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INVESTIGATIONS ON THE Eu^{3+} DOPED SnO_2 NANOPOWDER

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Nanostructured SnO_2 powder doped by Eu^{3+} has been prepared by sol-gel technique. The chemical composition, the morphology and the luminescence characteristics were studied. The samples were further investigated by XRD, SEM, EDX (energy dispersive X-ray spectroscopy) and fluorescence spectroscopy.

Keywords: Tin oxide, Nanopowder, Eu^{3+} doping, Luminescence, XRD, SEM, EDX

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1. Introduction

Recently a great interest is developed to nanosized semiconductors because of their characteristic: the so-called quantum-size effect. The band gap of nanostructured semiconductor powders is size-sensitive and this determines the liked absorption and luminescent properties [1-5].

The tin-dioxide is a semiconductor material used for many applications such as gas-sensor [6], optical transparent conductive electrode [7], solar cells [8], protective layers [9-12] and others. The SnO_2 has a unique characteristic: posses a wide band gap at 3.6 eV. This can be modified by the material dimensions when the particles of SnO_2 powder are nanosized. The obtaining of this material required a development of easy synthesis in a reproductive manner.

The nanosized SnO_2 can be doped with a trivalent rare-earth ions. The consequence of the excitation of SnO_2 band gap is the transmission of the absorption energy for lanthanide ion, which causes the appearance of the photoluminescence effect [3-5].

The synthesis of rare-earth ions doped nanostructured SnO_2 powder gives a possibility of applications for production of opto-electronic devices, for example as nanoscopic optical storage elements.

This paper present the preparation of Eu^{3+} doped nanostructured SnO_2 powder by sol-gel technique and the study of chemical composition, the morphology and the luminescence characteristics by XRD, SEM, EDX (energy dispersive X-ray spectroscopy) and fluorescence spectroscopy.

2. Experimental

The Eu^{3+} doped SnO_2 was prepared by the sol-gel techniques. The powder was doped by using two procedures:

a. The concentration of Eu^{3+} is 2 at.% as compared to the Sn content in the precursor solution.

b. The concentration of Eu^{3+} is 4 at.% atom as compared to the Sn content in the precursor solution.

The precursor was obtained from an A and B solution mixture. The A solution contains 7 g $SnCl_4 \times 5H_2O$ (Merck) in 10 ml 2M propanol. The B is an aqueous solution, which contains $Eu(NO_3) \times 5H_2O$ (Fluka). The obtained sol is neutralized with a 20 % ammonia solution. After one hour, the resulted precipitate is filtrated and dried 2 hours at 60 ºC. The half amount of the samples was calcinated for 30 min. in an electrical oven at 400 ºC, the remaining part was fired at 600 ºC.

3. Methods

The XRD measurements were carried out using a Phillips type Bragg-Bretano diffractometer with Cu-K_α radiation (Cu-target tube PW 3710/PW 1050) (λ=0.154186 nm).

The morphology and structure were investigated by SEM on a HITACHI S-570 electron microscope. The acceleration voltage was 20 kV and the magnification was 1000 and 10000.

The investigation of the chemical composition was performed with energy dispersive X-ray RÖNTEC EDR 258 spectrometer.

The luminescence characteristics were determined by a Perkin Elmer LS 50B type luminescence spectrometer.

4. Results and discussion

The as-prepared Eu^{3+}/SnO_2 nanostructure powder exhibits an yellow colour.

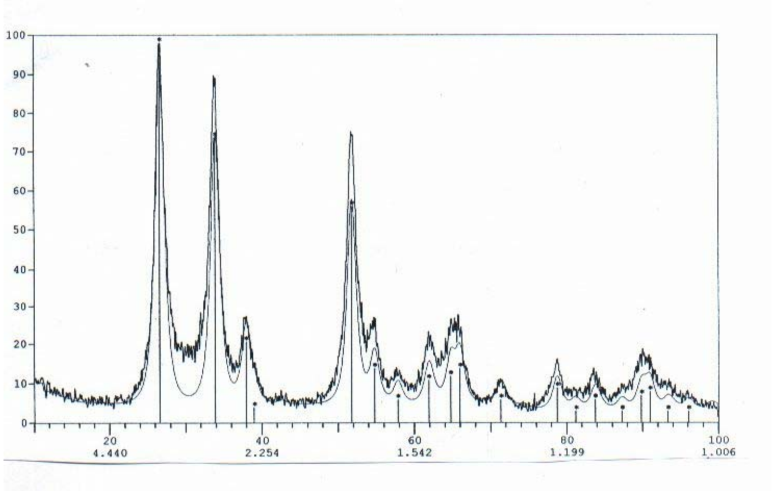

Fig. 1 . The XRD diagram of the Eu^{3+}/SnO_2 powder.x: 2 θ(deg.) y: intensity

The XRD measurements are presented on Fig. 1. For phase identification was used the ASTM Powder Diffraction File and the Fiche No. 41-1445 (Cassiterite). The conclusion was that the as prepared Eu^{3+}/SnO_2 nanostructured powder has a tetragonally rutil crystalline structure.No other phases have been identified, No separated Europium phase was observed.

The crystallite mean size has been estimated by using the Debye-Scherrer equation. In the calcinated powder, independent from the doping level, the size of the particles are 7.7 nm, at 400 ºC, and are 9 nm at 600 ºC. Higher calcination temperatures are favorable to the growth of the particles size.

The chemical composition of the nanopowders was investigated by EDX (fig.2 and fig.3). These spectrums show the percentage of Eu^{3+} from the samples; these values coincide with the quantity from the precursor solution.

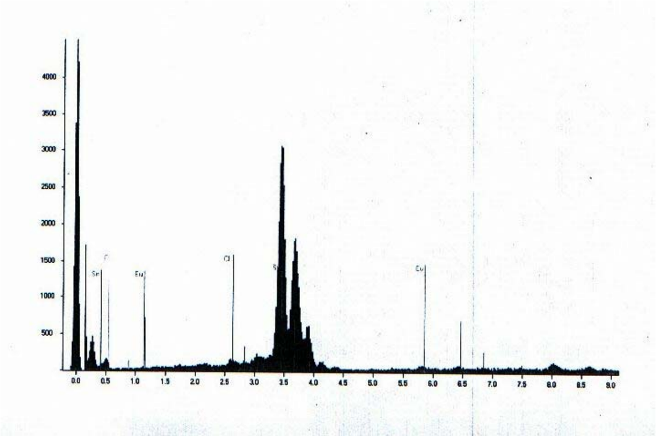

Fig. 2. Spectrum obtained by Röntgen analysis (2% doping level at 400 C˚) x: energy (keV) y: CPS; signal.

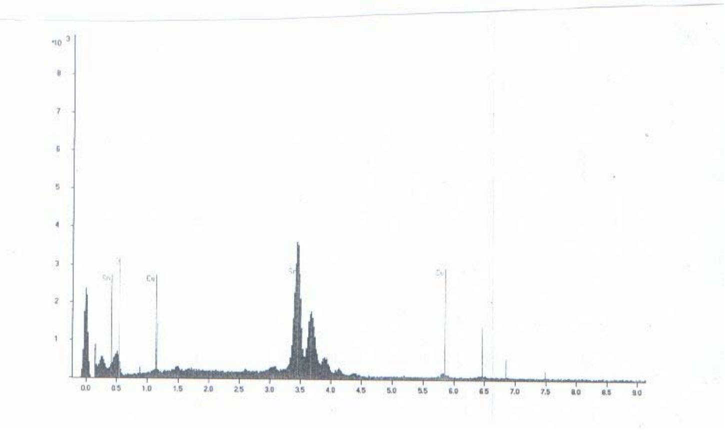

Fig. 3. Spectrum obtained by Röntgen analysis (4% doping level at 400 C˚) x: energy (KeV) y: CPS signal.

Table 1. The chemical c.omposition of the samples

Samples		Element concentration [%]			
		Sn	**O**	**Eu**	**Cl**
I	400 C˚	86.82	10. 69	2.11	0.38
I	600 C˚	76.69	20.96	2.04	0.20
II	400 C˚	62.58	33.15	4.27	-
II	600 C˚	71.64	24.48	3.88	-

The Table 1 shows the chemical composition of the nanopowders. The chlorine ion is an impurity due to precursor. The chlorine ions can affect the luminescence properties of SnO_2.

The morphostructural investigation (Fig. 4-7) demonstrates that the Eu^{3+}/SnO_2 powders are formed by nanosized particles agglomerations. Consequently, the increase of the calcination temperature determines a more homogeneous surface for these samples.

The investigation established the correlations between preparative parameters and morpho-structural and luminescence characteristics.

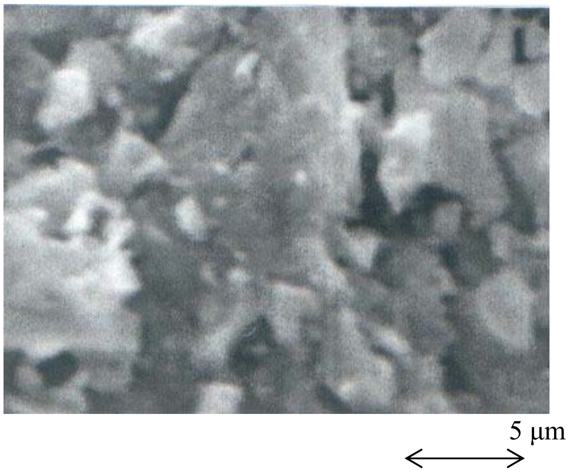

Fig. 4. SEM micrography at 2% doping level at 400 C°

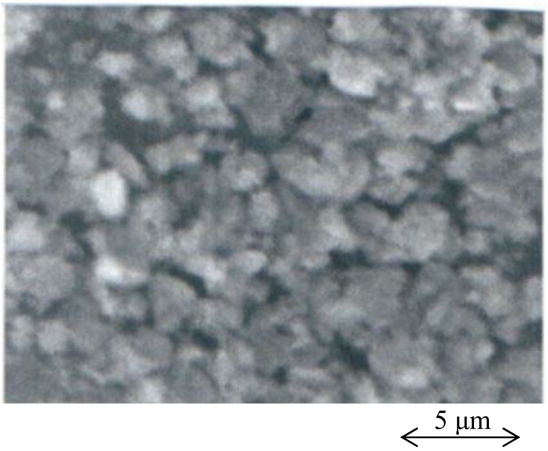

Fig. 5. SEM micrography at 2% doping level at 600 C°

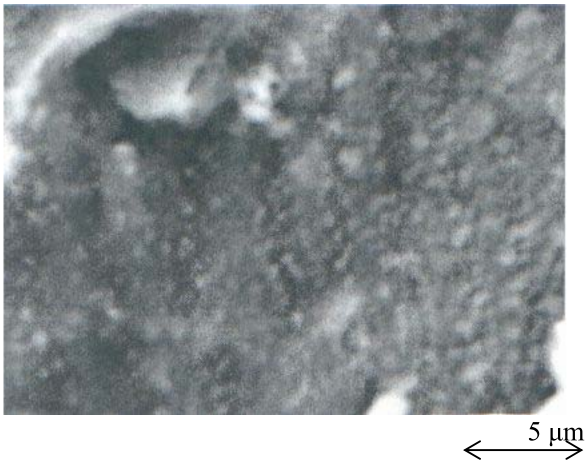

Fig. 6. SEM micrography at 4% doping level at 400 C°

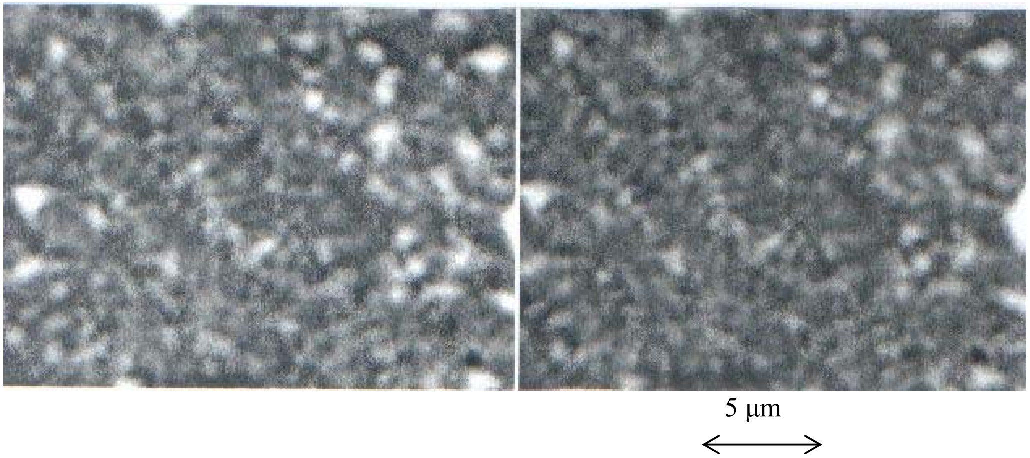

Fig. 7. SEM micrography at 4% doping level at 600 C˚.

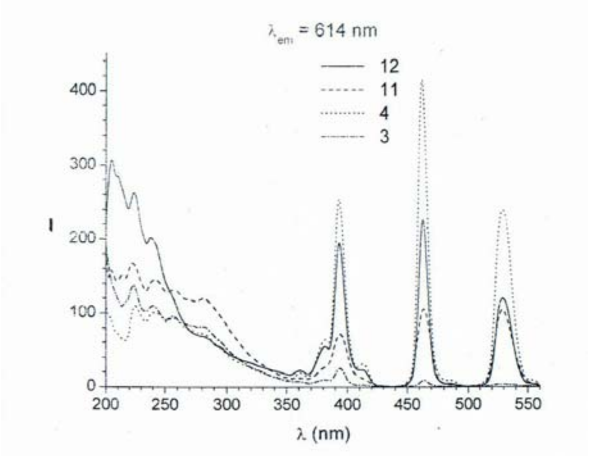

Fig. 8 The emission spectrum of Eu^{3+}/SnO_2 powder.

3: 2% doping level at 400 ˚C **11**: 2% doping level at 600 ˚C

12: 4% doping level at 400 ˚C **4**: 4% doping level at 600 ˚C

x: wavelength y: relative intensity

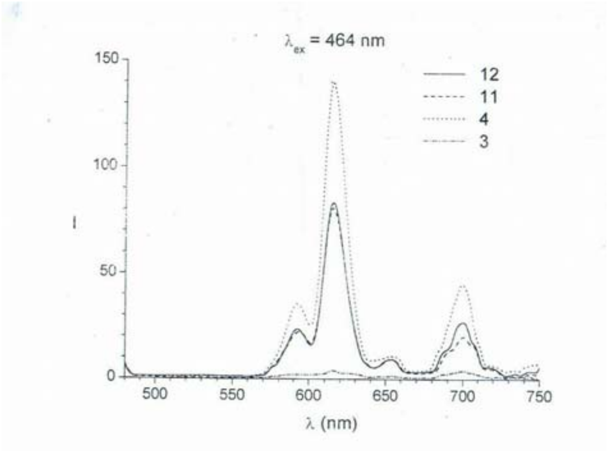

Fig. 9. The excitation spectrum of Eu^{3+}/SnO_2 powder.

3: 2% doping level at 400 ˚C **11**: 2% doping level at 600 ˚C

12: 4% doping level at 400 ˚C **4**: 4% doping level at 600 ˚C

x: wavelength y: relative intensity

The luminescence of the prepared nanopowder shows a very short lifetime, practically the samples show fluorescence. The intensity variation of the fluorescence depends on the doping level and calcination temperature and it is evidenced in an emission and excitation spectrum (Fig. 8 and 9). These spectra demonstrate the validity of theLambert Beer law, a linear dependence between the concentration of the fluorescence materials and the intensity values. In the same time, we can say that the fluorescent intensity is enhanced with the doping level and with the increase of the calcination temperature.

In pure SnO_2 host, the emission is ascribed to electron transition, mediated by defect levels in the band gap, such as oxygen vacancies, tin interstitials, etc.

The probable reason of the luminescence of Eu^{3+} doped SnO_2 is the existence of the excitation band corresponding to the band-gap energy and this is the evidence of the energy transfer from nanosized SnO_2 crystal to the Eu^{3+} ions. The electron-hole pairs are generated by the energy absorbed in the nanocrystals, the energies of which are recombined and then transferred to the Eu^{3+} ions.

5.Conclusions

The Eu^{3+}/SnO_2 powders prepared by sol-gel techniques are nanosized particles agglomerations which presents the so called quantum size effect, i.e. the size tunable materials properties. The luminescence processes are associated with oxygen vacancies in the host and related with the recombination of electrons in singly occupied oxygen vacancies with photo excited holes in the valence band. The homogeneity of their surface increases with the calcination temperature. The fluorescence intensity increases with the doping level and calcination temperature.

References

[1] S. J. L. Ribeiro, C.V. Santilli, S. H. Pulcinelli, L. F. C. Oliveira, J. Sol-Gel. Sci. Technol. **2** (1994).

[2] E. A. Morais, S. J. L. Ribeiro, C.V. Scalvi, C.V. Santili, S. H. Pulcinelli, Y. Messaddeq, J. Alloys and Compounds **344**, 217 (2002).

[3] F. Gu, S.F. Wang, M.K. Lu, G.J. Zhou, D.R. Yuan, Optical Materials **25**, 59 (2004).

[4] P. S. Chowdhury, S.Saha, A. Patra, Solid State Communication **25**, 131 (2004).

[5] F. Gu, S.F. Wang, C.F.Song, M.K. Lu, Y. X. Qi, G.J. Zhou, D. Xu, D.R. Yuan, Chem. Physics Letters, **372**, 451 (2003).

[6] S. Saukko, V. Lantto, Thin Solid Films 436, 137 (2003).

[7] F. Kormos, L. Sziraki, I. Tarsiche, Laboratory Robotics Automation **24**, 29 (2000).

[8] I. B. Bernardi, L.E. Soledade, I. A. Santos, E. R. Leite, E. Longo, J. A. Varela, Thin Solid Films **405**, 228 (2002).

[9] I. Puetz, F.N. Chalvet, M.A. Aegerter, Thin Solid Films, **442**, 53 (2003).

[10] I. Kurisawa, M. Shiomi, S. Ohsumi, M. Tsubata, Journal of Power Source **95**, 125 (2001).

[11] J. Szanyi, Applied Surface Science **185**, 161 (2002).

[12] A. P. Rizzato, L. Broussous, C. V. Santilli, S. H. Pulcinelli, A. F. Craievich, Journal of Non-Crystalline Solids **284**, 61 (2001).