



CHAPTER - III

ABSORPTION AND EMISSION SPECTRA

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## ABSORPTION AND EMISSION SPECTRA

### 3-1 INTRODUCTION:

Phosphors owe their practical importance due to their ability to emit different colours in visible spectral region. In general, impurity activation is needed for this purpose though vacancy may also be useful. The spectral distribution of absorbed bands is known as absorption spectra while the spectral distribution of emitted radiation is known as emission spectra. These studies are important in understanding the energy levels in the phosphors and many times yield valuable information about the nature of luminescent centres and energy transfer mechanism. It is said that the measurements of absorption and emission spectra are complimentary to each other (1) The process of luminescence can fully be explained resorting to energy level diagram constructed from spectral studies.

The aim of the present investigation is to analyse the observations of absorption and emission spectra so as to obtain the following information:-

- 1) Spectral distribution of emitted radiation,
- 2) Nature and origin of emission and absorption bands,
- 3) Effect of addition of activators and fluxes on emission and absorption characteristics,
- 4) An insight into mechanism of energy transfer, and;
- 5) To construct an energy level diagram for the phosphor system.

### 3-2 THEORETICAL BACKGROUND:

#### 3-2.1 Luminescence Spectra:

The spectral distribution of emission from a phosphor is a function of -

- i) structure and intrinsic degree of perfection of the host material,
- ii) the kind and amount of incorporated impurities, their valencies, and locations in the materials, and;
- iii) the temperature of the phosphor during the luminescence.

For instance, ZnS:Cu in a hexagonal structure emits a band close to  $5230 \text{ \AA}^{\circ}$ , while in cubic structure, emitted band is near  $5350 \text{ \AA}^{\circ}$ . The blue emission of self-activated ZnS shifts to longer wavelength side as the temperature is lowered down to  $90^{\circ}\text{K}$ , while the blue emission due to copper is shifted in opposite direction. The yellow to red emissions also appear when conventional ZnS phosphors are cooled rapidly after preparation.

#### 3-2.2 The Spectra of Free Ions:

The spectra of free ions can be described with the help of energy level diagram which may be derived from the Vector atom model. The Vector atom model includes two coupling schemes, namely, (i) L-S coupling, and (ii) J-J coupling.

In the L-S coupling scheme, several spin vectors (s) of the electrons combine to form a resultant Vector S, the several orbital vectors (l) of the electrons likewise combine to form a resultant vector l and then, S and L subsequently combine to form J. This is represented by -

$$\sum_i s_i + \sum_j l_j = S + L = J$$

L takes all integral values from zero i.e. 0, 1, 2, ... etc., while S is an integer or half integer; depending on the no. of electrons involved and on the direction of the spin vectors. The multiplicity of L is given by the quantity (2s+1).

In J-J coupling, each electron is considered separately, and its contribution to the orbital angular momentum of the atom is obtained by combining first its individual spin and orbital vectors by the relation  $J = l + s$ . The resultant vector J is obtained by -

$$\begin{aligned} & (l_1 + s_1) + (l_2 + s_2) + (l_3 + s_3) + \dots \\ & = j_1 + j_2 + j_3 + \dots \\ & = J \end{aligned}$$

### 3-2.3 Interaction of the Ions with the Lattice:

There are several manifestations of the interaction between the ion and the lattice. The crystal field splitting of atomic levels is the most obvious one. When an ion is incorporated in a solid, the electronic transitions responsible

for the emission spectra are governed by the Coulomb interactions ( $H_1$ ), the spin orbit interaction ( $H_2$ ) and the crystal field perturbation ( $H_3$ ).

The electrostatic Coulomb interaction amongst the electrons is given by the term.

$$H_1 = (e^2/r_{ij})$$

and is clearly a two electron operator. To calculate the effect of  $H_1$  on the electron states resulting from central field Hamiltonian; (considering the total orbital ( $L$ ) and the spin angular ( $S$ ) momenta of all the electrons, the electrons, the product states are constructed) the Coulomb term  $1/r_{ij}$  is then expanded in terms of spherical harmonics, and matrix elements of  $H_1$  are calculated between the product states.

The next level of approximation for an ion in crystal considers the perturbation terms arising due to spin orbit interaction ( $H_2$ ) and crystal field perturbation ( $H_3$ ).

The spin orbit interaction term is given as -

$$H_2 = \sum_{i=1}^n \xi_i s_i l_i$$

Where  $S$  is the spin quantum number,  $l$  is orbital quantum number, and  $\xi$  is the spin orbit parameter.

If the spin orbit interaction ( $H_2$ ) is much smaller than the Coulomb interaction ( $H_1$ ) then L-S coupling approximation can be used. The Hamiltonian ( $H_2$ ) splits  $(2S+1)$  multiplets into levels of total angular momentum.

$J = (L+S), (L+S-1), \dots, (L-S)$ , Each of these  $J$  levels is then  $(2J+1)$  fold degenerate. This can be perturbed by the application of electric and magnetic fields.

If the spin orbit interaction ( $H_2$ ) is not small compared to Coulomb interaction ( $H_1$ ) then  $L$  and  $S$  are no longer good quantum numbers. In the limit that  $H_2 \gg H_1$  the J-J coupling scheme is preferable. The spin and orbital components of the  $i^{\text{th}}$  electron couple to form angular momentum  $J$ , the various values of  $j$  then couple to form the total angular momentum. For rare earth ions, L-S coupling often serves a good to a first approximation but  $H_2$  is sufficiently larger to mix in wavefunctions of other multiplets and the true coupling is intermediate.

The crystal field perturbing potential encountered by placing an ion in the solid is

$$\begin{aligned} H_3 &= H(\text{stark}) + H(\text{exchange}) \\ &= V(\text{crystal field}) + 2A \sum_{ij} S_{ij} \end{aligned}$$

Where  $V(\text{crystal field})$  is the electronic potential generated by the nearest neighbours, electrons labelled

with subscript 1st reside on the perturbed ion, electrons with subscript 2nd reside on the exchange coupled neighbours and  $A$  is the exchange energy involved. In a special case of cubic symmetry, the crystal field Mamiltonian can be written as:-

$$H_3 = B_4 (C_4^0 + 5.C_4^4) + B_6 (O_6^0 - 21.O_6^4)$$

Where  $B_4$  and  $B_6$  are fourth order and sixth order cubic field parameters and  $O_n^m$  are angular momentum operator equivalent expressions for the spherical harmonics.

Crystal field spectra result from the effect of crystal field (environment) on the energy levels of the ions. They are recognised by their low intensity and their occurrence in the low energy spectral region (below  $50,000 \text{ cm}^{-1}$ ). An extensive literature on crystal field effect and its significance has been reviewed by McClure (2) and Ballhausen(3).

#### 3-2.4 Absorption & Emission Occuring at the same Centre:

Because of the surrounding lattice, the electronic transitions between different energy levels of a centre will be superposed by the vibrational transitions of the crystal through phonon interaction. This has the effect of broadening out the energy levels. Each discrete energy level corresponding to an isolated atom stretches out into a band of closely packed energy levels in the case of a

luminescence centre. The energy difference between an excited state of such a centre and its ground state, instead of being sharply single valued, has a quasi-continuous range of allowed values; consequently the frequency of an absorbed or emitted radiation, effected by the transition between excited and ground state and given by the equation  $\nu = (E_2 - E_1)/h$  has also a range of values. This explains the band nature of absorption, excitation and emission spectrum of a phosphor. In case of rare earth activated phosphor, the emission obtained from rare earth ion is line spectrum because of its incomplete 4f shell. This is shielded by outside shells which are completely filled and hence protected from the effects of surrounding lattice(5,7).

### 3-3 RESULTS AND DISCUSSION:

#### 3-3.1 Absorption Spectra:

Absorption characteristics of CaO:Bi:Sm phosphors without and with fluxes ( $\text{Na}_2\text{S}_2\text{O}_3$ ;  $\text{Na}_2\text{SO}_4$ ; NaF) have been studied in the wavelength range of 3500  $\text{\AA}^\circ$  to 6000  $\text{\AA}^\circ$ . The curves have been plotted after suitably shifting the ordinates to avoid overlapping and rendering their mutual comparison easier. Some of the curves thus obtained for various samples are shown in figures 3.1 to 3.7.

A) CaO:Bi Phosphors (with flux):

Figs.3.1 and 3.2 show the optical absorption spectra for samples containing varying concentrations of  $\text{Bi}^{3+}$ . It may be seen from the fig.3.1 that the undoped sample,  $\text{S}_0$ , exhibits absorption bands at about  $4200 \text{ \AA}^\circ$ ,  $4400 \text{ \AA}^\circ$ ,  $4600 \text{ \AA}^\circ$ ,  $4800 \text{ \AA}^\circ$ ,  $5000 \text{ \AA}^\circ$ ,  $5400 \text{ \AA}^\circ$ , and at  $5800 \text{ \AA}^\circ$  with an increase in absorption towards the shorter wavelength side ( i.e. from  $3700 \text{ \AA}^\circ$  ). The peaks observed at about  $5000 \text{ \AA}^\circ$  and  $5400 \text{ \AA}^\circ$  are pronounced while other ones are weaker. When activator  $\text{Bi}^{3+}$  is added to the host lattice, a band at about  $3700 \text{ \AA}^\circ$  appears and a band at about  $5800 \text{ \AA}^\circ$  shifts towards the shorter wavelength side (see curve 2, fig.3.1). With further increase in  $\text{Bi}^{3+}$  concentration no systematic change in band positions and intensities is observed. For example, the  $5800 \text{ \AA}^\circ$  band disappears for sample  $\text{S}_7$ ,  $3700 \text{ \AA}^\circ$  band shifts to  $3900 \text{ \AA}^\circ$  in case of samples  $\text{S}_3$  and  $\text{S}_6$  and bands observed at about  $4200 \text{ \AA}^\circ$  and  $4800 \text{ \AA}^\circ$  in case of sample  $\text{S}_1$  disappear for sample  $\text{S}_3$  and again appear for  $\text{S}_6$  and  $\text{S}_7$ . At higher concentration of  $\text{Bi}^{3+}$  however, some interesting results are observed. The intensities of bands in  $3700 \text{ \AA}^\circ$  and  $4500 \text{ \AA}^\circ$  wavelength range go on increasing (see fig.3.2) and absorption towards higher wavelength side becomes predominant. Moreover, a band at about  $4000 \text{ \AA}^\circ$  is seen for samples  $\text{S}_9$  and  $\text{S}_{10}$  (fig.3.2. curves 3 and 4).

From the above results it may be concluded that:

- 1) Addition of  $\text{Bi}^{3+}$  does give rise to new absorption bands but the observed bands appear and disappear with increase in  $\text{Bi}^{3+}$  concentration.
- 2) Higher concentration of  $\text{Bi}^{3+}$  causes to increase the intensity of absorption bands in the  $3500 \text{ \AA}$  to  $4500 \text{ \AA}$  wavelength range.
- 3) At higher concentration of  $\text{Bi}^{3+}$  absorption increases towards longer wavelength side.
- 4) The addition and changing  $\text{Bi}^{3+}$  concentration does influence the general feature of absorption spectra but the observed change is not systematic and notable.

B) CaO:Sm Phosphors (With flux):

Optical absorption spectra for samples containing varying concentration of  $\text{Sm}^{3+}$  is shown in figs. 3.3 and 3.4. From the figs. it may be seen that the addition of  $\text{Sm}^{3+}$  does not change the peak positions appreciably, but it causes for appearance and disappearance of some of the bands when compared with the spectra of sample  $S_0$ , the sample containing zero concentration of  $\text{Sm}^{3+}$ . For example, a band at about  $3700 \text{ \AA}$  is seen for samples  $S_{13}$ ,  $S_{14}$ ,  $S_{15}$ ,  $S_{19}$  and  $S_{20}$ , while  $4000 \text{ \AA}$  band is observed for samples  $S_{11}$ ,  $S_{12}$ ,  $S_{18}$ ,  $S_{19}$  and  $S_{20}$ .

Moreover, the band at about  $5800 \text{ \AA}^{\circ}$  is seen to be disappeared for samples  $S_{12}$ ,  $S_{13}$ ,  $S_{14}$ ,  $S_{15}$  and  $S_{16}$  but it again appears in case of samples  $S_{17}$ ,  $S_{18}$ ,  $S_{19}$  and  $S_{20}$ . Here, it should be noted that the absorption level of all bands remains almost the same.

Above results suggest that, whatever change has been observed as regards to the position of bands, band intensities, appearance and disappearance of bands with the addition of  $\text{Sm}^{3+}$  is small and unsystematic.

C) CaO:Bi:Sm Phosphors (With Flux):

In fig.3.5 optical absorption spectra for samples containing fixed concentration of  $\text{Sm}^{3+}$  and varying concentration of  $\text{Bi}^{3+}$  is shown while in fig.3.6, the absorption spectra for samples containing fixed concentration of  $\text{Bi}^{3+}$  and varying concentration of  $\text{Sm}^{3+}$  is given. These figs., when observed closely reveal that changing concentration of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  keeping other constant does influence the absorption characteristics. The absorption spectra obtained for sample CaO:Sm ( $S_{16}$ ) exhibits peaks at about  $3900 \text{ \AA}^{\circ}$ ,  $4200 \text{ \AA}^{\circ}$ ,  $4400 \text{ \AA}^{\circ}$ ,  $4800 \text{ \AA}^{\circ}$ ,  $5000 \text{ \AA}^{\circ}$  and  $5400 \text{ \AA}^{\circ}$ . However, with addition of  $\text{Bi}^{3+}$  additional peaks at about  $3700 \text{ \AA}^{\circ}$ ,  $4600 \text{ \AA}^{\circ}$  and at  $5800 \text{ \AA}^{\circ}$  are observed. When concentration of  $\text{Bi}^{3+}$  is made higher the peaks at about  $4400 \text{ \AA}^{\circ}$ , and  $4800 \text{ \AA}^{\circ}$  are seen to be disappeared (fig.3.5). With changing concentration of  $\text{Sm}^{3+}$  keeping  $\text{Bi}^{3+}$  constant (fig.3.6)

a band at about  $3700 \text{ \AA}^\circ$  appears and a band at about  $5800 \text{ \AA}^\circ$  disappears. Moreover, with the further addition of  $\text{Sm}^{3+}$  some of the bands appear ( $4200 \text{ \AA}^\circ$ , curves 4,5,6) and disappear ( $4400 \text{ \AA}^\circ$ , curves 4,5,6) in an unsystematic manner. The inference to be drawn from these results is that addition and varying concentration of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  in presence of other does give rise to new bands and affect the general nature of absorption spectra, but not in systematic manner.

D) Fluxed & Unfluxed Samples:

To see the effect of flux on absorption and emission characteristics, CaO, CaO:Sm and CaO:Bi samples prepared with and without flux ( $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_4$ , NaF) were studied. The absorption curves obtained for such samples are given in fig.3.7.

1) CaO:

Curves 1 and 2 of fig.3.7 show the absorption spectrum for unfluxed and fluxed CaO respectively. The absorption spectrum of unfluxed CaO exhibits peaks at about  $4000 \text{ \AA}^\circ$ ,  $4200 \text{ \AA}^\circ$ ,  $4400 \text{ \AA}^\circ$ ,  $4600 \text{ \AA}^\circ$ ,  $4800 \text{ \AA}^\circ$ ,  $5000 \text{ \AA}^\circ$ ,  $5400 \text{ \AA}^\circ$  and at  $5800 \text{ \AA}^\circ$  with decreasing absorption towards the shorter wavelength side (below  $4000 \text{ \AA}^\circ$ ). Addition of flux causes to suppress the band at about  $4000 \text{ \AA}^\circ$  with other bands remaining almost at same wavelength. The flux also causes to increase the absorption towards shorter wavelength side.

2) CaO:Sm:

The comparison of curves 3 and 4, which are for unfluxed and fluxed samples respectively, indicates that the spectra for unfluxed and fluxed samples are almost similar except that peak at about  $3900 \text{ \AA}^{\circ}$  appears and a peak at about  $4800 \text{ \AA}^{\circ}$  disappear for fluxed sample. Moreover, a little change is also observed in peak intensities for fluxed samples.

3) CaO:Bi :

Curves 5 and 6 of fig.3.7 correspond to CaO:Bi samples without and with flux respectively. Incorporation of flux gives interesting results as regards to the position and intensity of bands and also about the amount of absorption. The unfluxed CaO:Bi exhibits bands at about  $3700 \text{ \AA}^{\circ}$ ,  $3900 \text{ \AA}^{\circ}$ ,  $4400 \text{ \AA}^{\circ}$ ,  $4600 \text{ \AA}^{\circ}$ ,  $5000 \text{ \AA}^{\circ}$ ,  $5400 \text{ \AA}^{\circ}$  and at  $5800 \text{ \AA}^{\circ}$  while fluxed CaO:Bi has the bands at about  $3900 \text{ \AA}^{\circ}$ ,  $4000 \text{ \AA}^{\circ}$ ,  $4800 \text{ \AA}^{\circ}$ ,  $5000 \text{ \AA}^{\circ}$  and at  $5600 \text{ \AA}^{\circ}$ . Thus addition of flux causes to disappearance of bands at about  $3700 \text{ \AA}^{\circ}$ ,  $4600 \text{ \AA}^{\circ}$ ,  $5400 \text{ \AA}^{\circ}$  and  $5800 \text{ \AA}^{\circ}$  and appearance of additional bands at about  $4000 \text{ \AA}^{\circ}$ ,  $4800 \text{ \AA}^{\circ}$  and  $5600 \text{ \AA}^{\circ}$ . Moreover, addition of flux results into enormous increase in absorption level towards the longer wavelength side.

Above results lead to the following conclusions:

- 1) Absorption bands observed for unfluxed CaO is likely to be the property of host lattice.

- 2) Incorporation of flux into the CaO lattice either alone or alongwith  $\text{Sm}^{3+}$  or  $\text{Bi}^{3+}$  causes for appearance and disappearance of some of the bands indicating thereby flux introduces absorption centres into the host lattice.
- 3) Addition of flux in either presence or absence of activators ( $\text{Bi}^{3+}$ ,  $\text{Sm}^{3+}$ ) affects the amount of absorption either towards shorter wavelength side or longer wavelength side but the observed effect is not systematic in nature.

### 3-3.2 Nature & Origin of Absorption Bands:

Willi Lehmann (4) has studied extensively absorption and emission characteristics of CaO phosphor activated with various impurity elements and had reported a strong optical absorption at about 6.5 eV for purest CaO powder. Although part of this absorption might be due to various lattice defects obscuring true band gap of CaO which is likely to be some what under than 6.5 eV ( $\approx 191.2\text{nm}$ ). Moreover, according to Willi Lehmann CaO phosphors can not be excited optically across the band gap using 254 nm ( $= 4.9$  eV) radiations. In the present investigation, absorption spectra has been studied in the range 350 nm ( $= 3.5\text{eV}$ ) to 600 nm ( $= 2.07$  eV) the energy too small to excise the CaO phosphors across the band gap. Thus the absorption bands observed in the present investigation for various sample studied could be attributed

to the defects in the host lattice created during synthesis of phosphors at high temperature and/or due to incorporation of fluxes and activators ( $\text{Bi}^{3+}$ ,  $\text{Sm}^{3+}$ ) into the host lattice(5).

### 3-4 Emission Spectra:

The emission spectra for various samples are observed in the visible region (range  $4000 \text{ \AA}^{\circ}$  to  $6250 \text{ \AA}^{\circ}$ ) of the spectrum, under  $3650 \text{ \AA}^{\circ}$  UV. The measurements have been made at room temperature,  $302^{\circ}\text{K}$ . The curves have been plotted after normalising the intensity of a peak centered at  $5890 \text{ \AA}^{\circ}$  to a value 100 and suitably shifting the ordinates to avoid overlapping and rendering their mutual comparison easier. The emission spectra thus obtained for various samples are shown in figs.3.8 to 3.14 while the intensity of observed bands is summarised in table 3.1.

#### A) CaO:Bi Phosphors (With Flux):

Fig.3.8 and 3.9 show the spectral distribution of emission intensities for CaO phosphors doped with varying amounts of  $\text{Bi}^{3+}$ . The plot for undoped CaO is also shown in fig.3.8 (curve  $S_0$ ) for comparison. It is seen that undoped CaO exhibits three well defined peaks centered at about  $4500 \text{ \AA}^{\circ}$ ,  $5250 \text{ \AA}^{\circ}$  and  $5890 \text{ \AA}^{\circ}$ . With addition of  $\text{Bi}^{3+}$  a new peak at about  $4250 \text{ \AA}^{\circ}$  appears but with further increase in concentration of  $\text{Bi}^{3+}$  the general nature of emission spectra remains almost same. The inference to be drawn from these

results in that  $\text{Bi}^{3+}$  causes to emit in the violet-blue region.

B) CaO:Sm Phosphors (With Flux):

The emission spectra obtained for samples containing varying concentration of  $\text{Sm}^{3+}$  are shown in figs.3.10 and 3.11 alongwith the curve obtained for a sample containing zero concentration of  $\text{Sm}^{3+}$  (curve  $S_0$  fig.3.10). It may be seen from the figs. that the addition and changing concentration of  $\text{Sm}^{3+}$  has the following effects:-

- 1) a new band at about  $4250 \text{ \AA}^{\circ}$  appears,
- 2) intensity of band centered at about  $4500 \text{ \AA}^{\circ}$  decreases,
- 3) a band at about  $5250 \text{ \AA}^{\circ}$  disappears and;
- 4) emission in orange-red region i.e. from  $5890 \text{ \AA}^{\circ}$  goes on increasing with  $\text{Sm}^{3+}$  concentration.

Thus from these results it may be concluded that the addition of  $\text{Sm}^{3+}$  into the host lattice causes to absorb emission at about  $5250 \text{ \AA}^{\circ}$  and emit into orange-red region i.e. beyond  $5890 \text{ \AA}^{\circ}$ .

C) CaO:Bi:Sm Phosphors (With Flux):

Optical emission spectra for samples containing fixed concentration of  $\text{Sm}^{3+}$  and varying concentration of  $\text{Bi}^{3+}$  are shown in fig.3.12 while the emission spectra for samples with fixed concentration of  $\text{Bi}^{3+}$  and varying concentration

of  $\text{Sm}^{3+}$  are shown in fig.3.13. From the figs. it is clear that the addition of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  in presence of other influences the emission characteristics of studied phosphors. The changing concentration of  $\text{Bi}^{3+}$  has the tendency to give rise to a peak at about  $5250 \text{ \AA}^{\circ}$  and to entrance the emission in blue-violet region with quenching the emission in orange-red region. Whereas, addition of  $\text{Sm}^{3+}$  causes to enhance the emission in orange-red region with the decrease in emission intensity of a band at about  $5250 \text{ \AA}^{\circ}$ .

From these results it may be inferred that when  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  is added in the presence of each other they cause to give their own characteristic emission meaning thereby activators  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  introduce new luminescence centre into the host lattice.

D) Fluxed and Unfluxed Samples:

Fig.3.14 show the emission characteristics of fluxed and unfluxed samples. When fluxes ( $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_4$ , Naf) are added to CaO, a additional band is observed at about  $5250 \text{ \AA}^{\circ}$  (see curves 1 and 2). The emission spectra for fluxed and unfluxed samples containing either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  is more or less similar except that slight perturbation in peak positions and intensities. These results indicate that the effect of flux could only be observed in the absence of activators.

3-5 Summary:

The principal finding of this chapter can be summarised as follows:-

- 1) Unfluxed and unactivated CaO found to exhibit absorption bands at about  $4000 \text{ \AA}^{\circ}$ ,  $4200 \text{ \AA}^{\circ}$ ,  $4400 \text{ \AA}^{\circ}$ ,  $4600 \text{ \AA}^{\circ}$ ,  $4800 \text{ \AA}^{\circ}$ ,  $5000 \text{ \AA}^{\circ}$ ,  $5400 \text{ \AA}^{\circ}$  and at  $5800 \text{ \AA}^{\circ}$  with decreasing absorption towards the shorter wavelength side (below  $4000 \text{ \AA}^{\circ}$ ). These bands may be attributed to the defects in the host lattice probably created during the synthesis of phosphor at high temperature.
- 2) Incorporation of flux into the CaO lattice either alone or in presence of  $\text{Bi}^{3+}$  and/or  $\text{Sm}^{3+}$  causes for appearance and disappearance of some of the absorption bands and to change the intensities of observed bands.
- 3) The addition and changing concentration of  $\text{Bi}^{3+}$  markedly influences the general features of absorption spectra specially at high concentrations. At high concentrations of  $\text{Bi}^{3+}$  intensity of bands in  $3500 \text{ \AA}^{\circ}$   $4500 \text{ \AA}^{\circ}$  wavelength range is found to increase with greater enhancement of absorption towards the longer wavelength side.
- 4) The addition and changing concentration of  $\text{Sm}^{3+}$  causes for appearance and disappearance of some of the bands and also to change the band intensities.

But the observed effect is unsystematic and small. Similar are the results found with incorporation of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  in presence of each other.

5) Unactivated and unfluxed CaO exhibits emission bands at about  $4500 \text{ \AA}^{\circ}$  and at  $5890 \text{ \AA}^{\circ}$ .

6) Addition of flux gives rise to a band at about  $5250 \text{ \AA}^{\circ}$  suggesting thus incorporation of flux into CaO lattice introduces luminescence centres.

7) Emission characteristics of studied samples are found to depend sensitively upon the addition and changing concentration of activators ( $\text{Bi}^{3+}$ ,  $\text{Sm}^{3+}$ ).

8) Incorporation of  $\text{Bi}^{3+}$  gives rise to a band at about  $4250 \text{ \AA}^{\circ}$ .

9) With addition and increasing concentration of  $\text{Sm}^{3+}$  a band at about  $5250 \text{ \AA}^{\circ}$  disappears and intensity of a band at about  $4500 \text{ \AA}^{\circ}$  decreases with increase in emission in orange-red region.

10) The change in concentration of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  in the presence of each other found to affect sensitively general nature of emission spectra with their own characteristic emission.

Table No.3.1: Emission Intensities of Various spectral bands ( All fluxed samples unless mentioned) (The concentration of activator is in % of preparate).

Sample No.	Activator	Intensities in arbitrary units of the emission bands peaking at about			
		4250 <sup>o</sup> A	4500 <sup>o</sup> A	5250 <sup>o</sup> A	5890 <sup>o</sup> A
S <sub>0</sub>	-	-	26.1	45.3	100
S <sub>3</sub>	Bi(0.005 %)	21.5	22.7	37.5	100
S <sub>4</sub>	Bi(0.01 %)	23.6	25.3	40.3	100
S <sub>5</sub>	Bi(0.025 %)	21.7	23.2	40.3	100
S <sub>6</sub>	Bi(0.05 %)	20.06	22.1	36.6	100
S <sub>7</sub>	Bi(0.1 %)	19.8	21.6	35.8	100
S <sub>8</sub>	Bi(0.25 %)	24.5	25.5	42.0	100
S <sub>11</sub>	Sm(0.005 %)	18.00	19.00	-	100
S <sub>12</sub>	Sm(0.001 %)	18.0	19.3	-	100
S <sub>13</sub>	Sm(0.005 %)	17.7	19.0	-	100
S <sub>14</sub>	Sm(0.01 %)	18.2	19.0	-	100
S <sub>16</sub>	Sm(0.05 %)	18.0	19.4	-	100
S <sub>17</sub>	Sm(0.1 %)	17.8	19.0	-	100
S <sub>18</sub>	Sm(0.25 %)	17.5	18.7	-	100
S <sub>19</sub>	Sm(0.5 %)	17.9	18.6	-	100
S <sub>20</sub>	Sm(1.0 %)	17.1	18.0	-	100
S <sub>21</sub>	Bi(0.001 %) Sm(0.05 %)	20.0	20.3	-	100
S <sub>22</sub>	Bi(0.01 %) Sm(0.05 %)	21.2	22.1	39.1	100
S <sub>23</sub>	Bi(0.05 %) Sm(0.05 %)	20.7	21.2	36.4	100

..continued

Sample No.	Activator	Intensities in arbitrary units of the emission bands peaking at about			
		4250 <sup>o</sup> A	4500 <sup>o</sup> A	5250 <sup>o</sup> A	5890 <sup>o</sup> A
S <sub>25</sub>	Bi(0.00 %) Sm(0.05 %)	18.9	18.3	32.8	100
S <sub>26</sub>	Bi(0.05 %) Sm(0.001 %)	19.7	22.4	40.2	100
S <sub>27</sub>	Bi(0.05 %) Sm(0.01 %)	22.0	22.2	39.7	100
S <sub>29</sub>	Bi(0.05 %) Sm(0.25 %)	19.7	19.9	34.0	100
S <sub>30</sub>	Bi(0.05 %) Sm(0.00 %)	19.9	19.3	34.6	100
(Samples So <sub>1</sub> , So <sub>2</sub> and So <sub>3</sub> are without flux)					
So <sub>1</sub>	-	-	19.8	-	100
So <sub>2</sub>	Sm(1.0 %)	18.0	19.0	-	100
So <sub>3</sub>	Bi(1.0 %)	23.9	23.5	41.4	100
S <sub>10</sub> (with flux)	Bi(1.0 %)	20.8	20.6	36.1	100

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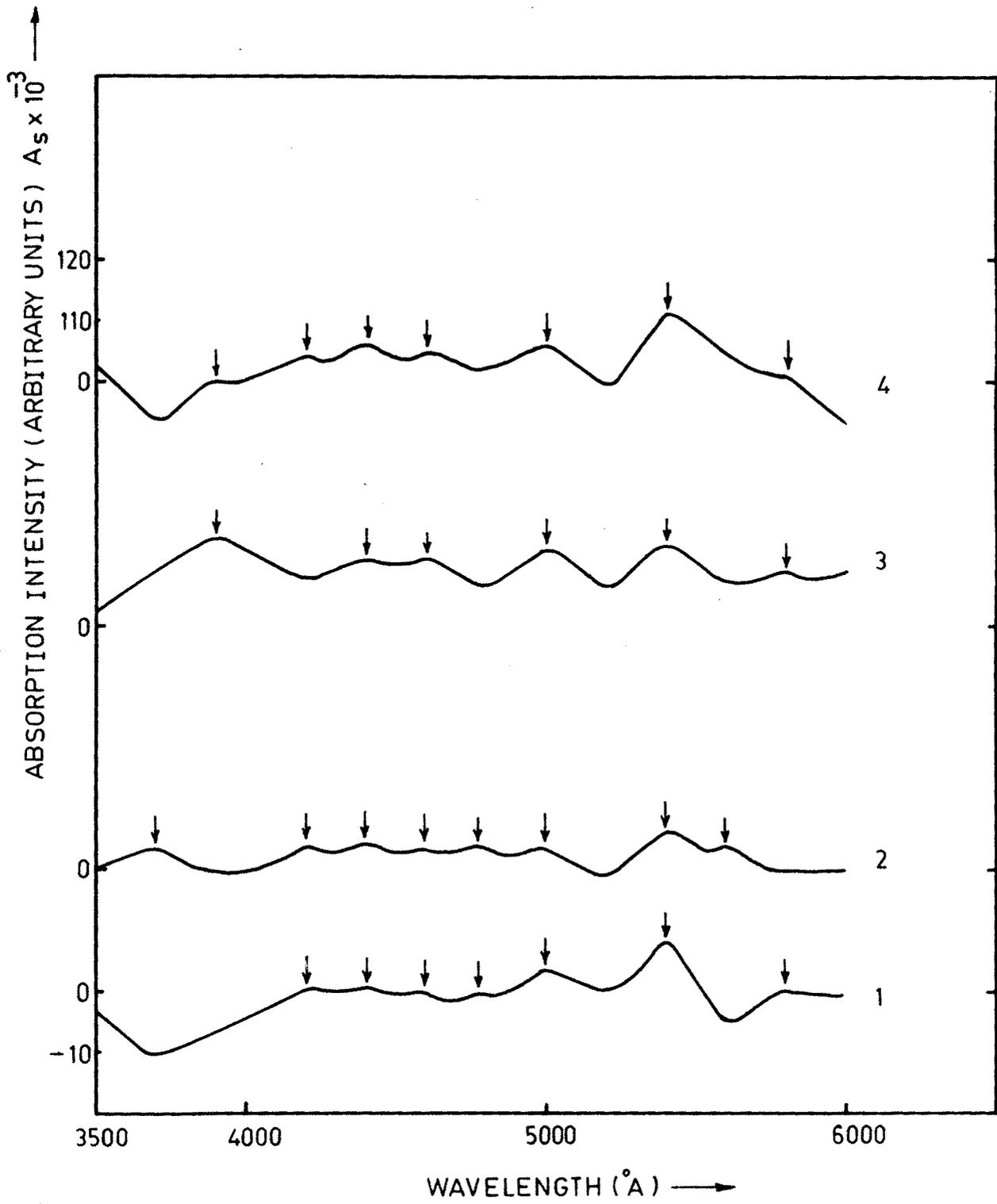


FIG. 3.1: ABSORPTION SPECTRA OF CaO:Bi PHOSPHORS.

( 1 : S<sub>0</sub> , 2 : S<sub>1</sub> , 3 : S<sub>3</sub> , 4 : S<sub>6</sub> )

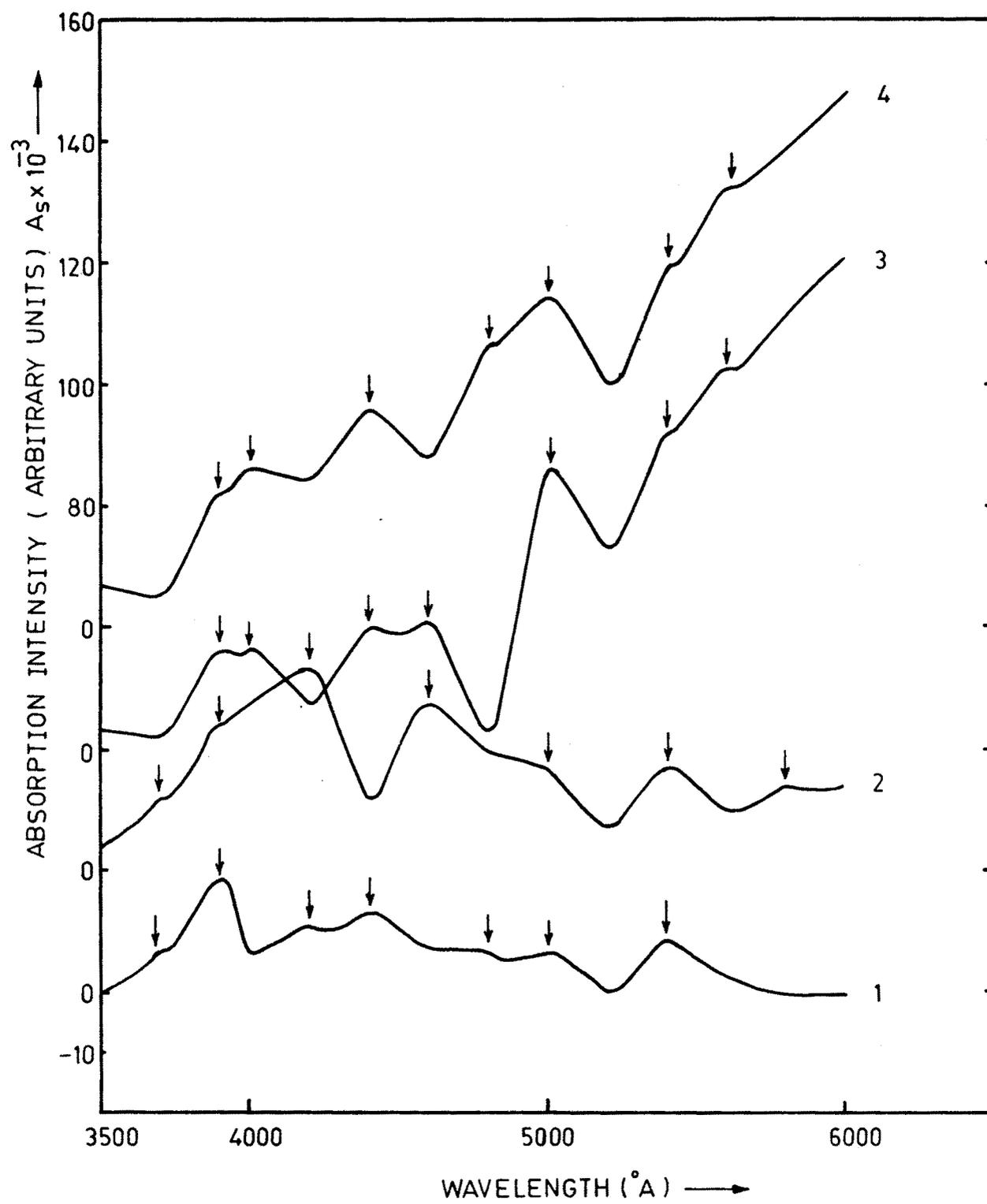


FIG. 3·2 : ABSORPTION SPECTRA OF  $\text{CaO}:\text{Bi}$  PHOSPHORS.

( 1 :  $S_7$ , 2 :  $S_8$ , 3 :  $S_9$ , 4 :  $S_{10}$  )

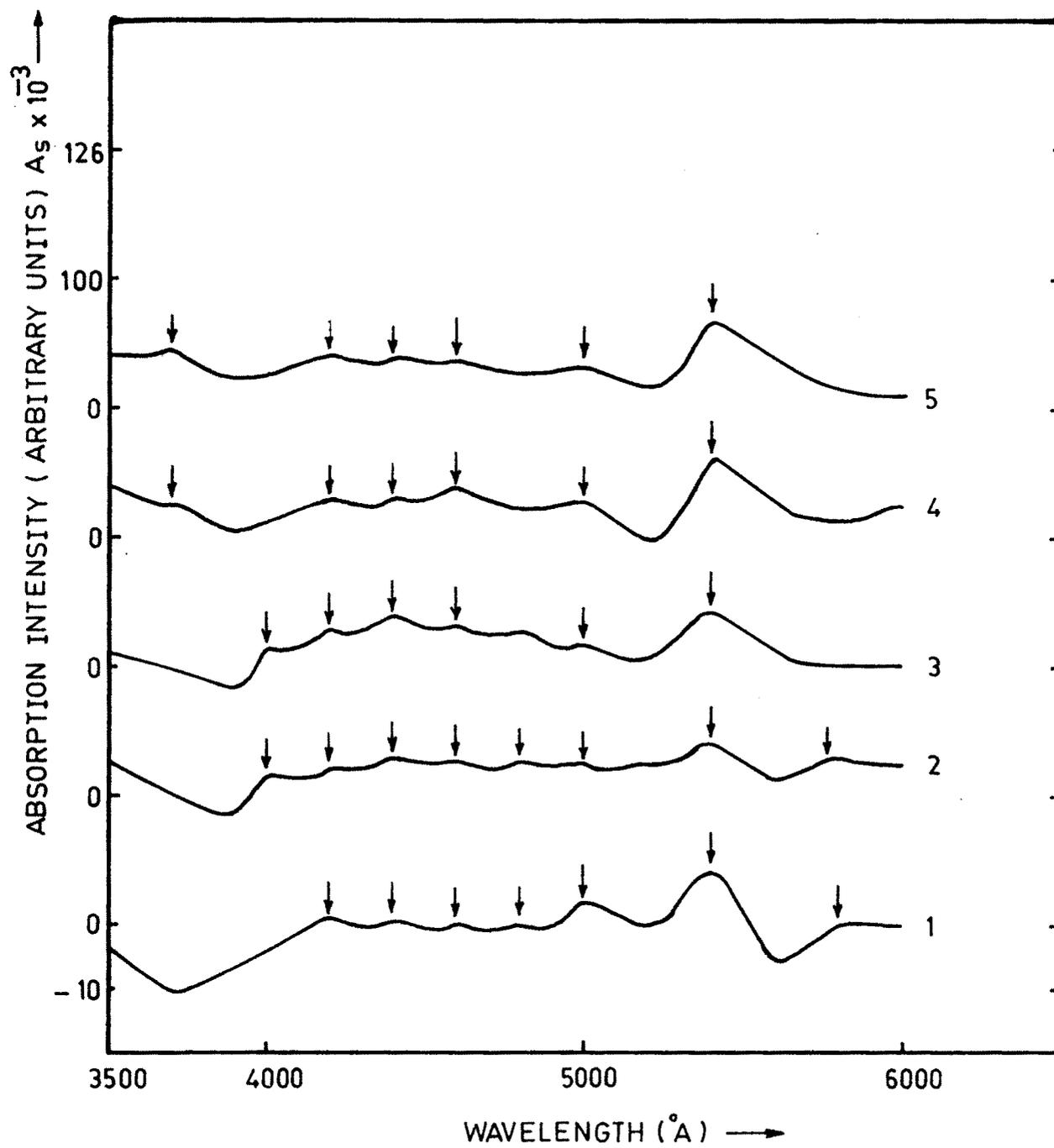


FIG.3-3: ABSORPTION SPECTRA OF  $\text{CaO}:\text{Sm}^{\uparrow}$  PHOSPHORS.

( 1 :  $S_0$  , 2 :  $S_{11}$  , 3 :  $S_{12}$  , 4 :  $S_{13}$  , 5 :  $S_{14}$  )

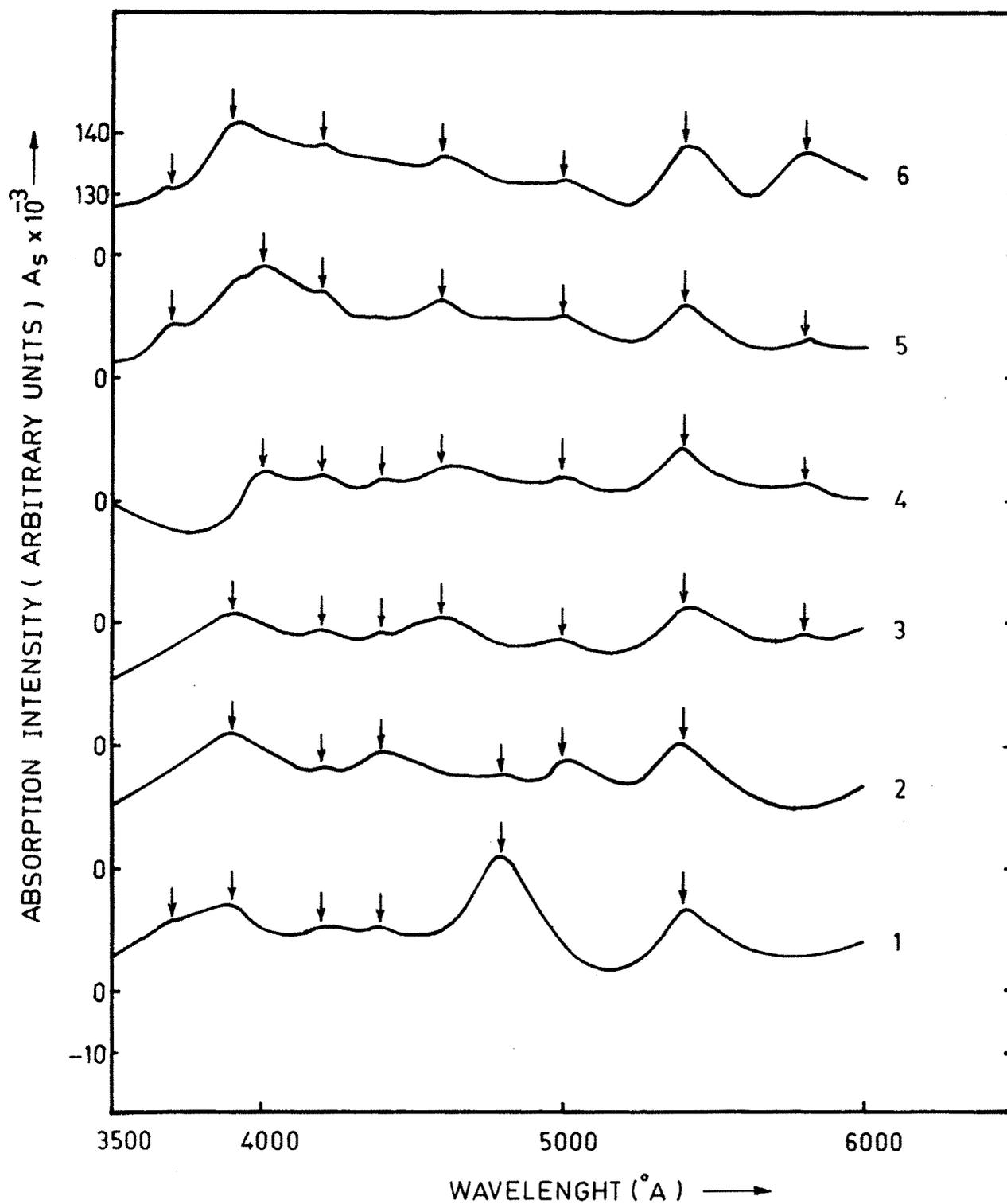


FIG. 3-4 : ABSORPTION SPECTRA OF CaO:Sm<sup>†</sup> PHOSPHORS .

( 1 : S<sub>15</sub>, 2 : S<sub>16</sub>, 3 : S<sub>17</sub>, 4 : S<sub>18</sub>, 5 : S<sub>19</sub>, 6 : S<sub>20</sub> )

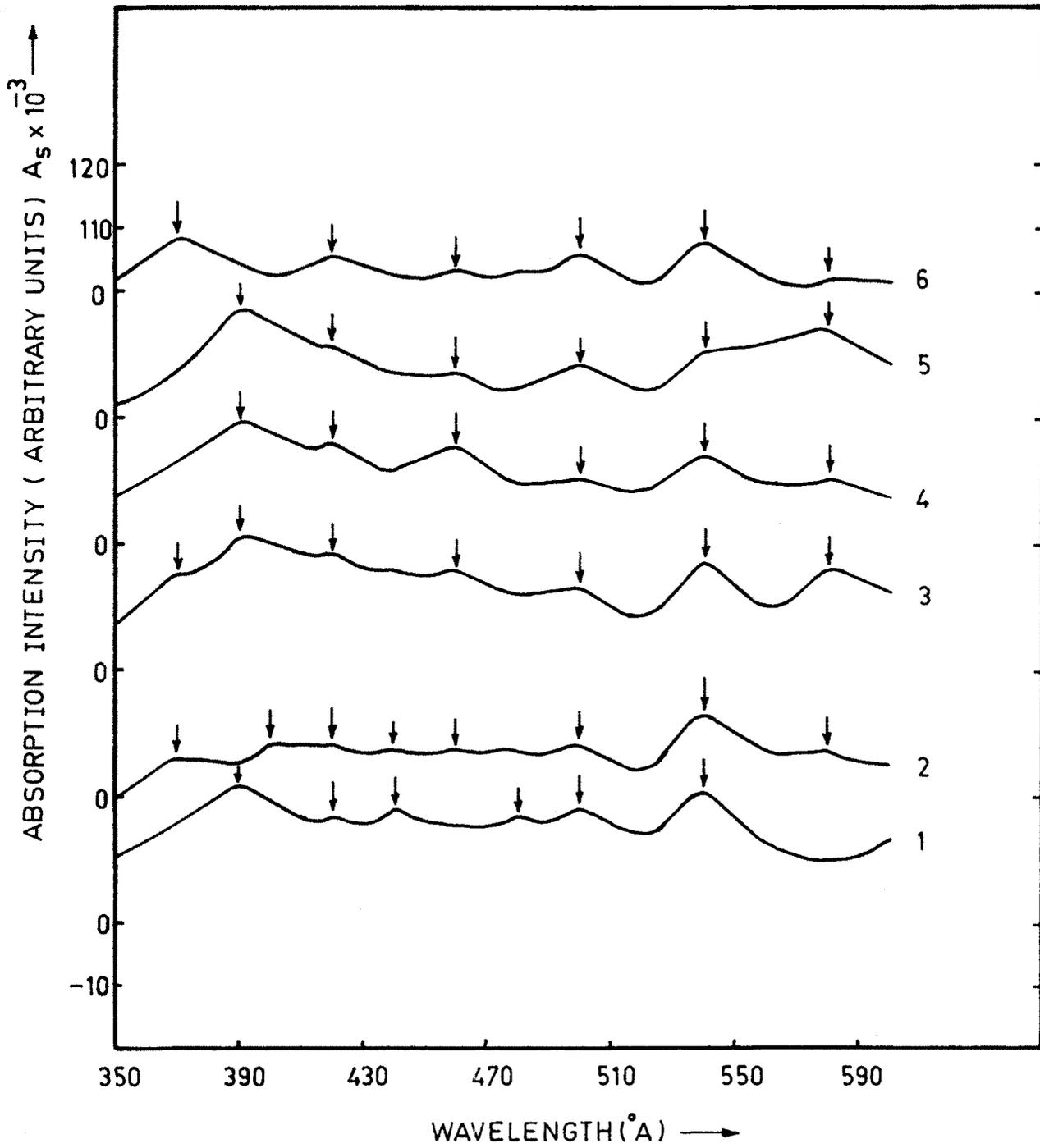


FIG. 3-5 : ABSORPTION SPECTRA OF  $\text{CaO}:\text{Bi}^{\uparrow}\text{Sm}$  PHOSPHORS .

( 1 :  $S_{16}$ , 2 :  $S_{21}$ , 3 :  $S_{22}$ , 4 :  $S_{23}$ , 5 :  $S_{24}$ , 6 :  $S_{25}$  )

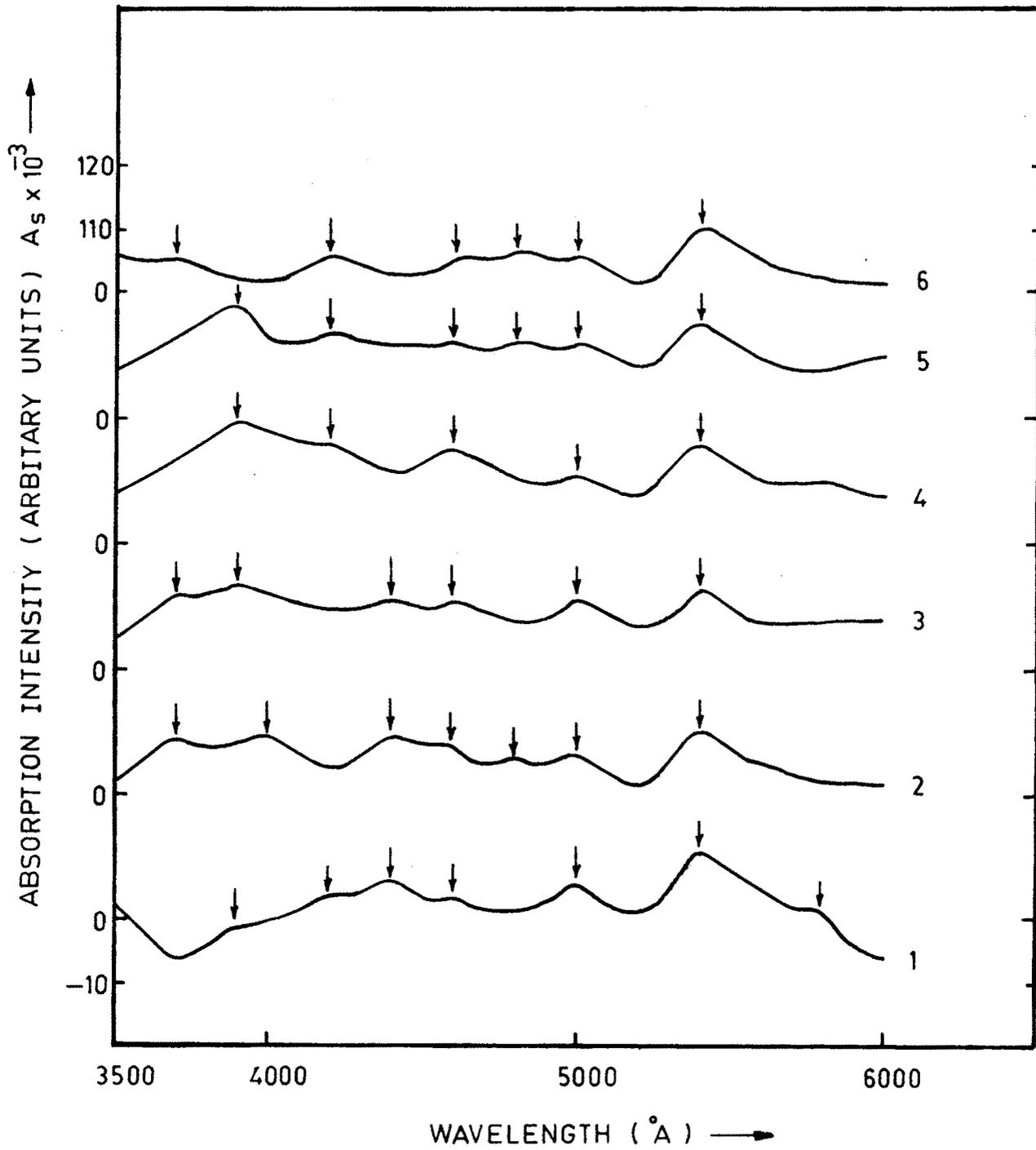


FIG.3-6 : ABSORPTION SPECTRA OF  $\text{CaO Bi:Sm}$  PHOSPHORS

( 1 :  $S_6$  , 2 :  $S_{26}$  , 3 :  $S_{27}$  , 4 :  $S_{28}$  , 5 :  $S_{29}$  , 6 :  $S_{30}$  )

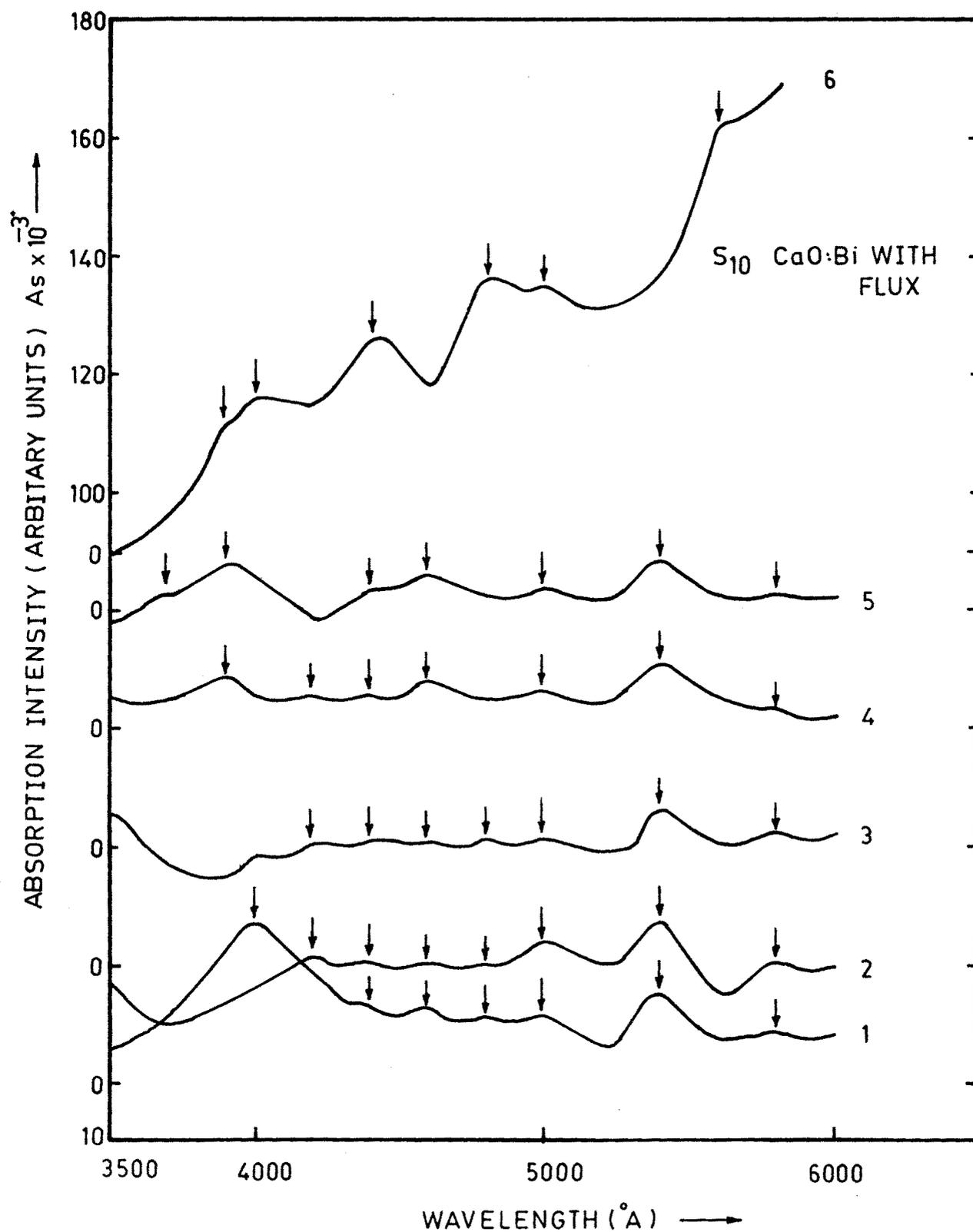


FIG.3-7 : CaO, CaO:Bi, CaO:Sm PHOSPHORS( WITH AND WITHOUT FLUX).

UNFLUXED-	1: S <sub>01</sub> , 3: S <sub>02</sub> , 5: S <sub>3</sub>
FLUXED-	2: S <sub>0</sub> , 4: S <sub>20</sub> , 6: S <sub>10</sub>

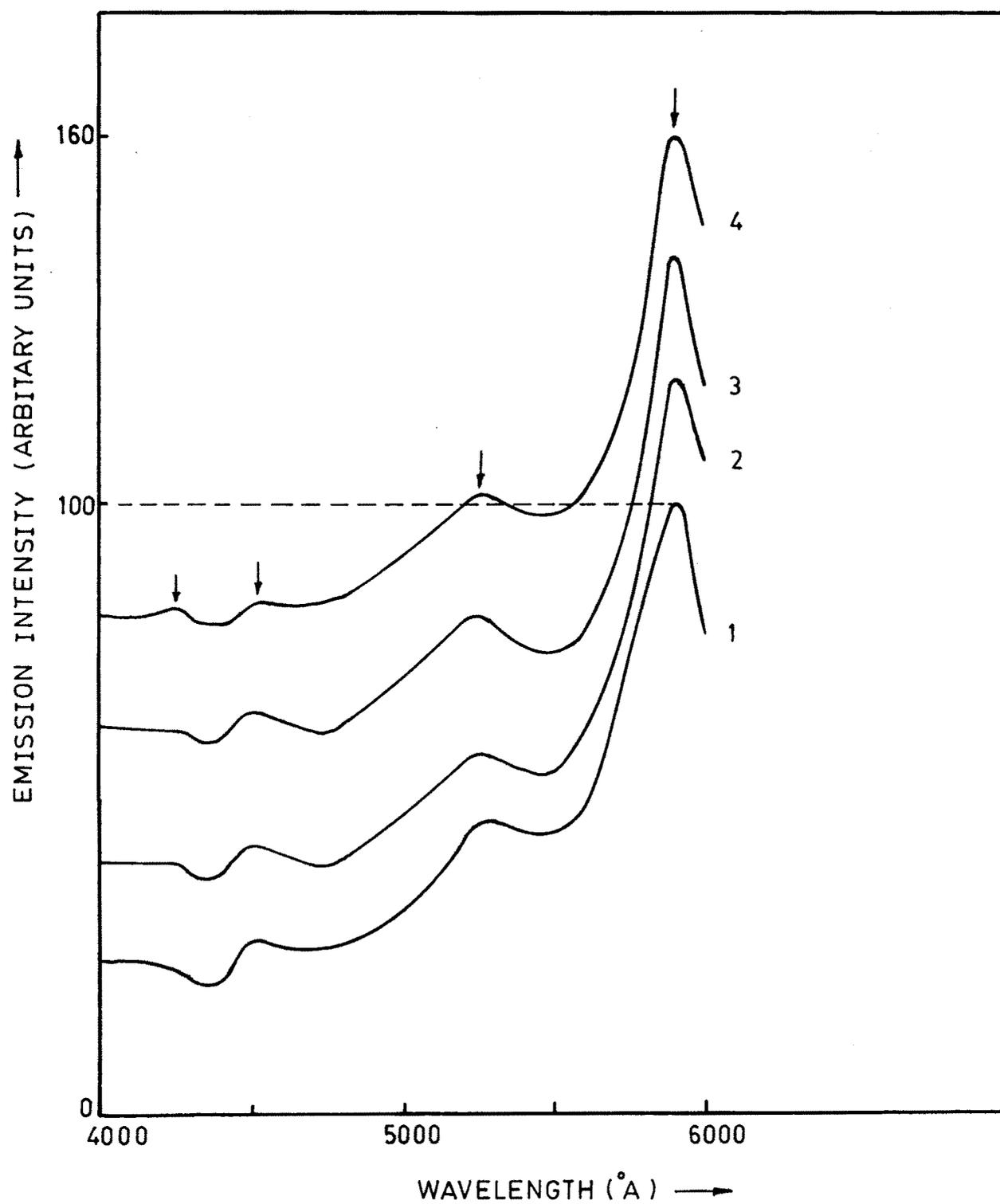


FIG. 3.8: EMISSION SPECTRA OF  $\text{CaO}:\text{Bi}$  PHOSPHORS UNDER UV EXCITATION.

1:  $S_0$ , 2:  $S_3$ , 3:  $S_4$ , 4:  $S_5$

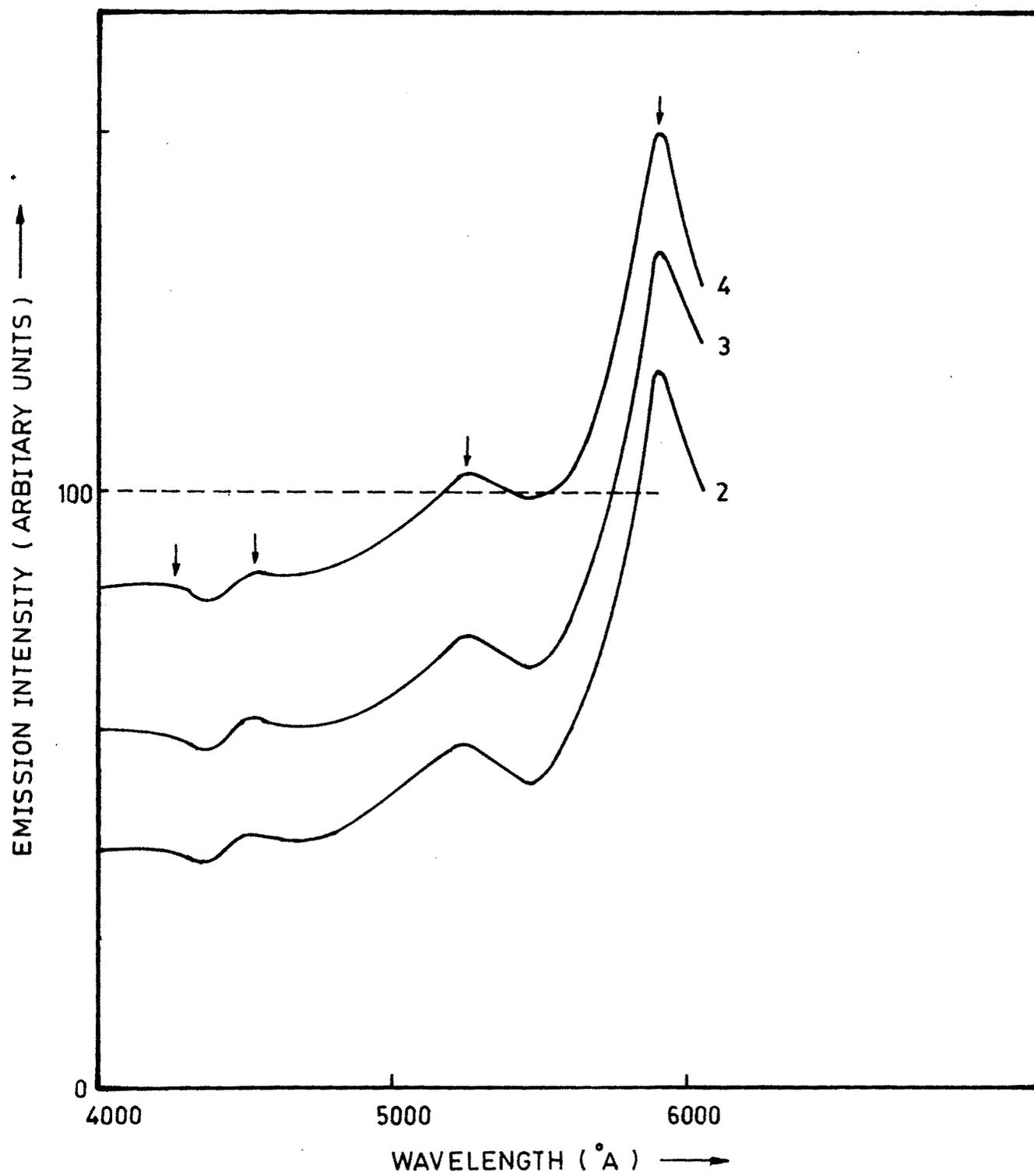


FIG. 3-9 : EMISSION SPECTRA OF  $\text{CaO}:\text{Bi}$  PHOSPHORS UNDER UV EXCITATION.

( 2 :  $S_6$  , 3 :  $S_7$  , 4 :  $S_8$  )

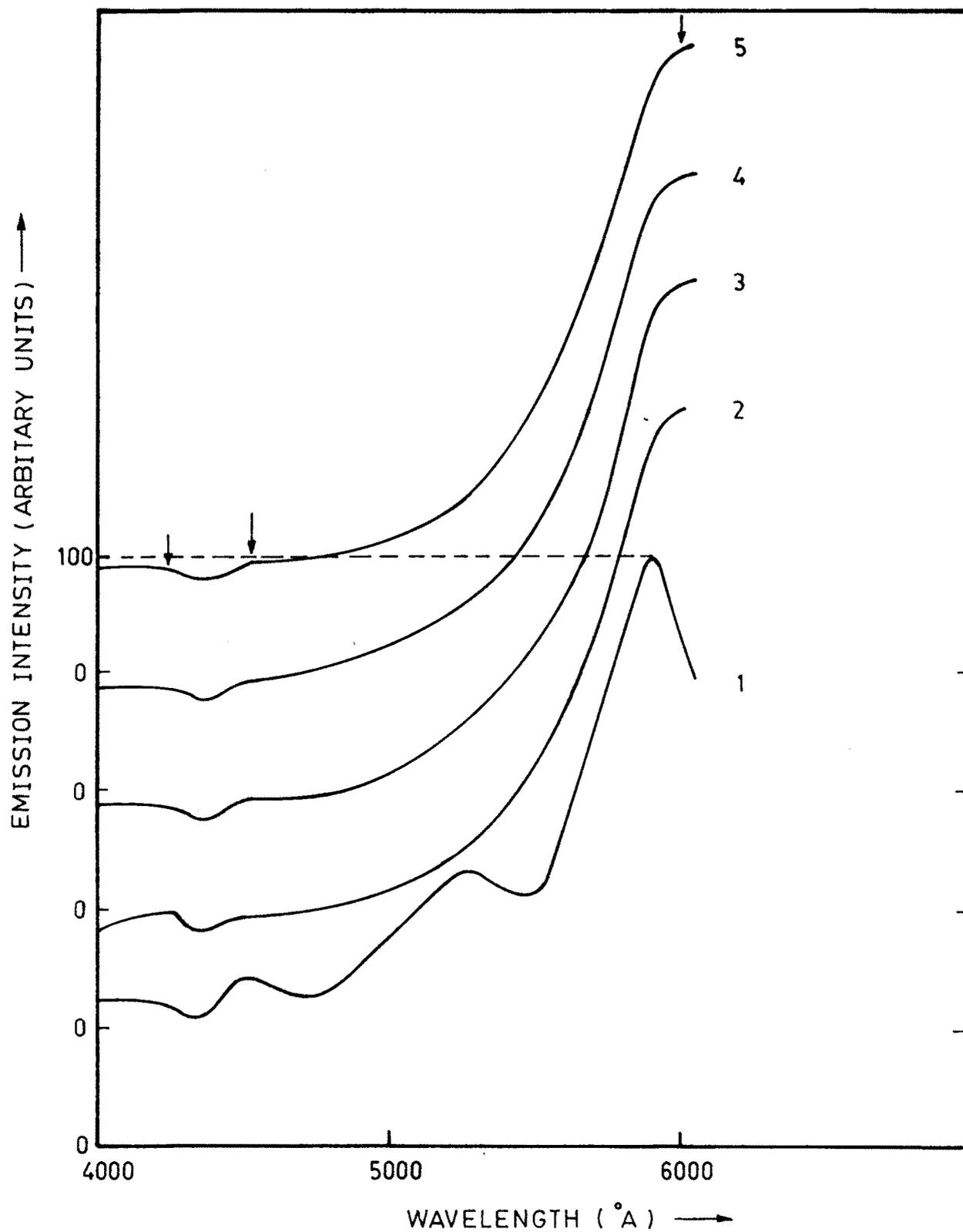


FIG. 3-10 : EMISSION SPECTRA OF  $\text{CaO}:\text{Sm}^{\uparrow}$  PHOSPHORS UNDER UV EXCITATION.

( 1:  $S_0$  , 2:  $S_{11}$  , 3:  $S_{12}$  , 4:  $S_{13}$  , 5:  $S_{14}$  )

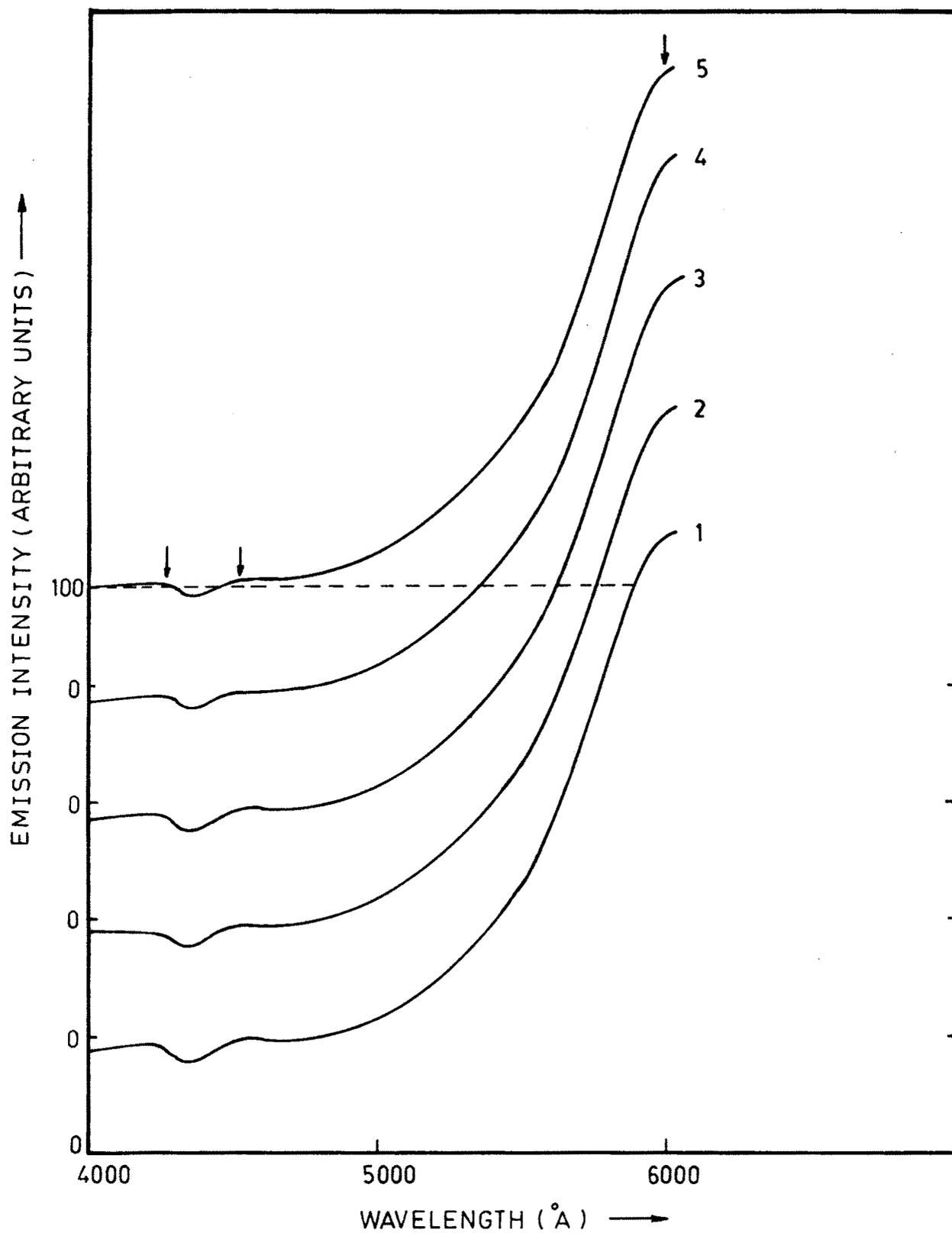


FIG. 3-11: EMISSION SPECTRA OF CaO:Sm PHOSPHORS UNDER UV EXCITATION.

( 1 : S<sub>16</sub> , 2 : S<sub>17</sub> , 3 : S<sub>18</sub> , 4 : S<sub>19</sub> , 5 : S<sub>20</sub> )

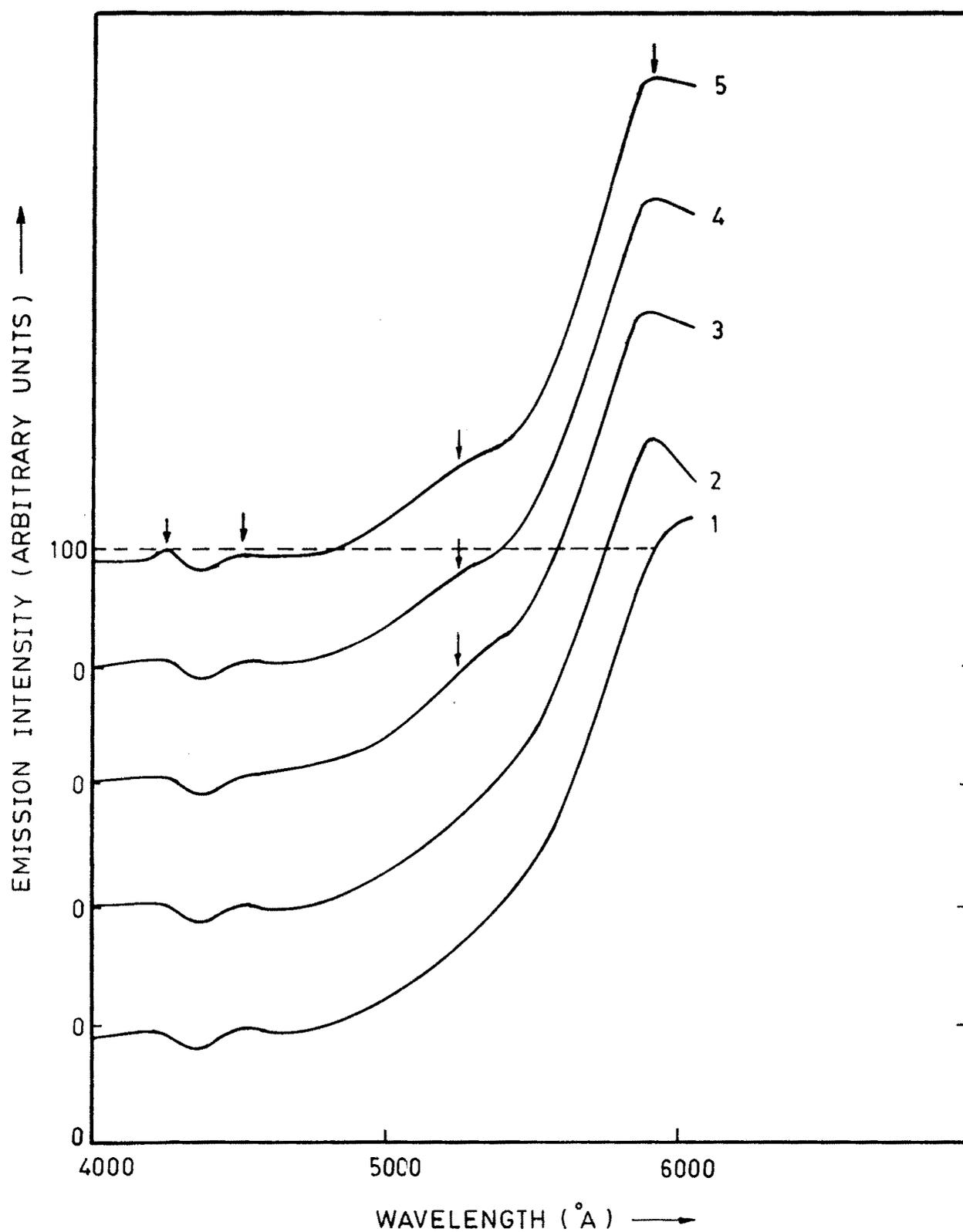


FIG. 3-12: EMISSION SPECTRA OF  $\text{CaO}:\text{Bi}^{\uparrow}\text{Sm}$  PHOSPHORS UNDER UV EXCITATION.

( 1:  $S_{16}$  , 2:  $S_{21}$  , 3:  $S_{22}$  , 4:  $S_{23}$  , 5:  $S_{25}$  )

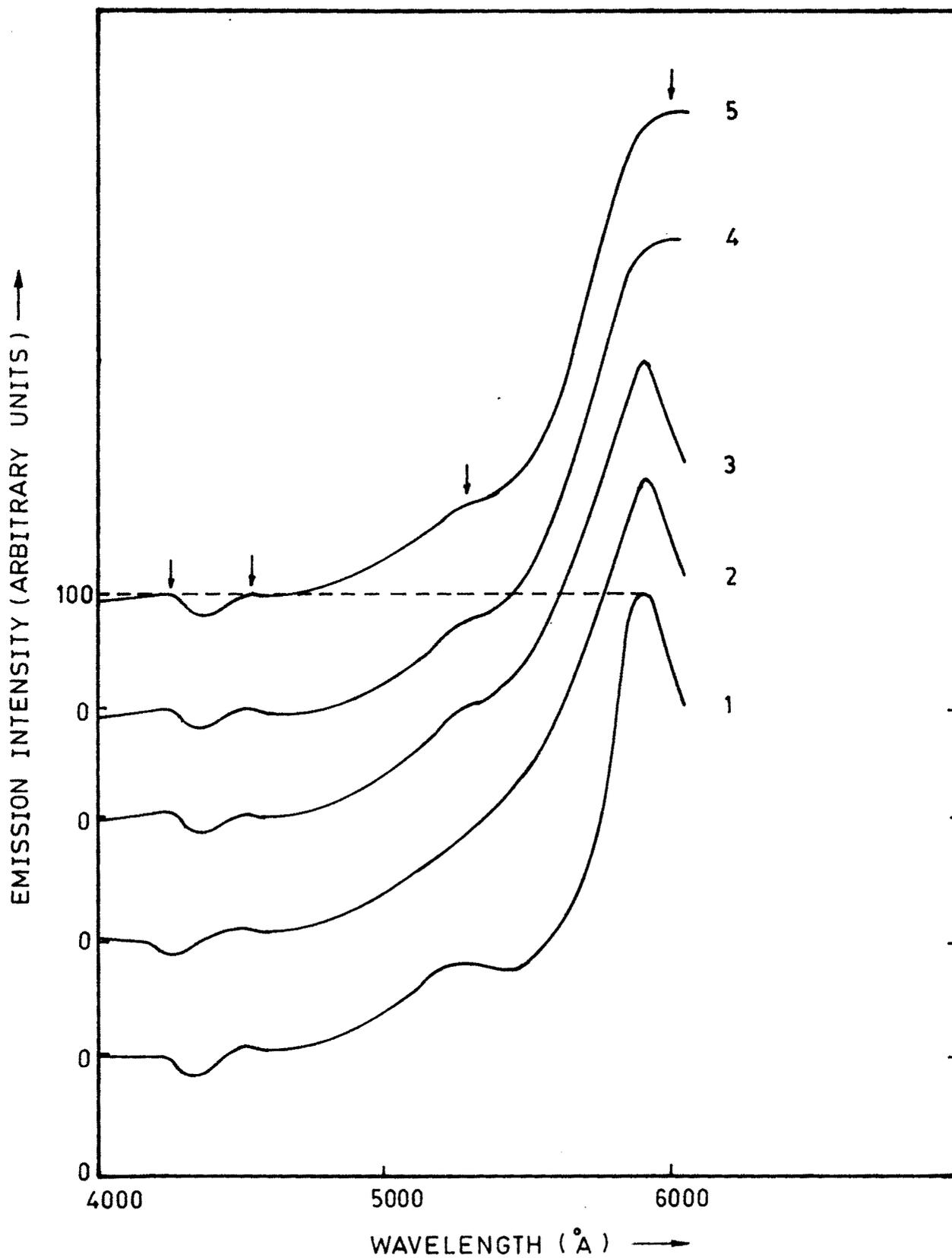


FIG. 3-13: EMISSION SPECTRA OF CaO:Bi:Sm PHOSPHORS UNDER UV EXCITATION.

( 1: S<sub>6</sub> , 2: S<sub>26</sub> , 3: S<sub>27</sub> , 4: S<sub>29</sub> , 5: S<sub>30</sub> )

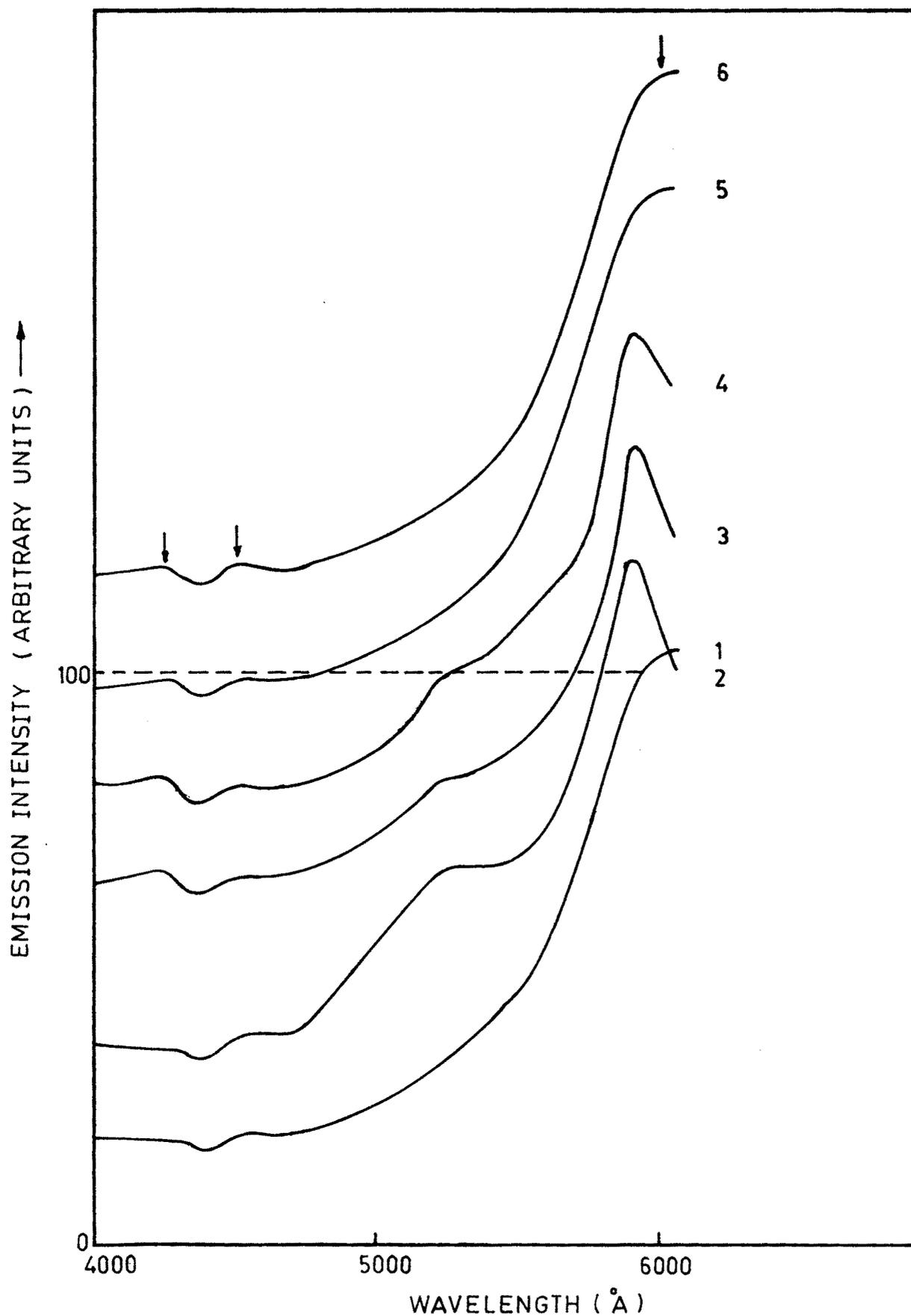


FIG. 3-14: EMISSION SPECTRA OF UNFLUXED AND FLUXED PHOSPHORS UNDER UV EXCITATION.

UNFLUXED-1: S <sub>01</sub> ,	3: S <sub>03</sub> ,	5: S <sub>02</sub>
FLUXED-2: S <sub>0</sub> .	4: S <sub>10</sub> .	6: S <sub>20</sub>