

Anomalous intensity of the $^5D_0 \rightarrow ^7F_0$ transition observed at decatungstoeuropate Langmuir films registered by in situ photoluminescence measurements

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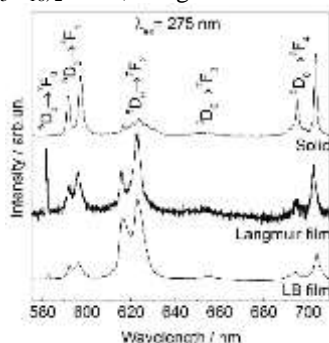
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Two-dimensional systems as nanostructured thin films on the solid surfaces have potential application in nanotechnology and self-assembly processes of these systems have been increasingly studied and employed [1-2]. Luminescent Langmuir-Blodgett films (LB) constitute two-dimensional systems with potential application in optoelectronics. The emission profile of the solid sodium decatungstoeuropate, $\text{Na}_9\text{Eu}(\text{W}_5\text{O}_{18})_2$, is different from that observed in Langmuir-Blodgett films of $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ heteropolyanion [3]. Therefore, the evaluation of the luminescent properties with the interfaces dynamics during the preparation of this two-dimensional system is important to understand the correlation between luminescent properties and two-dimensional organization. In this work, Langmuir films of DODA(dimethyldioctadecylammonium)/ $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ systems were successfully prepared and the luminescent properties of these films were investigated by *in situ* photoluminescence spectroscopy technique, assembled by the research group of the Luminescent Materials Laboratory (UNESP, Brazil). The luminescent properties of the DODA/ $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ mixed system is directly influenced by organization level of the monolayer in Langmuir films and it was possible to verify that the approximation of the molecules results on the luminescence quenching. Surprisingly, one of the most important observation is the anomalous intensity of the $^5D_0 \rightarrow ^7F_0$ transition on Langmuir film when compared with solid or LB film spectra (Figure 1). In the Langmuir film, the intensity of the $^5D_0 \rightarrow ^7F_0$ is higher than intensity of the $^5D_0 \rightarrow ^7F_1$ transition and it is similar to the intensity of the $^5D_0 \rightarrow ^7F_2$ transition. *In situ* spectra were recorded at different angles with respect to the air-subphase interface (90° , 45° and 0.5°). All spectra present the same characteristic, discarding the hypothesis that $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ species could be acting as waveguide at surface for the emission from $^5D_0 \rightarrow ^7F_{1,2,3,4}$ transitions. From $^5D_0 \rightarrow ^7F_J$ transitions, $^5D_0 \rightarrow ^7F_0$ presents the higher energy and probably because that, it is less influenced by the water multiphonon relaxation process.

Figure 1. Emission spectra of $\text{Na}_9\text{Eu}(\text{W}_5\text{O}_{18})_2$ solid, Langmuir and LB films of DODA/ $[\text{Eu}(\text{W}_5\text{O}_{18})_2]^{9-}$ system.



[1] ZHUANG, X. D. et al. *Advanced Materials* **2015**, 27, 403-427.

[2] SAKAKIBARA, K.; HILL, J. P.; ARIGA, K. *Small Journal* **2011**, 7, 1288-1308.

[3] ITO, T.; YASHIRO, H.; YAMASE, T. J. *Cluster Sci.* **2006**, 17, 375-387.

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