Tunable visible photoluminescence of powdered silica glass

P.S. Pizani a,*, M.R. Joya a, F.M. Pontes b, L.P.S. Santos c, M. Godinho Jr. c, E.R. Leite c, E. Longo c

a Departamento de Física, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, São Paulo, Brazil
b Departamento de Química, Faculdade de Ciências, Universidade Estadual Paulista, Av. Luis E. C. Cunha, 14-01, Bauru, São Paulo, Brazil
c Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, São Paulo, Brazil

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Abstract

Intense photoluminescence in the visible region was observed at room temperature in standard soda-lime-silica glass powder, mechanically milled in a high-energy attrition mill. The emission band maximum shows an interesting dependence on the exciting wavelength, suggesting the possibility to tune the PL emission. These findings indicate that the photoluminescence may be directly related to unsatisfied chemical bonds correlated with the high surface area. The Raman scattering and ultraviolet–visible optical reflectance measurements corroborate this assertion. Transmission electron microscopy measurements indicate that samples milled more than 10 h present the formation of nanocrystallites with about 10–20 nm.

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1. Introduction

During the last years, it has been reported intense photoluminescence (PL) emission in the visible region of the electromagnetic spectrum, at room temperature, of several different nanostructured or highly disordered materials as nanowires and porous silicon, silica-based mesoporous, ferroelectrics with ABO3 type perovskite structure (A = Ca, Ba, Pb, Sr), and AWO4-type, only to cite some [1–6]. The origin of this type of luminescence is always attributed to unsatisfied chemical bonds. In the ferroelectric case, the PL emission in the visible region was correlated with the high degree of structural disorder: as their energy band gap are at about 3–4 eV, in their highly local disordered state it is expected many localized electronic levels within the optical gap, given rise to luminescence in the visible region [7]. The fact that standard silica glass is transparent in the visible region with a strong absorption in the ultraviolet (UV) makes it a good candidate to test this model and to show that a so important material may present very interesting optical properties after suitable intervention.

In this work, to reach to a very high disordered state of standard soda-lime-silica glass, the samples were milled in a high-energy attrition mill during different times. To probe the local disorder on the structure, it was used Raman scattering, ultraviolet–visible optical absorption (UV–vis) and transmission electron microscopy (TEM) techniques. The results of PL measurements showed a different behavior from that reported in the literature for silica-based mesoporous or nanoscale materials, in which the PL peak positions do not vary with different excitation wavelengths [1].

2. Experimental procedures

Standard soda-lime-silica glass was mechanically milled in a high-energy attrition mill for different times, from 10 to
600 min. Zirconia balls with 1 mm diameter were used, in a commercial attrition mill turning at 450 rpm. The PL emission was performed using a U1000 Jobin–Yvon double monochromator coupled to a cooled GaAs photomultiplier and a conventional photon counting system. Several exciting wavelengths from 458 to 633 nm of an Ar and He–Ne lasers were used. The Raman spectra were performed in the same equipment, using the 488 nm as excitation. To prevent overheating of the samples, cylindrical lens and laser power below 100 mW were used at the output of the laser, a care very important to be adopted in measurements of amorphous materials in very fine powder samples. The UV–vis measurements were performed using a Cary 5G equipment, in the total reflection mode. All measurements were taken at room temperature.

3. Results

Transmission electron microscopy was used to follow the structural changes as a function of the milling time. Fig. 1 shows results after 10 h milling time demonstrating formation of crystallites with diameter of about 10–20 nm, immersed in the amorphous media. The density of nanoparticles increases with the milling time up to 24 h preserving their size.

Fig. 2 shows the photoluminescence spectra of the standard silica glass used in this work exhibiting two broad bands at about 530 and 680 nm. Among the PL bands, the two sharp features near the excitation line are the characteristic Raman peaks of silica glasses, localized at 600 and 1100 cm$^{-1}$ from the exciting wavelength. As can be observed from the spectra, the maximum PL peak positions are independent of the excitation energy. This behavior is indicative that the origin of these PL emissions comes from electronic transitions between well-defined energy levels. It can be attributed probably to impurities.

Fig. 3 displays the evolution of the PL spectra for glass milled for different times. Increasing the milling time, a new intense band emerges at about 540 nm. After 10 h, no more important changes occurs in the PL spectra. Fig. 4 displays the PL spectra of the sample milled for 10 h for six different exciting energies. It is noticeable the dependence of the

Fig. 1. Transmission electron micrograph a glass milled by 10 h, showing the formation of nanocrystallites with sizes of about 10–20 nm immersed in an amorphous media.

Fig. 2. Photoluminescence spectra of the standard silica glass without treatment, excited with the 514 nm, 488 nm and 458 nm lines of an argon ion laser. The two sharp peaks near the excitation are the characteristics Raman peaks of the silica glass.

Fig. 3. Evolution of the photoluminescence spectra of the standard silica glass for different milling times: without treatment, 1 h, 3 h and 10 h. Spectra excited with the 488 nm, at room temperature.
maximum peak position with the exciting wavelength, which can be well described by a linear dependence between the ratio emission wavelength/exciting wavelength versus excitation wavelength, showed in the graph of Fig. 5. This behavior indicates that the origin of this luminescence is different from that at 530 and 680 nm. A very similar dependence was already observed in amorphous ferroelectric materials with ABO$_3$ type perovskite structure (A = Ba, Ca, Pb, Sr and B = Ti, Zr) prepared by the polymeric precursor method, at room temperatures and also on the ultra fine PbTiO$_3$ powder milled in the high-energy attrition mill [8].

To follow the milling effect on the vibrational spectrum, Raman scattering measurements were performed on the samples. The results, displayed in Fig. 6, show that increasing the milling time increases the structural disorder. The spectra of the samples milled for 10 h present a very weak and broadened peaks characteristic of the silica glass, indicating that after these milling times there are still a feeble memory of the original symmetry, but in a highly disordered state.

Fig. 7 displays the reflectance spectra of the glass before milling (full line) and after milling for 10 h (dotted line). The spectra show that the absorption increases after mill-
ing, indicating the generation of electronic energy levels in the visible region. This result is also strongly indicative of the formation of a highly disordered state, confirming the Raman and photoluminescence results.

4. Discussion

The above results are strongly indicative that the PL emission stems from the highly disordered state of the materials in both cases, milled glasses or ABO3 type perovskites. Furthermore, it is possible to explain why the PL peak position change with the exciting photon energy if we assume that, in highly structural disordered materials (at local level), instead a well-defined energy band gap, there is a distribution of localized electronic states, coupled with local vibrational modes, forming a distribution of vibronic states [9]. Here, it is worth to remember that the details of the band structure in solids are mainly determined by the potential within the unit cell rather than by the long-range periodicity. In our case, the PL may come from radiative decay of vibronic states and the peak position must follow the excitation, as observed experimentally in our measurements. In the perovskites, the high disordered state is due to disorder in the Ti–O octahedron: XANES (X-Ray Absorption Near Edge Spectroscopy) measurements showed five-fold oxygen Ti co-ordination [10]. Our first principle molecular calculations for BaTiO3 and SrTiO3 indicate that the energy band gap is strongly dependent on the distance Ti–O: for five-fold oxygen co-ordination, there is a reduction of about 20–30% in the energy band gap. For crystalline perovskites, the conduction band is formed mainly by 3d states of the titanium, while the valence band by the 2p states of the oxygen [11]. In the glass case, probably the high disordered state may be related to the increases in the density of electronic surface states, since the mill process increases the surface area. For nanostructured silica-based materials, the most accepted is that the PL emission is related to non-bridging oxygen (NBO) located in both, surfaces and bulk [12]. However, in our case, Nuclear Magnetic Resonance measurements showed no changes in the chemical shift of the Si-29 signal, indicating that no important changes in the Si–O bonds occurred within the NMR sensitivity [13]. Then, the most probable is that the PL emission comes from NBO’s located at the small grain surfaces or even adsorption of impurities can not be disregarded.

5. Conclusion

Intense photoluminescence was observed at room temperature in ultra fine silica glass mechanically milled in a high-energy attrition mill. The photoluminescence spectra present a broad band in the visible region, with the maximum peak position depending on the exciting wavelength, indicating the possibility to tune the PL emission with the exciting energy. The results indicate that the PL emission comes from the highly structural disordered state, probably due to the high density of surface dangling bonds or adsorbed impurities. This assertion was corroborated by the Raman and UV–vis measurements.

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