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V.U.V absorption coefficient measurements of borate matrices

B. Moine[a,*], J Mugnier[a], D. Boyer[b], R. Mahiou[b], S. Schamm[c], G. Zanchi[c]

[a]*LPCML, UMR 5620 du CNRS, Université Lyon 1, Villeurbanne, 69622 France*
[b]*LMI, Université Blaise Pascal, Aubière, 63177 France*
[c]*CEMES, CNRS, Toulouse, 31055 France*

Abstract

We present results obtained by direct absorption coefficient measurement on YBO_3 thin films in the wavelength range from 120 to 240 nm. Indirect determination of the absorption coefficient by treatment of the low-loss part of electron energy loss spectra has also been investigated. The YBO_3 films (few tenths of nanometers) were layered by the Sol-Gel technique on a MgF_2 substrate. The results of both experiments are compared. The absorption coefficient of YBO_3 is found to be 6.3×10^5 cm^{-1} at 147 nm. We show that electron energy loss spectroscopy (EELS) results may be reliable in the low energy range, between 5 and 10 eV.

Keywords: Light absorption; EELS; Optical properties; Phosphors; Thin films

1. Introduction

Scientific research on phosphors has a long history, going back more than 100 years. However, recently, the appearance of new kinds of displays (plasma display, field emission display, etc.) has induced an increase in the research of new phosphors with better luminous efficiency than those available up to now. It has been shown that the behaviour of 'classical' phosphors in a plasma display panel is quite different than in a cathode ray tube and that the vacuum ultraviolet (v.u.v.) excitation process has to be studied with care in order to improve the phosphor's efficiency.

The v.u.v. energy of the plasma discharge is essentially absorbed by the phosphor matrices and then transferred to the luminescent centres. Thus, it is of primary importance to measure the absorption coefficient of these matrices in order to know the penetration depth of the exciting photons. Indeed, if the v.u.v. energy is absorbed in a very thin layer at the surface of the phosphor grain, the size and the surface quality of this grain may be very important for the luminous efficiency, and surface energy losses may explain the low light output intensity of some phosphors under v.u.v. excitation. The fundamental absorption coefficient of inorganic insulating materials is generally not known with good precision because it is, most of the time, too high to be measured with a simple spectrophotometer, especially when the forbidden gap of the material is wider than 7 eV, inducing measurements in the v.u.v. range. Generally, we assume that this absorption coefficient is of the order of 10^6 cm^{-1}.

Here, we present results obtained by direct absorption measurement on thin films of YBO_3 (a few tenths of a nanometer) layered by the Sol-Gel technique on a MgF_2 substrate in the wavelength range from 120 to 240 nm.

We have also performed electron energy loss spectroscopy (EELS) on these samples. Quantitative information on optical constants, such as the absorption coefficient, can be extracted with good spatial resolution, down to the nanometer range, by performing EELS experiments in a transmission electron microscope (TEM). This information is obtained from the exploitation of the low-loss domain (up to hundred eV) of the EELS spectra.

The main purpose of this paper is to estimate the penetration depth in phosphors of v.u.v. radiation and to compare two techniques that allow this measurement.

Recently, the preparation of orthoborates $LnBO_3$ (Ln= rare earth) thin films has received great attention because of their potential applications as luminescent materials, for example, in flat plasma display panel (PDP) screens. The present tendency of developing such materials is oriented mostly towards the preparation of thin crystalline films, with the idea that the small crystals in the film will

*Corresponding author.

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suppress the optical loss due to the direct or back-scattering of light at grains boundaries.

2. Experimental

The sol-gel method is the most convenient and unique route to our knowledge to prepare orthoborate films using the dip-coating technique [1,2]. As previously known, the sol-gel method is one of the most important techniques for fabricating high-tech materials, since it permits high purity, low temperature synthesis, precise composition control and direct formation of thin films without powder processing.

Coating solutions of YBO_3 were prepared, starting from the synthesis of heterometallic alkoxides sol with lanthanide salts (Y) and boron alkoxide [3]. MgF_2 single crystal plates were used as substrates. Coating procedures were performed in a chamber placed under a regulated flow of dry nitrogen. The substrate was dipped in the coating solution, withdrawn at a fixed speed of 8 cm min^{-1} and dried at 80°C for 15 min. The film was then heat-treated at 700°C for 15 min. Crystallisation of the film was examined using an X-ray diffractometer.

Direct absorption measurements were made with a v.u.v. spectrophotometer equipped with a 150-W deuterium lamp. Sodium salicylate is known to have a regular fluorescence efficiency in the v.u.v. range below 300 nm. So, we used its blue fluorescence to calibrate the intensity of the v.u.v. beam, which goes through a reference plate of MgF_2 and through the studied samples. Two samples were studied, one with a YBO_3 film on one side of the MgF_2 plate (YBO_3 single film) and another with a film on both sides of the plate (YBO_3 double film). The thickness of the film was measured using an ellipsometry technique and is approximately equal to 50 ± 5 nm.

For electron energy loss experiments, the measurements were performed on a Philips CM20 TEM operating at 100 kV. The microscope is equipped with a Gatan PEELS spectrometer, the energy resolution and dispersion of which were 1 and 0.1 eV per channel, respectively. Spectra were acquired in the image mode with a probe size of around 10 nm^2. The spectra are corrected for noise and detector gain via the Gatan procedure.

Suitable TEM samples were prepared from the YBO_3 single film. A cross-section of the YBO_3 film was prepared by mechanical polishing followed by ion argon milling to electron transparency. This allows the observation of the film in a direction perpendicular to its growth direction, from the MgF_2 substrate to the top of the film.

3. Results and discussion

3.1. Optical absorption

We have recorded the transmission (Fig. 1) of a reference plate of MgF_2 (0.5-mm thick and 15 mm diameter). The beam dimension on the sample is 10×3 mm^2, which leads to a good average value of the transmission. The intensity of the beam after the sample is given by the relation (neglecting the reflection):

$$I_{MgF_2} = I_0.\exp(-\alpha.d_1)$$

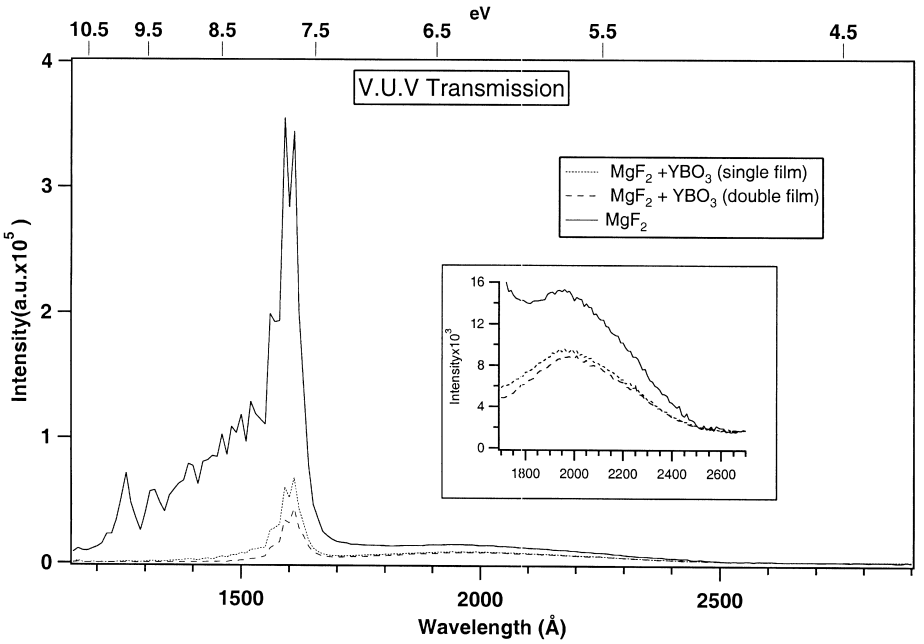

Fig. 1. V.U.V. transmission experiments. The special shape of these spectra is due to the variation in intensity of the deuterium lamp spectrum. The inset shows that YBO_3 absorption is negligible over 2500 Å.

For the same conditions, we have recorded the light transmitted through the two films. The intensities for the YBO_3 single film and for the YBO_3 double film are, respectively:

$$I_1 = I_0.\exp(-\alpha.d_1.\exp(-\alpha_{YBO_3}.d_2)$$

and

$$I_2 = I_0.\exp(-\alpha.d_1.\exp(-\alpha_{YBO_3}.2d_2)$$

where d_1 and d_2 are the thickness of the MgF_2 substrate and of the YBO_3 film, respectively. The curves corresponding to the values of $\log(I_{MgF_2}/I_1)$ and $\log(I_{MgF_2}/I_2)$ are shown in Fig. 2. This ratio is equal to one in the spectral region where $\alpha_{YBO_3}=0$, and should be equal to 2 in the spectral domain where $\alpha_{YBO_3}\neq 0$. The maximum value of the ratio that we got was 1.5. This is probably due to the YBO_3 film thickness ratio, which is not exactly equal to two between both samples. So we calculated the average value of α_{YBO_3} considering fluctuations of the film thickness of between 25 and 75 nm (which have been confirmed by EELS analysis) in the wavelength range of a Xe–Ne plasma discharge of a plasma display panel. These values are gathered in Table 1 with the distance corresponding to an absorption of 99% of the incident v.u.v. photons. The value of 147 nm is a rough approximation since the intensity of the v.u.v. beam going through the samples is extremely weak, inducing probably an important error. Anyway, the main information is that all the v.u.v. photons of the plasma discharge are absorbed into one standard phosphor grain, which typically has a diameter of 2–4 μm.

Table 1

λ(nm)	147	160	170	180
α_{YBO_3} (10^5 cm^{-1})	6.3±0.5	3.4±0.5	2.2±0.5	1.3±0.5
d (nm)	73	135	210	354

3.2. TEM/EELS

The first TEM observation of the YBO_3 single film shows that it is polycrystalline with an irregular thickness, with the heights of the crystals ranging from 25 to 75 nm, with a mean value of 50 nm. EELS analysis of the chemical composition of the film reveals that it is not only made of the YBO_3 phase but probably also of the Y_3BO_6 phase. This result must be confirmed by further observations of the second film deposited on both sides of the MgF_2 substrate. As a consequence, some differences in the low-loss spectra acquired on nanometric zones appeared, essentially in the energy range of 5–20 eV. This can be seen on the absorption coefficient curves shown in Fig. 3 for three cases, which are representative of the sample.

The low-loss spectra were processed using EPSILON software[1]. It consists of different stages [4], which concern the extraction of the low-loss function $Im(-1/\varepsilon(E))$ from an experimental spectrum $I(E)$, after which, $\mathrm{Re}(1/\varepsilon(E))$ is obtained from the Kramers-Krönig relation, thereby yielding the real part, $\varepsilon_1(E)$, and the imaginary part, $\varepsilon_2(E)$, of

[1]Described in detail by S. Schamm at the Euro Summer School, NANOANALYSIS 2000, Nanoscale Diagnosis in condensed matter with high energy electron, May 22–June 3, 2000, Cargèse, Corse, lab session 'Processing low-loss spectra, calculation of optical constants'.

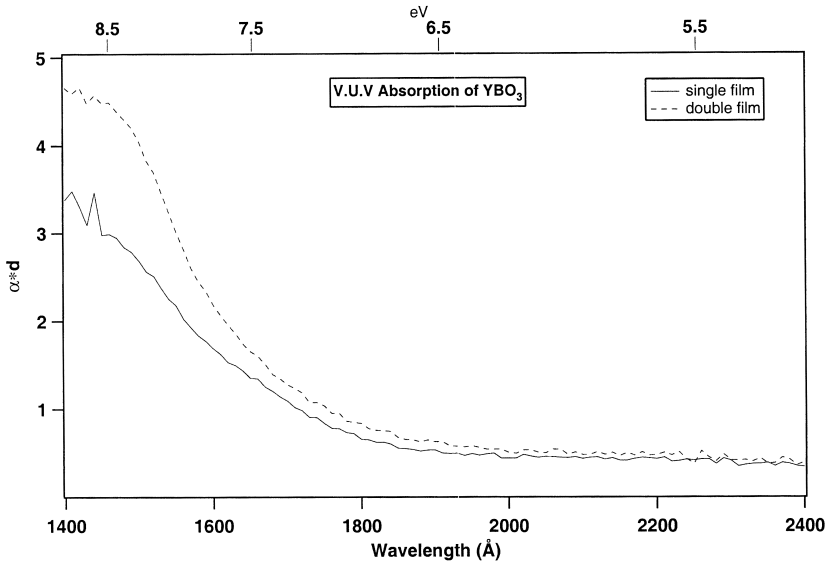

Fig. 2. V.U.V. absorption of YBO_3. These curves represent the product of the absorption coefficient, α, and the thickness, d, for the YBO_3 single film and the YBO_3 double film. The thickness of each film is around 50 nm.

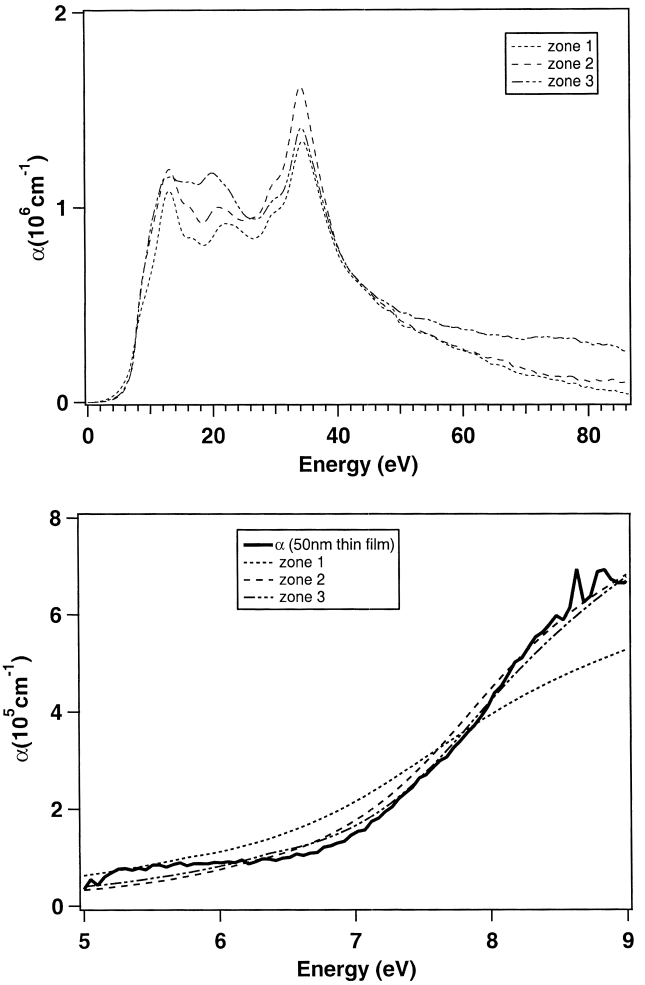

Fig. 3. YBO_3 thin film absorption coefficient determined from EELS experiments. The best fits to the low-energy part of the optically measured spectrum is obtained for the value of refractive index $n=1.64$–1.76, which is slightly higher but consistent with that obtained by ellipsometry [1].

the dielectric function. The absolute scale of $Im(-1/\varepsilon(E))$ is obtained using the Kramers-Krönig sum rule at zero energy. $\varepsilon(0)$ is taken to be the square of the refractive index. In this case, we chose a value of n^2 between 2.8 and 3.1 for a best fit with the optical curve. These values are slightly higher than, but are consistent with, those obtained by ellipsometry. The variation of some optical constants with energy or wavelength can then be deduced, such as the refractive index, n, the extinction coefficient, κ, the absorption coefficient, α and the reflectance, R. In this paper, we concentrate only on the α coefficient, which is defined by

$$\alpha(E) = 2\frac{E}{\hbar}\frac{\kappa}{c} \quad \text{and} \quad \kappa(E) = \sqrt{\left(-\varepsilon_1(E) + \sqrt{\varepsilon_1(E)^2 + \varepsilon_2(E)^2}\right)}$$

where c = velocity of light, $\hbar = h/2\pi$, and h = Planck's constant.

The $\alpha(E)$ curves corresponding to our indirect measurement and to the optical experiment on the YBO_3 single film (Fig. 3) have comparable profiles and intensities for two cases. Discrepancies appear only in the third one. Relative error can be as high as 50%. This result is not so surprising and is often encountered when results of local analysis on the nanometric scale are compared to global analysis on the millimetric scale. Thus, if we consider the results of the three cases observed by EELS, they can be considered as being representative of the optical measurements.

4. Conclusion

For the first time, to our knowledge, we have performed direct measurement of the YBO_3 absorption coefficient in the v.u.v. range up to 10 eV. Our experimental results have been compared to those of EELS experiments. The agreement is good enough and it is worth continuing but both methods need to be improved. The quality of the thin film must also be improved, its thickness should be reduced and the annealing process leading to crystallisation should be more accurately controlled, as suggested in reference [1]. As we said, the film is probably not only made up of YBO_3 crystals, thus, complementary EELS experiments are needed on Y_3BO_6 single crystals. We must not forget that EELS experiments are done on the single crystal scale (nm scale) whereas optical measurements are macroscopic (mm scale). Some other efforts have to be made to perform quantitative comparison between the results of these two techniques.

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