Interference effect in surface modified ZnS nanoparticles / Poly (methylmethacrylate) nanocomposites

N. Romcevic[1], B. Hadzic[1], M. Curcic[1], V. Radojevic[2], N. Paunovic[1], and M. Romcevic[1]

[1] *Institute of Physics Belgrade, University of Belgrade, Belgrade, Serbia*

[2] *Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia*

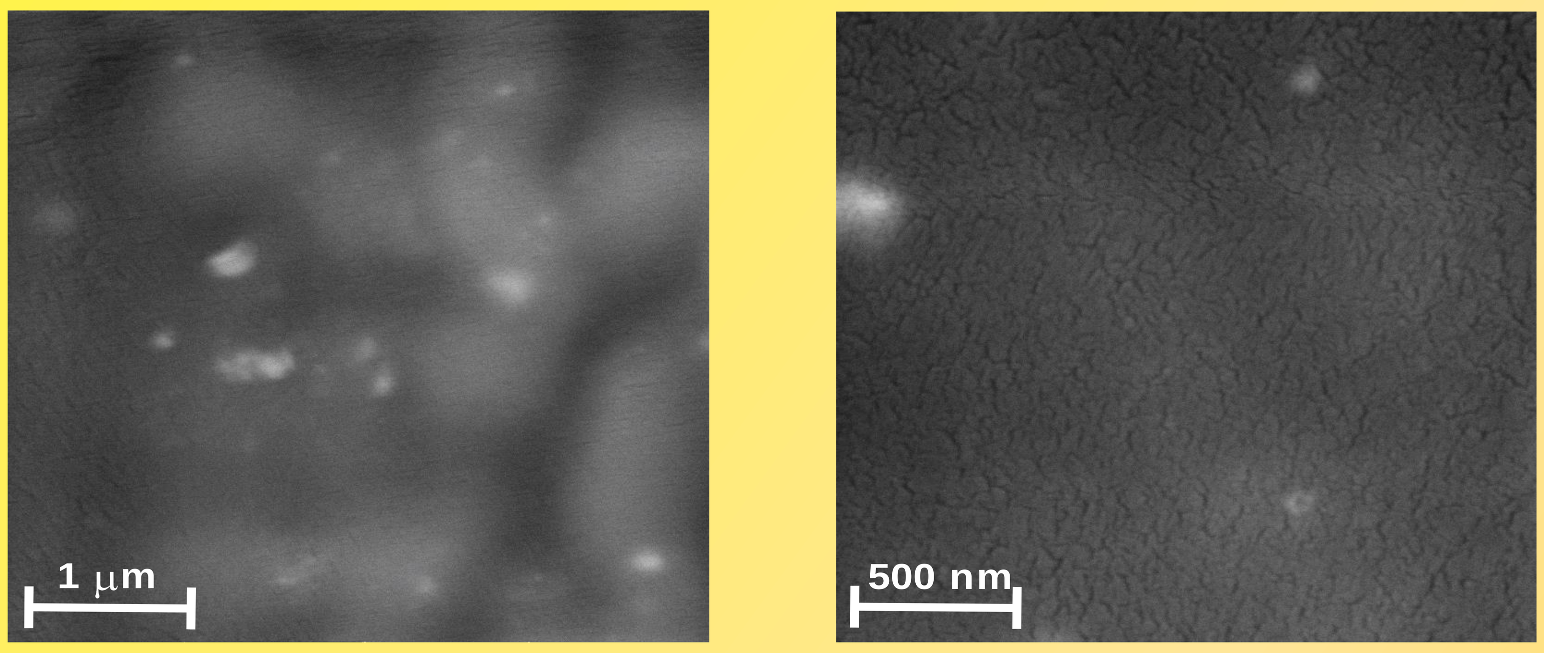
1. Methods and materials

The ZnS nanoparticles were synthesized by mechanochemical treatment. The milling time was 10 min and the crystallite size of the obtained ZnS nanoparticles was estimated to be 2.3 nm. Surface modification of ZnS is achieved by using a 3-Mercaptopropyltrimethoxysilane (MPTMS) – Dynasylane, Evonik Industries and toluene, hexane (Sigma Aldrich) as solvent.

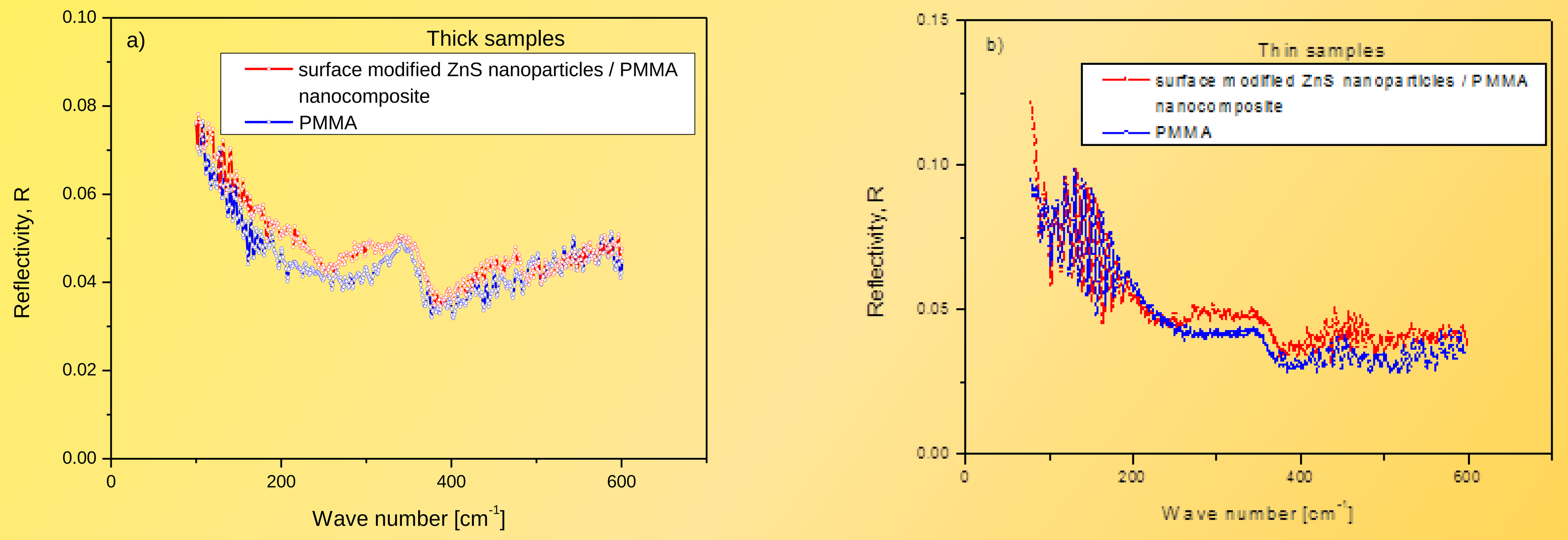
Surface modified ZnS nanoparticles / poly (methylmethacrylate) - PMMA nanocomposites were prepared by the solution casting method. The ZnS nanoparticles modified with MPTMS were added in the solution of the PMMA (concentration of 22 % wt.) to achieve the nanoparticles concentration of the 0.06 % wt. The thin films were obtained by casting the solutions in Petri dishes and dried. Considering the thickness of the thin film we obtained the same types of the samples: conditionally thin - about 290 mm and thick - over 2mm.

The samples morphology was analyzed using the high-resolution MIRA3 TESCAN scanning electron microscope (SEM) operated at the accelerating voltage of 5, 12, and 20 kV. Far-infrared reflection spectra were recorded in the wave number range up to 600 cm^{-1} utilizing an A BOMEM DA - 8 FTIR spectrometer with a deuterated triglycine sulfate (DTGS) pyroelectric detector.

SEM: ZnS/PMMA



Experimental far-infrared (FIR) reflection spectra



2. Results and discussion

FIR spectra was fitted according to the model of thin or thick plate of nanocomposites in air. Thin sample have three-layer structure: medium 1 is air (ε_1=1); medium 2 is a surface modified ZnS nanoparticles / PMMA nanocomposite of thickness; medium 3 is air (ε_3=1); this third layer doesn't exist in thick sample.

Dielectric function for LO phonon-plasmon interaction, for thick samples:

$$(1)\quad \varepsilon(\omega)=\varepsilon_\infty \frac{\prod_{j=1}^{2}\left(\omega^2+i\gamma_{lj}\omega-\omega_{lj}^2\right)}{\omega(\omega+i\gamma_P)\left(\omega^2+i\gamma_t\omega-\omega_t^2\right)}\prod_{m=1}^{s}\frac{\omega^2+i\gamma_{LOm}-\omega_{LOm}^2}{\omega^2+i\gamma_{TOm}-\omega_{TOm}^2}$$

Effective medium theory – Maxwell-Garnet mixing rule, for thick samples:

$$(2)\quad \varepsilon_{eff}=\varepsilon_1+3f\varepsilon_1\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_2+2\varepsilon_1-f(\varepsilon_1-\varepsilon_2)}$$

with reflection coefficient $R=\left(\sqrt{\varepsilon_{eff}}-1\right)/\left(\sqrt{\varepsilon_{eff}}+1\right)$

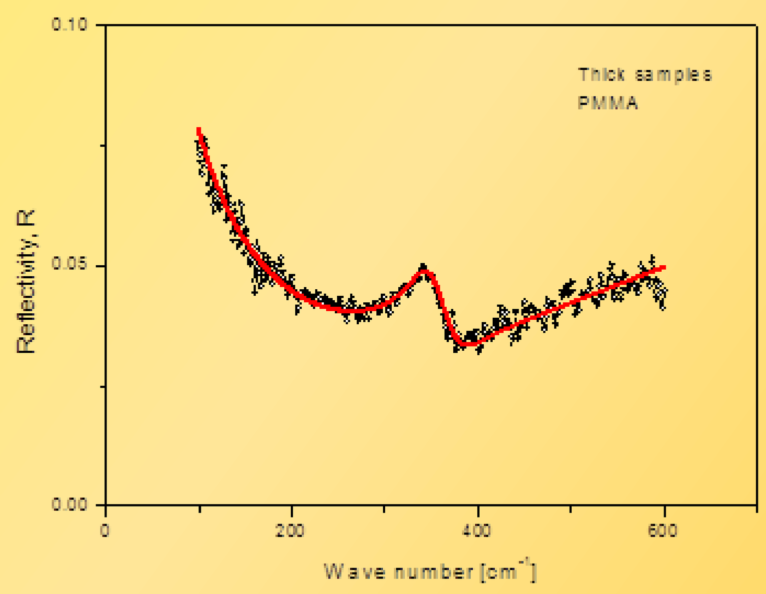
For thin samples, theoretical spectrum was obtained by model:

$$(3)\quad R_A=\frac{A_r}{A_i}=\frac{r_{12}e^{-i\alpha}+r_{23}e^{i\alpha}}{e^{-i\alpha}+r_{12}r_{23}e^{i\alpha}}$$

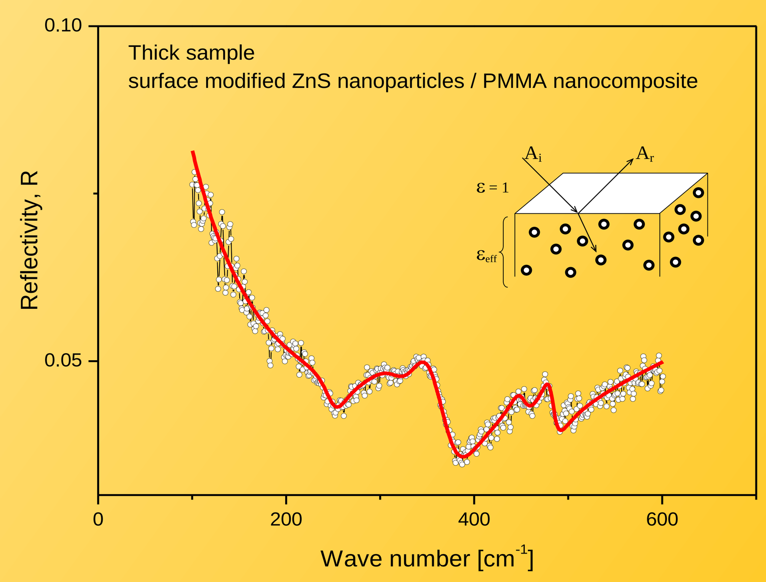
$r_{ij}=(n_i-n_j)/(n_i+n_j)=\left(\sqrt{\varepsilon_i}-\sqrt{\varepsilon_j}\right)/\left(\sqrt{\varepsilon_i}+\sqrt{\varepsilon_j}\right)$ are the Fresnel coefficients, A_i and A_r represent amplitudes of the incident and reflection beams, respectively, *n* is complex index of refraction, *ε* is the dielectric constant and $\alpha = 2\pi\omega d(\varepsilon_2)^{1/2}$ is the complex phase change related to the absorption in the crystal layer with the thickness *d*.

Reflectance, *R,* is given as: $R=|R_A|^2$.

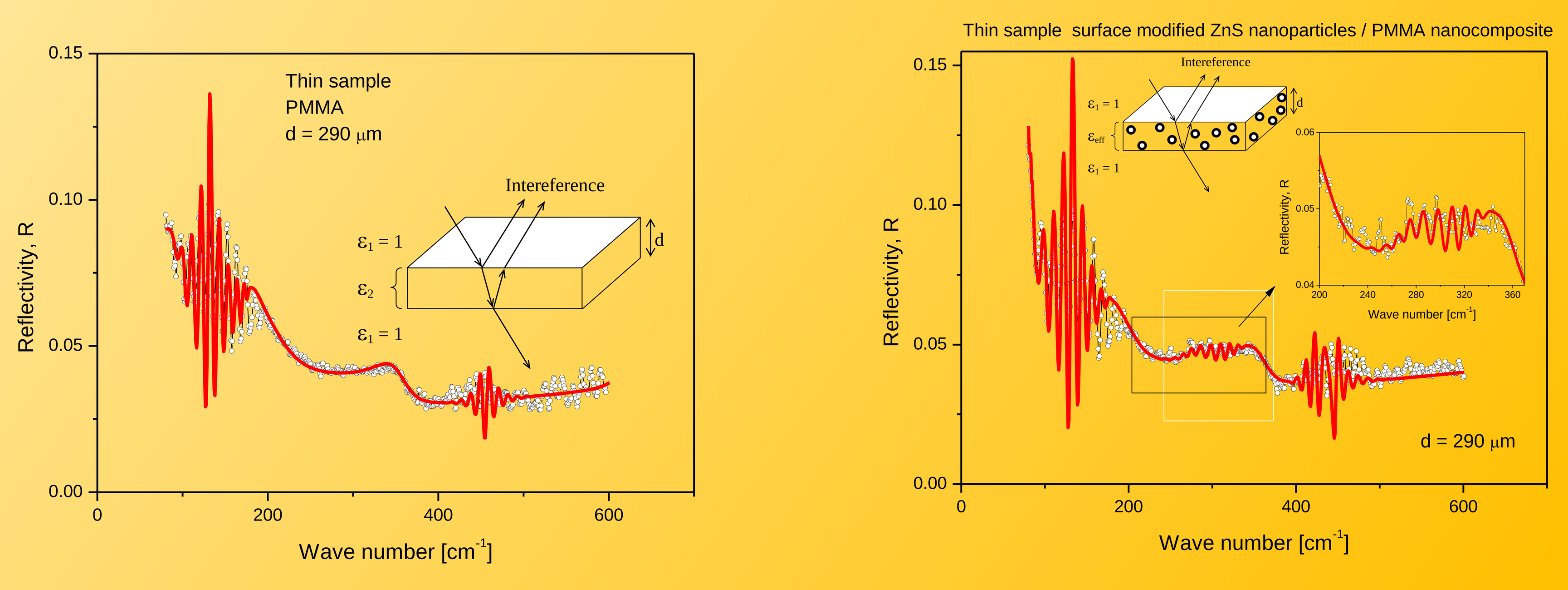
FIR: theoretical spectrum obtained by eq. 1 and fitting procedure



FIR: theoretical spectrum obtained by eq. 2 and fitting procedure



FIR: theoretical spectrum obtained by eq. 3 and fitting procedure



3. Conclusion

In PMMA thin sample (about 290mm) intense, well-defined interference was registered in the range of 90 to 200cm^{-1}, while significantly weaker and less well-defined interference was registered in the range around 450cm^{-1}. In the thin surface modified ZnS nanoparticles / poly (methylmethacrylate) - (PMMA) nanocomposites sample, in addition to the interference induced by sample thickness, interference induced by the existence of ZnS nanoparticles (crystallite size at about 2.3 nm) was also observed, located between TO and LO phonons of ZnS. The specific nature of the effect is related to the fact that for the same thin film thickness we can modify the basic interference effect by designing the properties of nanocomposites. We registered the new effect - modified semiconductor nanoparticles induced interference in thin polymer samples, suitable for use in interferometry.

Acknowledgment

This research was supported by the Science Fund of the Republic of Serbia, Grant No. 7504386, Nano object in own matrix – Self composite – NOOM-SeC.