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Microstructure and optical absorption of silver granules in oxide glasses produced by ion-exchange and reduction treatments

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An electron micrographic investigation has been carried out on two oxide glasses containing alkali ions and subjected to a sodium⇌silver ion-exchange followed by reduction treatments at various temperatures. The presence of metallic silver in the silver-rich droplet phases has been confirmed by selected-area electron diffraction. The silver-rich phases are found to have diameters ranging from 3 to 50 nm. The nucleus density of these particles is found to have a maximum value at temperatures in the range 250 to 300° C. The optical absorption spectra of the reduced glasses show a maximum around a wavelength of 400 nm. Maxwell–Garnett theory has been used to calculate the optical absorption and the predicted wavelength for maximum absorption is in reasonable agreement with the experimental value.

1. Introduction

The optical behaviour of colloidal metal spheres in different media (mostly glasses) has been investigated in recent years because of the technological importance of such composite materials. The optical absorption of gold [1] and silver [2, 3] spheres dispersed in either water or a glass matrix have been analysed using the Mie theory. The metal spheres in these experiments were nucleated in the glass matrix by ultraviolet irradiation followed by suitable heat treatment. In the spectrofloat process, metal microspheres are precipitated within the surface layer of the float glass by an ion-exchange and reduction process [4]. Electrically conducting layers can also be induced in certain glasses by this technique [5, 6]. The microstructural characteristics of ion-exchanged and reduced glasses in the float glass system were studied earlier in relation to their optical behaviour with the metallic phase being copper [7]. In this paper, we report on similar investigations carried out on some common oxide systems with silver as the metallic species.

2. Experimental procedure

The compositions of the two glasses used in the present investigation are given in Table I. Glass 2 is the commercial C-glass supplied by Seraikella Glass Works Pvt Ltd, Kandra, Singhbhum (Bihar), India. Glass 1 was prepared from reagent-grade chemicals. Boric oxide was introduced as boric acid, sodium oxide as sodium carbonate and silica as sea sand. The mixture was melted in an electrically heated furnace in the temperature range 1300 to 1350° C. The glass was cast by pouring the melt on to an aluminium plate. The specimen was subsequently annealed at 400° C for 3 h and allowed to cool in the furnace. Samples of both glass 1 and glass 2 were cut and ground to the dimensions 25 mm × 10 mm × 3 mm with an optical finish obtained by polishing with 0.05 μm alumina powder.

Fibres having diameters in the range 10 to 15 μm were also drawn from both glasses using high alumina ceramic bushings [8, 9]. These were essentially for electron microscopic investigations as described below.

Sodium⇌silver exchange was carried out at 330° C for 6 h by immersing glass samples and a bunch of glass fibres of the same composition in a molten bath of reagent-grade silver nitrate kept in a Pyrex crucible. After this treatment, the samples were taken out of the molten bath, cooled and cleaned under running water to dissolve any

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TABLE I Compositions of glasses investigated

Oxide	Glass 1 (mol %)	Glass 2* (mol %)
SiO_2	64	65.2
Na_2O	10	8.3
B_2O_3	26	4.4
Al_2O_3	–	2.4
MgO	–	4.5
CaO	–	15.0
Fe_2O_3	–	0.2

*Analysis supplied by Seraikella Glass Works Pvt Ltd, Kandra, Singhbhum (Bihar), India.

silver nitrate adhering to the surface. The ion-exchanged samples were then reduced in a tube furnace by passing hydrogen gas at a rate of 100 $cm^3 min^{-1}$. The reduction temperature and time were varied in the ranges 150 to 300° C and 0.5 to 2 h, respectively.

For electron microscopic studies, thin films of carbon were first prepared by vacuum evaporation on a precleaned glass slide. These films were then cut into small squares and made to float on the surface of double distilled water in a crystallizing dish. They were subsequently removed with copper grids such that the films rested on the matt side of the grid for better adhesion. A bundle of ion-exchanged and reduced glass fibres were ground in an agate mortar to a fine powder and kept in suspension in acetone. A few drops of the suspension were applied to the grids with carbon side up. After evaporating the acetone, the grids were coated with a thin film of 0.5 wt% collodion solution in amyl acetate. In this way the specimen was sandwiched between collodion and carbon films with a supporing copper grid. The samples were examined in a Philips EM 301 transmission electron microscope operated at 100 kV.

For optical absorption measurements the ion-exchanged and reduced glass samples were polished with 0.05 μm alumina powder to remove the treated layer from one of the faces [7]. The optical density of the samples was measured in a CARY-17 D spectrophotometer in the wavelength range 300 to 700 nm. For each measurement, a glass sample of identical composition and dimension but not subjected to ion-exchange and reduction treatments was used as a reference.

3. Results and discussion

Both the glasses exhibit a homogeneous structure in the untreated condition. The structures which develop in glasses 1 and 2 after ion-exchange treatment at 330° C for 6 h, are shown in Fig. 1a and b, respectively. It is evident that a hetero-phase structure is induced in these glasses after ion-exchange, the dimensions of the interspersed phases being in the range 4 to 10 nm. However, some of the phase-separated regions have dimensions of the order of 100 nm. Such gross structures contain dispersed phases of much smaller dimension. No clear explanation is available as to their origin. The electron diffraction patterns from these regions do not show any sharp rings indicating thereby that the dark regions consist of amorphous phases rich in silver ions. Fig. 2a and b show typical microstructures of ion-exchanged and reduced samples of glasses 1 and 2, respectively. The corresponding selected-area electron diffraction pattern (Fig. 3) contain sharp rings and are identified (Table II) as arising due to the presence of metallic silver. The electron micrographs show particles of varying sizes between 3 and 50 nm. Fig. 4 gives a typical histogram obtained for the particle sizes of an ion-exchanged and reduced

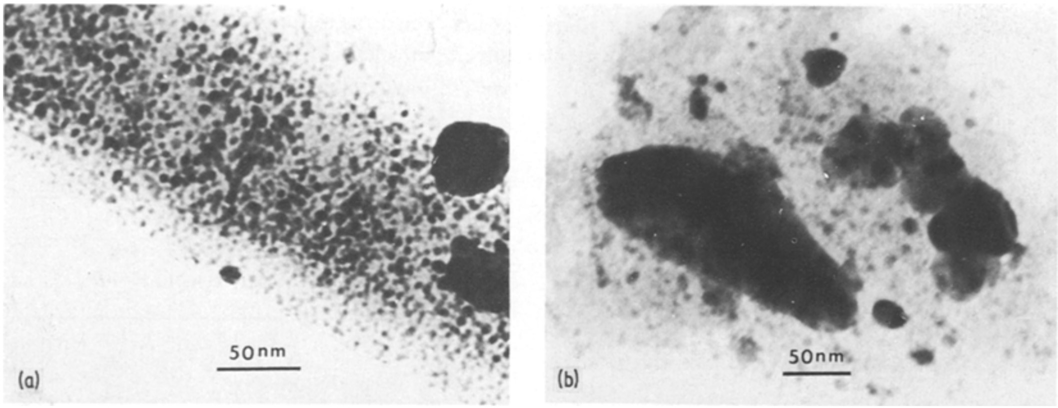

Figure 1 Electron micrographs of glass after ion-exchange at 330° C for 6 h. (a) Glass 1, (b) glass 2.

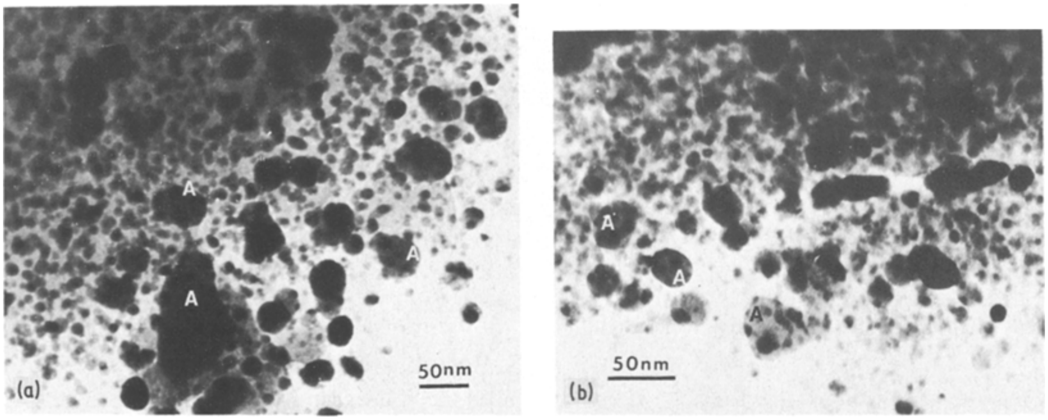

Figure 2 (a) Electron micrograph of glass 1 ion-exchanged at 330° C for 6 h and reduced at 300° C for 1.5 h. (b) Electron micrograph of glass 2 ion-exchanged at 330° C for 6 h and reduced at 200° C for 1 h.

sample of glass 1. Such histograms were used for calculating the statistical weighted average values of particle diameters. Table III summarizes the diameters obtained in ion-exchanged glasses reduced at different temperatures for various time intervals. The calculated average diameters have values in the range 5 to 18 nm. It can be seen (Table III) that the particle diameter in any specimen decreases as the reduction temperature or time is increased. This anomalous behaviour is believed to arise due to the dark regions in the electron micrographs not consisting entirely of metallic silver but rather comprising a silver-rich glassy phase in which silver particles are precipitated. Evidence of such a composite phase structure can be seen in the electron micrographs given in Fig. 2a and b. The areas indicated as A in Fig. 2b consist of a dark phase in which several smaller particles are dispersed. It is likely that in the present glass system, the metal phase precipitation is preceded by a phase separation involving silver ions. A similar model was proposed earlier in the case of metallic copper precipitation in float glass [7].

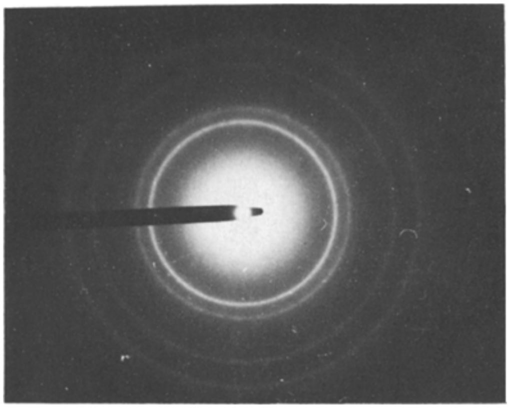

Figure 3 Selected-area electron diffraction pattern of glass 2 having the microstructure given in Fig. 2b.

Fig. 5a and b show the variation of the nucleus density of the silver-rich phase as a function of reduction temperature of glasses 1 and 2, respectively, reduced for different periods of time. It is found that the nucleus density is maximum at temperatures of 300 and 250° C, respectively, for the two glass compositions. These temperatures should also correspond to the maximum nucleation density for metallic silver because of the conclusions drawn in the previous paragraph.

Fig. 6a and b give the optical density as a function of wavelength obtained for glasses 1 and 2, respectively, ion-exchanged and reduced at different temperatures and for various durations. It is evident that all the samples exhibit an absorption maximum at around 400 nm wavelength. The absorption also increases as the reduction temperature and time are increased. The optical absorption is believed to arise due to the presence of metallic silver particles in the glass matrix as discussed in the following paragraph.

TABLE II Comparison of d_{hkl} values for silver as obtained from selected-area electron diffraction of ion-exchanged and reduced (300° C for 2 h) glass 2

Calculated d-values from S.A.D. (nm)	ASTM silver (fcc) data		
	d (nm)	$\frac{I}{I_{\max}}$	hkl
0.2361	0.2359	100	111
0.2063	0.2044	40	200
0.1453	0.1445	25	220
0.1241	0.1231	26	311

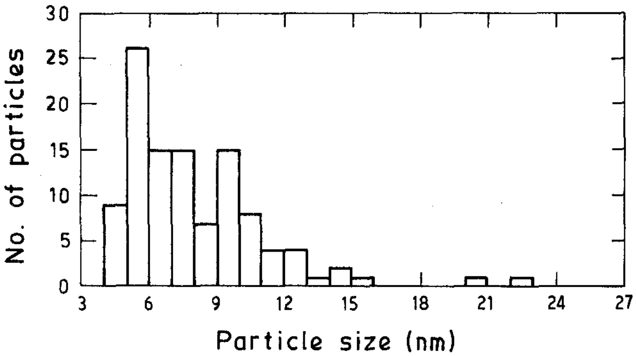

Figure 4 Histogram of particle sizes in glass 1 ion-exchanged at 330° C for 6 h and reduced at 300° C for 2 h.

According to the Mawell–Garnett (MG) theory the effective dielectric permeability $\bar{\epsilon}^{\mathrm{MG}}$ of the composite consisting of spherical particles dispersed in a matrix characterized by a dielectric constant ϵ_{m} is given by [10]:

$$\frac{\bar{\epsilon}^{\mathrm{MG}} - \epsilon_{\mathrm{m}}}{\bar{\epsilon}^{\mathrm{MG}} + 2\,\epsilon_{\mathrm{m}}} = f\,\frac{\epsilon - \epsilon_{\mathrm{m}}}{\epsilon + 2\,\epsilon_{\mathrm{m}}} \tag{1}$$

where ϵ is the dielectric constant of the particles and f is the filling factor.

The size- and frequency-dependent dielectric permeability, $\epsilon_j(\omega)$, of silver particles is given by [11]:

$$\epsilon_j(\omega) = \epsilon_{\mathrm{exp}}(\omega) - \epsilon_{\mathrm{exp}}^{\mathrm{Drude}}(\omega) + \epsilon_j^{\mathrm{Drude}}(\omega), \tag{2}$$

where, $\epsilon_{\mathrm{exp}}(\omega)$ is the experimentally determined frequency-dependent dielectric permeability of bulk silver [11], and the two Drude terms are

$$\epsilon_{\mathrm{exp}}^{\mathrm{Drude}}(\omega) = 1 - \omega_{\mathrm{p}}^2/\omega\,(\omega + i/\tau_{\mathrm{b}}) \tag{3}$$

$$\epsilon_j^{\mathrm{Drude}}(\omega) = 1 - \omega_{\mathrm{p}}^2/\omega\,(\omega + i/\tau_j), \tag{4}$$

where ω_{p} is the bulk plasma frequency, τ_{b} is the mean electron life time for bulk silver, and τ_j is given by:

$$\tau_j^{-1} = \tau_{\mathrm{b}} + 2V_{\mathrm{f}}/x_j, \tag{5}$$

V_{F} being the Fermi velocity and x_j the diameter for particles of size j. The bulk parameters as given in the literature [11]:

$$\left.\begin{aligned} \hbar\omega_{\mathrm{p}} &= 0.70\,\mathrm{eV} \\ \hbar/\tau_{\mathrm{b}} &= 0.079\,\mathrm{eV} \\ V_{\mathrm{F}}/c &= 4.7 \times 10^{-3} \end{aligned}\right\} \tag{6}$$

c being the velocity of light.

The absorption coefficient, α, is related to the Maxwell–Garnett permeability by [11]:

$$\alpha = (\omega/c)\,[\bar{\epsilon}_2^{\mathrm{MG}}/(\bar{\epsilon}_1^{\mathrm{MG}})^{1/2}] \tag{7}$$

where $\bar{\epsilon}^{\mathrm{MG}} = \bar{\epsilon}_1^{\mathrm{MG}} + i\bar{\epsilon}_2^{\mathrm{MG}}$ and where the α values were evaluated using the above equations for different glasses reduced under various conditions by taking the average values of particle diameters and the corresponding filling factor as evaluated from the microstructural data. For comparison the experimental absorption coefficients were calculated from optical density (OD) data by the equation.

$$\alpha_{\mathrm{exp}} = \frac{2.303\,(\mathrm{OD})}{t}, \tag{8}$$

where t is thickness of the metal-rich layer in the different glasses and was arbitrarily chosen to be equal to $2\,\mu$m. The latter is a reasonable approximation in view of the silver diffusion profile in

TABLE III Diameters of silver-rich particles in ion-exchanged glasses reduced at different temperature for various time intervals

Reduction treatment		Average diameter of silver-rich phase (nm)	
Temperature (° C)	Time (h)	Glass 1	Glass 2
150	2.0	16.3	12.2
200	0.5	16.0	12.4
200	1.0	15.4	12.4
200	1.5	15.4	13.2
200	2.0	13.9	12.6
250	0.5	16.5	14.0
250	1.0	–	12.4
250	1.5	18.1	16.6
250	2.0	16.8	13.2
300	0.5	11.5	15.8
300	1.0	11.3	13.2
300	1.5	10.7	12.4
300	2.0	8.0	11.4
325	0.5	12.8	14.7
325	1.0	8.9	9.0
325	1.5	6.4	9.0
325	2.0	7.4	7.4
350	0.5	9.6	9.8
350	1.0	9.0	–
350	1.5	–	5.0
350	2.0	5.9	–

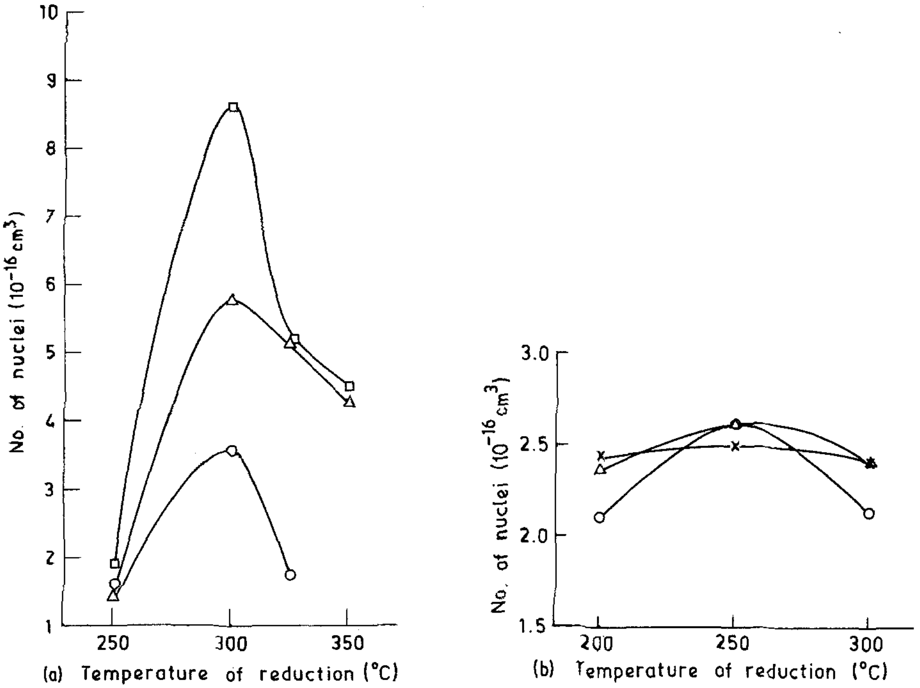

Figure 5 Variation of nucleus density of the silver-rich phase in glasses ion-exchanged at 330° C for 6 h and reduced at different temperatures for various duration. (a) Glass 1: ○ 0.5 h; △ 1.5 h; □ 2.0 h. (b) Glass 2: ○ 0.5 h; △ 1.0 h; × 2.0 h.

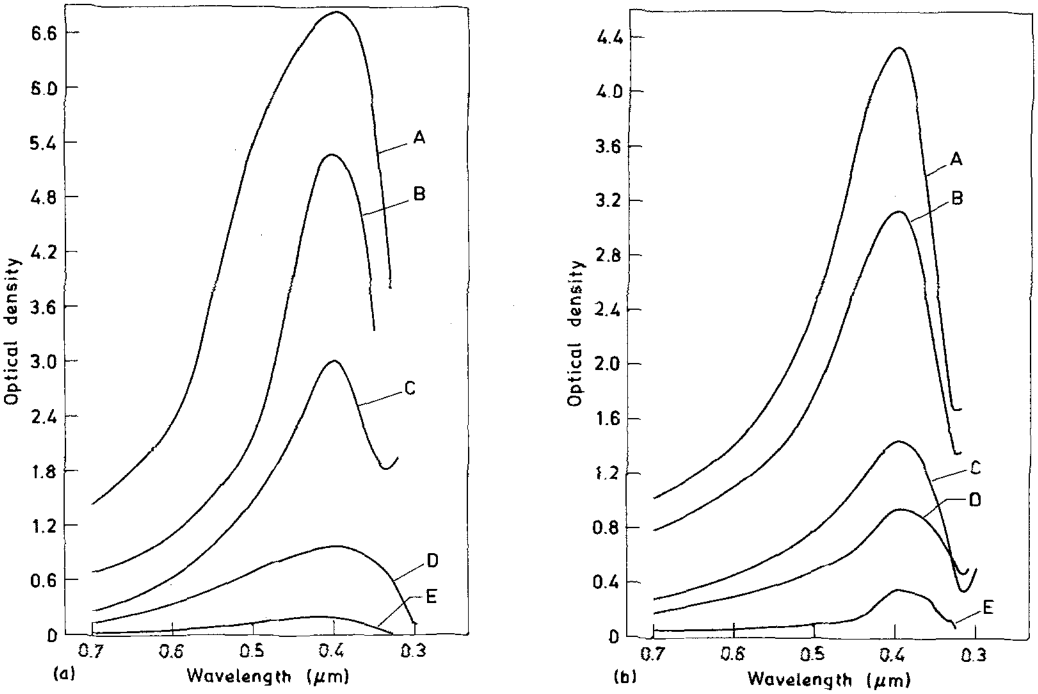

Figure 6 Optical absorption spectra of glasses ion-exchanged at 330° C for 6 h and reduced at different temperatures for various duration. (a) Glass 1 reduction treatments: A, 300° C for 2 h; B, 300° C for 0.5 h; C, 250° C for 1.5 h; D, 250° C for 0.5 h; E, 200° C for 0.5 h. (b) Glass 2 reduction treatments: A, 300° C for 2.0 h; B, 300° C for 1.0 h; C, 250° C for 1.5 h; D, 250° C for 0.5 h; E, 200° C for 0.5 h.

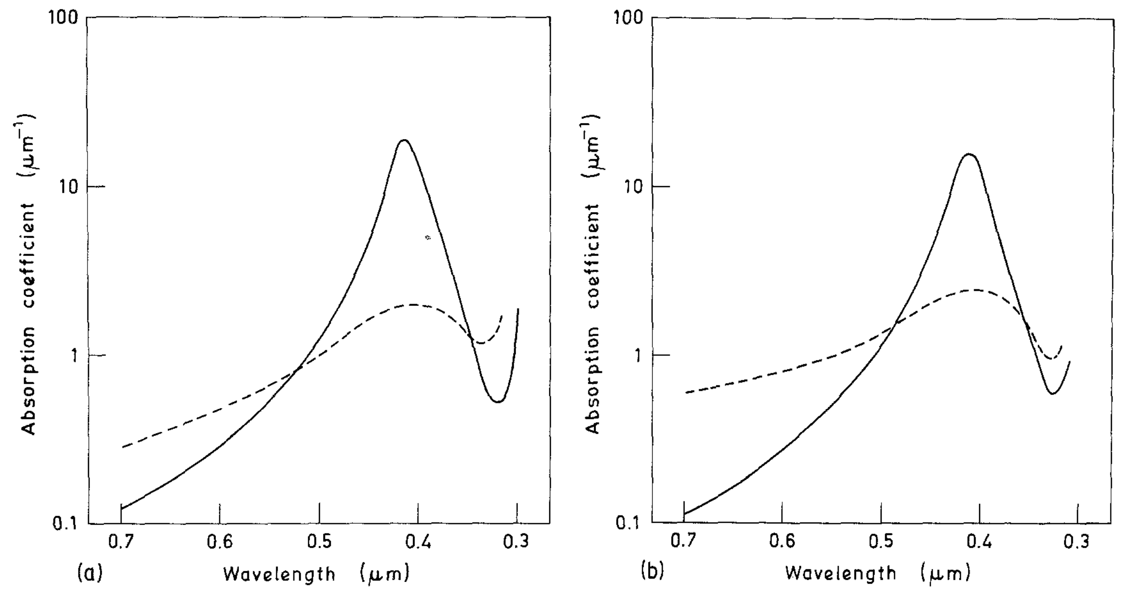

Figure 7 Theoretical and experimental optical absorption coefficients for different reduced glasses. (a) Glass 1: —— theoretical (fill factor = 0.04; – – – experimental (reduced at 250° C for 2 h). (b) Glass 2: —— theoretical (fill factor = 0.04); – – – experimental (reduced at 300° C for 2 h).

these glasses [12]. In Fig. 7a and b the theoretical and experimental absorption coefficients for glass 1 (reduced at 250° C for 2 h) and glass 2 (reduced at 300° C for 2 h), respectively, are shown. The comparison for glasses treated at other temperatures/times looks similar to Fig. 7a and b. It is evident that the wavelength at which the maximum in absorption occurs as predicted by the Mawell–Garnett model is in reasonable agreement with the experimental value. There is, however, a substantial disagreement with regard to the magnitude of the absorption coefficient. This is to be expected because of the error involved in estimating the true volume fraction of the metal phases. It is apparent from the above discussions that the volume fraction of the metal phase has been overestimated in our analysis.

4. Conclusions

(1) Sodium⇌silver ion exchange followed by reduction treatments at various temperatures in commercial C- and sodium borosilicate glasses result in phase separation with the emergence of silver-rich glassy phase regions or particles. Reduction temperatures in the range 250 to 300° C produce the highest nucleation density of such particles.

(2) The optical absorption spectra of ion-exchanged and subsequently reduced glasses show a maximum around 400 nm wavelength. The extent of absorption increases with temperature and time of reduction.

(3) Maxwell–Garnett theory predicts the wavelength corresponding to maximum optical absorption in satisfactory agreement with experimental data. However, there is a substantial disagreement of the experimental and theoretical values of the magnitude of absorption coefficient. This is ascribed to an overestimate of the volume fraction of the metallic silver phase as deduced from electron micrographs.

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