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Carbon-in-silica Composite Selective Solar Absorbers:
A Determination of Composition and Dielectric Properties

G KATUMBA[1], T BAISITSE[2], A FORBES[2], L OLUMEKOR[1] & E WÄCKELGÅRD[3]
[1]Department of Physics, University of Zimbabwe, Harare, Zimbabwe
[2]CSIR National Laser Centre, PO Box 395, Pretoria 0001, South Africa
[3]Department of Materials Science, Uppsala University, Uppsala, Sweden

INTRODUCTION

The Bruggeman and Maxwell-Garnett effective medium approximations (EMAs) have been used to investigate optical properties of composite materials. The EMA assumptions are based on random unit cell models in which metal particles are embedded in a dielectric medium. The embedded particles can be varied between spherical, ellipsoidal and cylindrical shapes. An interesting structure of connected short chains of amorphous carbon intermixed with silica chains at nanoscale level has been observed. The Bruggeman and Maxwell-Garnett EMAs could not model the optical properties of these materials; neither could the Bergman-Milton bounds approach. A generalised Bergman representation is applied on these carbon-in-silica samples with successful fitting between experiment and theory. The curve-fitting procedure resulted in information such as volume fraction of carbon relative to silica, percolation threshold and film thickness.

EXPERIMENT

The details of the synthesis process of C-SiO$_2$ samples have been reported ealier.[1] The reflectance of the C-SiO$_2$ samples was measured in the wavelength range 400 to 2500 nm using a Lambda 900 spectrophotometer.

The Bruggeman, Maxwell-Garnett and Bergman-Milton EMAs shown in equations (1), (2) and (3), respectively, were fitted to the experimental reflectance measurements using the Fresnel formalism:

$$f_A \frac{\varepsilon_A - \bar{\varepsilon}_{Br}}{\varepsilon_A + 2\bar{\varepsilon}_{Br}} + (1 - f_A)\frac{\varepsilon_B - \bar{\varepsilon}_{Br}}{\varepsilon_B + 2\bar{\varepsilon}_{Br}} = 0 \tag{1}$$

$$\bar{\varepsilon}_{MG} = \varepsilon_B \frac{\varepsilon_A + 2\varepsilon_B + 2f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_A + 2\varepsilon_B - f_A(\varepsilon_A - \varepsilon_B)} \tag{2}$$

$$\varepsilon_{BM} = \frac{\varepsilon_A\varepsilon_B + 2\varepsilon_h(f_A\varepsilon_A + f_B\varepsilon_B)}{2\varepsilon_h + f_A\varepsilon_B + f_B\varepsilon_A} \tag{3}$$

with the bounds $\varepsilon_h = x\varepsilon_A + (1-x)\varepsilon_B$ for the Bergman-Milton EMA.

In these equations ε_A, ε_B, ε_{Br}, ε_{MG} and ε_{BM} are the respective dielectric functions of a-carbon, silica, effective Bruggeman, Maxwell-Garnett and Bergman-Milton composites. The carbon volume fraction is given by f_A and $f_B = 1-f_A$ is the silica volume fraction. The parameter x determines the mixing ratio for ε_{BM}.

A generalised Bergman representation, described in equations (4) to (6), was used to fit the reflectance spectra. The important fit parameters are volume fraction of carbon relative to silica, percolation threshold, the thickness of the coatings and effective dielectric function of the composite layer.

$$\varepsilon_{eff} = \varepsilon_M\left(1 - f\int_0^1 \frac{g(n,f)}{t-n}dn\right) \tag{4}$$

The function *g(n,f)* is the spectral density which contains all topological details of the microgeometry of the composite layer and *f* is the volume fraction of the filling material of dielectric function ε embedded in a matrix of dielectric function ε_M. The spectral density is a real and non-negative function that is normalised for n in the interval [0,1]. In equation (5) *t* is given by the expression:

$$t = \frac{\varepsilon_M}{\varepsilon_M - \varepsilon} \tag{5}$$

In the case of an isotropic medium there is a condition for the first moment of the spectral density given by:

$$\int_0^1 g(n,f)\,dn = 1, \text{and} \int_0^1 ng(n,f)\,dn = \frac{1-f}{3} \tag{6}$$

The microstructure of the samples was studied by cross-sectional high resolution transmission electron microscopy (X-HRTEM). A representative X-HRTEM image is shown in Figure 1.

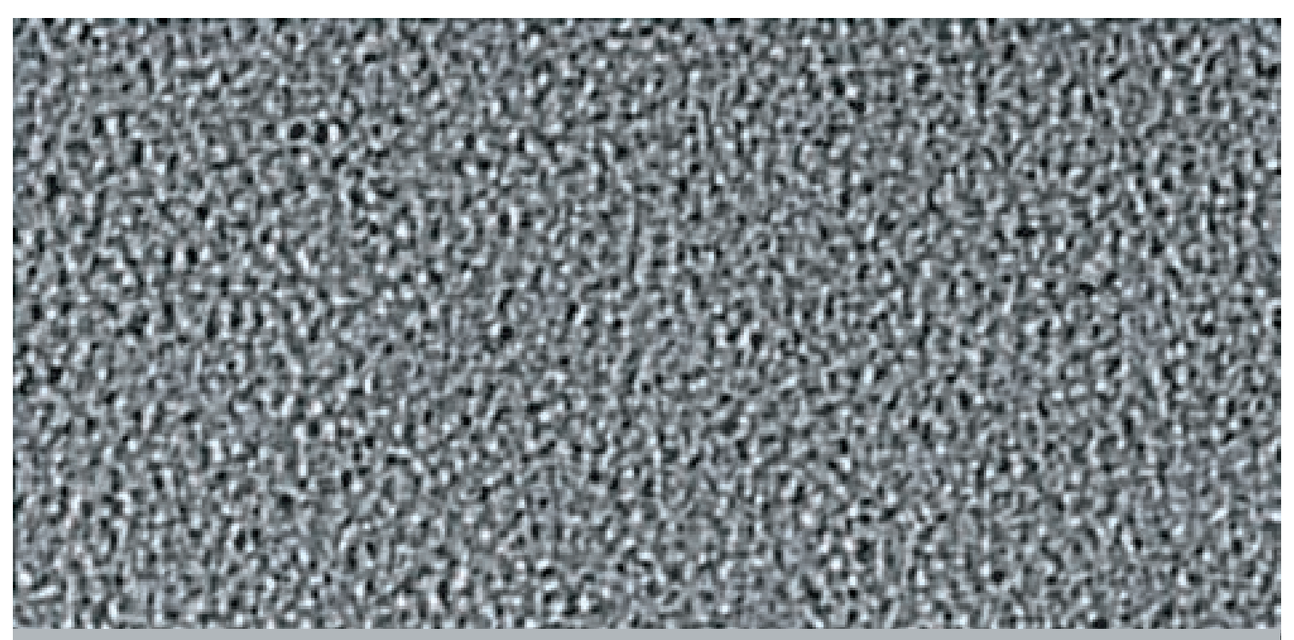

Figure 1: X-HRTEM image of C-SiO$_2$ composite showing the chain-like microstructure

RESULTS AND DISCUSSION

The theoretical reflectance calculations for the Bruggeman, Maxwell-Garnett and the Bergman-Milton EMAs are compared with experiment in Figures 2 to 4, respectively.

There is evident disparity in all the three comparison fit attempts.

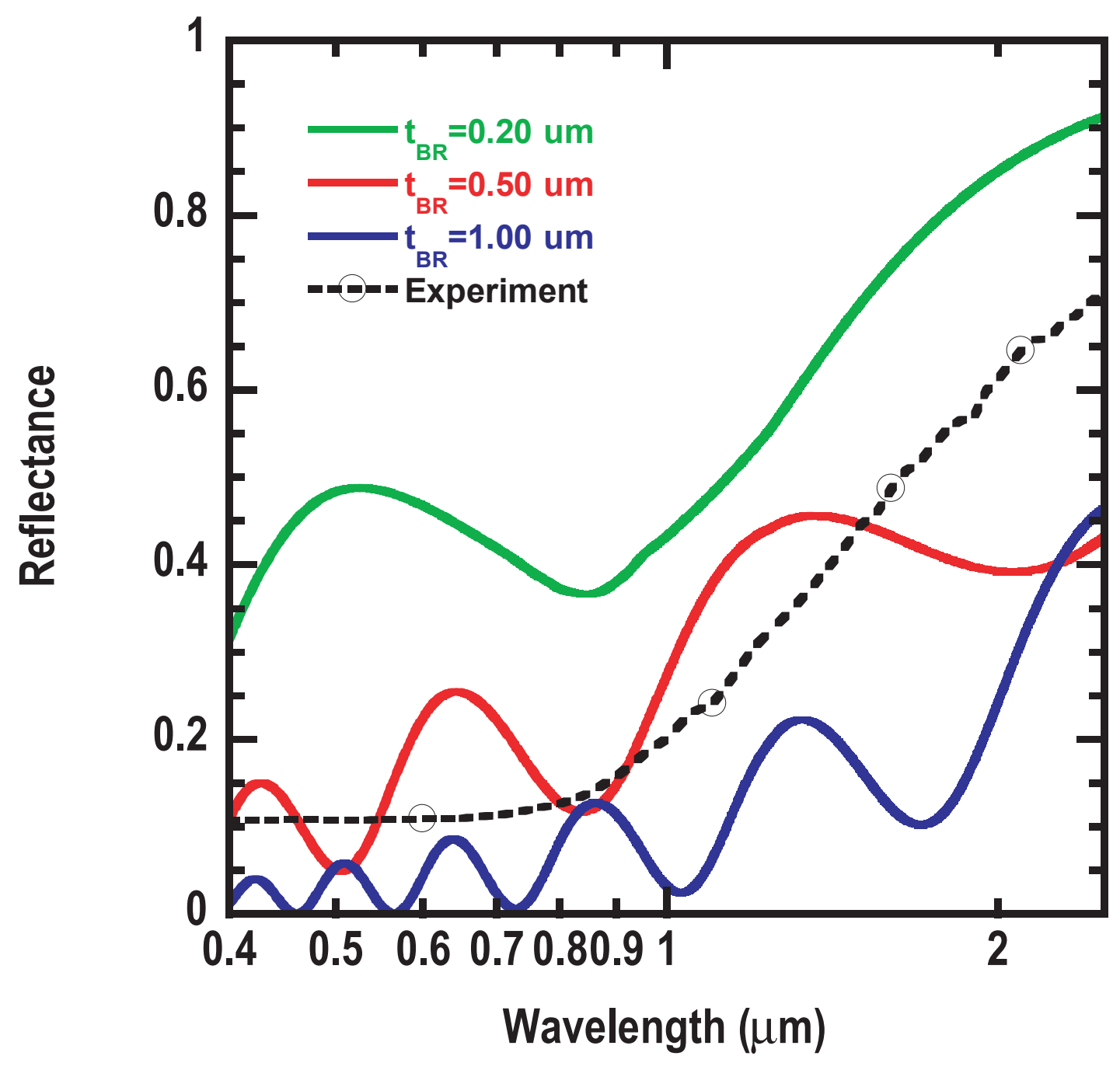

Figure 2: Comparison of Bruggeman EMA with fill factor 0.33 to experiment. There is great disparity between theory and experiment for many other fill factors and coating thicknesses

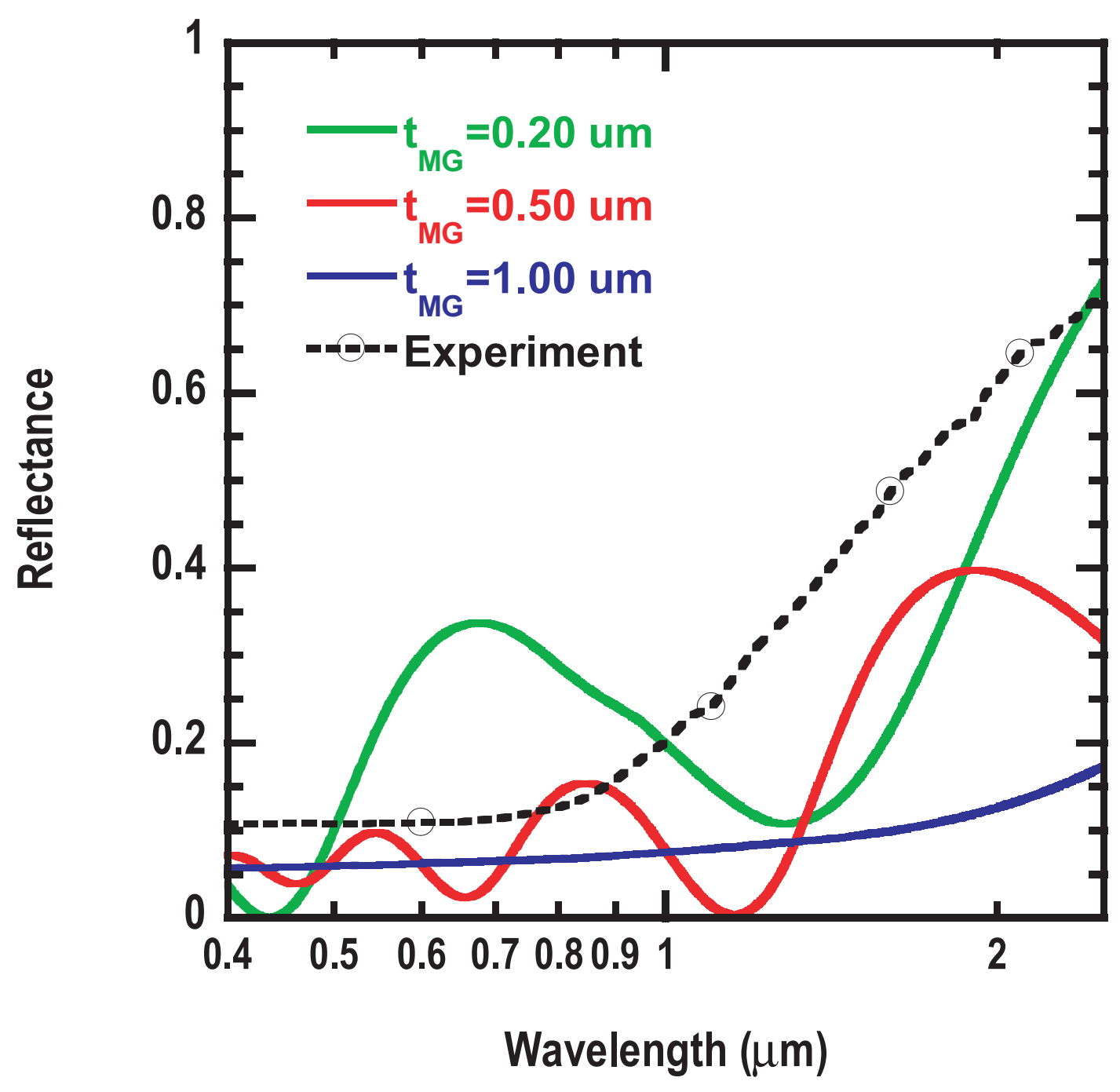

Figure 3: Comparison of the Maxwell-Garnett EMA with fill factor 0.33 to experiment. There is great disparity between theory and experiment for many other fill factors and coating thicknesses

The Bergman representation fits to reflectance measurements of three samples are shown in Figure 5. The parameters extracted from the curve-fitting are presented in Table 1. Independent measurements of some of the parameters, where possible, have been made for comparison.

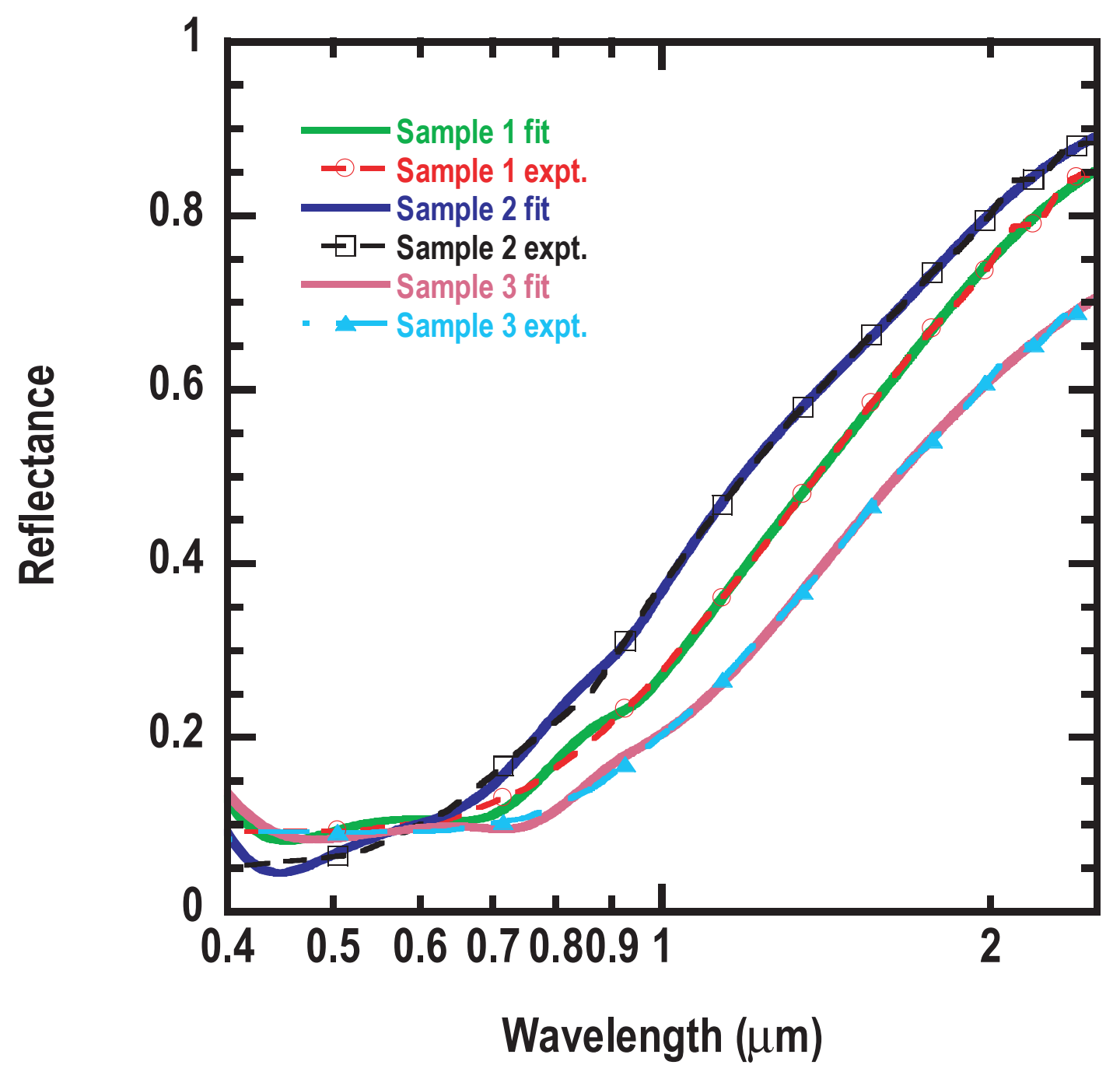

Figure 5: The Bergman representation fitted to experimental data. There is agreement between theory and experiment

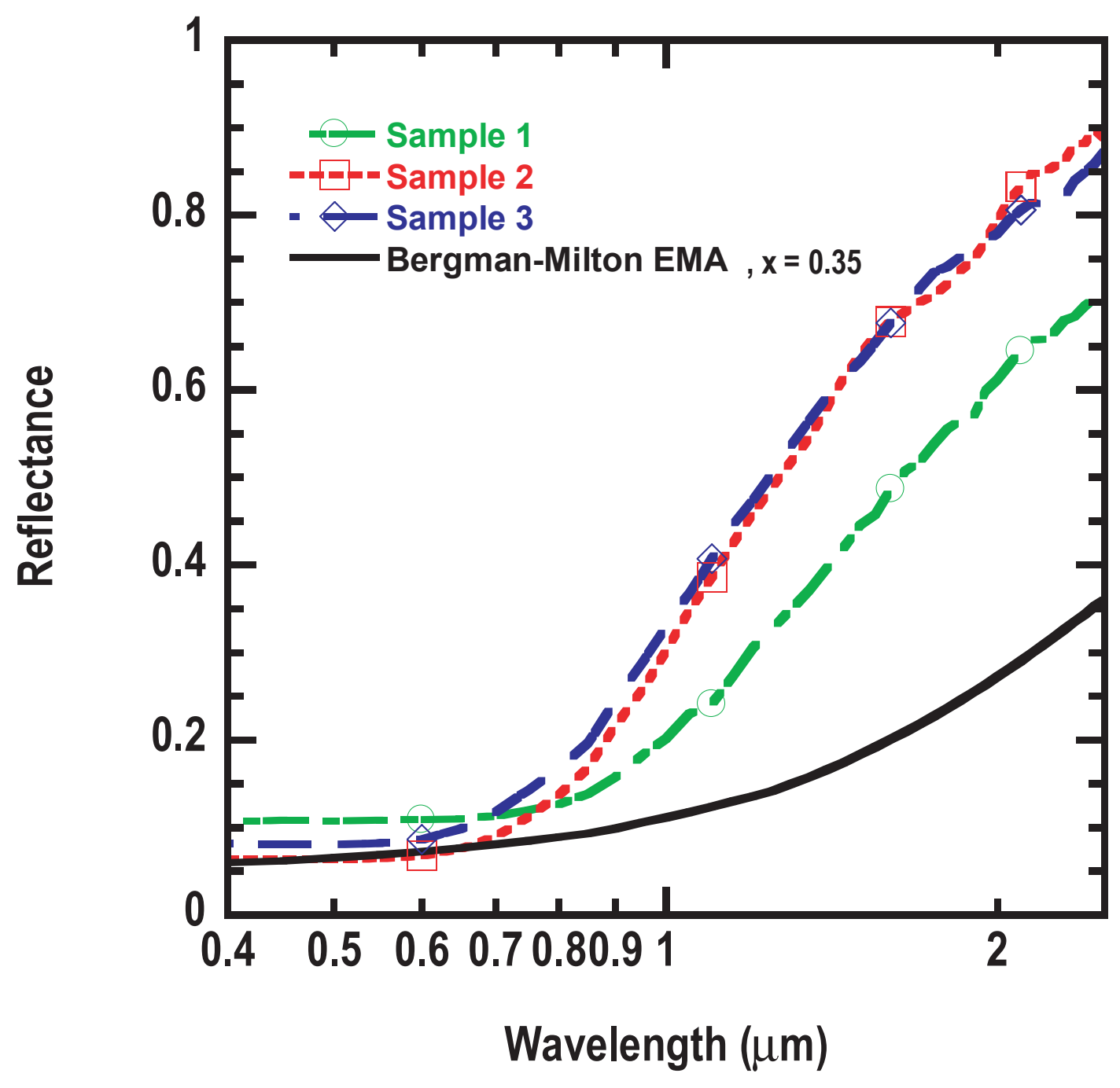

Figure 4: The Bergman-Milton bounds EMA compared with experiment for x=0.35. There is great disparity between theory and experiment for many other fill factors and x parameter values

Sample	Fit thickness (μm)	TEM Thickness (μm)	Fit carbon volume fraction	Carbon volume fraction (LIBS)	Percolation threshold
1	1.02	1.14	0.33		0.51
2	1.12	1.00	0.28	0.29	0.54
3	0.87	0.92	0.35		0.55

Table 1: Data extracted from the Bergman fit. There is agreement within experimental limits between the fit values and the independent measurements

CONCLUSION

The Bergman EMA representation has been fitted successfully to composite coatings of carbon nano-chains embedded in silica. Film thickness, carbon volume fraction and percolation threshold were extracted.

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