curves can be divided in three portions: the first has a quasi-constant luminous intensity; the second has a maximum at about 230° K; the third presents a rapid decrease of luminous intensity.

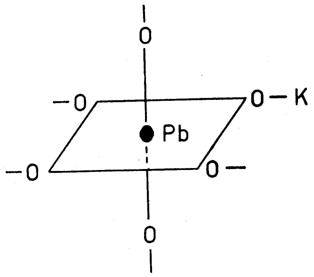
7 *b*: the luminous intensity of the curves are constantly decreasing, but a flex is present at about 230÷240° K. These curves are related to the samples of fig. 3.

7 *c*: The luminous intensity is pratically always decreasing, beginning at the low temperature. This curve is related to the $PbO—SiO_2$ sample.

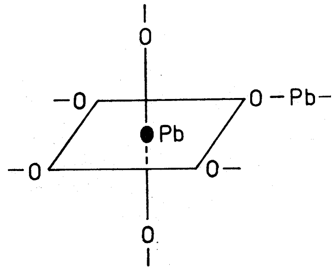
In our case, the elevated value of the concentration which gives the quenching permits one to believe that the luminous emission be due to well-screened groups as the uranile group. It seems permissable then to attribute luminous emission to the PbO_6 or PbO_4 groups.

The mechanism by means of which this group produces luminous emissions has not been clarified. In general it is necessary that one of the oxygens be attached to a cation or to a different oxyanionic group. Therefore it seems proven by fact that very pure silica does not produce any luminous emission, even if irradiated with light having wavelengths corresponding to the maximum of optical absorption, whereas the introduction of a small quantity of alkalies or germanium give rise to a luminous emission [16]. In Ca metasilicate, the luminous intensity of the SiO_4 group is increased by introduction of TiO_2 [17]. In the lead glasses studied by the authors, the introduction of K_2O in modest quantities gives rise to a considerable increase in luminous intensity without altering the spectral composition.

From the exposed facts a probable hypothesis concerning luminous emission could be that they may be connected to the levels of the ligand field of Pb^{++} in the 6 or 4 coordination, analogous to what seems to happen with Mn^{++} [18]. In fact, the introduction of K_2O modifies the ligand field because an O of the coordination would be non-bridging and thus non-equivalent.



The weak luminescence emission of lead glasses without alkali can be explained by imagining that the Pb could act as the developer of a modest amount of non-bridging oxygen.



Regarding the behaviour of the thermal dependance of the luminous emission many various interpretations have been given from which we shall record the two most accepted. The first, by Mott and Seitz [19, 20], starts from the hypothesis that the configuration coordinates of the excited state be closer to the configuration coordinates of the fundamental state. When the temperature of the solid increases, the transitions occur between the vibrational levels of greatest energy and thus increase the probability of non-radiative transitions. When the vibrational levels are very close to the energetic level of the temperature break point, the probability of non-radiative transitions is maximum. The activation energy of the process is connected to a luminous efficiency by the relation:

$$\eta = \frac{1}{1 + C \exp(-E/kT)} \cdot$$

The second theory, by Moeglish and Rompe [21], starts from the hypothesis that a simultaneous emission could occur consisting of many phonons and thus producing a non-radiative transition between band and band. In such a case the efficiency of the luminous process becomes.

$$\eta = \frac{1}{1 + \mathrm{CT}g}$$

where $g = \mathrm{E}_{\mathrm{gap}}/(n/2\,\pi)\,w$ and $\mathrm{E}_{\mathrm{gap}}$ is the wavelength of the emitted phonons. The g obtained experimentally is much inferior to that obtained theoretically

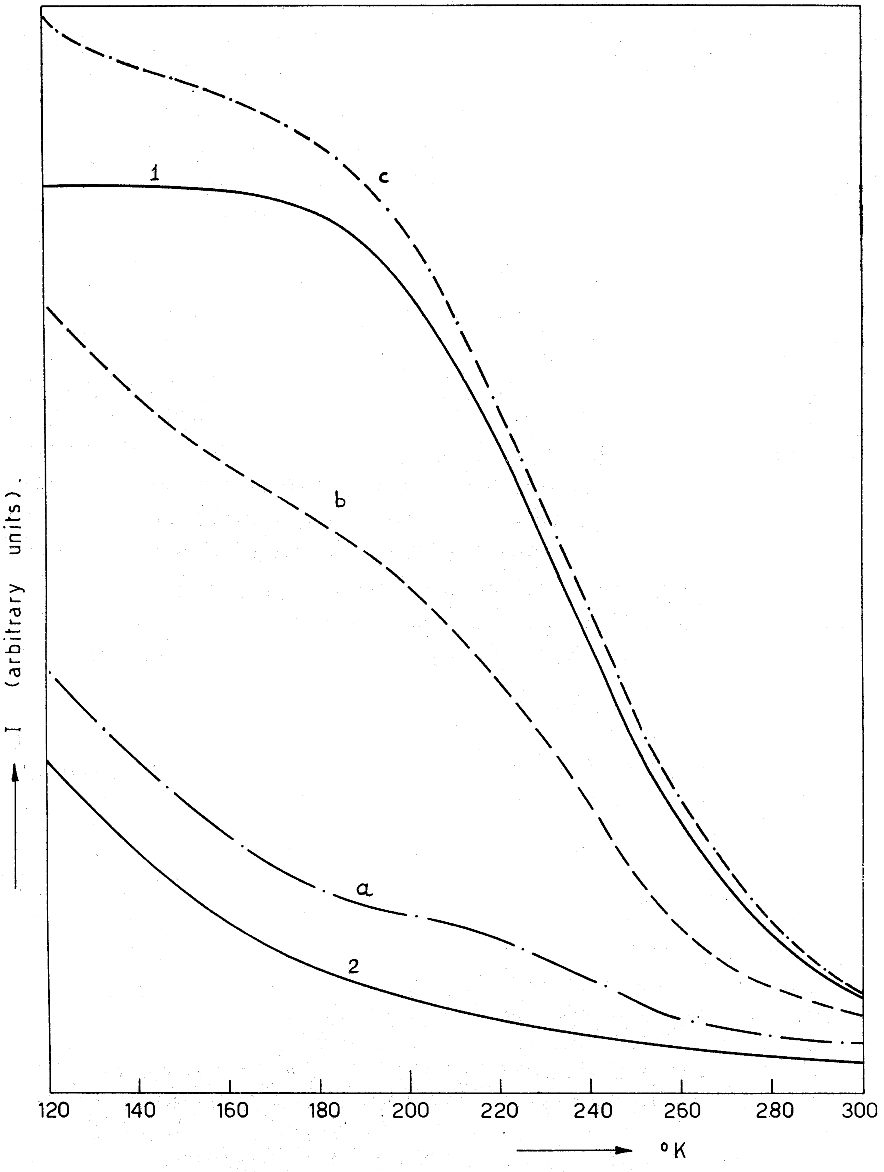


Fig. 8. – Theoretical thermal quencing curves of luminous intensity calculated with arbitrary values of E and C, according to Mott and Seitz (curve 1) and Moeglish and Rompe (curve 2) theories. Curves *a*, *b* and *c* were constructed assuming the contemporaneous presence of the two laws.

(deduced for an ideal crystal) where the lattice defects introduce new levels and thus decrease the energy of the gap. Since the materials under study were glasses it was possible to foresee a very low value for g. In fig. 8 curves are reported relative to the two theories and calculated by means of arbitrary values. Curve 1 corresponds to Mott and Seitz's theory while curve 2 corresponds to that of Moeglish and Rompe. Supposing that there be a contemporaneous presence of the two phenomena, one would obtain curves of the types *a*, *b*, and *c*. From the figure it is possible to see that curve 2 is somewhat similar to the curve of type C (fig. 7) which is typical of glasses of high lead content. The curves of fig. 7 *a* and 7 *b* seem to be more or less a combination of the two phenomena (curves *a*, *b*, and *c* of fig. 8). These are not sufficiently complete proofs to establish whether such behaviours are due to the different ways of non-radiative emission of the same center or if they are due to the presence of distinct centers having different properties.

CONCLUSION.

All the examined glasses of the PbO—SiO_2—K_2O system presented luminous emissions if excited at 120° K with short UV light (2537 Å). The spectral composition of the light emitted, due to lead, varied as the PbO content was varied: the maximum of the spectrum displaced itself from the 440 to 510 mn as to Pb content increased. The samples having a constant SiO_2/PbO ratio showed an increase in luminous intensity as the K_2O content was increased. The shape of the intensity vs. temperature curve varied according to the chemical composition of the sample. Three types of temperature dependance of luminous intensity were thus ascertained in function of the lead content.

Acknowledgements. – The authors thank the National Research Council (CNR) for the financial support of this work.

REFERENCES.

[1] N. J. KREIDL, « J. Opt. Soc. Am. », *35*, 249 (1945).
[2] H. WITZMANN and G. HERZOG, « Z. Phys. Chem. », *225*, 197 Lipsia (1964).
[3] N. E. LUSCHIK, CH. B. LUSHCHIK, « Optics and Spectroscopy », *8*, 441, (1960).
[4] A. BOHUM, J. SAK and J. DOLEJSI, « Phys. Status Sol. », *9*, 341 (1965).
[5] H. WITZMANN, G. HERZOG and K. BRACHMANN, « Z. Phys. Chem. », *225*, 26 Lipsia (1964).
[6] P. J. BOTDEN and F. A. KRÖGER, « Physica », *14* (8) 553 (1948).
[7] C. VLAM, « Physica », *15*, 609 (1953).
[8] H. W. LEVERENZ, *An Introduction to Luminescence of Solids*, p. 239, J. Wiley N.Y. (1950).
[9] C. BETTINALI and G. FERRARESSO, « Z. Phys. Chem. NF. », *48*, 16 (1966).

[10] A. BRIL, *Luminescence of Organic and Inorganic Materials,* ed. H. P. Kalmann, G. M. Spruch, J. Wiley, pp. 479–493 (1962).

[11] S. SHIONOYA, T. KODA, K. ERA and H. FUJIWARA, see ref. 10, pp. 353–390.

[12] A. KATS and J. M. STEVELS, « Philips Res. Rep. », *11*, 115 (1956).

[13] G. O. BAGDYKYANTS and A. G. ALEKSEEV, « Structure of Glass », Vol. II Consultant Bureau, p. 198, N. Y. (1960).

[14] M. LEVENTHAL and P. J. BRAY, « Phys. and Chem. of Glasses », *6* (4), 113 (1965).

[15] P. L. DEXTER and J. H. SCHULMAN, « J. Chem. Phys. », *22*, 1063 (1954).

[16] V. GARINO-CANINA, « Ver. et Refr. », *10*, 63 and 151 (1956); *12*, 313 (1958).

[17] H. W. LEVERENZ (ref. 8), p. 217 and foll.

[18] H. S. LINWOOD and W. A. WEYL, « J. Opt. Soc. Am. », *32*, 443 (1942).

[19] N. F. MOTT and R. W. GURNEY, *Electronic Processes in Ionic Crystals,* pp. 219–224, Clarendon Press, Oxford (1948).

[20] F. SEITZ, « Trans. Faraday Soc. », *35*, 79 (1939).

[21] F. MOEGLISH and R. ROMPE, « Z. für Phys. », *115*, 707 and *117*, 119 (1940).