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Modeling and Characterization of Microspheres with Silver Molecular Clusters for Sensor Applications †

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Abstract: This study explores silver molecular cluster-containing microspheres for advanced sensors. These microspheres are synthesized through an ion exchange process with silver nitrate and sodium nitrate, creating unique optical properties. Simulation shows enhanced radiation interaction due to extended fundamental mode propagation. The study investigates luminescence in the visible range (400–600 nm) when excited by long-wavelength UV light (360–410 nm), offering potential for sensing applications. These microspheres find use in environmental sensing (pollutant detection), biomedicine (drug delivery, bioimaging), and industrial process monitoring.

Keywords: microspheres; silver molecular clusters; advanced sensor applications; ion exchange; glass matrix; refractive index gradient; optical characteristics; luminescence; UV light excitation; sensor technologies

1. Introduction

In recent years, Whispering Gallery Mode (WGM) microcavities have garnered significant attention as potent optical sensors for the label-free detection of various biological and chemical molecules and particles. These sensors can identify a range of molecules with refractive indices differing from that of the surrounding environment, eliminating the need for labeling. They rely on the observation of frequency shifts in WGM resonance due to minute perturbations in the mode volume. The efficacy of these sensors has been demonstrated in the detection of a variety of objects, including individual proteins, DNA molecules, and viruses [1,2].

In our current research, we are exploring a novel material for use in these WGM sensors. We are focusing on silicate glass microspheres containing ions and neutral molecular clusters (MC) of silver. These glasses are exceptional materials that exhibit intense luminescence in the visible spectrum [3]. They are characterized by high quantum yields and resistance to degradation, making them more appealing than organic dyes. The primary limitation of such sensors lies in the requirement for physical coupling between the WGM resonator and external optics, such as a tapered fiber or bus waveguide, to provide phase-matched evanescent coupling [4]. An alternative approach is the concept of WGM sensors with optically active resonators [5], which enables pumping in the UV region via LEDs and remote measurements through free space optics.

The ion exchange (IE) method is currently widely utilized for synthesizing multifunctional glasses. This method is straightforward to execute and enables the attainment of a high concentration of silver ions near the glass surface. Although studies on glasses

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with Ag+ ions and silver ions obtained through the IO method have been conducted for more than half a century, their potential remains far from being fully explored.

In soda-silicate glass, silver initially exists in its ionic form as Ag^+. Structural defects in the glass may contain uncompensated negative charges. These defects can arise from various factors, including defects in the crystal lattice of the glass or the presence of additional ions that can form negatively charged sites. In the presence of electronic defects near glass structural defects, silver ions Ag^+ can readily be reduced to neutral silver atoms Ag^0. This reduction occurs when the glass is heated, and electrons are released from electronic defects. Neutral silver atoms Ag^0 can aggregate into molecular clusters, potentially comprising multiple silver atoms, each with unique optical and electronic properties. The formation of these molecular clusters can be induced by the characteristics of glass structure defects and heating conditions.

2. Materials and Methods

To create the silicate glass microspheres, we employed glass with the composition detailed in Table 1. The production process involved several steps. Initially, we crafted a thin fiber, and subsequently, we formed the microspheres by melting the fiber's end using a propane flame. The microspheres were then subjected to the Low-Temperature Ion Exchange (LTIE) process.

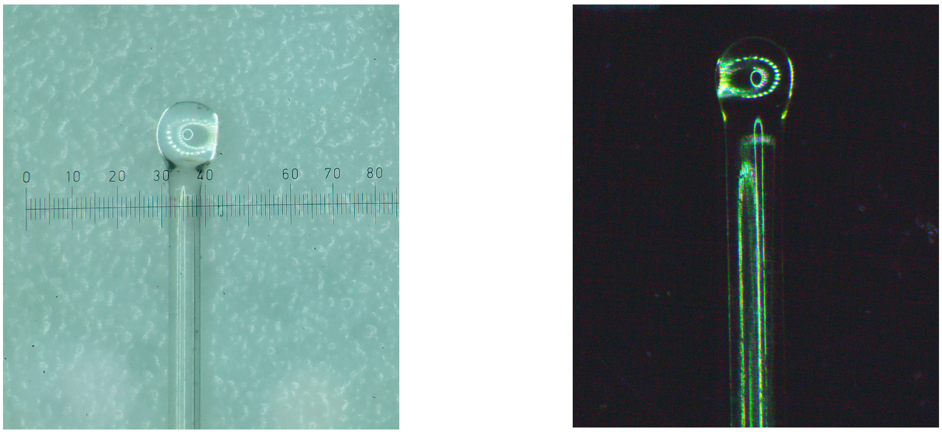
Table 1. Composition of glass used for making samples.

Chemical Constituents	**Glass (% Mass)**
SiO_2	72.2%
Na_2O	14.3%
K_2O	1.2%
CaO	6.4%
MgO	4.3%
Al_2O_3	1.2%
Fe_2O_3	0.03%
SO_3	0.3%

The ion exchange process occurred in a molten salt mixture of silver nitrate ($AgNO_3$) and sodium nitrate ($NaNO_3$) at a temperature of 330 °C for a duration of 15 min. To monitor the progress of the process, we also included witness glasses with the same composition. These glasses, with a thickness of 0.17 mm, underwent the ion exchange process alongside the microspheres in a common crucible.

Following the LTIE process, we meticulously cleansed the samples. This cleansing process involved washing with distilled water and then with isopropyl alcohol to eliminate any residual salts remaining on the surface after the process.

Figure 1 display photographs of the samples we obtained. Notably, the smallest sample achievable through the described method had a diameter of 200 microns. Figure 2 shows one of the witness samples that was not completely immersed in the crucible; when the sample was illuminated with a LED with a wavelength of ≈390 nm, the luminescence of molecular clusters of silver is clearly visible, and the area where the glass passes where the glass was not immersed in the molten salts.



(**a**) (**b**)

Figure 1. The obtained microsphere samples: (**a**) microsphere with a diameter of 380 μm; (**b**) microsphere with a diameter of 200 μm.

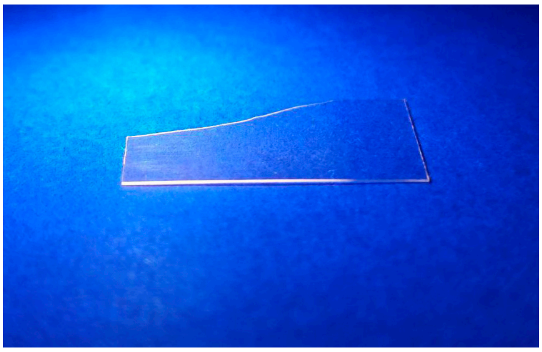


Figure 2. Witness sample visible luminescence.

Comsol Multiphysics was employed to determine the resonant frequencies and fundamental modes of the resonator. For an effective modeling of the WGM resonator, a two-dimensional axisymmetric approach was adopted. The grid was manually adjusted to facilitate a two-dimensional axisymmetric natural frequency analysis.

The investigation of the properties of silicate glass containing silver molecular clusters, synthesized through the LTIE method, encompassed both absorption measurements and luminescence spectra measurements. Absorbance measurements were conducted on the witness samples using a UV-VIS spectrophotometer (PB 2201). Luminescence spectral acquisition measurements were performed using a Fluorolog®-3 instrument with FluorEssence™. For all luminescence measurements integration time was 0.1 s.

3. Results and Discussion

3.1. Investigation of the Properties of Silicate Glass Containing Silver Molecular Clusters

An experiment was conducted to measure the absorption of glass samples that underwent Low-Temperature Ion Exchange (LTIE), and transparent glass samples that were not subjected to LTIE treatment. The resulting spectrum is depicted in Figure 3. Notably, the absorption spectrum of the samples after the LTIE process lacks characteristic absorption peaks. This absence is attributed to the fact that, under the same process parameters used treatment, predominantly silver molecular clusters, such as $Ag_{2...5}$, are formed [6].

Figure 4 presents the results of measuring luminescence intensity. When excited at wavelengths of 370 nm and 390 nm, the luminescence spectra of all synthesized glasses exhibit a broad luminescence band within the visible spectrum. This broadband luminescence spanning from 500 to 900 nm corresponds to the emission emanating from a small quantity of silver microcrystals formed directly during the LTIE process [7]. To generate molecular clusters (MC), it is imperative to reduce silver ions to their atomic state. This transformation leads to the creation of a certain quantity of silver microcrystals during the LTIE process, consequently giving rise to weak luminescence across the entire visible range.

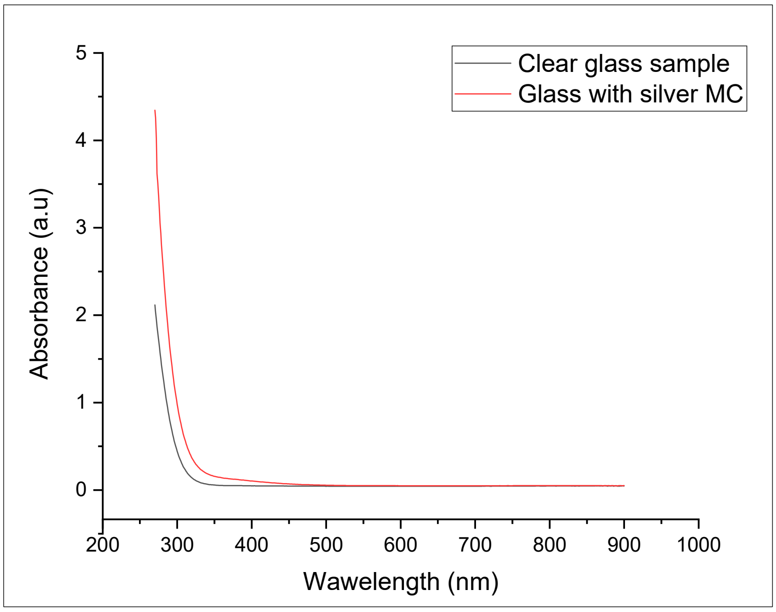


Figure 3. This is a figure. Schemes follow the same formatting.

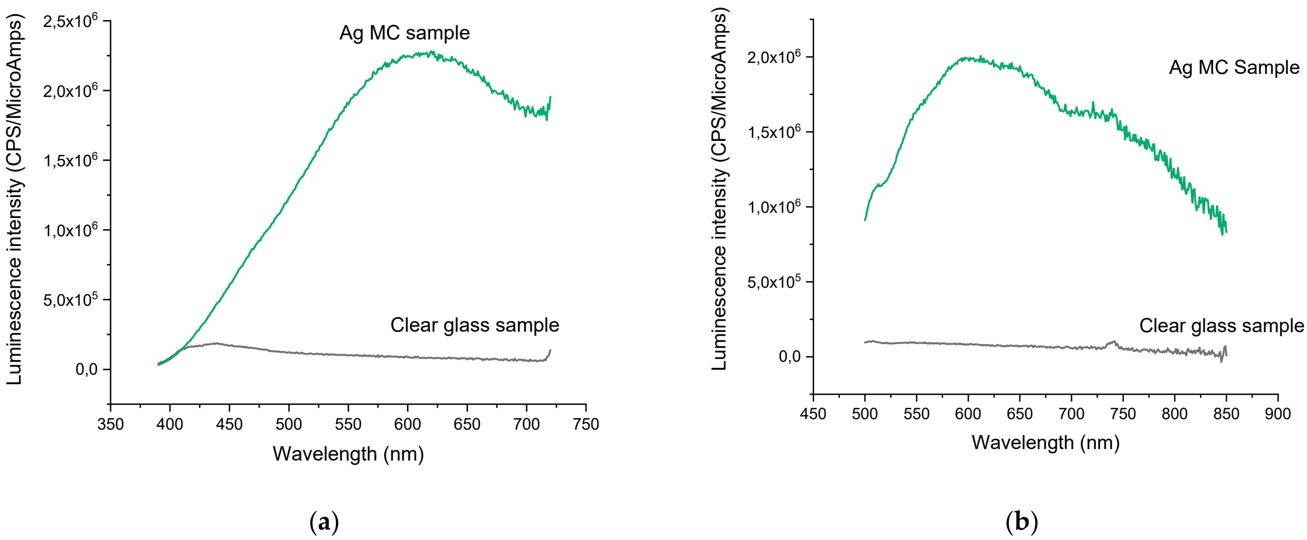
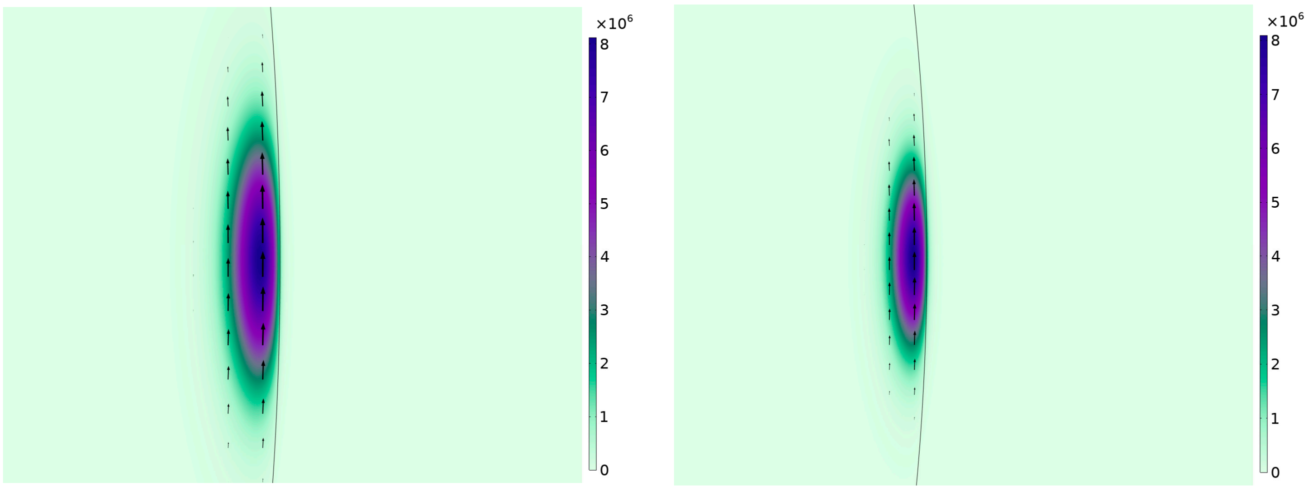


Figure 4. Luminescence intensity: (**a**) First sample λ_{exc} 370 nm; (**b**) Second sample λ_{exc} 390 nm.

3.2. Modelling WGM Resonators

The simulated microspheres had a radius of 100 µm. During the LTIE process with silver, glass changes its refractive index from 1.585 on the surface to 1.515. The simulated microsphere had a gradient refractive index from the edge of the microsphere to the center. To explore the potential of this material, simulations of microspheres in air and water were carried out. Figure 5 shows the distribution of the EM field in the cross section of the microcavity in air (a) and water (b). The resonant wavelength for the fundamental mode of the microresonator near the luminescence peak was determined. For a microsphere in air, the resonant wavelength for the fundamental TE mode with azimuthal number 1608 was 600.988. For a microsphere in water, the resonant wavelength for the fundamental TE mode with azimuthal number 1608 was 601.294. The difference between the resonant wavelengths was 0.25 nm.



(**a**) (**b**)

Figure 5. Fundamental mode localization: (**a**) Microsphere in air; (**b**) Microsphere in water.

4. Conclusions

We have obtained a new material that is suitable for use in label-free sensors with active WGM resonators. This material is very simple to obtain and cost-effective. The experiment showed that glass samples subjected to low temperature ion exchange (LTIE) showed distinct absorption characteristics, in particular the absence of characteristic absorption peaks, which was attributed to the formation of $Ag_{2...5}$ molecular clusters of silver. Luminescence measurements demonstrated a broad emission band in the visible spectrum, especially in the 500–900 nm range, confirming the formation of silver microcrystals during the LTIE process.

According to the simulation results, the difference between the resonant wavelengths for media with different refractive indexes was 0.26 nm. This allows the material to be used for microsphere sensors without direct physical connection. The results obtained show the potential of soda silicate glass with molecular silver clusters as a material for WGM sensors.

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