Spectroscopy and Electron Microscopy for the Characterization of CdSxSe1-x Quantum Dots in a Glass Matrix

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Abstract : When semiconductor particles are reduced in scale to nanometer dimension, their optical and electro-optical properties strongly differ from those of bulk crystals of the same composition. Since sampling is often not allowed concerning cultural heritage artefacts, the potentialities of two non-invasive techniques, such as Raman and Fiber Optic Reflectance Spectroscopy (FORS), have been investigated and the results of the analysis on some original glasses of different colours (from yellow to orange and deep red) and periods (from the second decade of the 20th century to present days) are reported in the present study. In order to evaluate the potentialities of the application of non-invasive techniques to the investigation of the structure and distribution of nanoparticles dispersed in a glass matrix, Scanning Electron Microscopy (SEM) and energy-disperse spectroscopy (EDS) mapping, together with Transmission Electron Microscopy (TEM) and Electron Diffraction Tomography (EDT) have also been used. Raman spectroscopy allows a fast and non-destructive measure of the quantum dots composition and size, thanks to the evaluation of the frequencies and the broadening/asymmetry of the LO phonons bands, respectively, though the important role of the compressive strain arising from the glass matrix and the possible diffusion of zinc from the matrix to the nanocrystals should be taken into account when considering the optical-phonons frequency values. The incorporation of Zn has been assumed by an upward shifting of the LO band related to the most abundant anion (S or Se), while the role of the surface phonons as well as the confinement-induced scattering by phonons with a non-zero wavevectors on the Raman peaks broadening has been verified. The optical band gap varies from 2.42 eV (pure CdS) to 1.70 eV (CdSe). For the compositional range between $0.5 \leq x \leq 0.2$, the presence of two absorption edges has been related to the contribution of both pure CdS and the CdSxSe1-x solid solution; this particular feature is probably due to the presence of unaltered cubic zinc blende structures of CdS that is not taking part to the formation of the solid solution occurring only between hexagonal CdS and CdSe. Moreover, the band edge tailing originating from the disorder due to the formation of weak bonds and characterized by the Urbach edge energy has been studied and, together with the FWHM of the Raman signal, has been assumed as a good parameter to evaluate the degree of topological disorder. SEM-EDS mapping showed a peculiar distribution of the major constituents of the glass matrix (fluxes and stabilizers), especially concerning those samples where a layered structure has been assumed thanks to the spectroscopic study. Finally, TEM-EDS and EDT were used to get high-resolution information about nanocrystals (NCs) and heterogeneous glass layers. The presence of ZnO NCs (< 4 nm) dispersed in the matrix has been verified for most of the samples, while, for those samples where a disorder due to a more complex distribution of the size and/or composition of the NCs has been assumed, the TEM clearly verified most of the assumption made by the spectroscopic techniques.

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