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Optical properties of bismuth granules in a glass matrix

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Abstract. Optical absorption chracteristics for ultra-fine bismuth particles having dimensions around 10 nm and dispersed in both silicate and vanadium phosphate glass matrices have been investigated in the wavelength range 300 to 700 nm. Bismuth particles in vanadium phosphate matrix show an absorption peak around 440 nm whereas in silicate glass matrix they give two peaks in the ranges 500 to 530 nm and 420 to 430 nm respectively. The peak positions in all the glass-bismuth metal systems are predicted in fair agreement with experiment by Maxwell–Garnett (MG), as extended by Polder and van Santen (MG-PvS) and Bruggeman (BR) effective medium theories. It is observed, however, that MG-PvS and BR models give the best fit to experimental data over the entire wavelength range studied.

Keywords. Optical absorption; ultra-fine bismuth particles; silicate glass matrix; vanadium phosphate glass matrix; effective medium theories

1. Introduction

Optical properties of ultrafine metal aggregates with mean diameters around 10 nm have been studied extensively in recent years (Granqvist 1978). The metal particles of these dimensions have been prepared by various experimental techniques, *viz.*, by making colloids suspended in an aqueous solution (Kreibig and Zacharias 1970), precipitating gold or silver granules in a photosensitive glass by UV radiation followed by heat-treatment (Maurer 1958; Smithard and Dupree 1972), by preparing granular cermet films (Priestley *et al* 1975) and by gas evaporation in the presence of oxygen (Granqvist and Hunderi 1977) or in a reduced atmosphere of an inert gas (Granqvist and Buhrman 1976).

Recently it has been shown that bismuth particles of diameters of the order of 10 nm can be dispersed in an oxide glass matrix by a suitable choice of the starting composition, which is then melted and quenched (Chakravorty 1974). The presence of such micro-granules is found to alter the electrical properties of the base glass significantly (Chakravorty *et al* 1977). We have studied the optical absorption characteristics of these glass-metal particulate systems in the wavelength range 300 to 700 nm and analysed the data in terms of the various effective medium theories developed so far (Granqvist and Hunderi 1978). The results are reported in this paper.

2. Experimental

The glass compositions used for the present investigation are given in table 1. All glasses were prepared from reagent grade chemicals. P_2O_5 was added as $(NH_4)_2$ HPO_4, B_2O_3

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Table 1. Compositions of glass-bismuth microcomposites investigated (in mole %).

Micro-composite No.	V_2O_5	P_2O_5	SiO_2	B_2O_3	Na_2O	Bi_2O_3
1	80	20	—	—	—	—
2	80	15	—	—	—	5
3	70	20	—	—	—	10
4	—	—	64	26	10	—
5	—	—	64	18	10	8
6	—	—	64	14	10	12

as H_3BO_3, Na_2O as Na_2CO_3 and the others as their respective oxides. Glass batches were weighed, thoroughly mixed in acetone and melted in alumina crucibles in an electrically heated furnace in the temperature range 1300° C to 1400° C. Films of glasses having thicknesses around 10 μm were made by a blowing method (Chakravorty *et al* 1979). To increase the volume fraction of bismuth phase in the glass matrix the glass samples were also subjected to reduction treatments. The latter were carried out in a pyrex tube inserted in the mullite muffle of an electrically heated furnace. Glass films sandwiched between perforated metal sheets were kept at the centre of the pyrex tube and hydrogen gas was passed through it at a rate of 100 cc/min. For electron micrographic analysis, powdered samples dispersed in acetone were mounted on carbon coated grids. A thin film of collodin was applied on the sample. The microstructure and selected area diffraction patterns were taken using an electron microscope (Phillips EM 301) operated at 100 kV. The average particle diameter $\bar{x}$ for each sample was estimated by the following relation,

$$\bar{x} = \sum_{j=1}^{n} x_j n_j / N, \tag{1}$$

where, x_j is the diameter in the jth interval of histogram; n_j is the frequency of the jth interval; n is the number of intervals and N is the total number of particles measured ($\sim$ 100).

The standard deviation s was calculated from

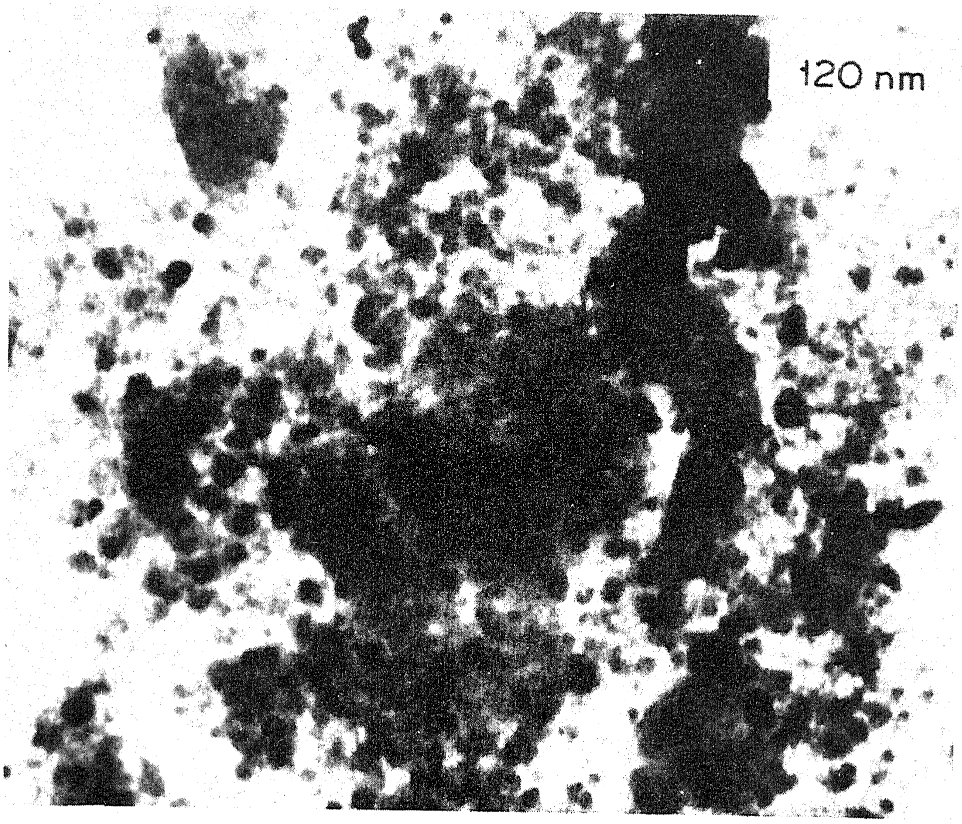
$$s = \left[\sum_{j=1}^{N} (x_j - \bar{x})^2 / (N-1) \right]^{1/2}. \tag{2}$$

The optical density of the samples was measured in a spectrophotometer (Cary 17D) in the wavelength range 300 to 700 nm. For samples in the system V_2O_5-P_2O_5-Bi_2O_3 glass no. 1 was used as the reference whereas for specimens in the Na_2O-B_2O_3-SiO_2-Bi_2O_3 system glass no. 4 was used as the reference.

3. Results

In figures 1 and 2 are shown the typical electron micrographs and selected area electron diffraction patterns of glass no. 3 (reduced at 200°C for 2 hr) and glass no. 6 respectively. Table 2 compares the interplanar spacings (d_{hkl}) as calculated from the diffraction rings obtained for these samples with standard values for metallic bismuth (Selected Powder Diffraction Data for Minerals 1979). These results confirm that the particles observed

(a)



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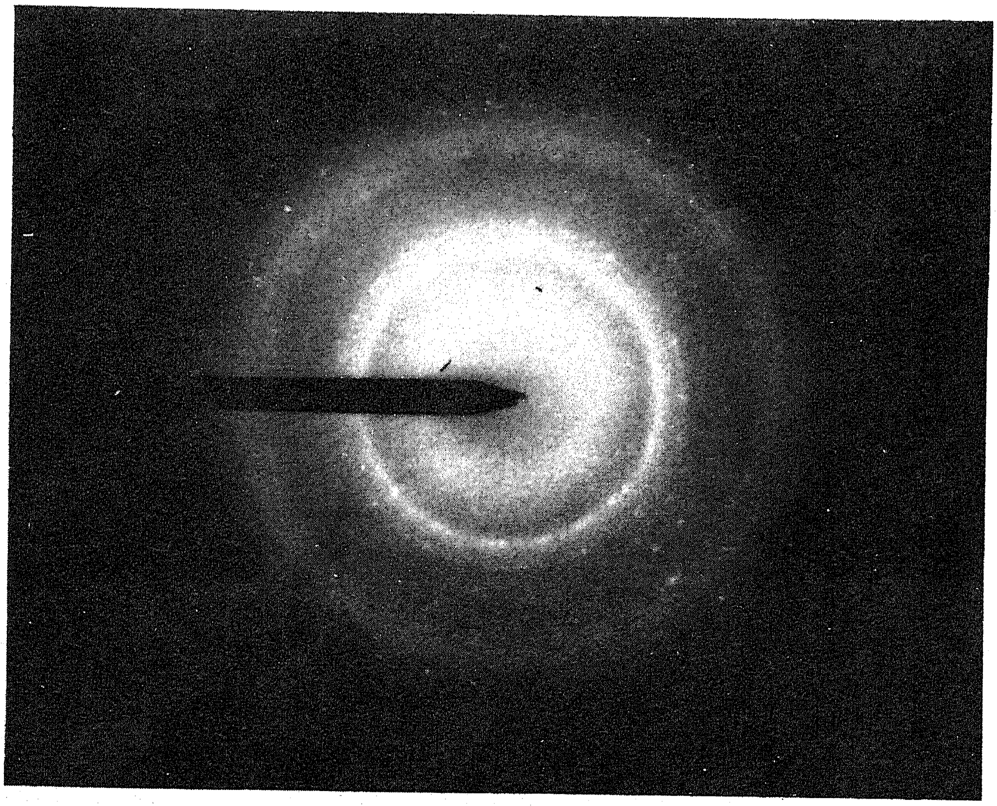
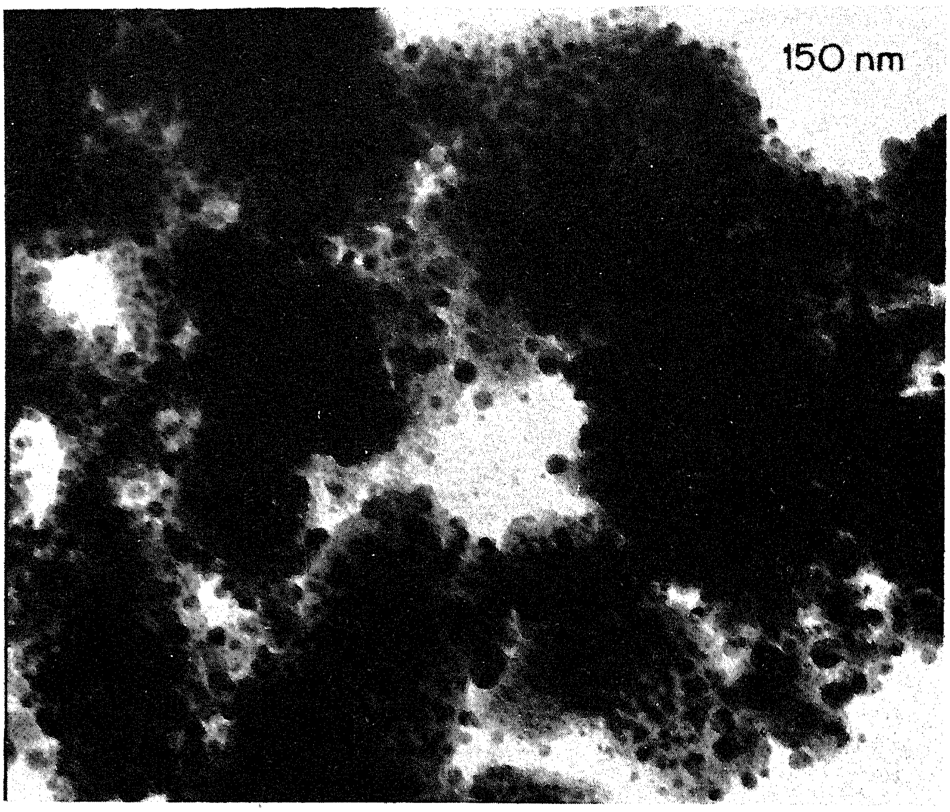


Figure 1. **a.** Electron micrograph of microcomposite no. 3 reduced at 200°C for 2 hr. **b.** Selected area electron diffraction pattern of microcomposite no. 3 reduced at 200°C for 2 hr.

(a)



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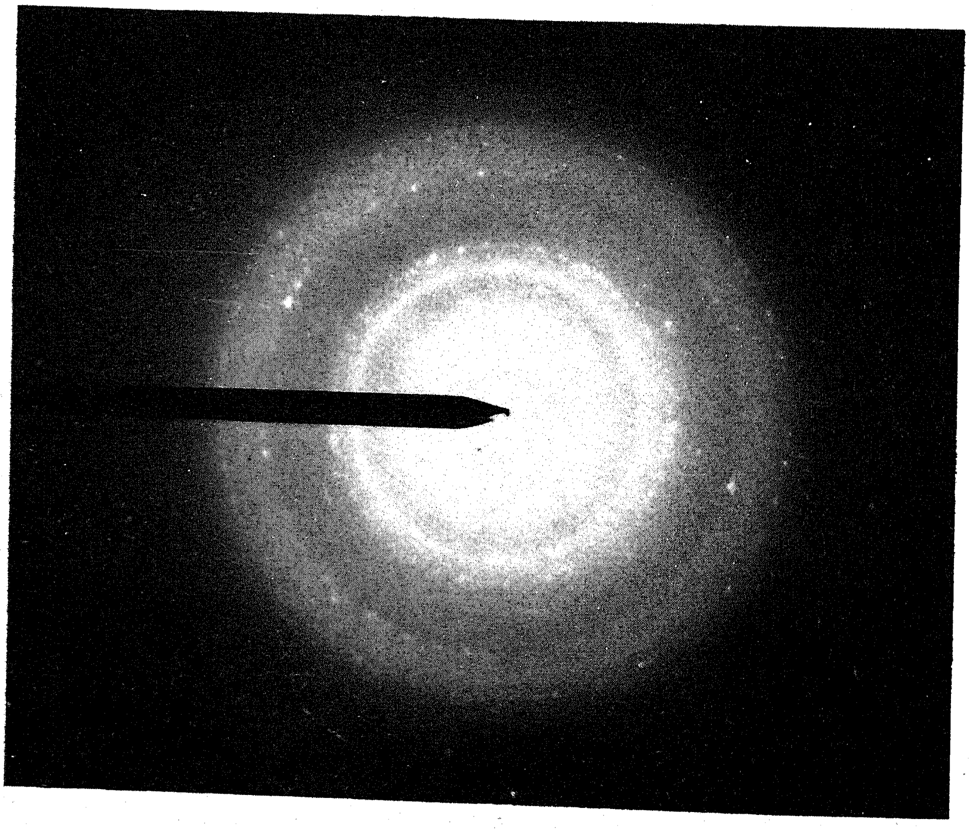

Figure 2. **a.** Electron micrograph of microcomposite No. 6. **b.** Selected area diffraction pattern of microcomposite No. 6.

Table 2. Comparison of d_{hkl} values obtained from electron diffraction data of different specimens.

d_{hkl} from diffraction data (Å) Micro composite no.3 reduced at 200°C for 2 hr	Micro-composite no. 6	Standard d_{hkl} (Å)
2·17	2·20	2·27
1·84	1·89	1·87
1·30	1·33	1·33
1·10	1·12	1.12

* Selected Powder Diffraction Data for Minerals (1979).

in the electron micrographs consist of bismuth metal. In table 3, the average particle diameter $\bar{x}$ and the standard deviation s of the metal phase in different samples are summarised. It is seen that in general the average particle diameter of the metallic phase increases as the reduction temperature or time is increased. The average diameter varies in the range 7·5 to 16 nm. The decreasing trend in the $\bar{x}$ values in glass 6 could be due to the fact that the dark spheres in this glass consists of a bismuth-rich phase which has a distribution of bismuth particles of smaller radii within itself (Sarkar *et al* 1982). Hence the diameter values calculated from the micrographs are believed to be overestimated.

The optical absorption coefficients for glasses 2 and 3 at various stages of reduction are shown in figure 3. It is evident that for longer reduction treatments the absorption coefficient attains higher values. The absorption peaks for various samples occur at a wavelength around 440 nm. Figure 4 gives the absorption data for glasses 5 and 6. In

Table 3. Bismuth grain sizes in different micro-composites investigated.

Microcomposite No.	Reduction Treatment	Average particle diameter $\bar{x}$ (nm)	Standard deviation in particle diameter s (nm)
2	Virgin	9·0	4·0
	200°C/1 hr	10·9	5·7
	200°C/2 hr	10.2	6·0
3	Virgin	7·7	2·2
	200°C/1 hr	11.6	4·6
	200°C/2 hr	15·2	4·5
5	Virigin	8·1	3·0
	300°C/1 hr	9·4	2·9
	300°C/1·5 hr	9·5	3·5
6	Virgin	15·6	3·6
	300°C/1 hr	12·9	5·6
	300°C/1·5 hr	8·9	3·2

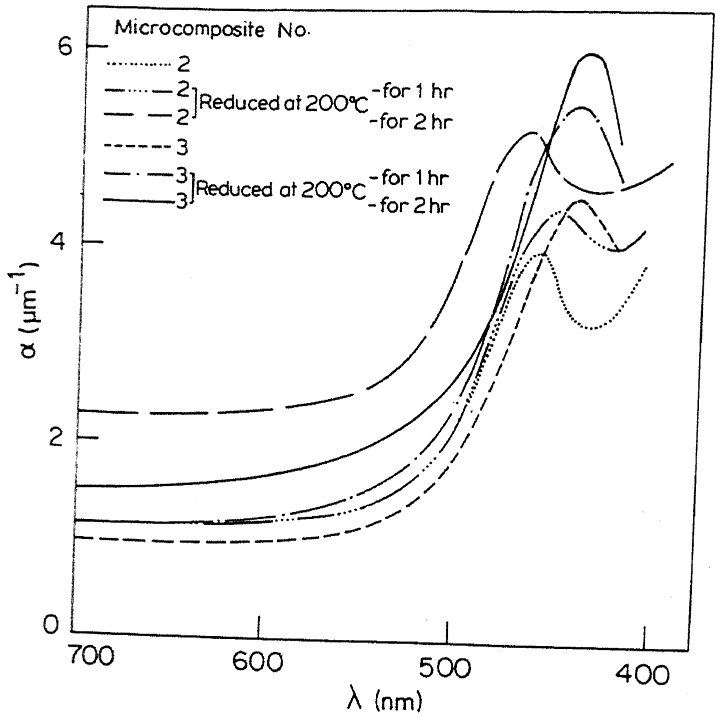

Figure 3. Optical absorption coefficient α as a function of wavelength λ for V_2O_5-P_2O_5 glasses containing bismuth granules.

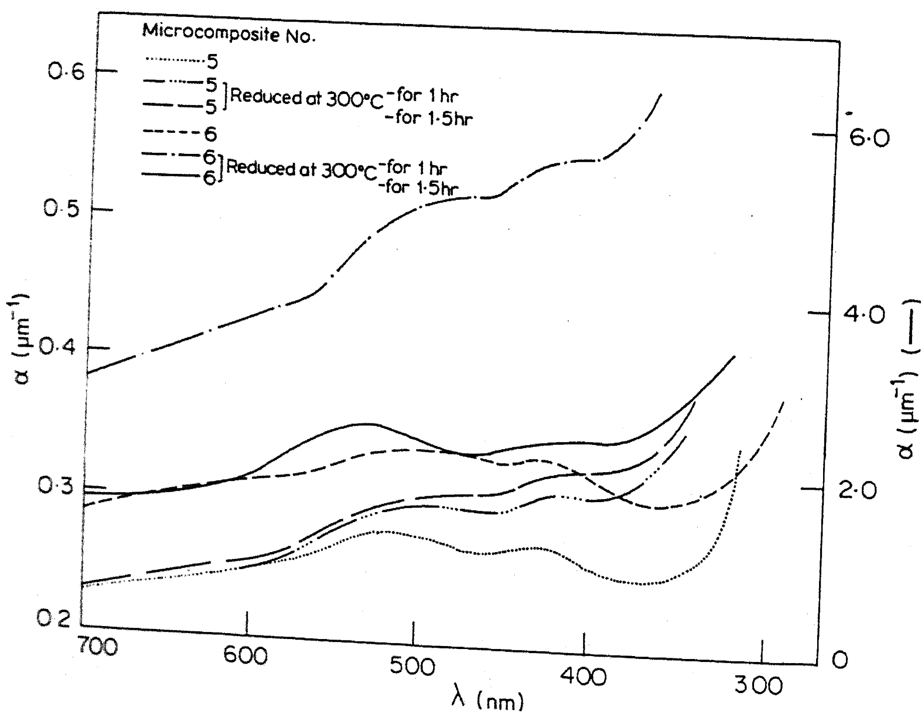

Figure 4. Optical absorption coefficient α as a function of wavelength λ for silicate glasses containing bismuth granules.

these glasses two absorption peaks are observed in the ranges 500 to 530 nm and 420 to 430 nm respectively.

4. Calculations

A number of effective medium theories have recently been used to explain the optical behaviour of metal-dielectric multiphase mixtures (Granqvist and Hunderi 1977). According to Maxwell–Garnett (1904) the effective permittivity $\bar{\varepsilon}^{MG}$ – is given by

$$\frac{\bar{\varepsilon}^{MG} - \varepsilon_m}{\bar{\varepsilon}^{MG} + 2\varepsilon_m} = f \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}, \tag{3}$$

where, ε_m is the dielectric permittivity of the matrix, f the fill factor and ε the permittivity of an individual particle. In this model, the particles are assumed to be equal-sized spheres and separated sufficiently from each other to ensure independent scattering.

Polder and van Santen (1946) by incorporating Onsager's (1936) 'reaction field' derived an improved effective medium permittivity $\bar{\varepsilon}^{MG-PVS}$ for particles of ellipsoidal shapes as given by the following

$$\bar{\varepsilon}^{MG-PvS} = \varepsilon_m \frac{1 + \frac{2}{3}\sum_j f_j \delta_j}{1 - \frac{1}{3}\sum_j f_j \delta_j}, \tag{4}$$

where f_j is the fill factor of particles having diameters around x_j such that $\sum_j f_j = f$, f being the overall fill factor of the metallic-phase. δ_j is proportional to the polarizability of particles in the jth class and for an ellipsoidal shape it is given by,

$$\delta_j = \frac{1}{3} \sum_{k=1}^{3} \frac{\varepsilon_j - \bar{\varepsilon}}{\bar{\varepsilon} + L_k(\varepsilon_j - \bar{\varepsilon})} \tag{5}$$

where, ε_j is the size dependent dielectric permittivity of particles in the jth class, $\bar{\varepsilon}$ is the effective medium permittivity and L_k's are the depolarisation factors for the jth particles.

Bruggeman's (1935) theory considers the particles to be embedded in an effective medium and the properties of the composite are determined in a self-consistent manner. The effective medium permittivity $\bar{\varepsilon}^{BR}$ in this model is given by

$$\bar{\varepsilon}^{BR} = \varepsilon_m \frac{1 - f + 1/3 \sum_j f_j \delta_j}{1 - f - 2/3 \sum_j f_j \delta_j}, \tag{6}$$

where the symbols have their significance as described earlier.

To compute the effective permittivity values in the present glass-metal system by the different theories mentioned above, the size-dependent dielectric permittivity of bismuth has been obtained from the bulk data (Gray 1972) by the following relation (Granqvist and Hunderi 1977)

$$\varepsilon_j(\omega) = \varepsilon_{exp}(\omega) - \varepsilon_{exp}^{Drude}(\omega) + \varepsilon_j^{Drude}(\omega), \tag{7}$$

where ω is the angular frequency of the radiation used. The last two terms on the right side of the above equation are given by

$$\varepsilon_{\rm exp}^{\rm Drude}(\omega) = 1 - \omega_{pb}^2/\omega(\omega + i/\tau_b), \tag{8}$$

$$\varepsilon_j^{\rm Drude}(\omega) = 1 - \omega_{pxj}^2/\omega(\omega + i/\tau_j), \tag{9}$$

where ω_{pb} and τ_b are the bulk plasma frequency and the mean electron life time respectively, ω_{pxj} is the apparent plasma frequency of particle of size x_j and τ_j is given by

$$\tau_j^{-1} = \tau_b^{-1} + 2v_{fb}/x_j \tag{10}$$

where v_{fb} is the bulk Fermi velocity of electrons. A value of $\hbar\omega_{pb} = 16$ eV has been used (Tools and Marton 1969). Values of $\tau_b/\hbar = 2{\cdot}84$ eV and $v_{fb} = 1{\cdot}82 \times 10^8$ cm/sec have been estimated using the free electron model (Kittel 1974). For bismuth in SiO_2 and V_2O_5–P_2O_5 matrices the ε_m values have been assumed to be 2·2 (Granqvist and Hunderi 1978) and 10 (Man Singh *et al* 1975) respectively.

Equations (5) and (7) giving $\bar{\varepsilon}^{\rm MG\text{-}PvS}$ and $\bar{\varepsilon}^{\rm BR}$ values respectively contain size-dependent fill factors f_j which can be related to f by the following equation

$$f_j = w_j f, \tag{11}$$

where w_j is the weight factor and is given by,

$$w_j = \frac{x_j^3 n_j}{\sum_j x_j^3 n_j}. \tag{12}$$

The symbols have their usual significance.

In the present calculations the fill factor f is used as an adjustable parameter chosen by the least squares method such that the theoretical α values give the closest fit to experimental results (Granqvist and Hunderi 1977).

The optical absorption coefficient α in all the above models is calculated from the relation

$$\alpha(w) = (w/c)(\bar{\varepsilon}_2/\bar{\varepsilon}_1^{1/2}), \tag{13}$$

where $\bar{\varepsilon}_1$ and $\bar{\varepsilon}_2$ are the real and imaginary parts of the effective medium permittivity.

Figures 5 and 6 give the frequency dependent α values computed on the basis of various models for glasses 2 and 6 respectively. The experimental results are plotted in these figures for comparison. Computed data for these glasses with other reduction treatments are similar to the ones shown in these figures. BR and MG-PvS theories give almost identical results and hence only the BR values are plotted in the figures. Theoretical values for V_2O_5-P_2O_5 glasses containing bismuth show an absorption peak at 650 nm and for silicate glasses with bismuth a small dip at around the same wavelength is observed. However, these features are not exhibited by experimental data. In V_2O_5-P_2O_5-Bi_2O_3 system, BR and MG-PvS theories give better agreement with experimental results than MG theory for the peak around 450 nm. In the SiO_2-B_2O_3-Na_2O-Bi_2O_3 system also BR and MG-PvS theories predict results (530 nm and 460 nm) which are in better agreement with the experimentally observed peak positions (515 nm and 425 nm).

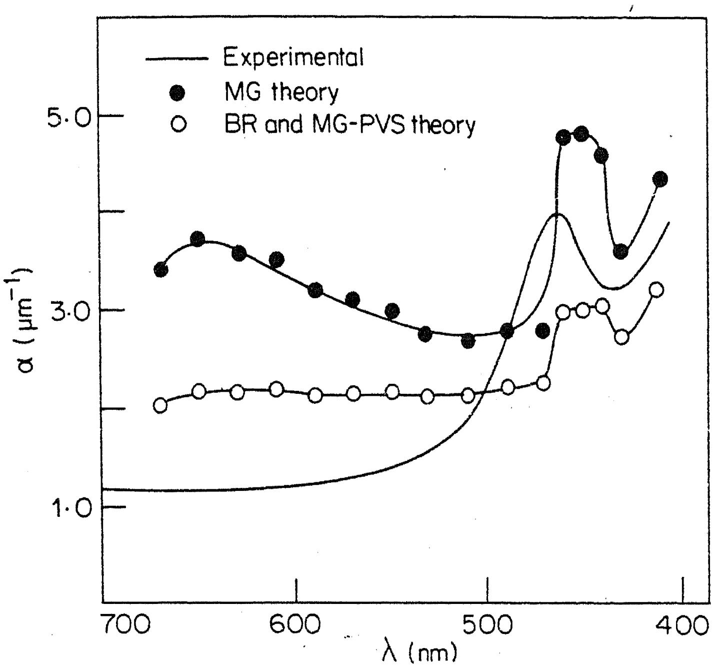

Figure 5. Experimental and theoretical absorption coefficients for microcomposite no. 2; $f = 0{\cdot}03$

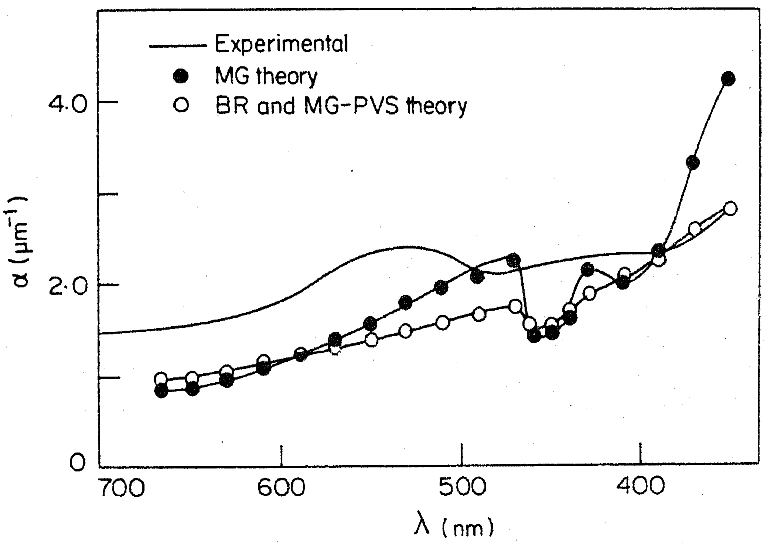

Figure 6. Experimental and theoretical absorption coefficients for microcomposite no. 6 reduced at 300°C for 1·5 hr; $f = 0{\cdot}03$

5. Conclusions

(i) Vanadium phosphate glasses containing bismuth granules having dimensions ranging from 7 to 15 nm show an absorption maximum at around 450 nm. (ii) Silicate glasses containing bismuth granules ranging from 8 to 16 nm show absorption maxima at 515 nm and 425 nm respectively. (iii) MG, MG-PVS and BR theories predict the optical absorption peak positions in fair agreement with the experimentally observed values in the case of ultrafine bismuth particles dispersed in either a silicate or a vanadium phosphate glass matrix. (iv) MG-PvS and BR theories predict values over the entire wavelength range which are in better agreement with experimental data than those obtained from MG theory in vanadium phosphate as well as silicate glasses containing bismuth particles.

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