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PMMA nanocomposite films
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CHARACTERIZATION OF PbS / PMMA NANOCOMPOSITE FILMS ELABORATED BY DIRECT INCLUSION METHOD

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Abstract - PbS / PMMA nanocomposite films were prepared by dispersion of PbS crystallites in PMMA solution and dip-coated on glass substrates. The X-ray diffraction (XRD) results of the composite films show that the introduced PbS crystallites in PMMA matrix are nanometric with cubic crystalline structure. Raman spectrometry analysis reveals a peak at 220 cm^{-1} due to the PbS LO mode. Characterization by infrared spectroscopy of the PbS / PMMA nanocomposite films demonstrate the existence of an absorption band due to Pb-O bond stretching vibration at 433 cm^{-1}. The optical absorption measurements in the UV-visible-near infrared spectrum show the presence of several absorption bands. These results suggest that the introduction of PbS nanoparticles into PMMA matrix can be used as color centers in biological applications and medical imaging.

Résumé - Elaboration et caractérisations de films nanocomposites PbS/PMMA par la méthode d'inclusion directe. Des films nanocomposites PbS/PMMA ont été préparés par dispersion des cristallites de PbS dans le PMMA en solution et déposés sur des substrats en verre par la technique dip-coating. Les résultats de la caractérisation par diffraction des rayons X (DRX) ont montré l'introduction de particules de PbS nanométriques de structure cubique dans le PMMA. L'analyse par spectrométrie Raman a révélé un pic relatif au mode LO de PbS centré à 220 cm^{-1}. La caractérisation par spectroscopie infrarouge du nanocomposite PbS/PMMA a permis de mettre en évidence l'existence d'une bande d'absorption due à la vibration d'élongation de la liaison Pb-S à 433 cm^{-1}. Les mesures d'absorption optique dans la gamme UV-visible- proche infra-rouge ont montré la présence de plusieurs bandes d'absorption. Ceci indique que les particules du PbS introduites dans le PMMA pourraient être utilisées comme centres colorés dans les applications en biologie et en imagerie médicale.

1. INTRODUCTION

The semiconducting particles in nanometric size are characterized by very different and interesting physical properties compared to those of the same material in bulk state. These particularities are the result of the quantum confinement. Therefore, nanoparticles have particular interest in various research laboratories in order to obtain new materials. This is due to various

potential applications of these nanomaterials in electronics, optics and catalysis [1-4]. With the improvement of nanoscale materials synthesis methods and processes, significant advances have been made in controlling the particle size distribution. Thereby, semiconducting nanoparticles can find new applications in other fields such as biology, light emission and photovoltaics [5, 6].

However, the aggregation phenomenon leads to very important surface / volume ratios of the nanoparticles and generates an amplification of the surface effects. To avoid these constraints, the nanoparticles were dispersed in crystalline or amorphous matrices such as polymers, ceramics glass and organic polymer [7-9]. The role of the matrix is to improve the stability of the particles and to reduce the surface effects.

Lead sulphide (PbS) in the nanocrystalline state, has a single spectral emission in the near infrared [10]. It is also characterized by a large Bohr radius (20 nm), high dielectric constant and a low band gap energy (0, 41 eV). This value can be increased up to 5 eV by decreasing the particle size [11]. It is also being studied for use in photovoltaic solar cells [5].

PMMA (poly (methyl methacrylate)) is a widely employed material in polymeric optical fibers used in computer data exchange [12]. Thus, PbS quantum dots dispersed in PMMA (composite PbS / PMMA) can be used as an excellent polymeric optical fibers in the infrared optical communication [12].

In this work, PbS / PMMA nanocomposite films were prepared by soft chemistry method associated with the dip-coating technique. The structural, optical and vibrational properties of the elaborated nanocomposites films were investigated and discussed.

2. MATERIALS AND METHODS

In a first step, PbS nanometric-sized crystallites were isolated by sedimentation in a chloroform solution. 100 mg of PbS commercial powder (Aldrich, 98 %) are introduced in 20 ml of chloroform at room temperature. The solution was kept under magnetic stirring to obtain homogeneous dispersion. Then, the mixture was left to stand to achieve the sedimentation of large particles. For the preparation of the PbS / PMMA composite films, only the near-free surface solution part is used.

In the second step, PMMA was dissolved in chloroform under room temperature magnetic stirring for 6 hours. The final solution used for the films deposition was obtained by mixing 5 ml of the solution prepared in the first step with 15 ml of the PMMA solution.

The deposition of PbS / PMMA composite films was carried out using a KSV type dip coater. The pulling speed and the number of deposited layers were fixed to 100 mm / min and 20, respectively.

The crystalline structure of the prepared nanocomposite films was investigated by X-ray diffraction (XRD) with a PanAnalytical diffractometer, operating at 40 kV and 30 mA using Cu Ka radiation (wavelength k = 1.54059 Å). Raman spectra were measured with Bruker Optik GmbH Senterra microscope type using an Olympus 100x objective MPLN with 532 nm excitation wavelength. Infrared absorption spectra (FTIR) were performed by Shimadzu IRaffinity-1 spectroscope. The optical density spectra were recorded at room temperature using a Safas UVmc2 spectrophotometer.

3. RESULTS AND DISCUSSION

Figure 1 shows XRD diffractogram of the prepared PbS / PMMA nanocomposite film. Several diffraction peaks at 25.91 °, 30.02 °, 43.03 ° and 50.97° are observed. They are related with reflection peaks (111), (200), (220) and (311), respectively, and all these diffraction peaks can be perfectly indexed to diffractograms of the PbS particles displaying the zinc blende (ZB) crystalline phase according to reference patterns JCPDS 05-0592. The PbS / PMMA composite DRX spectrum

is characterized by a more pronounced (200) diffraction peak, which shows a preferred orientation of PbS particles in PMMA matrix. The average size of PbS crystallite dispersed in the PMMA film was estimated using the Scherrer formula $D = 0.9 \lambda/(\beta \cos\theta)$, where λ is the X-ray wavelength (1.54 Å), θ is the diffraction angle and β is the full width at half maximum (FWHM) of the diffraction peak (in radians). The average size was found to be around 46 nm.

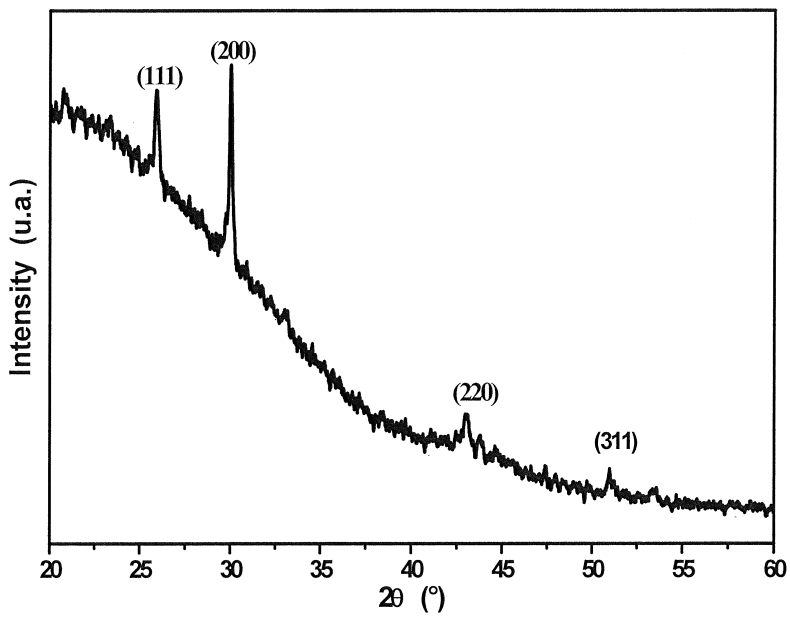

Figure 1. X-ray diffraction (XRD) spectrum of PbS / PMMA composite film.

Figure 2 shows the Raman spectrum of the elaborated PbS / PMMA nanocomposite film. The intense peaks observed in the spectrum are due to vibrations of bonds of the PMMA matrix and substrate, while the peak appeared at 220 cm^{-1} is assigned to LO mode of PbS crystallites [13, 14]. All the others bands are due to the vibrations of PMMA matrix molecules. The peaks centred at 260 and 366 cm^{-1} are due respectively to the C–C out-of-plane vibration [15] and C-O out of plane bending vibration [16]. The bands centred at 483 and 556 cm^{-1} are assigned to the vibration in plane of C-C bond [16]. The bands located at 601 and 667 cm^{-1} are due respectively to C-C-O bond vibration [17] and C-H out-of-plane vibration [18]. The little peak located at 620 cm^{-1} is due to Si-O bond vibration of the substrate [19].

FTIR spectrum of the elaborated PbS / PMMA nanocomposite film is shown in *Figure 3*. The band observed at 433 cm^{-1} is due to the Pb-S bond stretching vibration. The band centred at 502 cm^{-1} is attributed to the in-plane deformation vibration of C-C bond in PMMA [14] and the other, located at 754 cm^{-1}, is due to the stretching vibration of the C-H bond of the PMMA matrix [20].

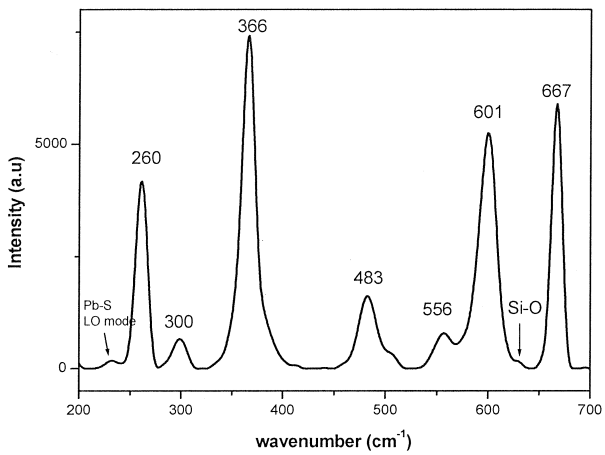

Figure 2. Raman spectrum of the PbS / PMMA nanocomposite film

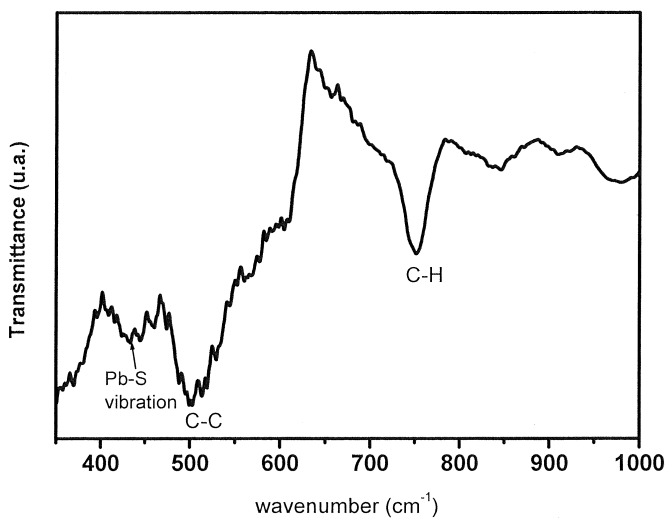

Figure 3. FTIR spectrum of the PbS / PMMA nanocomposite film.

Figure 4 shows the normalized absorption spectra in the UV-visible range of the PbS / PMMA nanocomposite film. The observed undulations in the absorption spectrum of the

PbS / PMMA nanocomposite film indicate that the sample is of good optical quality. These undulations result from the Fabry-Perot interferences. These results show that the PbS nanoparticles can act as color centers when introduced into the PMMA matrix.

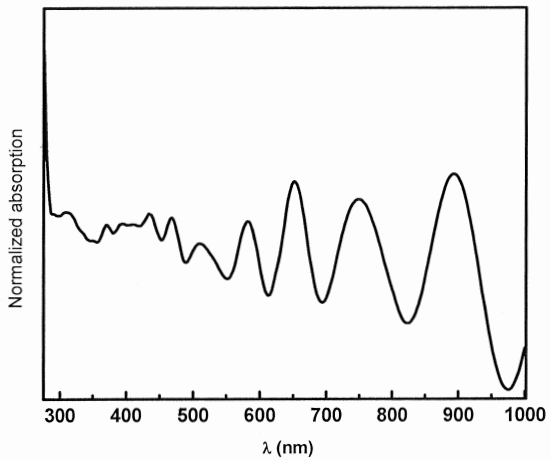

Figure 4. Normalized optical absorption spectrum of PbS / PMMA nanocomposite film

The optical transmittance spectra of the pure PMMA and PbS / PMMA composite films are shown in *figure 5*. The transparency of the samples exceeds 80 %. However, a shift toward higher wavelengths is observed in the transmittance threshold after the introduction of the PbS crystallites in PMMA matrix.

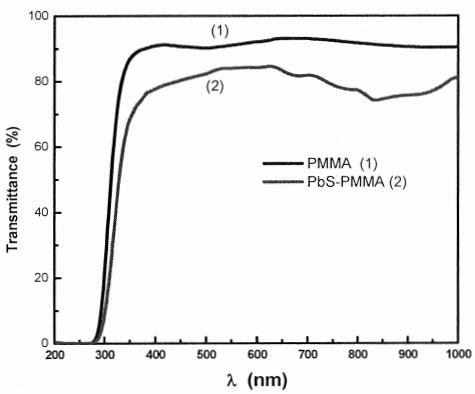

Figure 5. Optical transmittance spectra of the pure PMMA and PbS / PMMA composite films.

4. CONCLUSION

PbS/PMMA nanocomposite films have been dip-coated from solution obtained by direct dispersion of PbS particles in liquid PMMA. XRD results confirmed the nanometric size and the cubic structure of the PbS particles after their introduction in transparent PMMA matrix. The Raman spectrometric analysis of PbS / PMMA nanocomposites showed a low intensity band near 220 cm^{-1} due to LO phonons mode of PbS. FTIR characterization of PbS /PMMA nanocomposite films showed an absorption band around 433 cm^{-1}due to the Pb-S bond stretching vibration. The optical transmission spectrum showed a shift of the transmission threshold to the higher wavelengths and a transparency over than 80%. The undulations observed in the normalized optical absorption spectrum testify the good optical quality of the elaborated nanocomposite films. According to the obtained results, PbS/PMMA nanocomposite films can find applications as color centers in biology and medical imaging

5. REFERENCES

[1] C.N.R. Rao, A.K. Cheetham, J. Mater. Chem. 11 (2001) 2887-2894.
[2] C.N.R.Rao, A. Govindaraj, Nanotubes and Nanowires, Royal Soc. Chem. (London), 2005
[3] R.H.Baughman, A.A. Zakhidov, W.A. de Heer, Science, 297 (2002) 787-792.
[4] Z.L.Wang, Ann. Rev. Phys. Chem., 55 (2004) 159-196.
[5] I. Chakraborty, S.P.Moulik, J. Nanoparticle Res. 6 (2004) 233-240.
[6] S.A. McDonald, G. Konstantatos, S.Zhang, L.Levina, E.H.Sargent, Nat. Mater.4 (2005) 138-142.
[7] J.M.Benoit, B. Corraze, S. Lefrant, W. Blau, P. Bernier,O. Chauvet, Synth. Met., 121 (2001)1215-1216.
[8] D. Qian, E.C. Dickey, R. Andrews, and T. Rantell, Appl. Phys. Lett., 76 (20) (2000) 2868-2870.
[9] A.R.Bhattacharyya, T.V.Sreekumar, T.Liu, S.Kumar, L. M.Ericson, R.H. Hauge, R.E. Smalley, Polymer 44 (2003) 2373-2377.
[10] X.S.Zhang, X.Y.Dong, Y.G.Liu, G.Y Kai, Z.Wang, L. Li, X. Han, Y.Li, Optoelectron. Lett. 3 (2007) 337-338.
[11] R.Thielsch, T. Bohme, R. Reiche, D. Schlafer, H.D. Bauer, H.Bottcher, Nanostruct. Mater. 10 (1998)131-149.
[12] X.S. Zhang, G.Y. Kai, L. Li, Y. Li, X.Han, Z.Wang, Y.G. Liu, X.Y. Dong, J. Optoelectron. Laser, 17 (2006)1487-1491.
[13] R. G. Pérez, G H. Téllez, U.P. Rosas, A. M.Torres, J. H. Tecorralco, L. C. Lima, O.P. Moreno, J. Mat. Eng. A 3 (2013) 1-13.
[14] Ovsyannikov, S. V. , Shchennikov, V. V. , Cantarero ,A. , Cros, A., Titov, A. N., Mater. Sci.Eng. A 462 (2007) 422–426
[15] M. K. Murali, V. Balachandran, M. Murugan, M.Karnan, J. Basic and Appl. Phys. 1 (2012) 79-88.
[16] R. H. Mas, H. Mas, S. Kathiresan, S. Mohan, Der Pharma Chemica 2 (2010) 316-323.
[17] K. J.Thomas, M. Sheeba, V.P.N. Nampoori, C.P.G.Allabhan, P.Radhakrishnan, J. Opt. A: Pure Appl. Opt. 10 (2008) 055303-055308.
[18] D. K. B. Renuka, R. Madivanane, Eng. Sci. Technol. 2 (2012) 795-799.
[19] T.Lopez, P.Bosch, M.Asomoza, R. J. Gomez, Catal.133 (1992) 247-259.
[20] S. Umamaheswari, M. Murali, Chem. Engg. 64 (2013) 19159-19164.

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