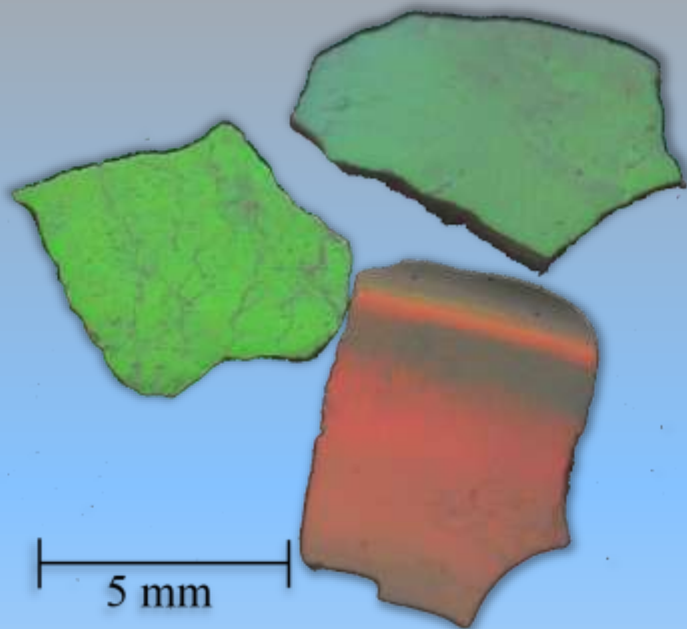
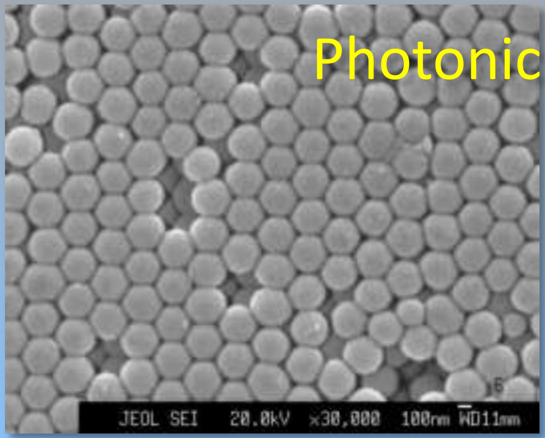
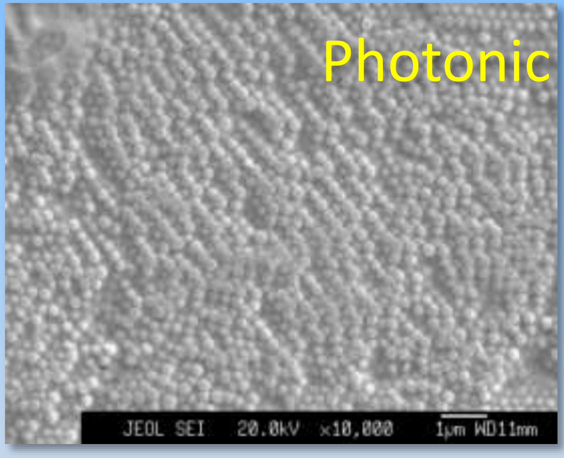
Raman spectroscopy of nanocomposites on basis of synthetic opals and active dielectrics

A.V. Yevchik, **V.N. Moiseyenko, M.P. Dergachov**

Oles Honchar Dnipropetrovsk National University







Synthetic opal samples fabricated in Oles` Honchar Dnipropetrovs`k National University

Size of the SiO_2 globules is about 250nm

Microphotographs of samples surface. photographs were obtained using X-ray microanalyzer JEO JXA 8200 (Technical Center of the National Academy of Sciences of Ukraine, Kyiv)

Bragg diffraction features of synthetic opal

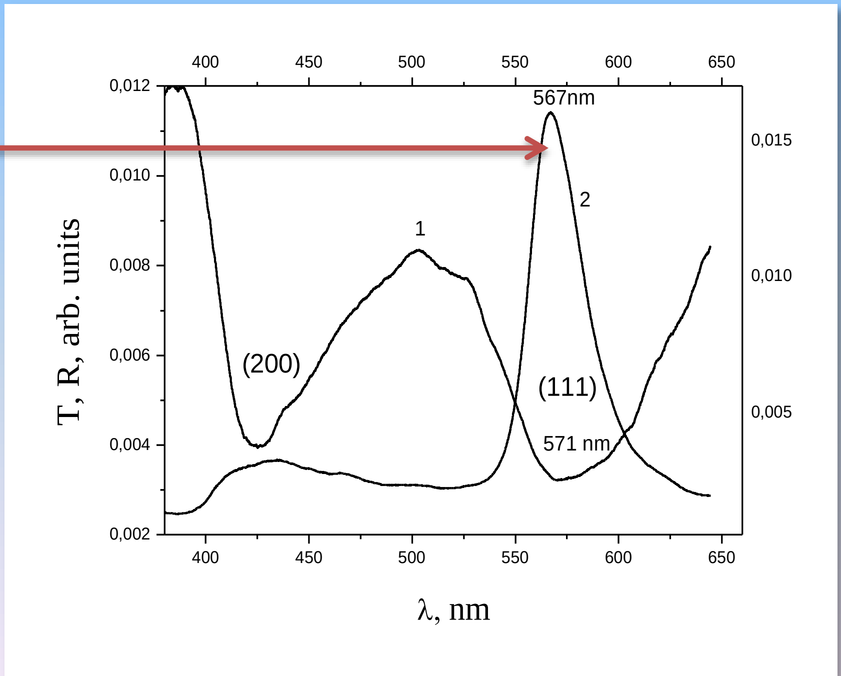
$$\lambda(\theta) = 2d\sqrt{\varepsilon_{eff} - \sin^2(\theta)};$$

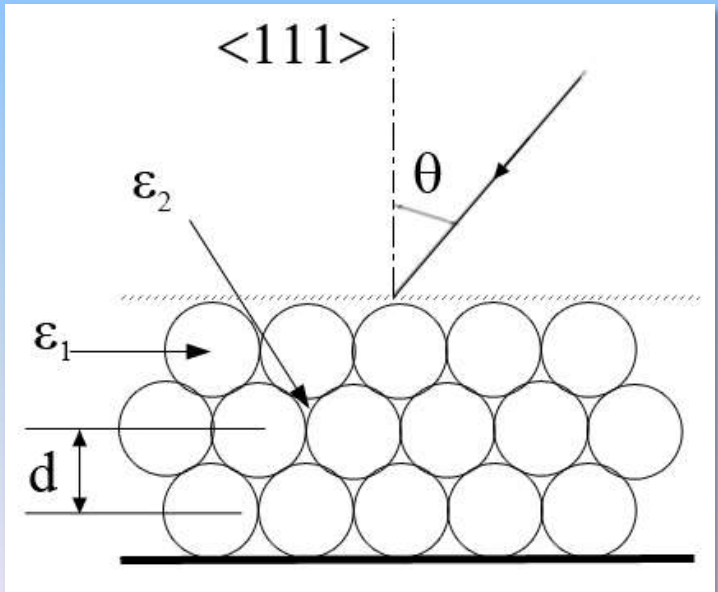
$$\varepsilon_{eff} = \varepsilon_1 f_1 + \varepsilon_2 f_2; \quad f_2 = 1 - f_1;$$

$\varepsilon_1,\ f_1$ - permittivity and fill factor of SiO_2 globules;

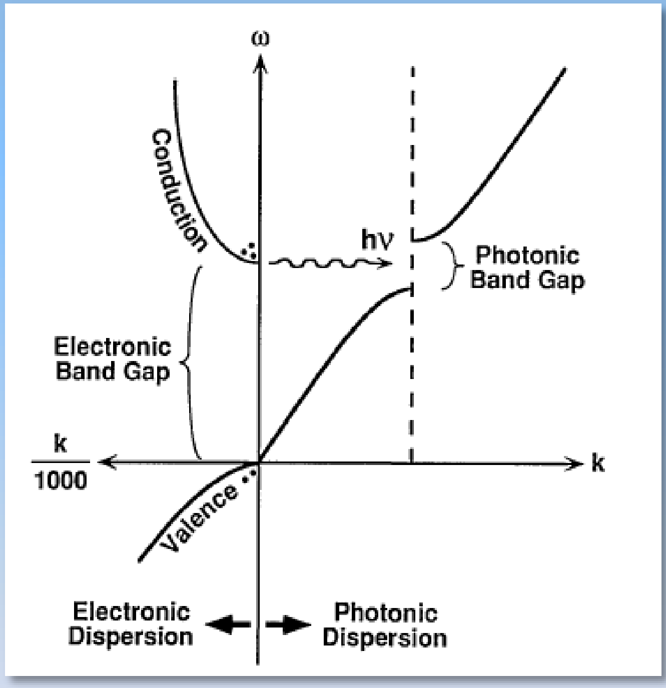
$\varepsilon_2,\ f_2$ - permittivity and fill factor of material in pores;

For *fcc* lattice $f_1 = 0.74,\ f_2 = 0.26;$

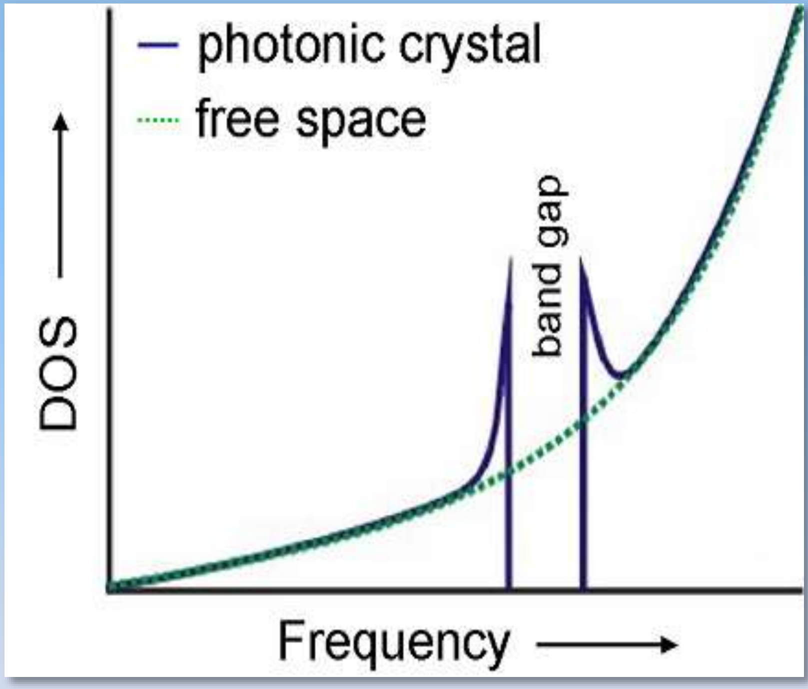




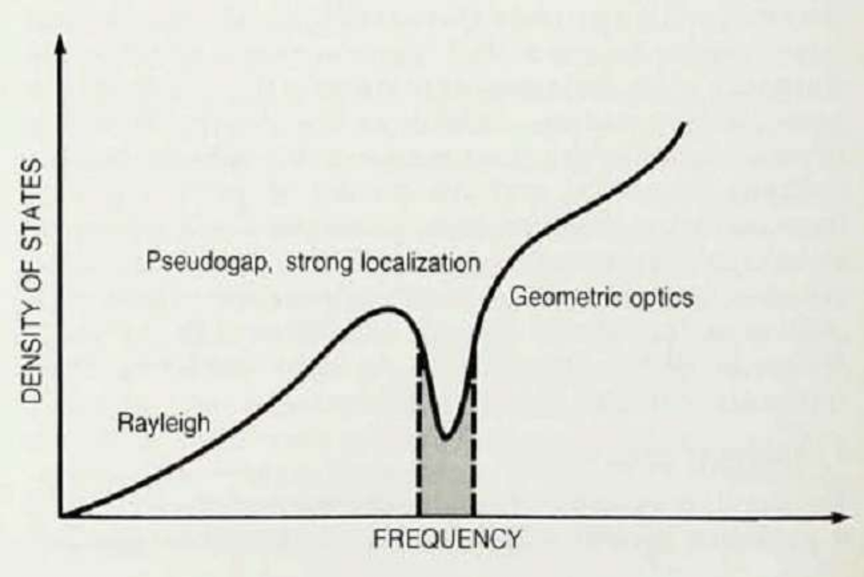
E.Yablonovitch. J. Opt. Soc. Am. B., V.10, No.2, P.283 (1993)



Bartl Group, Department of Chemistry, University of Utah, Salt Lake City UT 84112



Sajeev John, Localization of light, Physics Today, May 1991

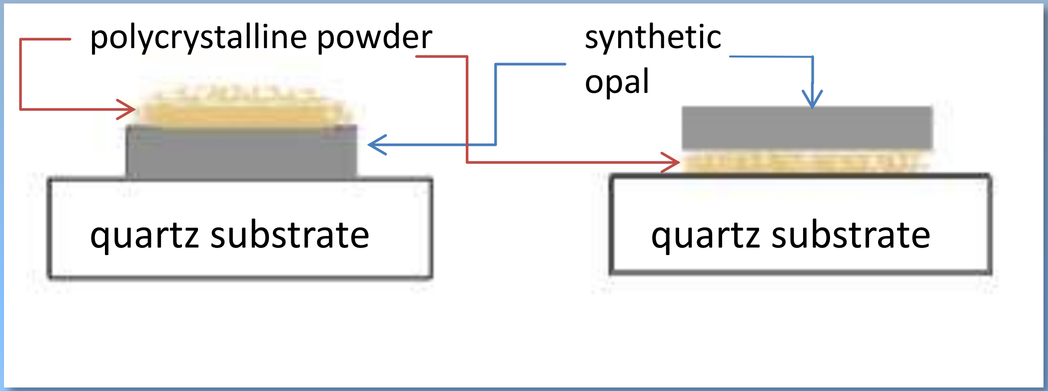


Density of states for photons in a disordered lattice is dominated by Rayleigh scattering at low frequencies and by classical ray optics at high frequencies. The photonic gap of the ordered structure is now replaced by a pseudogap. The states in the pseudogap are strongly localized.

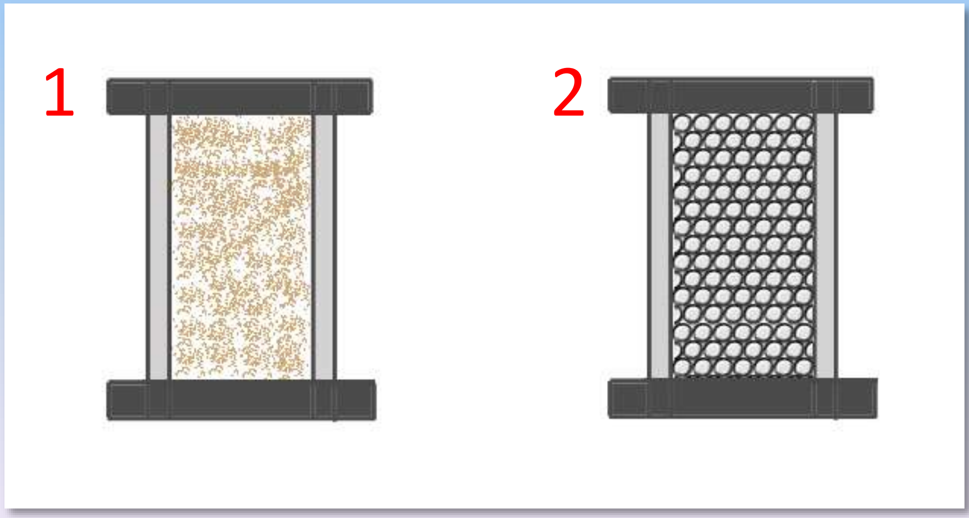
Goals and objectives

- Fabricate nanocomposite samples with synthetic opals and active dielectrics possess high electro-optic efficiency ($Bi_{12}Si(Ge)O_{20}$) and acousto-optic efficiency ($NaBi(MoO_4)_2$);
- Measure the Raman spectra obtained nanocomposites;
- Interpret the results using comparative analysis of the Raman spectra of nanocrystals and compounds in polycrystalline and monocrystalline state;

Technology of samples preparation



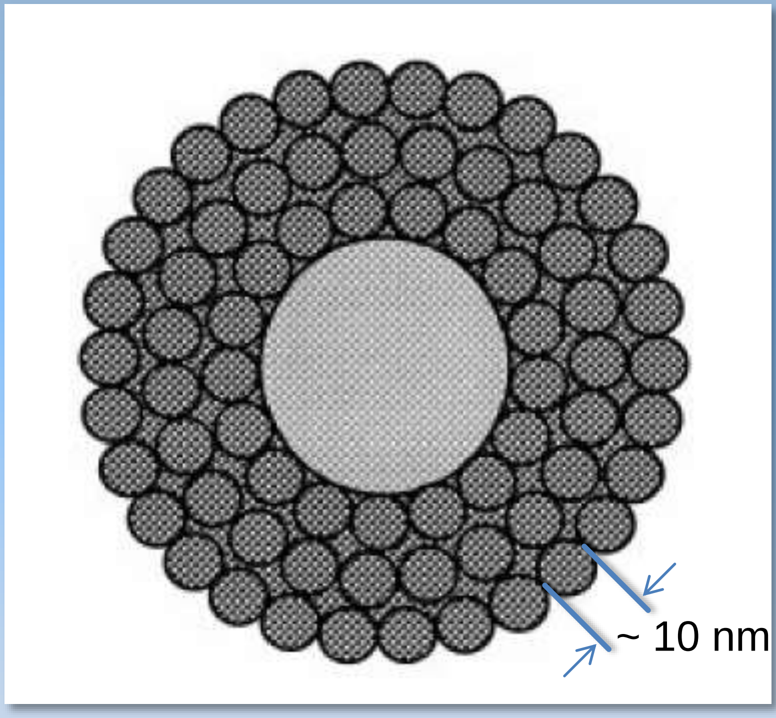
The filling-in of opal pores was carried out by melting-in of $Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$ and $NaBi(MoO_4)_2$ fine-dispersed polycrystalline powder at corresponding fusion temperatures:
$Bi_{12}SiO_{20}$ – 895 ^{0}C; $Bi_{12}GeO_{20}$ – 920 ^{0}C;
$NaBi(MoO_4)_2$ – 840 ^{0}C.



1 – Cell with the polycrystalline powder of material under research. Material volume fraction consist of 80% per volume unit;
2 – cell with the synthetic opal sample filled material under research. Material volume fraction consist of 10 - 20% per volume unit;

I. A. Karpov, Physics of the Solid State, **47**, 334 (2005)

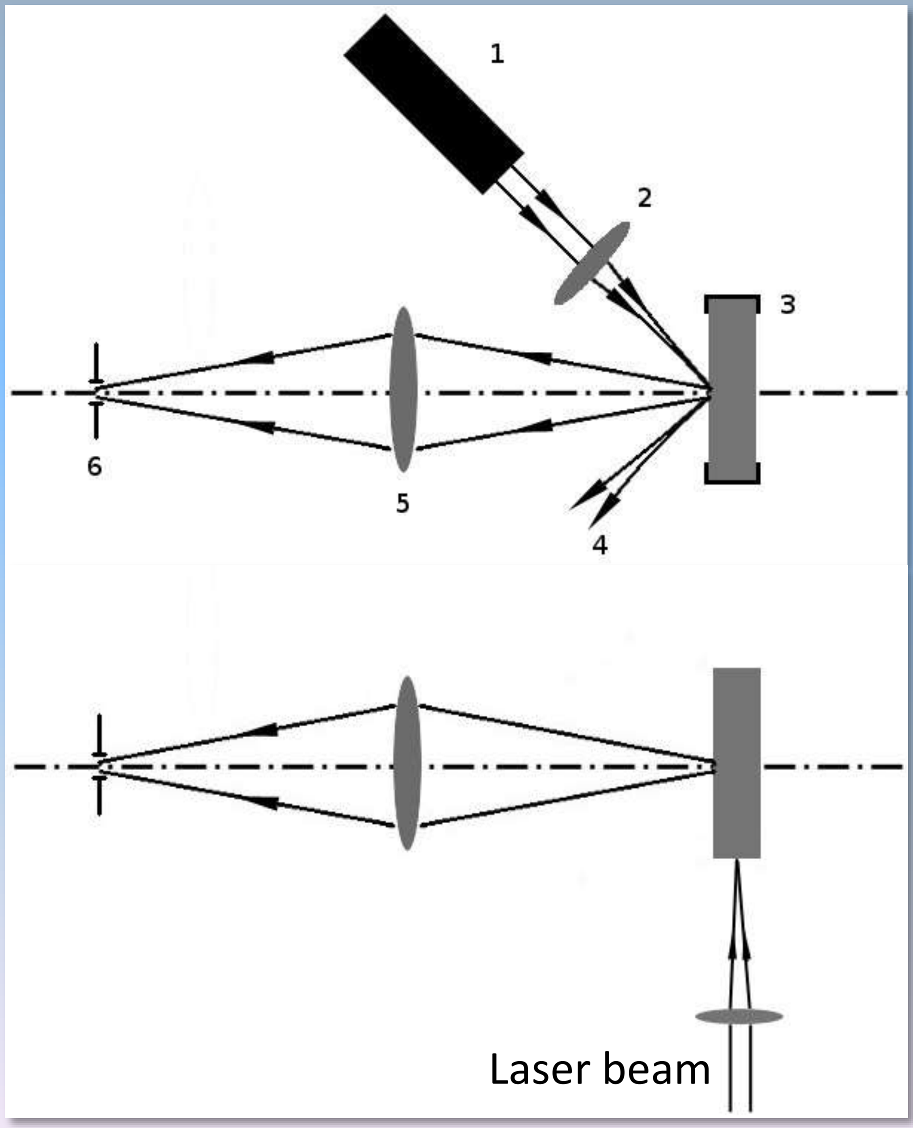
Structure of globule



Due to the surface inhomogeneity occurs heterogeneous formation of the crystalline phase on spherical substructure of globule.

This leads to the formation of a few hundred to thousands of nanocrystals with the size of 10 - 30 nm in pore volume (130 nm)^3.

Optical schemes of the experiment



1 – DPSS laser, wavelength 532 nm, 100 mw power;

2, **5** – collecting lens;

3 – sample;

4 – mirror component of radiation;

6 – spectrometer slot.

Experiment results

Raman spectra
a – photonic crystal and $Bi_{12}SiO_{20}$ nanocomposite; **b** – photonic glass and $Bi_{12}SiO_{20}$ nanocomposite.

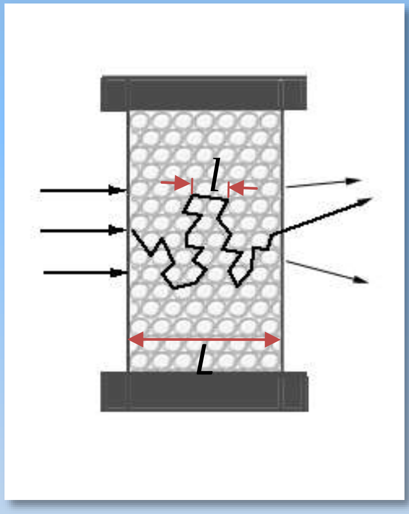
Raman spectra (Reduced to a one value of amount of matter per volume unite).
a – polycrystalline powder of $Bi_{12}SiO_{20}$,
b,c (different melting processes) – photonic crystal and $Bi_{12}SiO_{20}$ nanocomposite.

Raman spectra
a – $Bi_{12}GeO_{20}$ monocrystal;
b – photonic glass and $Bi_{12}GeO_{20}$ nanocomposite.

Raman spectra
a – polycrystalline powder of $NaBi(MoO_4)_2$;
b - photonic glass and $NaBi(MoO_4)_2$ nanocomposite.

The offered interpretation

1. Overall gain of the Raman spectrum intensity.



$$s = n \cdot l >> L,$$

s - full photon path inside the synthetic opal

$n+1$ - number of photon collisions.

l -mean free path of photon;

2. Redistribution of the spectral lines intensity as well as line shift caused by a change of structure and bond lengths during the melting.

3. Appearance of new lines proposed to interpret in new bonds terms of **Bi** atom and **O** atom of the globule.

So, the time of the photon interaction with the material under research increase!

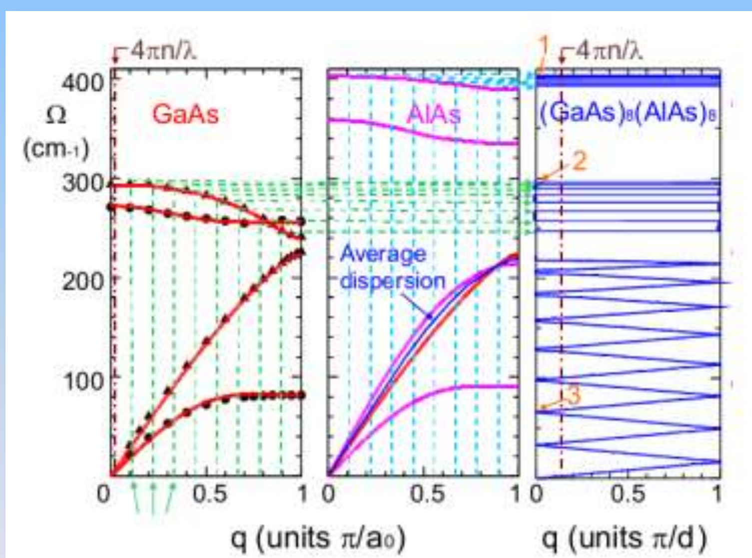
4. Splitting of nondegenerate lines* caused by the manifestation of size effects in the vibrational spectra (Confinement modes).

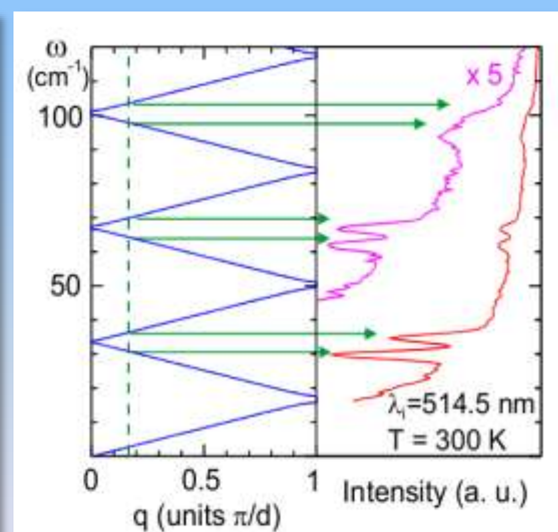
$$N^3/2 > 6\cdot N^2; \qquad \Delta q = \frac{2\pi}{Na}; \qquad \frac{\Delta q_{nanocryst}}{\Delta q_{monocryst}} \approx 10^6$$

N - number of cells in certain direction;

a - Cell size in certain direction.

Quasimomentum selection rule is broken! The phonons from other point of Brillouin zone can appear in the Raman spectrum.





Karpov S. V., Phonons in Nanocrystals, Saint Petersburg State University (2006)

* Venugopalan S., Ramdas A. K., Phys. Rev. B **5**, 4065 (1972).

CONCLUSIONS

- Structure of a substance is highly dependent on the melting conditions in synthetic opal pores;
- The overall intensity gain of nanocomposites Raman spectra is established ;
- New intensive lines in the internal vibrations region and splitting of nondegenerate lines of opal-$Bi_{12}Si(Ge)O_{20}$ nanocomposites Raman spectra are revealed;
- Enhancement and redistribution of spectral lines intensity are observed;

Thank you for attention!