

1. Meeting of the luminescence group of the European  
section of the electrochemical society  
Meudon-Bellevue (France) 16-17 Jul 1984  
CEA-CONF--7410

F RPSO 0554

Ce<sup>+3</sup>-and Tb<sup>+3</sup>-luminescence in glasses.--Ce<sup>+3</sup>-activated bulk silica  
and silica thin films.-An $\alpha$ -particle detector based on a Ce<sup>+3</sup>-activated  
silica thin film.-A Ce<sup>+3</sup>-Tb<sup>+3</sup>-energy transfer in a high melting point  
phosphate glass.

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I - Introduction.

The recent interest in plutonium as a substitute for uranium isotopes in atomic energy reactors had made it necessary to develop scintillators having an acceptable life-time (i.e. 1 year) in continuous use, and which are able to measure quantitatively both high and low Pu-concentrations in the presence of other,  $\beta$ - and  $\gamma$ -radiating, elements.

The quantitative detection of the  $\alpha$ -emitting Pu in the presence of strong  $\beta$  and  $\gamma$  radiators is possible using scintillators having a thickness less than 40 microns. The  $\alpha$  particles lose their energy completely in about 40 microns of material while  $\beta$  and  $\gamma$  rays interact little.

In this special case - the control and the command of a large separation unit of Pu - the detector has to work in direct contact with a hot 4N nitric acid solution of the radioelement. Furthermore, only little adsorption of radioactive ions on the detector surface must occur.

Phosphors based on ZnS, NaI,  $\text{YPO}_4 : \text{Ce}^{+3}$  and EPM : Au respond strongly to  $\alpha$ -particle activation,  $\text{Eu}^{+3}$  and  $\text{Tb}^{+3}$  - activated rare-earth oxides and  $\text{BaSi}_2\text{O}_5 : \text{Eu}^{+2}$  somewhat less. Plastic scintillators and dpm (= dipivaloylmethanolate of Tb) which show both a high sensibility towards  $\gamma$  and  $\beta$  radiation do not respond at all.

These phosphors are not stable in contact with the hot acid; thus we tried to protect the phosphor layers by very thin sputtered films of Pt or Ta, but the homogeneity of the metal film on the phosphor powder layers is insufficient to protect them over an extended period of time. Only glassy  $\text{BaSi}_2\text{O}_5 : \text{Eu}^{+2}$  can be efficiently protected after optical polishing, but the  $\text{Eu}^{+2}$  emission decreases with time when exposed (i.e. 8 days) to  $\alpha$ -particles; apparently oxidation of  $\text{Eu}^{+2}$  to  $\text{Eu}^{+3}$  occurs which emits only weakly in this host.

Sputtered activated thin films of ZnS, R.E.-oxysulfides or  $\text{BaSi}_2\text{O}_5$  have a smooth surface and can therefore be protected efficiently by metal films, but these thin films which are amorphous show only weak fluorescence.

Their luminescence can be restored by annealing (fig. 1 and 2), but then the films recrystallize and show poor adherence to their substrates (glass or silica).

Therefore, we decided to investigate the possibility to use  $Ce^{+3}$ -activated glass systems as  $\alpha$ -particle detectors; The bulk glass pieces obtained by classical glass-preparation (melting) were to be brought down to a thickness of about 40 microns by grinding or etching. Furthermore, because of practical reasons an emission in the visible region was desired; there fore also  $Tb^{+3}$  and  $Ce^{+3}/Tb^{+3}$  - activated glasses were prepared.

Conveniently, the initial spectroscopic examinations were performed under U.V. -excitation. Samples showing good emission were then excited by  $\alpha$  and  $\beta$  radiations.

## II - Short review on rare-earth-fluorescence in glasses.

Before the discovery of the Nd-glass-Laser in 1961 by Snitzer (2) there had been little work on R.E.-luminescence in amorphous materials. Since this invention hundreds of Nd-glasses have been investigated (3), mostly to determine their potential use for thermonuclear fusion reactions. Spoward (1,4,5) has later developed neutron - scintillators based on an "in situ" nuclear reaction between neutrons and  $^6Li$  in the  $Ce^{+3}$  -activated- Li - silicate - glass. The energy liberated excites the  $Ce^{+3}$  - UV - luminescence-. Amorphous  $Ba Si_2O_5 : Eu^{+2}$  has been suggested as a possible X.R. screen material.

The theoretical side of R.E - luminescence in low melting glasses has been enriched by the work of Ziman (6), Reisfeld (7), Duffy and Ingram (8,9) and more recently by Brawer (10). Their conceptions are also valuable for high melting point systems.

In brief, the amorphous state is characterized by the absence of the long-range order common to the crystalline state, and the occurrence of a short range order.

Thus, the main optical properties of a R.E. in a glass are characterized by its immediate environment, which differs only slightly from one to another short-range "motif". But because of the fortuitous linking between these "motifs" over the whole solid, small site - to - site differences in the local crystal field appear which introduce perturbation effects into the activator energy levels, i.e. line broadening and non-exponential decay. In spite of this, the main features of the optical properties of a R.E. in a glass are similar from one site to another, and therefore Reisfeld concludes that they may be analyzed

in the same way as in crystals and that the R.E. may even be used as a probe to determine the microsite-symmetry.

This representation is perhaps oversimplified. It is improbable that the immediate surroundings of the R.E., i.e. the microsites, are perfectly ordered and exempt of faults. "Micro-faults" occur surely and will interact with the activator ion. In all cases, because of the broadening of the absorption- and emission bands and lines the interpretation of the spectra becomes very difficult.

III. Experimental:--Bulk glass was prepared by melting the raw materials in a iridium crucible. The melt was poured onto a platinum sheet. The pieces were annealed, cut and polished down to 1 mm thickness. The starting material were of analytical grade (Rhone-Poulenc R.P.), the rare-earth oxides of 99.995 purity (Rhone-Poulenc, Chimie fine). High purity  $\text{SiO}_2$  (powder) was bought from "Quartz et Silice", Paris (Tetrasil) and from Degussa. (Ultrasil).--The  $\alpha$ -emitting isotope was  $\text{Am}^{241}$  (100 C) and the  $\beta$ -emitting  $\text{Sr}^{90}$ - $\gamma^{90}$  (50mC), both furnished by the French Atomic Energy Center of Fontenay-aux-Roses.--Spectrometry by nuclear particles was performed with the help of the device shown in fig. 3.--The  $\text{Ce}^{+3}$ -ion repartition and concentrations were checked with a Cameca Castaing electron microprobe.--The decay times were recorded using a boxcar Parr and the optical spectra with a Cary 17.--Transparent  $\text{Ce}^{+3}$ -activated silica and  $\text{SiO}_2$ - $\text{CeO}_2$ -ceramics have been prepared for us by "Quartz and Silice 3, Paris.  $\text{SiO}_2$ - $\text{CeO}_2$ -pellets have been obtained by pressing hydrostatically the powder mixtures and sintering them in air at 1150°C-1300°C.--The sputtering experiments were performed with the help of a magnetron-cool plasma unit especially designed for the deposition of high purity films and built at the "laboratoire de physique des matériaux" CNRS Bellevue.

IV. Results:    A.  $\text{Ce}^{+3}$  and  $\text{Ce}^{+3}, \text{Tb}^{+3}$ -activated high melting point glasses and sputtered glass films.

A. Excitation by UV-radiation. (253,7 nm)

1. Bulk glass: Fig. 4 and 5 show the emission spectra of  $\text{Ce}^{+3}$  in phosphate-, silicate-, borosilicate and boroaluminate glasses, compared to  $\text{YPO}_4/\text{Ce}^{+3}$ . The chemical composition has a strong effect on the intensity and on the shape of the emission spectra. Fig. 6 shows some excitation spectra. Fig. 7 presents the

luminescence of the two best Tb-activated glasses; the emission intensity is high. After grinding the glass to a powder the luminescence decreases strongly. Fig. 8 shows curves which demonstrate an efficient energy transfer from  $Ce^{+3}$  to  $Tb^{+3}$ -ions in a double activated phosphate glass.-(Energy transfer between other rare-earth ions ( $Tm^{+3}$  to  $Er^{+3}$  and  $Gd^{+3}$  to  $Tb^{+3}$ ) in low melting point glasses has already been described by Reisfeld). (11,12).--Table 2 shows the decay-times of the  $Ce^{+3}$ -ions in different glass systems. Two decay times have been found in each type of glass investigated. Thus, the  $Ce^{+3}$ -ions must occupy two different sites in all these very different glasses. Reisfeld has concluded (7) that the  $Ce^{+3}$ -ions in silicate glasses can occupy sites having a microsite-symmetry  $C_5$  or  $C_2$ .--Table 1 shows also the results of the etching experiments. (500hrs, 70°C, 4n nitric acid).

2. Glass films:  $Ce^{+3}$ -activated glass films (phosphate and silicate glasses) have been deposited by sputtering onto glass substrates by a Ar- $H_2$  (10%) plasma. The films have then to be treated in a Ar- $H_2$ -atmosphere in order to obtain the  $Ce^{+3}$ -emission. These films showed always a very inhomogenous luminescence; they had no useful luminescence properties.--The dependence of the  $Ce^{+3}$ -emission intensity of the Ce-concentration has been investigated in the phosphate glass type 3078, from .5 to 10 cation-%. The strongest emission has been obtained with a Ce-concentration of 10%. (See also table 1). This is remarkable enough: Apparently no concentration quenching occurs at such a high Ce-doping level. Yet this agrees with the finding of Blasse and Brill (14) who could not reveal a strong concentration quenching in the series  $La_{1-x}Ce_xPO_4$ . (polycrystalline powder).--When more  $CeO_2$  is introduced into the glass it remains yellow even after reduction and does no longer show useful luminescence properties. It was not possible, during the course of this work--the amount of experiments to do would have been too enormous--to evaluate the influence of the variation of the  $Ce^{+3}$ -concentration on its emission intensity in other glass types.

B.  $Ce^{+3}$ -luminescence in transparent bulk silica, silica-ceramic and sputtered silica films.

a. Transparent bulk silica: The max. concentration of  $Ce^{+3}$ -ions which can be introduced into this material prepared by fusion in an arc furnace is about

4 000 ppm. After reduction at 800 °C, 2 hrs, in Ar-10% H<sub>2</sub>, this material shows a strong luminescence. (fig. 9). Its decay times are given in table 2.

b. SiO<sub>2</sub>-CeO<sub>2</sub>-ceramics: Arc-furnace melted mixtures of SiO<sub>2</sub> and CeO<sub>2</sub> with Ce-concentrations from 4 000 ppm to 5 mole-% yield hard, mechanically very stable ceramics consisting of 2 phases: One is glassy silica containing some dissolved cerium ions, the second is a Ce-silicate. (fig. 10). After reduction in Ar-H<sub>2</sub>, the glassy part shows a strong Ce-emission under 253,7 nm excitation. The emission has been examined under a microscope.

c. Sputtered Ce<sup>+3</sup>-activated silica films.--It has been found impossible to prepare at acceptable costs, by grinding or etching of bulk material (glass or silica) slices having a thickness of 40 microns or less which show some reasonable surface qualities and retain some mechanical strength. Ion-beam etching may be a solution but we have no access, actually, to such an apparatus. We have therefore prepared Ce<sup>+3</sup>-activated SiO<sub>2</sub> thin films of suitable properties by high frequency sputtering. The targets were mixtures of SiO<sub>2</sub> and CeO<sub>2</sub>-powders or the SiO<sub>2</sub>-CeO<sub>2</sub>-ceramic described above, the substrate being transparent silica. The deposition rate is 4 000 to 8 000 Å/hr. The films were annealed in a Ar-H<sub>2</sub> (10%) atmosphere for 2 hrs, at 800°C. --Films having a thickness of 2 to 20 microns have been prepared. --Results: These amorphous films show a perfect adherence to their substrates, even after annealing. They emit strongly the typical Ce<sup>+3</sup>-fluorescence under UV (253,7 nm) and  $\alpha$ -radiation excitation. The emission differs somewhat from that of the doped bulk silica. (fig. 9). The optimum Ce-concentration is about 3 atom-%, but higher doped films (till 8%) still show a good luminescence. ---The introduction of such a high concentration of Ce-ions into the SiO<sub>2</sub>-films is only possible using the sputtering technic. Indeed the deposition of the molecules onto the cooled substrate freezes the material far from its thermodynamic equilibrium, i.e. the cerium oxide and silica molecules cannot move to form aggregates of silicates.

Conclusion.

While many  $\text{Ce}^{+3}$ -activated glasses of different type emit strongly under UV (253,7 nm) and  $\beta$ -ray excitation, only the commercial silicate glass NE 905 shows an useful emission when exposed to  $\alpha$ -particles.

Only phosphate glasses have given the green  $\text{Tb}^{+3}$ -emission, when doped by it, under UV and  $\alpha$  and  $\beta$  radiation.

Sputtered films of  $\text{Ce}^{+3}$ -activated silica have appropriate luminescence properties, adherence to the substrate and a perfect chemical resistance to hot nitric acid.

A  $\alpha$ -particle detector has been built which has permitted the quantitative detection of plutonium in the presence of other radiative ions.--A patent application has been made.(13)

We thank "Quartz et Silice", Paris, for the preparation of  $\text{Ce}^{+3}$ - activated transparent silica and  $\text{SiO}_2$ - $\text{CeO}_2$ -ceramic.

We are indepted to Dr. Blanzat, CNRS, for the decay time measurements.

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Emission spectra of some thin films. - X-excitation.

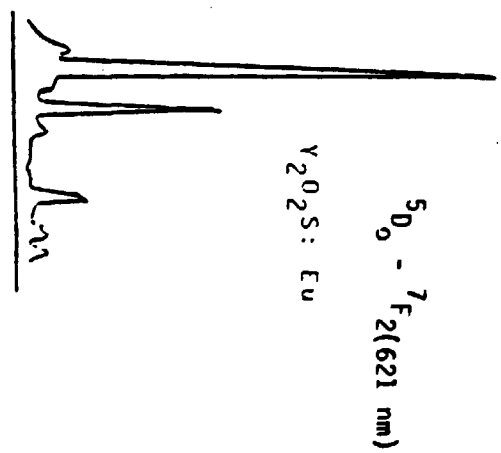
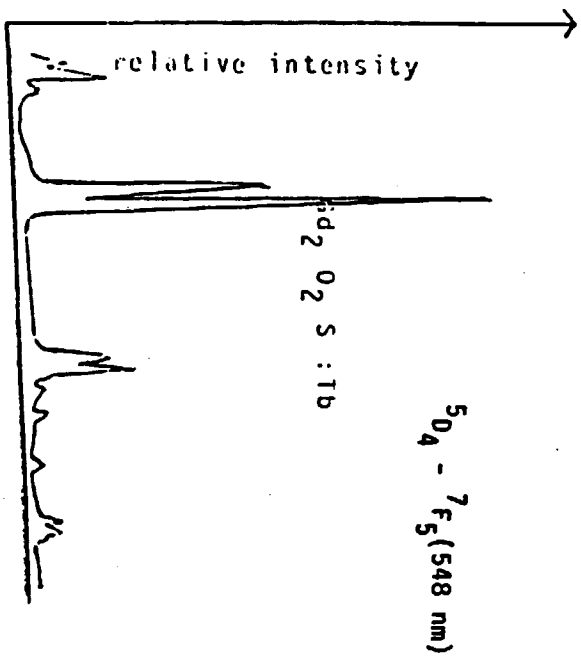


Fig. 1

$\alpha$ -excitation of some sputtered thin films.

EMISSION SPECTRA.

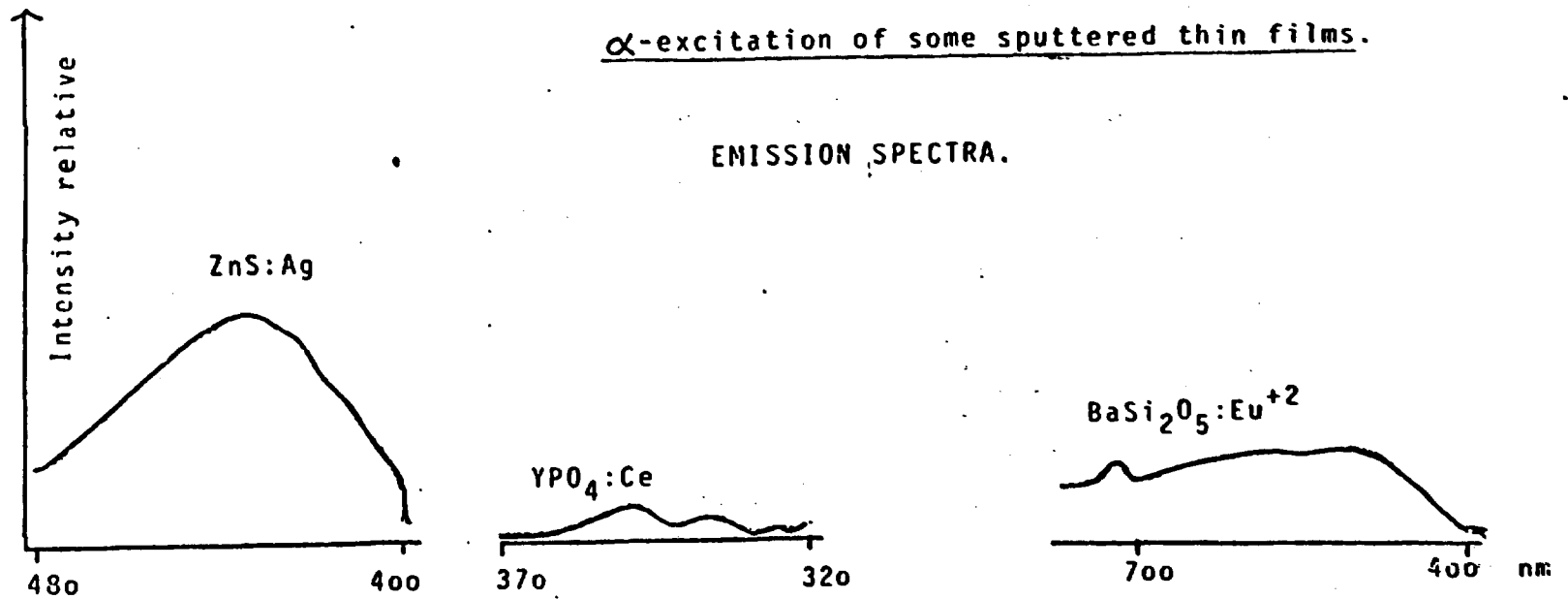


FIG. 2

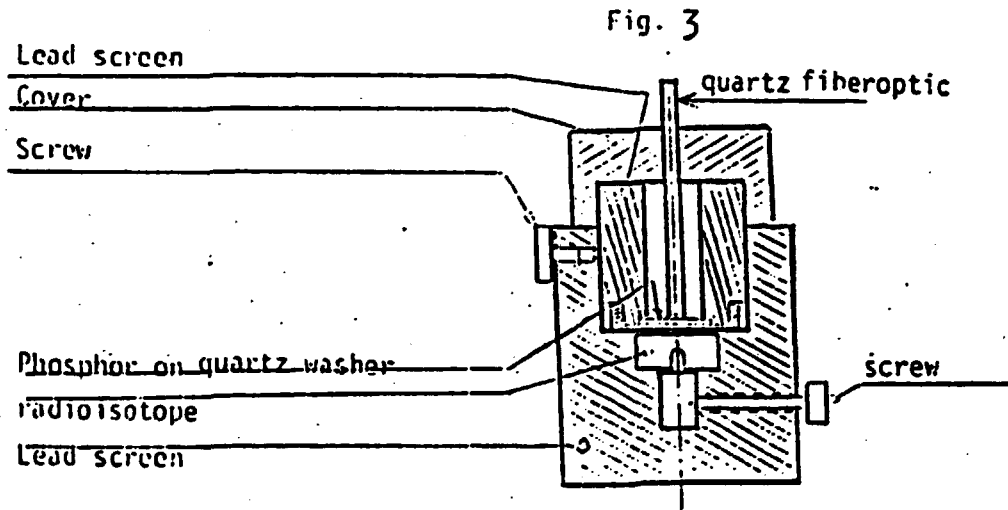
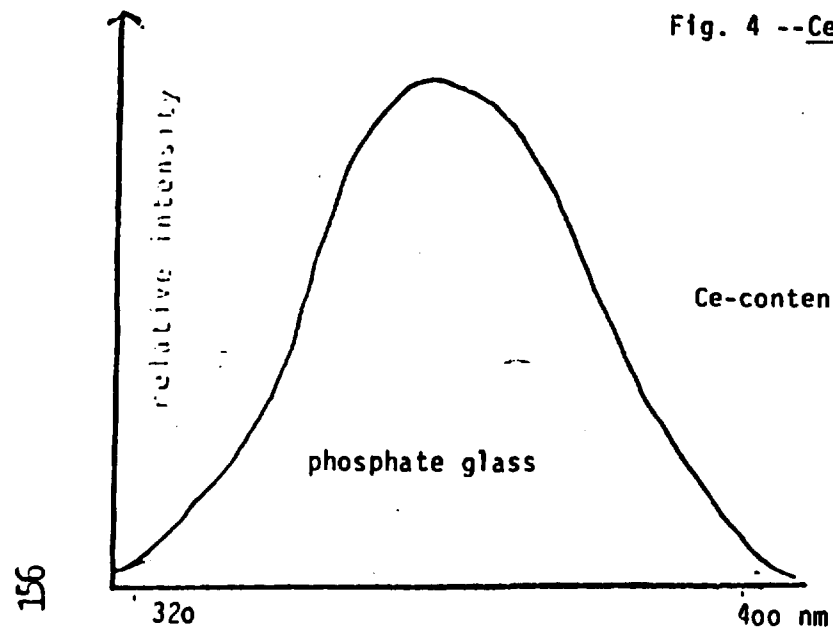
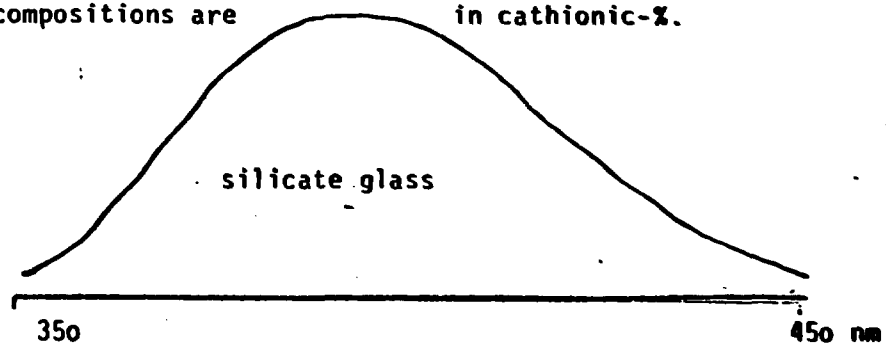


Fig. 4 --Ce<sup>+3</sup>-emission spectra.



P/ 56.3--Ca:5.3--Na:31.6--Al: 4.8  
type nr. 3078

Ce-content: 2 %.- The compositions are in cationic-%.



Si:56.2--Ba:17.3--K:24.5  
type nr. 5 007

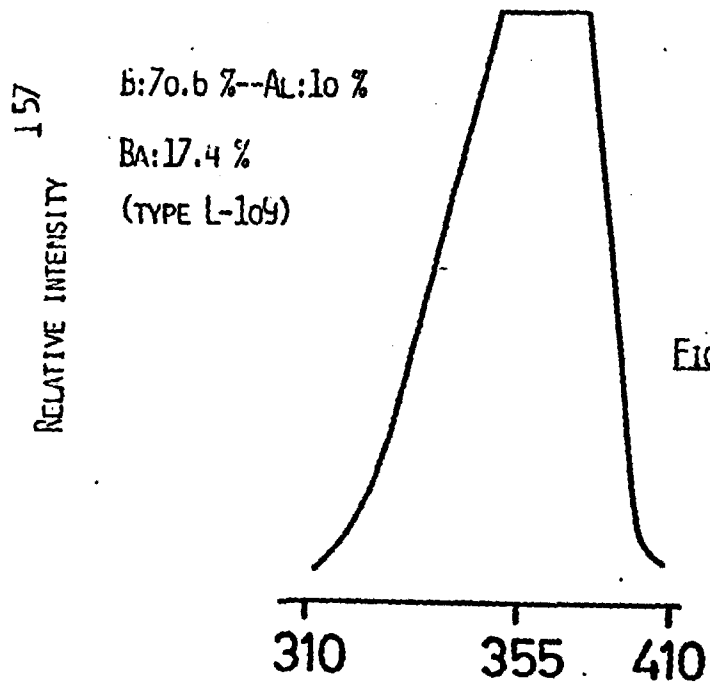
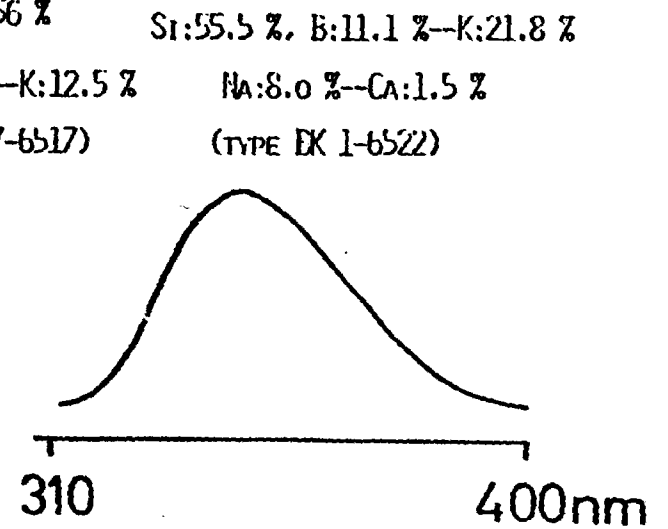
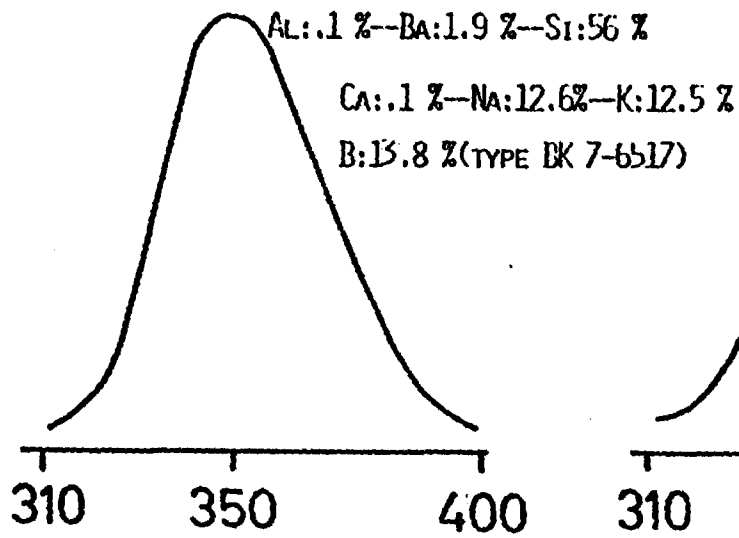
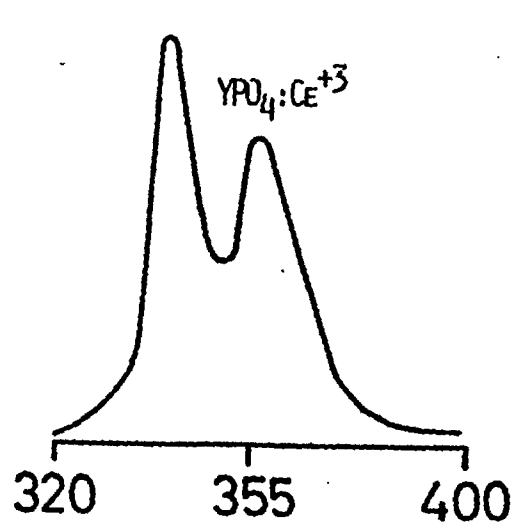
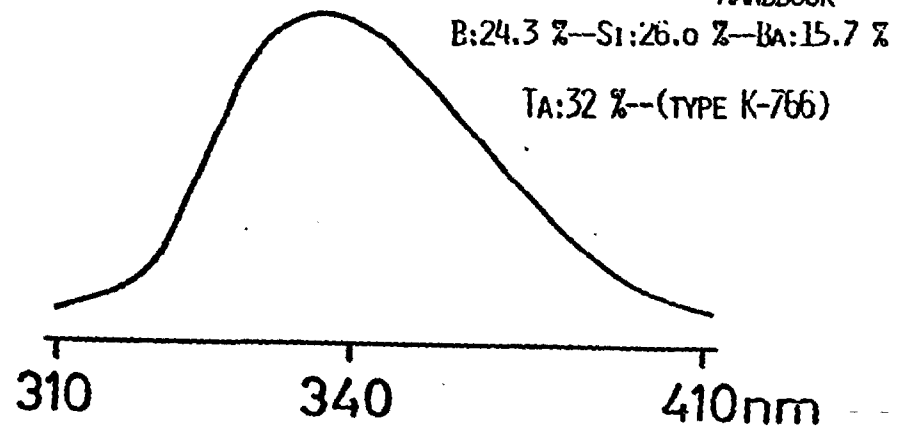


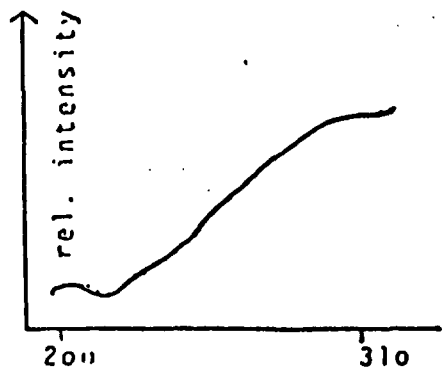
FIG. 5

Ce<sup>+3</sup>-EMISSIONSPECTRA--EXCITATION: 253.7 nm

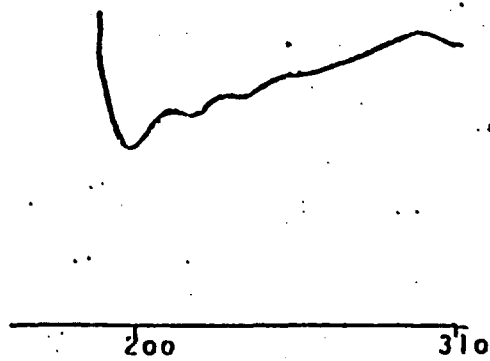
THE CERIUM CONTENT IS 2%.- THE COMPOSITIONS ARE IN CATHIONIC-%.

THE GLASS TYPES HAVE BEEN CHOSEN IN THE L.LIVERMORE UNIVERSITY GLASS HANDBOOK

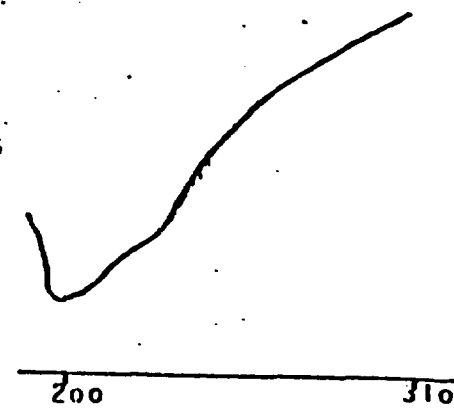




phosphate glass, type 3o78



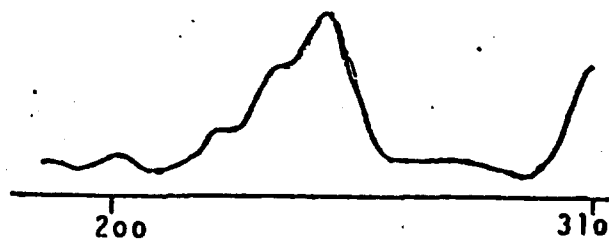
borosilicate glass, type BK 7  
6517



silicate glass C 9o5

EXCITATION SPECTRA of  $Ce^{+3}$  in some glasses.  
(2% Ce-content).

Fig. 6



$YPO_4:Ce^{+3}$  (2 mole-%)

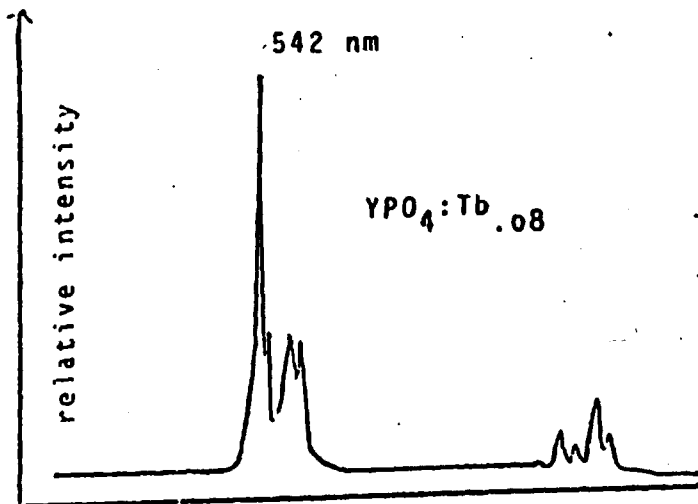
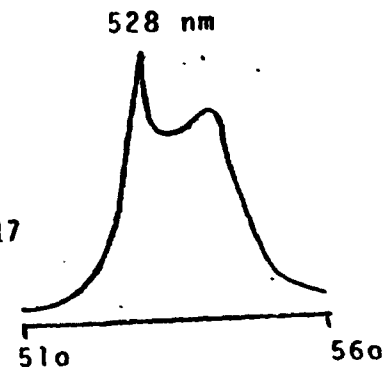


Fig. 7



EMISSIONSPECTRA of  $\text{Tb}^{+3}$  in some glasses.

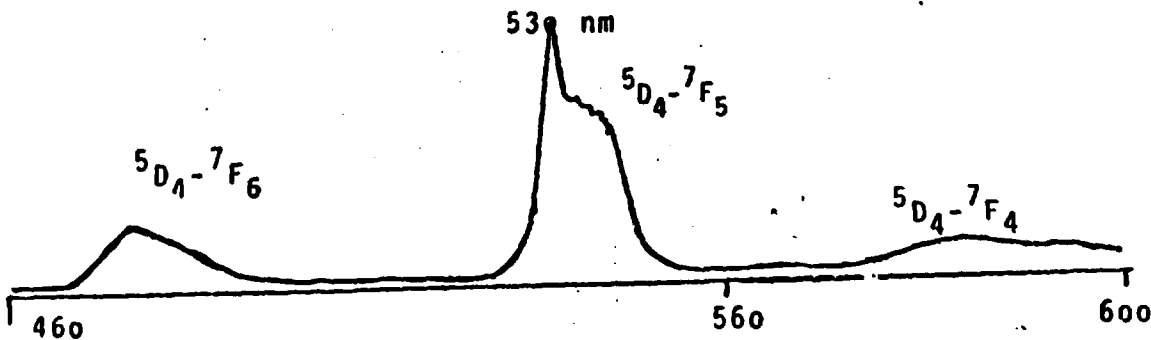
Excitation: 253.7 nm

Tb-content: 2 cationic-%.

159

phosphate glass-  
type 3078

phosphate glass,  
(powder)  
type 3078

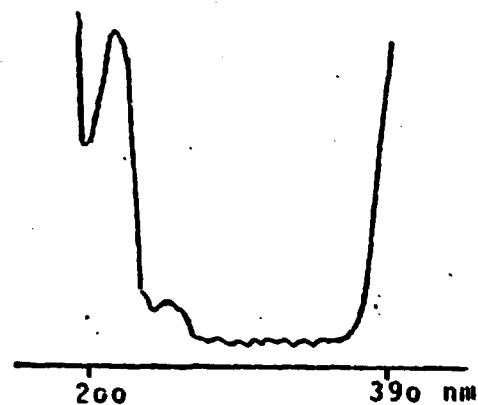
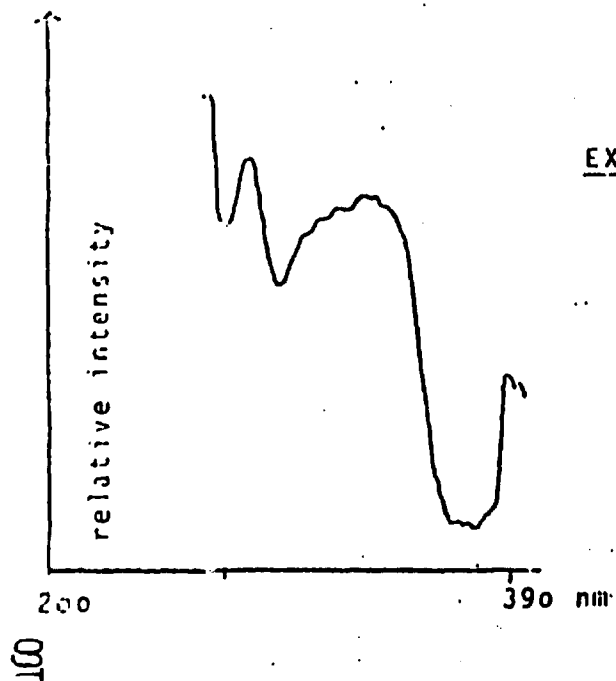


Energy transfer Ce—Tb in a phosphate glass.  
(type 3o78)

EXCITATIONSPECTRA

(Tb-emission)

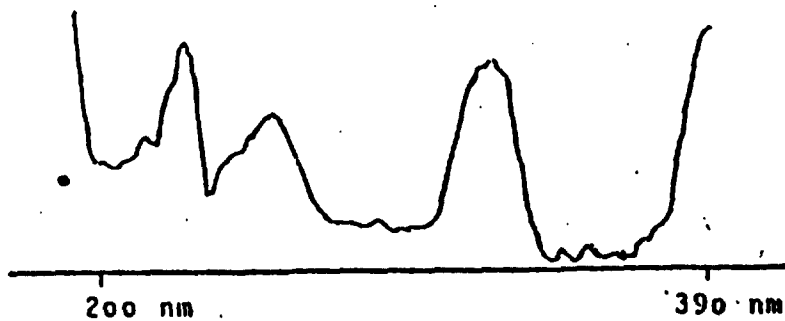
Fig. 8



glass activated by  
4% Ce<sup>+3</sup> and 2% Tb<sup>+3</sup>.

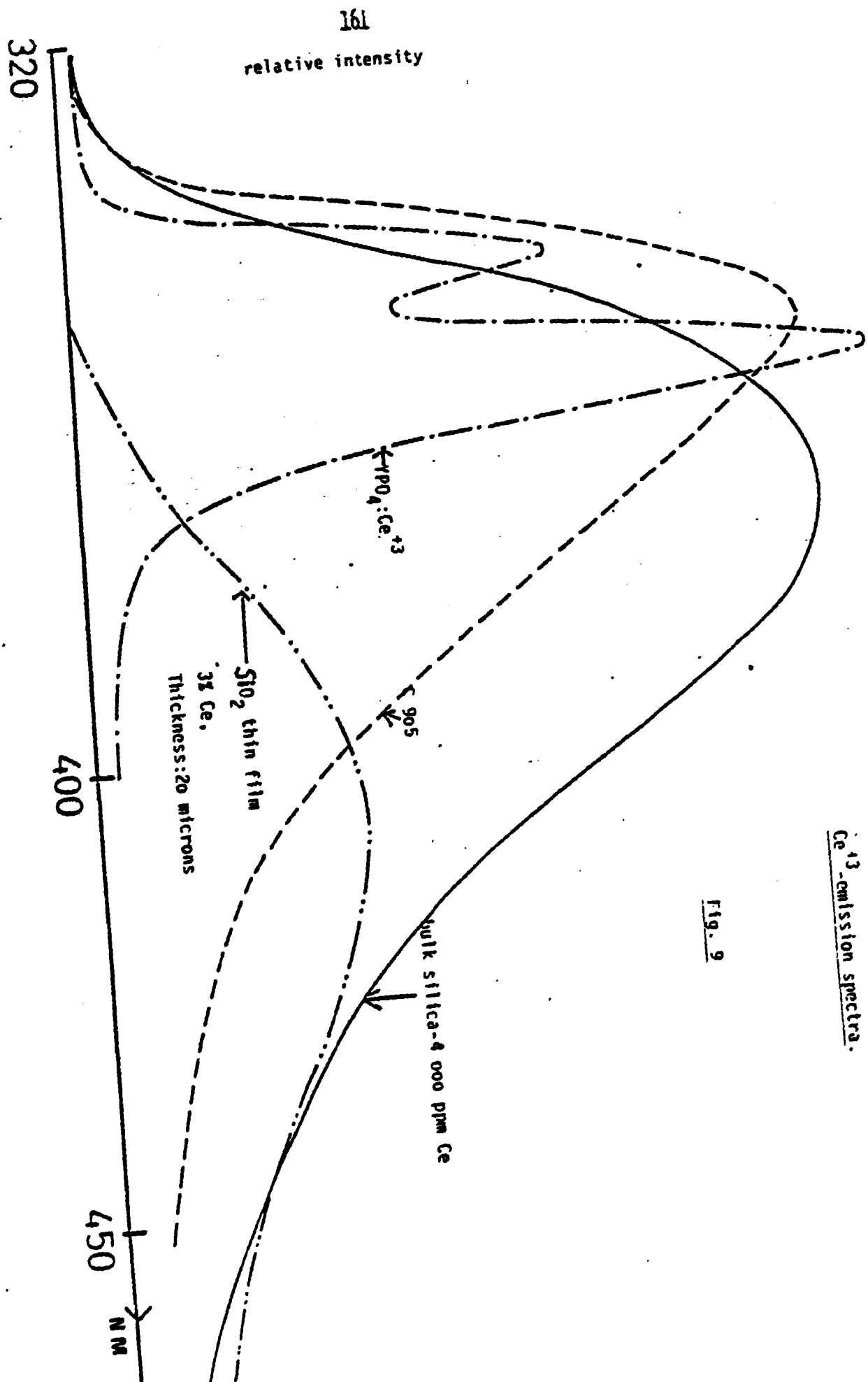
glass activated by  
2% Tb<sup>+3</sup>

The concentrations are in the glasses  
in cationic-%



YPO<sub>4</sub>: 4 mole-% Ce<sup>+3</sup>, 2 mole-% Tb<sup>+3</sup>

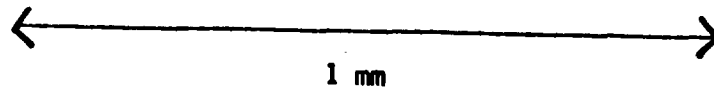
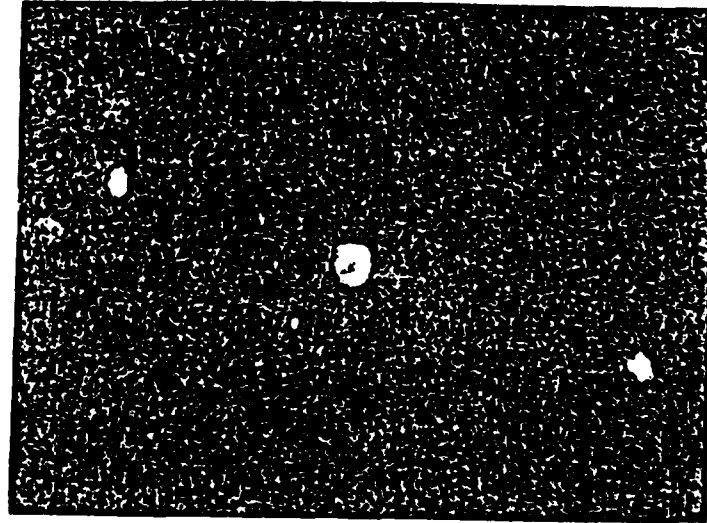




<sup>137</sup>Ce emission spectra.

Fig. 9

Fig. 10.



Micrograph of a  $\text{SiO}_2\text{-CeO}_2(4\%)$  ceramic.

White spots: Ce-silicates

Table 1

type	chemical attack	relat. emis- sion intensity	excitation	maximum of the emission.
NE C 905-silicate glass.-see also table 2	very slight	2	$\alpha$	340
		60	$\beta$	
borosilicate glass type BK 7-6517	slight	0	$\alpha$	350
		220	$\beta$	
phosphate glass, type nr. 3078-10%Ce	strong	0	$\alpha$	355
		160	$\beta$	
phosphate glass type nr. 3078, 3% Ce	strong	0	$\alpha$	355
		120	$\beta$	
phosphate glass, type nr. 3078, 2% Tb (1)	strong	3	$\alpha$	530
		80	$\beta$	
YPO <sub>4</sub> :Ce <sup>+3</sup> (2%)		100	$\alpha$	355, 330
		100	$\beta$	

1: Compared to YPO<sub>4</sub>-2 mole-% Tb

Table 2.

Type of glass	decaytime I (nsecs.)	decaytime II (nsecs.)
phosphate glass nr. 3078	51	23,5
silicate glass: SiO <sub>2</sub> :60.-MgO:27.-Al <sub>2</sub> O <sub>3</sub> : 9 CeO <sub>2</sub> : 4 mole-% (type NE C 905)	58	23
SiO <sub>2</sub> -4 000 ppm CeO <sub>2</sub>	61	24
borosilicate type BK 7 6517 (2 % CeO <sub>2</sub> )	54	22
borosilicate BK 1- 6522	52	20.5
borate glass L-109	50	22