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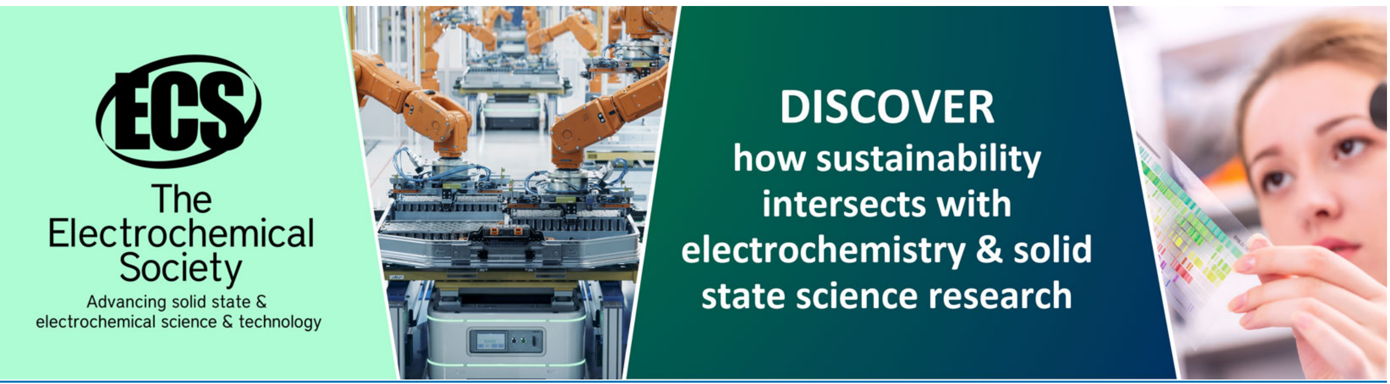

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Refractive index investigations of nanoparticles dispersed in water

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Abstract. The refractive index of nanoparticles dispersed in water is measured, using the total internal reflection method. The critical angle is determined by the disappearance of diffraction orders from a metal grating. The investigated nanoparticles are titanium dioxide (anatase phase), (35 nm diameter), zinc oxide, (<50 nm diameter), zirconium dioxide, (<100 nm diameter). The refractive index is measured with the experimental uncertainty of 1%. The Lorentz-Lorenz, Maxwell Garnett and Bruggeman relations are applied in the nanoparticle's refractive indices calculations.

1. Introduction

More than 120 years ago LeBlanc [1] has proposed a critical angle method for refractive index (RI) measurement of powders. In fact, that is an immersion technique, where critical angle is fixed when particle's RI is equal to the RI of the immersion liquid. In this case the light scattering is minimized. The Abbe refractometer ensures satisfactory measurement precision. However, the LeBlanc's method is time consuming; limited to the short list of high RI immersions; and high RI particles are measured with inflammable and toxic immersion liquids. In 1991 one of the authors [2] has proposed RI measuring method based on the critical angle determination by the disappearance of the diffraction pattern, created by a metal grating, placed in contact with the liquid or solid sample with a thickness varying from 250 nm to several μm. Applying this method, RI of turbid samples, cow butter for example, could be measured [3].The maximum experimental uncertainty is ±0.001 [4].

In the present paper the RI of high RI nanoparticles are measured. The samples are water dispersions of ZnO, TiO_2 and ZrO_2 nanoparticles with filling factors (f) 0.15, 0.012 and 0.02, respectively. The thickness of the liquid layer's is 6 μm. After RI determination of water dispersion's RI, RI of the nanoparticles are calculated using well-known Lorentz-Lorenz [5], Maxwell Garnett [6] and Bruggeman [7] mixing models. He-Ne laser (632.8nm) and semiconductor laser (532nm) are utilized as light sources in the present RI measurements.

The RI data at these two laser wavelengths is used for one oscillator Sellmeier dispersion relation.

2. Theoretical background

Our considerations are based on the most popular mixing theories. According Lorentz-Lorenz [5], in the optical spectral range we have:

$$\frac{n_e^2-1}{n_e^2+2}=f\,\frac{n_i^2-1}{n_i^2+2}+\left(1-f\right)\frac{n_m^2-1}{n_m^2+2}, \qquad (1)$$

where n_e is experimentally obtained effective RI; n_i is RI of inclusions; n_m is RI of matrix.

Filling factor f is defined as ratio between the total particles' volume and full volume:

$$f=\frac{V_i}{V_m+V_i}. \qquad (1a)$$

Using the effective dielectric function, Maxwell Garnett [6] obtained:

$$n_e^2=n_m^2\,\frac{\left(n_i^2+2n_m^2\right)+2f\left(n_i^2-n_m^2\right)}{\left(n_i^2+2n_m^2\right)-f\left(n_i^2-n_m^2\right)}. \qquad (2)$$

In 1935, Bruggeman [7, 8] proposed another mixing relation:

$$f\,\frac{\left(n_i^2-n_e^2\right)}{\left(n_i^2+2n_e^2\right)}+\left(1-f\right)\frac{\left(n_m^2-n_e^2\right)}{\left(n_m^2+2n_e^2\right)}=0. \qquad (3)$$

Solving the equation (1), (2) and (3), for RI of embedded nanoparticles we have:

$$n_i^{L-L}=\left[\frac{2\left(n_e^2-n_m^2\right)+fn_m^2\left(n_e^2+2\right)}{\left(n_m^2-n_e^2\right)+f\left(n_e^2+2\right)}\right]^{\frac{1}{2}}, \qquad (4)$$

$$n_i^{MG}=n_m\left[\frac{2\left(n_e^2-n_m^2\right)+f\left(n_e^2+2n_m^2\right)}{f\left(n_e^2+2n_m^2\right)-\left(n_e^2-n_m^2\right)}\right]^{\frac{1}{2}}, \qquad (5)$$

$$n_i^{Br}=n_e\left[\frac{3fn_m^2-2\left(n_m^2-n_e^2\right)}{3fn_e^2+\left(n_m^2-n_e^2\right)}\right]^{\frac{1}{2}}, \qquad (6)$$

where n_i^{L-L}, n_i^{MG} and n_i^{Br} are the RI of nanoparticles, embedded into liquid or solid matrix and calculated using different mixing rules.

3. Experimental

3.1. Samples

All investigated samples are in the form of nanoparticles dispersed in water. The ZnO nanoparticles with diameter less than 50 nm, product of "Sigma-Aldrich", are 50 wt.% dispersion concentration in water. Titanium dioxide nanoparticles with diameter 35 nm are in anatase form and 5 wt.% dispersion concentration in water. The ZrO_2 nanoparticles with diameter less than 100 nm are also product of "Sigma-Aldrich" and 10 wt.% dispersion concentration in water. The 5 μl of the liquid sample is spread over 800 mm^2 of the grating and its thickness of is calculated to be 6 μm.

3.2. Refractive index measurements

The refractive index of the liquid sample is measured with a two-wavelength laser micro-refractometer at 632.8 nm and 532 nm. A 1 mW "Spectra Physics" He-Ne laser and second harmonic 20 mW semiconductor laser are used in the present investigations as light sources.

The laboratory device is illustrated in figure 1.

As described [9], the critical angle φ_c is determined by the observed diffraction pattern disappearing on the screen (10).

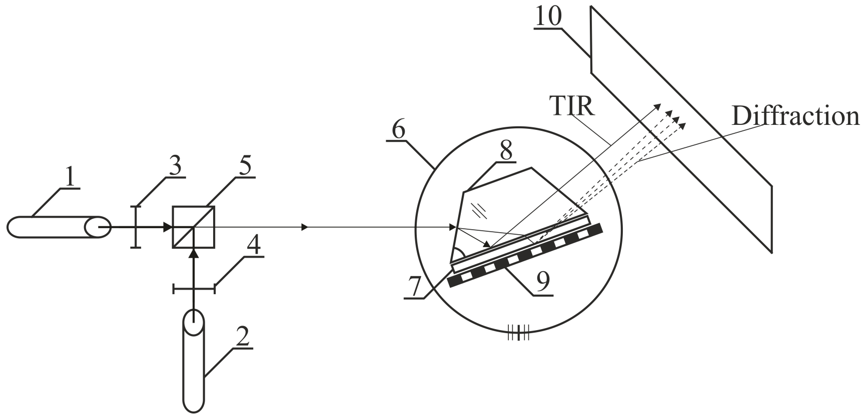

Figure 1. Two-wavelengths laser micro-refractometer: 1 – He-Ne laser (632.8 nm); 2 – 532 nm semiconductor laser; 3 and 4 – choppers; 5 – beam splitter; 6 – rotary stage with vernier; 7 – sample; 8 – glass prism; 9 – metal diffraction grating; 10 – screen.

The refractive index is calculated by the following equation:

$$n = N \sin\left[A \pm \arcsin \frac{\sin \varphi_{cr}}{N} \right]. \tag{7}$$

The sign (+) and (-) corresponds to the clockwise and the counter-clockwise determination of φ_{cr}, respectively. In our case the sign is (-). In equation (7) $A = 65°$ is the reflecting angle of the prism, N is the refractive index of the prism and has the values 1.7347 and 1.7480 for the used wavelength of 632.8 nm and 532 nm, respectively.

The optical properties of the materials are usually presented by their dispersion dependences. The most appropriate dispersion relation in dielectric and non-magnetic materials far from the fundamental absorption band is the Sellmeier relation:

$$n^2 - 1 = \frac{s\lambda^2}{\lambda^2 - \lambda_s^2}. \tag{8}$$

In the one-oscillator Sellmeier's model the dependence of refractive index as a function of wavelength λ is expressed by two constants, s and λ_s, which are called Sellmeier's coefficients.

4. Results and discussion

The obtained experimental results calculated by equations (4), (5) and (6) are listed in table 1. The RI of water n_m is measured by the laser micro-refractometer (see part 3.2) with the experimental uncertainty 0.01%. The nanoparticle concentration uncertainty is 0.05%. The nanoparticles RI uncertainty is $\Delta n = \pm 0.02$ and mainly depended from effective RI measurements.

Table 1. Refractive index of investigated nanoparticles.

Sample	**TiO_2**		**ZrO_2**		**ZnO**	
λ, nm	532	632.8	532	632.8	532	632.8
n^{MG}, $\Delta n = \pm 0.02$	2.52	2.46	2.19	2.14	2.06	2.02
n^{Br}, $\Delta n = \pm 0.02$	2.54	2.49	2.20	2.16	2.04	2.01
n^{L-L}, $\Delta n = \pm 0.02$	3.79	2.81	3.94	2.76	2.37	2.13

Table 1 represents a good correlation, between experimentally obtained RI of nanoparticles and those described in the literature within our experimental uncertainty. The results obtained by Maxwell Garnett and Bruggeman mixing relations match. According to the data published in [10] refractive index of anatase is 2.49 at 589.3 nm wavelength. According to the data published on Internet (www.refractiveindex.info) and references therein the averaged RI of ZnO is $n^{532} = 2.03$ and $n^{633} = 1.99$. For ZrO_2 $n^{532} = 2.17$ and $n^{633} = 2.15$. The experimental results are very close, which has been theoretically proved earlier [9]. The Lorentz-Lorenz mixing rule is not applicable for RI investigations of nanoparticle dispersions. The experimental uncertainty in the present research is not high because scattered light background hinders the exact critical angle determination. Due to the Mie scattering theory [11], the scattered light intensity is very high - proportional to $\left|\left(n_i^2 - n_m^2\right)\right|^2$.

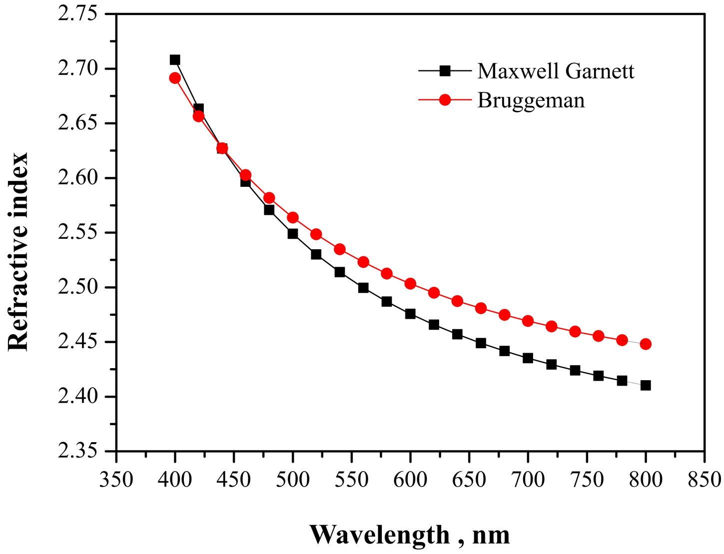

Figure 2. Sellmeier approximation of the dispersion dependences of the refractive index of TiO_2 nanoparticles obtained by Maxwell Garnett and Bruggeman relations.

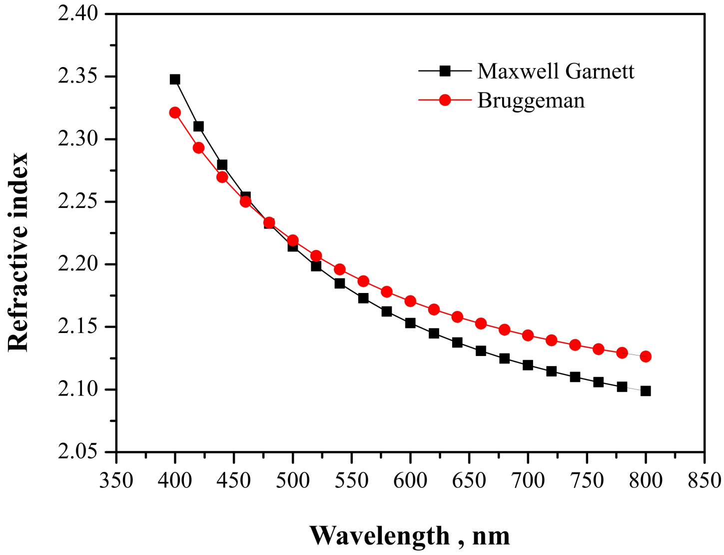

Figure 3. Sellmeier approximation of the dispersion dependences of the refractive index of ZrO_2 nanoparticles obtained by Maxwell Garnett and Bruggeman relations.

In order to attain an experimental uncertainty better than ±0.001 it is necessary to increase signal-to-noise ratio in diffraction pattern detection. It could be achieved by CCD camera detection followed by computer processing for scattered light background suppression. The simultaneous sample's thickness diminishing in the range 0.5 µm – 1.0 µm will also increase signal-to-noise ratio.

The refractive index dispersion dependencies of the investigated nanoparticles are obtained by fitting using equation (8) and listed below.

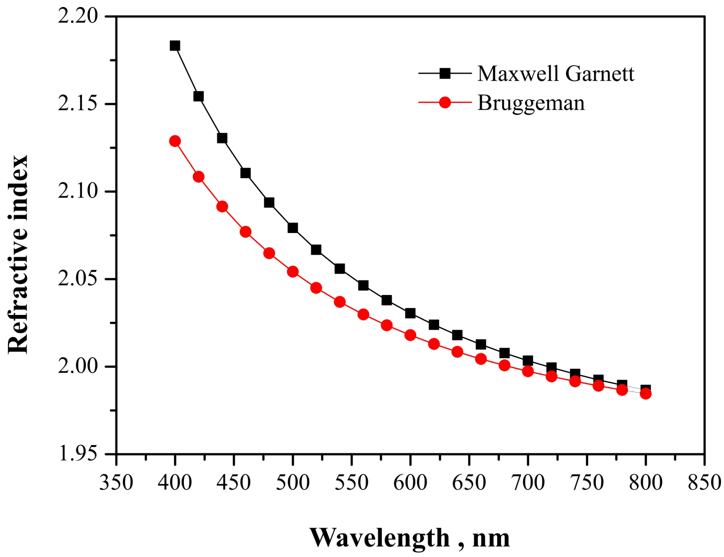

Figure 4. Sellmeier approximation of the dispersion dependences of the refractive index of ZnO nanoparticles obtained by Maxwell Garnett and Bruggeman relations.

5. Conclusion

The refractometric method of the disappearing diffraction pattern is applicable for RI investigation of nanoparticles. In the present work high RI nanoparticles are dispersed in water - i.e. the case with the biggest RI difference and consequently, very high light scattering background.

Acknowledgements

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