

Phosphorescent Composites Based on Polyethyleneterephthalate

CORNELIU SERGIU STAN, DOINA SIBIESCU*, MARIUS SEBASTIAN SECULA, IOAN ROSCA, IGOR CRETESCU

"Gh. Asachi" Technical University, Faculty of Chemical Engineering and Environmental Protection, 71 D. Mangeron Blvd., 700050, Iasi, Romania

Photoluminescent composite of poly-ethyleneterephthalate-SrAl₂O₄:Eu²⁺, Dy³⁺ was prepared by of a new procedure based on mixing the constituents in specific solvents for PET. In a first step it was studied the possibility of preparing europium and dysprosium doped strontium aluminate using a method that allows obtaining crystals in nanometric range compatible with polymer matrix. Also, the dependence of transparency in UV-VIS range of the polymer matrix density and experimental paths for obtaining a low crystallinity of PET at co-precipitation from solution were investigated. Characteristics of absorption / photonic emissions, phosphorescent decay time were investigated for europium/dysprosium doped strontium aluminate, and respectively for the composite prepared. The prepared photoluminescent composite presents a series of applications in optoelectronics, highway/ railway and utilitarian signaletics.

Keywords: long persistence phosphorescent compounds, phosphorescent composites, polymer matrix, polyethyleneterephthalate

Phosphorescent inorganic compounds having persistent emission in the visible spectrum have been of particular interest in recent years due to their potential applications in optoelectronics [1]. One of the most promising applications lies in the use of these compounds in lightning systems that allow energy storage of solar radiation and capitalization of phosphorescent emission in its absence. This allows obtaining energy efficiencies higher than those of conventional lighting systems. In the same context of energy saving can be considered the use of phosphorescent films at highway or railway signaling systems, utilitarian or emergency lightning of buildings.

The embedment of phosphorescent chemical compounds in polymer matrices [2] is aimed at both obtaining of new materials adapted to certain applications and maintaining the integrity of the crystalline structure of the phosphorescent compound by its decoupling from the external environment.

Phosphorescent composites obtained nowadays are based on the embedment of copper doped zinc sulphide (ZnS:Cu) or strontium aluminates in the polymer-matrices like polystyrene (PS) [3] or polymethylmethacrylate (PMMA) [4].

In order to obtain a phosphorescent composite adapted to the applications already mentioned, the present study aims at the use of poly-ethyleneterephthalate (PET) as polymer matrix due to the specific advantages provided by this polymer (high physical-chemical stability, high degree of transparency, high melting and transition temperatures, lack of toxicity). The preparation method has good reproducibility at laboratory scale and presents a high potential of scalability at industrial scale. Also, there is the possibility of the valorization of PET wastes resulted from single-use PET packaging.

The achievement of PET - SrAl₂O₄:Eu²⁺,Dy³⁺ composite can be approached by one of the following methods. In melt, by introducing strontium aluminate in the poly-condensation reactor in the final stage of the process followed by granulation of the obtained composite by conventional methods. In this way, a composite that may be subjected to subsequent extrusion processes to achieve films with photo luminescent properties can be obtained. In melt, by introducing strontium aluminate directly into an extruder able to achieve a pronounced homogeneity,

and provided with a rapid cooling system for the obtained film in order to avoid composite crystallization (and implicitly opacitization). Both procedures are possible due to the high thermal stability and temperature specific to strontium aluminate (stable, with preservation of the phosphorescent properties up to approx. 1000 to 1090 °C) allowing maintaining the crystalline structure and consequently its phosphorescent properties at temperatures specific to the obtaining methods in melt (270-280°C). In solution, by dissolving poly-ethyleneterephthalate in the appropriate solvent [5] and adding the strontium aluminate under vigorous stirring, then sharp cooling followed by the composite precipitation and its separation from the solution.

In this paper the preparation method of the composite in solution was selected due to its experimental simplicity and the possibility of using the recycled PET from packaging waste, followed by the investigation of the obtained composite. Among the specific solvents (phenol-tetracloroethane mixture, ortocresol, benzyl alcohol) benzyl alcohol was selected due to its moderate toxicity compared with the other solvents.

Experimental part

The analytical reagents of aluminum nitrate (Al(NO₃)₃·xH₂O, 99.997%); Sr(NO₃)₂ – strontium nitrate (99.995%); Eu(NO₃)₃ – europium nitrate (Eu(NO₃)₃·xH₂O, 99.99%); Dy(NO₃)₃ – dysprosium nitrate (Dy(NO₃)₃·xH₂O, 99.9%) were purchased from Sigma-Aldrich. Benzyl alcohol (99.5%) and camphor (95%) were analysis grade and purchased from Fluka. Technical grade nitrogen was used for fast cooling of the reaction mass in the final stage of synthesis.

The preparation of europium and dysprosium doped strontium aluminate is performed in solid phase by mixing and heating the corresponding reactants to temperatures ranged between 600 and 1200°C as a function of the adopted method [6].

One commonly used synthesis method [6,7] of europium and dysprosium doped strontium aluminate involves a reaction in solid phase. Practically, the method involves in the first step the mixing of nitrates of Sr, Al in molar ratio of 1:1, doping agents Eu-1%, Dy-2% together with the combustion agent such as urea or camphor. The

* email: dsibiesc@ch.tuiasi.ro

mixture is lead to a paste consistency by the addition of demineralized water, being then brought into a thermo resistant recipe and exposed for about 5 min. at a temperature of 500-600°C. The combustion agents in volatile state ignite creating thus the necessary conditions to include doping agents within the crystalline matrix. The resulting gases prevent the agglomeration and sinterization facilitating the formation of nanocrystalline structures. From the reaction, nanocrystals of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ are generated. The phosphorescent characteristics are essentially dependent on keeping the integrity of the crystalline structure of strontium aluminate, which involves selecting preparation methods of the composite in order to maintain its initial characteristics during the entire process. Eu, Dy doped strontium aluminate in crystal state dissolves rapidly in acid media and is sensitive (slow dissolution) in aqueous environments.

Then in a typical procedure of composite synthesis, an amount of 180 g of fine chopped PET and 1.2 L of benzyl alcohol are inserted into the reactor, the stirring is started and the temperature is raised to the boiling temperature of benzyl alcohol (205 °C). Benzyl alcohol vapors are condensed in a reflux refrigerant returning into the reaction mass. These conditions are maintained for about 2-3 h until total dissolution of PET occurs. The source of heating is stopped and the stirring is stopped at temperatures of 190°C, when a quantity of 85 g strontium aluminate doped with Eu and Dy is added. Then, the stirring is resumed for about 20-30 min. followed while stopping agitation by nitrogen bubbling into the reaction mass. This has a double role for homogenization and for sharp cooling to temperatures below 60-65°C. For best results, it can be added 200-300 mL of benzyl alcohol cooled to -10C in order to reduce the cooling time. The composite in reaction mass is discharged through the bottom outlet of the reactor and filtered under a vacuum of 60-100 mmHg. Further, the composite is subjected to a separating operation to remove benzyl alcohol under a vacuum of 3-5 mmHg at a temperature of 50-55 °C. The method allows obtaining the a fine powder composite having phosphorescent characteristics strongly dependent on the transparency degree of the PET matrix therefore the cooling process is critical in order to obtain a high transparency index which allows efficient absorption and emission processes in Eu, Dy doped strontium aluminate.

Absorption/emission characteristics of nanocrystalline powder of the prepared strontium aluminate were investigated using a Perkin-Elmer LS-50 spectrophotometer.

Phosphorescence decay time was measured with an ET Enterp. 9828WB photomultiplier tube connected to an Agilent Tech. U1242a digital millivoltmeter. Before measurements, the samples were excited for 5 min by means of a set-up consisting of 10 electroluminescent diode emitting in UV ($\lambda = 380 \text{ nm}$).

Results and discussions

Among the inorganic compounds having persistent phosphorescent properties [8], europium and dysprosium doped strontium aluminates ($\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$) [9] are distinguished by a number of advantages which could stay at the basis of high efficiency phosphorescent composites with various applications. Among these, the most important are as follows: the phosphorescent time of 20-40 h, emission in the visible spectrum (530 -540 nm) and high physical-chemical stability.

The mechanism of the persistent phosphorescence [10,11] specific to strontium aluminate doped with

elements from lanthanide group are not completely understood, being assumed the formation of electron traps and holes followed by photon emission. Europium has a key role in the formation of photon emission centers, being assumed the existence of some mechanisms (fig. 1) of direct or valence band transfer of holes and their recombination with the emitting center formed in Eu^{2+} due to the thermal phenomena of deactivation of traps or holes. In order to establish the role of Eu^{2+} in achieving the property of persistent phosphorescence of strontium aluminate, strontium aluminate samples doped only with Eu and respectively with both Eu and Dy were investigated [10].

Both samples were excited under the same conditions, using a UV source, both samples showed phosphorescent emissions in the green range of the visible spectrum ($\lambda = 510 - 530 \text{ nm}$). It was found that in both cases the absorption characteristics and those of emissions are approximately identical (Fig. 2) indicating the existence of identical emission centers for both cases due to Eu^{2+} . Establishing Dy role [12] as co-activator of the persistent phosphorescence property of strontium aluminate involves assessing its role in the formation of the crystalline lattice, of its influence on the density of for hole traps / electrons.

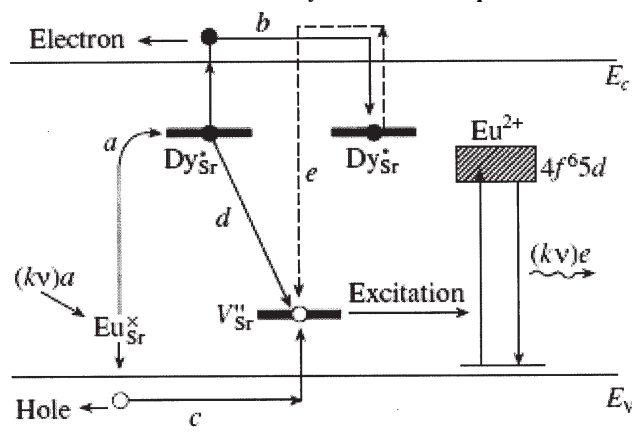


Fig.1. Phosphorescence mechanism in Eu, Dy doped strontium aluminate

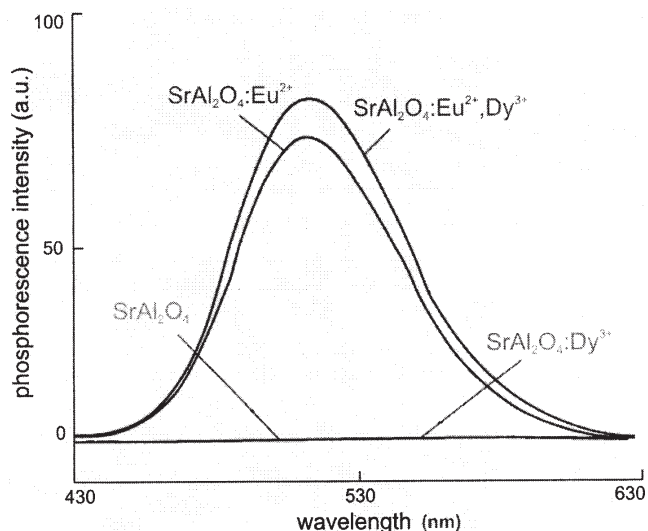
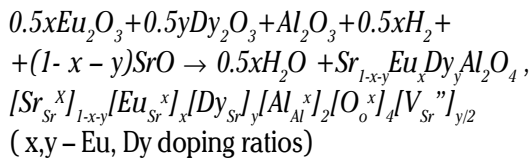


Fig.2.Role of dopants in phosphorescence

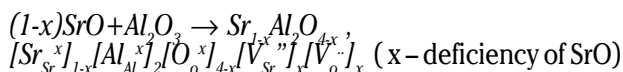
Comparing samples of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ doped or undoped with Dy indicates a negligible influence on the wavelength of the radiation emitted by phosphorescence. Dy influence is significant on the absorption spectrum of excitant radiation as well as on the phosphorescence process efficiency. In the current state of research, the Dy role in obtaining the persistent phosphorescence property of

strontium aluminate doped with Eu and Dy is not fully elucidated. By co-doping of strontium aluminate, Eu^{2+} and Dy^{3+} ions will replace mainly Sr^{2+} ions in the crystalline lattice because the dimensional characteristics (ionic diameter) of Eu^{2+} and Dy^{3+} ions are comparable with those of Sr^{2+} and very different (much higher ionic diameter) in comparison to those of Al^{3+} ions.

Doping reactions of strontium aluminate with Eu and Dy are described by the following chemical reactions [13]:



Substituting Sr^{2+} by Eu^{2+} is an equivalent substitution that creates a crystalline defect Eu_{Sr}^x . Being a non-equivalent substitution, the replacing the $\text{Sr}_{\text{Sr}}^{2+}$ by Dy^{3+} leads to the formation of two types of defects Dy_{Sr} and $\text{Sr}^{2+} [\text{V}_{\text{Sr}}^{\prime\prime}]$ vacancy in order to preserve the balance of electric charge. After ionic substitution, the crystalline lattice presents inherently aberrations due to the dimensional differences between Eu^{2+} , Dy^{3+} , Sr^{2+} ions. According to the stoichiometric ratio, the complete doping of the crystalline matrix is not possible with Eu^{2+} and Dy^{3+} for which reason will permanently be a deficiency of SrO and consequently Sr^{2+} and O^{2-} vacancies ($\text{V}_{\text{Sr}}^{\prime\prime}$ and $\text{V}_{\text{O}}^{\bullet}$) will be formed according to the following equations [13,14]:



Thus, $\text{V}_{\text{O}}^{\bullet}$, $\text{V}_{\text{Sr}}^{\prime\prime}$, Eu_{Sr}^x and Dy_{Sr} will coexist as crystalline defects into the crystalline lattice of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$. Since Dy_{Sr} has a positive electric charge and $\text{V}_{\text{O}}^{\bullet}$ has two positive electric charges, they develop an affinity for the free electrons and can be considered electron traps. In contrast, having two negative charges, $\text{V}_{\text{Sr}}^{\prime\prime}$ traps present behaviour of hole traps.

The phosphorescent characteristics are essentially dependent on keeping the integrity of the crystalline structure of strontium aluminate, which involves selecting preparation methods of the composite in order to maintain its initial characteristics during the entire process. Crystalline Eu, Dy doped strontium aluminate dissolves rapidly in acid media and it is sensitive (slow dissolution) in aqueous environments. Decoupling of the crystalline structure of the potentially aggressive media specific to the aimed applications is achieved by its adding in stable polymer matrix. The polymer matrix must present a high transparency index to allow the energy transfer to the phosphorescent compound, and the visible radiation resulted from the phosphorescence phenomenon. The used polymer must be stable under the conditions of long exposure to radiations with wavelengths in the UV area. For the applications related to obtaining of phosphorescent films, a key criterion for selecting the polymer matrix is its sensitivity to specific organic solvents (toluene, methyl ethyl ketone, butyl acetate, acetone). All these requirements can be met by using polyethyleneterephthalate as polymer matrix. In addition, this has the advantage of moderate manufacturing cost and offering also the possibility of higher capitalization of disposable packaging waste based on this material.

Absorption / emission characteristics of nanocrystalline powder of the prepared strontium aluminate are shown in figures 3 and 4.

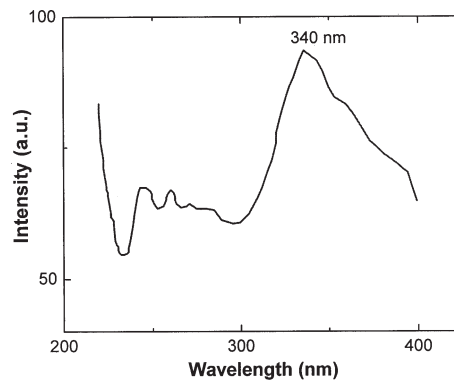


Fig.3. Absorption spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$

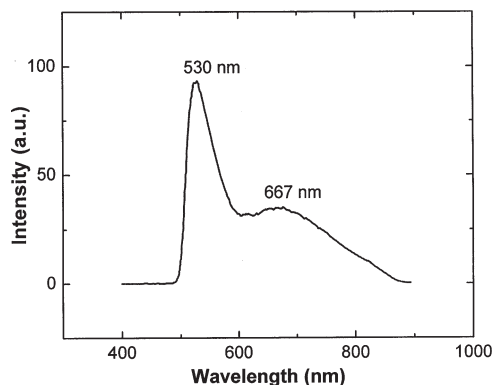


Fig.4. Emission spectra of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$

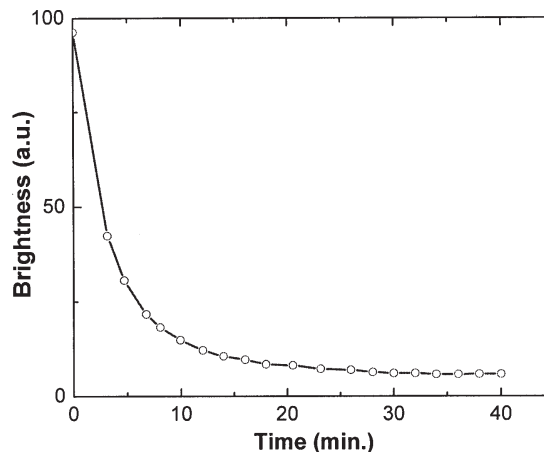


Fig.5. Phosphorescence decay time of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$

A maximum absorption is observed at wavelengths of excitant radiation of 340 nm in the UV range of the spectrum. The phosphorescent emission presents a maximum located in the green-blue area of the visible spectrum ($\lambda = 530$ nm).

In order to measure the phosphorescence decay time (fig.5), the sample was excited for 5 min by means of a set-up consisting of 10 electroluminescent diode emitting in UV ($\lambda = 380$ nm) and then was measured with a ET Enterp. 9828WB photomultiplier tube connected to an Agilent Tech. U1242a digital millivoltmeter.

At longer exposure time (hours) using a UV source of greater power (50-100 W) or by exposure to solar radiation, it may be obtained phosphorescent decay times of 20-30 h.

The achievement of the composite following the preparation method in solution involves the preliminary testing of the obtaining conditions of a polymer matrix with a high degree of transparency. For this purpose there were studied the needed conditions maintaining a low crystallinity of the polyethyleneterephthalate precipitated

from solution. The crystallinity is determined on a measuring column of density gradient (CCl_4 + metaxylene) followed by the calculation of crystallinity using the Wlochowicz and Jeziorny equations [15].

In figure 6 is presented the variation of crystallization index as a function of the PET density and its influence on the transparency. To prepare the phosphorescent composite, some rapid cooling processes were prior investigated to obtain powders of amorphous PET with high transparency index. It was found that the introduction of nitrogen into the reaction vessel after complete dissolution of PET in benzyl alcohol allows decreasing the temperature from 190 to 60°C at a rate of cca.10-12°C/min., which allows obtaining of a satisfactory transparency degree. The best results were obtained by introducing additionally benzyl alcohol previously cooled at -10°C, which provides temperature decreasing rate of more than 18-20°C/min. Thus, it is obtained a high degree of transparency.

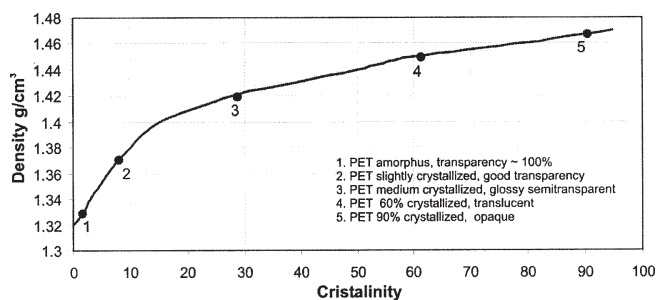


Fig.6. Relation between PET density and cristallinity

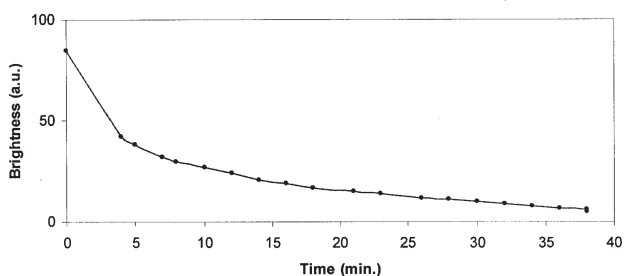


Fig.7. Phosphorescence decay time of prepared composite



Fig.8. Composite sample after UV excitation

Using PET as polymer matrix does not influence the absorption / emission characteristics of strontium aluminate in pure state (figs. 3 and 4) and as regards phosphorescence time, it is noticed a small influence most probably due to the diminished luminous transfer of light when passes through the polymer matrix.

In figure 7 is presented the phosphorescent decay time. The sample of $\text{PET-SrAl}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ composite was excited for 5 min under the same conditions as in the case of determinations made on samples of $\text{SrAl}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ in pure state. In this way, it was used a set-up composed of 10 electroluminescence diodes emitting in UV ($\lambda = 380$

nm). Then the phosphorescent time was measured by means of the same photomultiplier tube connected to a digital millivoltmeter.

In figure 8 is shown a composite sample of $\text{PET-SrAl}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ prepared by the method described in the paper. The sample was photographed after 5 min. of exposure to a UV lamp ($\lambda = 350$ nm) for approx. 60-70 s.

Conclusions

A new preparation method based on mixing the constituents in specific solvents for PET of phosphorescent composite of polyethyleneterephthalate- $\text{SrAl}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ was described.

The possibility of preparing Eu, Dy doped strontium aluminate crystals in nanometric range compatible with polymer matrix was investigated.

Characteristics of absorption / photonic emissions, phosphorescent decay time were investigated for europium/dysprosium doped strontium aluminate, and for the composite prepared by the new developed method.

Composites of $\text{PET-SrAl}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ prepared by the described method have a high potential to be applied in the fields of optoelectronic devices, especially in illumination sources with high energy efficiency and in autonomous display / warning systems.

Due to low sensitivity of PET polymer matrix against typical solvents, the composites might be used to obtain phosphorescent films lacquers and paints.

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