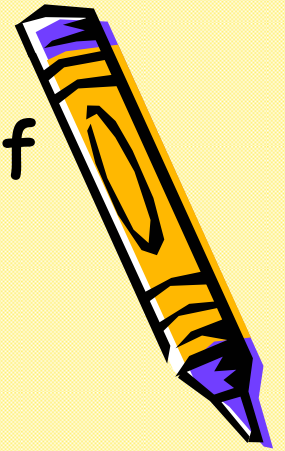


Study of Phase Transitions by Means of Raman Scattering



M. Mahbubur Rahman

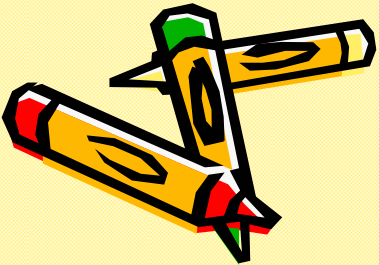
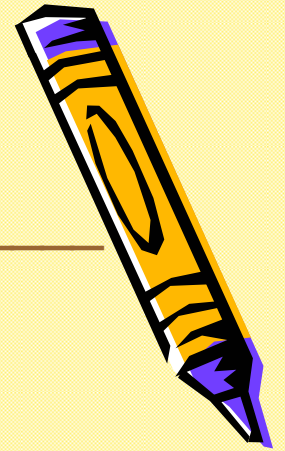
Department of Physics & Physical Oceanography

Memorial University, Canada

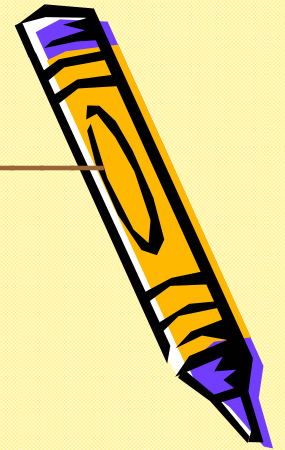


Outlines

- Introduction
- Advantages of Raman spectroscopy?
- Typical Experimental Set-up for Raman Scattering
- Selected Applications of Raman Spectroscopy
- Summary



Introduction



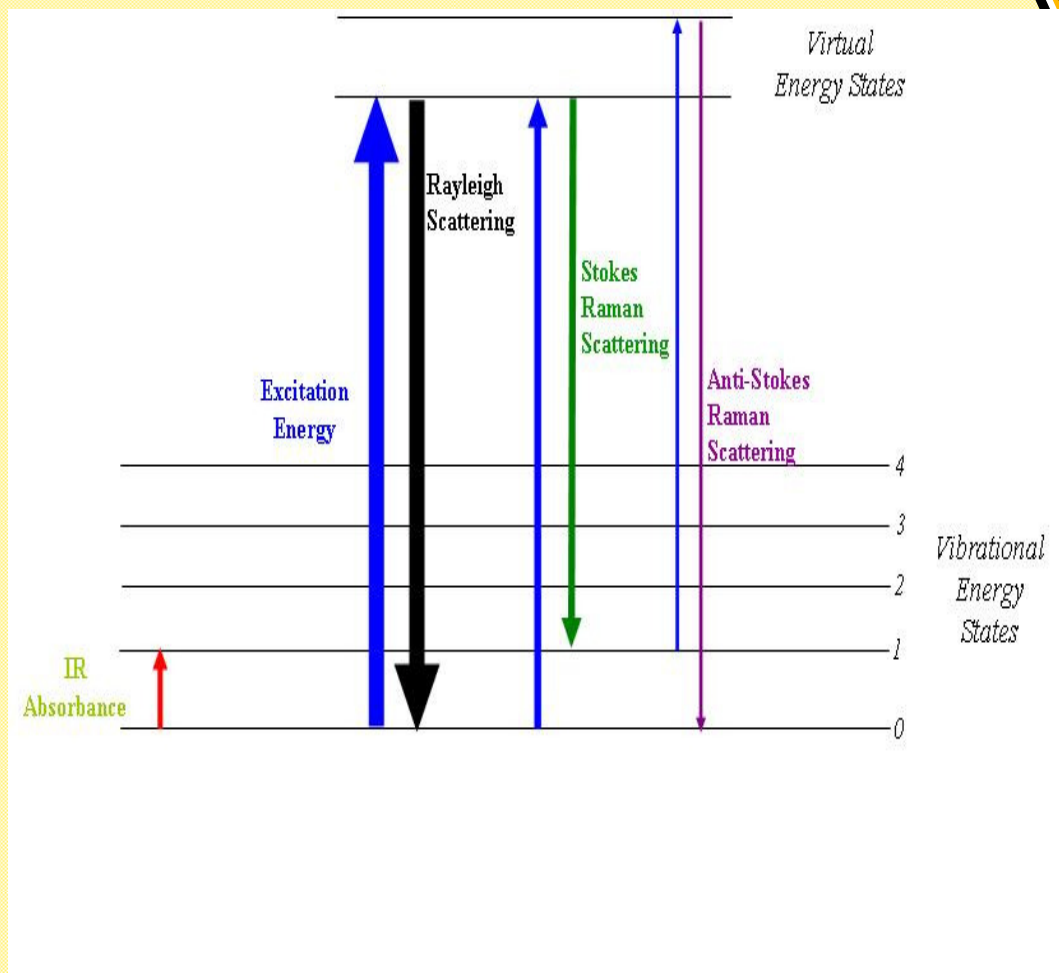
- Raman spectroscopy is based on inelastic scattering of light
- When photons incident on a crystal it shows three phenomena:
 - (1) Most of the incident radiation is scattered elastically in all possible directions, a phenomenon known as **Rayleigh scattering**
 - (2) Molecule absorbs energy. The scattered photon has lower energy and thus shifted towards the red end of the spectrum - **Stokes Raman scattering**
 - (3) Molecule loses energy. The scattered photon has higher energy and thus shifted towards the blue end of the spectrum - **anti-Stokes Raman scattering**
- **Stokes scattering is stronger comparing with the anti-Stokes scattering**



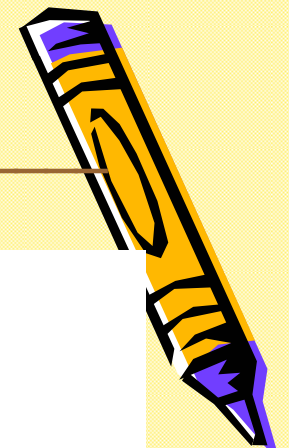
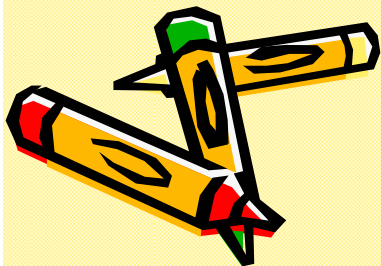
Stokes & anti-Stokes Raman Scattering

Stokes- > A molecule is raised from ground state to virtual state and then drops back down to a higher vibrational state; scattered photon loses energy and wavelength is increased

anti-Stokes- > A molecule is in vibrational state to start with; after scattering is in its ground state; scattered photon gains energy and the wavelength is decreased

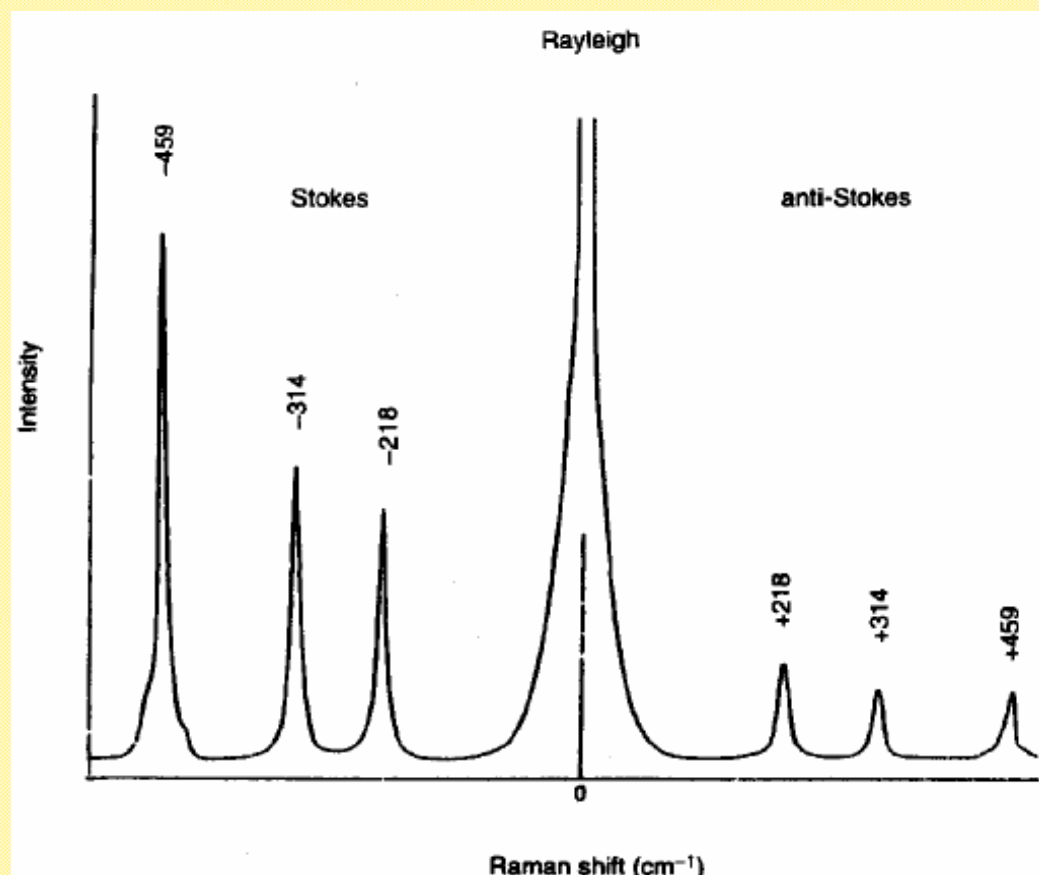


http://en.wikipedia.org/wiki/Raman_spectroscopy



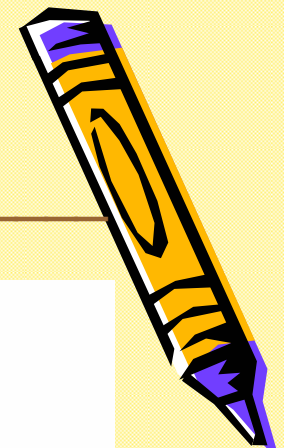
Stokes & anti-Stokes Raman Scattering

Stokes lines are stronger than the anti-Stokes lines and both of them give the same information and it is customary to measure the Stokes side of the spectra

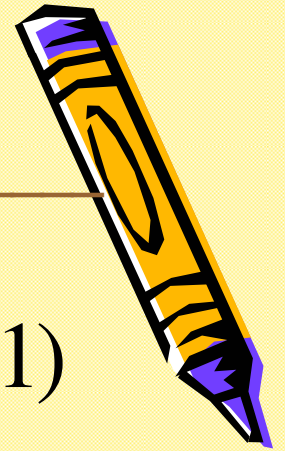


Raman Spectra of CCl₄ irradiated by 488 nm laser beam

Ferraro, J. R., Introductory Raman Spectroscopy, Academic press, Harcourt Brace & Co. Pub. (1994)



Origin of Raman Scattering



The strength of electric field of the laser

$$E = E_0 \cos(2\pi\nu_0 t) \dots\dots\dots(1)$$

Electric dipole moment

$$P = \alpha E = \alpha E_0 \cos(2\pi\nu_0 t) \dots\dots\dots(2)$$

Nuclear displacement

$$q = q_0 \cos(2\pi\nu_m t) \dots\dots\dots(3)$$

Where ν_m is the frequency of molecular vibration

q_0 is the vibrational amplitude



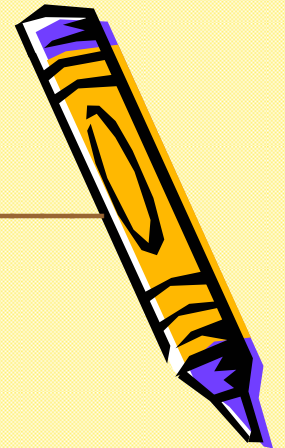
Origin of Raman Scattering

Electronic polarizability is a function of q

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q} \right)_0 q + \dots \dots \dots (4)$$

Where $\left(\frac{\partial \alpha}{\partial q} \right)_0$ is the rate of change of α w. r. t. q evaluated at equilibrium

$$\begin{aligned} P &= \alpha E_0 \cos(2\pi\nu_0 t) \\ &= \alpha_0 E_0 \cos(2\pi\nu_0 t) + \left(\frac{\partial \alpha}{\partial q} \right)_0 q E_0 \cos(2\pi\nu_0 t) \\ &= \alpha_0 E_0 \cos(2\pi\nu_0 t) + \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \cos(2\pi\nu_0 t) \cos(2\pi\nu_m t) \\ &= \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 [\cos\{2\pi(\nu_0 + \nu_m)t\} + \cos\{2\pi(\nu_0 - \nu_m)t\}] \dots \dots \dots (5) \end{aligned}$$



Origin of Raman Scattering

1st Term → **Rayleigh** scattering (an oscillating dipole radiates at frequency ν_0)

2nd Term → **anti-Stokes** scattering with a frequency $(\nu_0 + \nu_m)$

3rd Term → **Stokes** scattering with a frequency $(\nu_0 - \nu_m)$

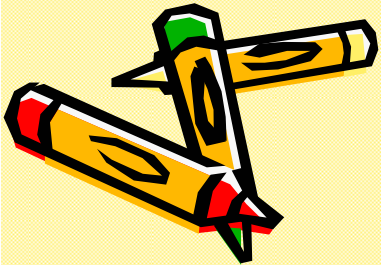
To be **Raman active** $\left(\frac{\partial \alpha}{\partial q}\right)_0 \neq 0$



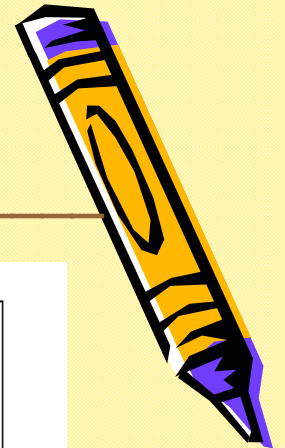
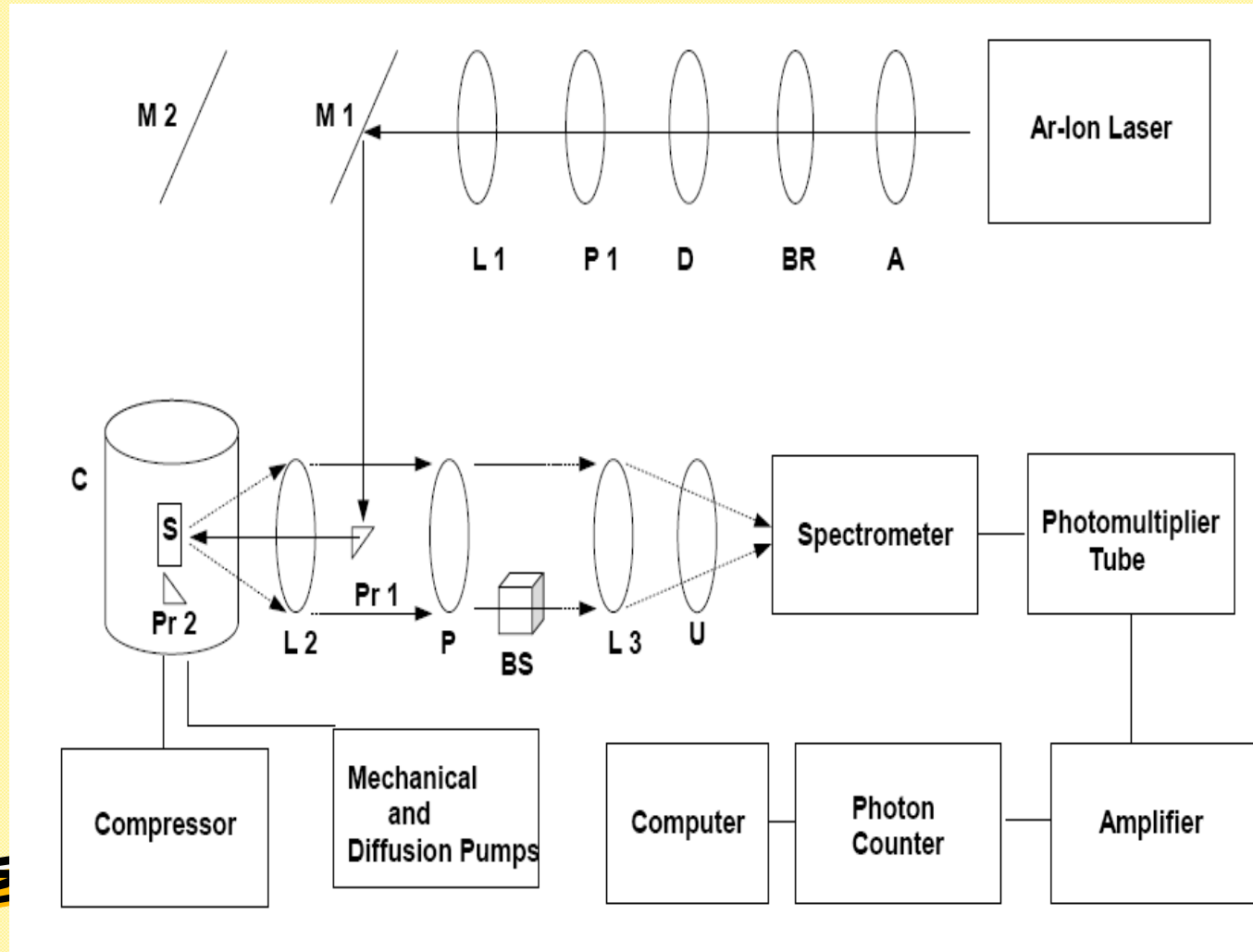
Advantages of Raman Spectroscopy



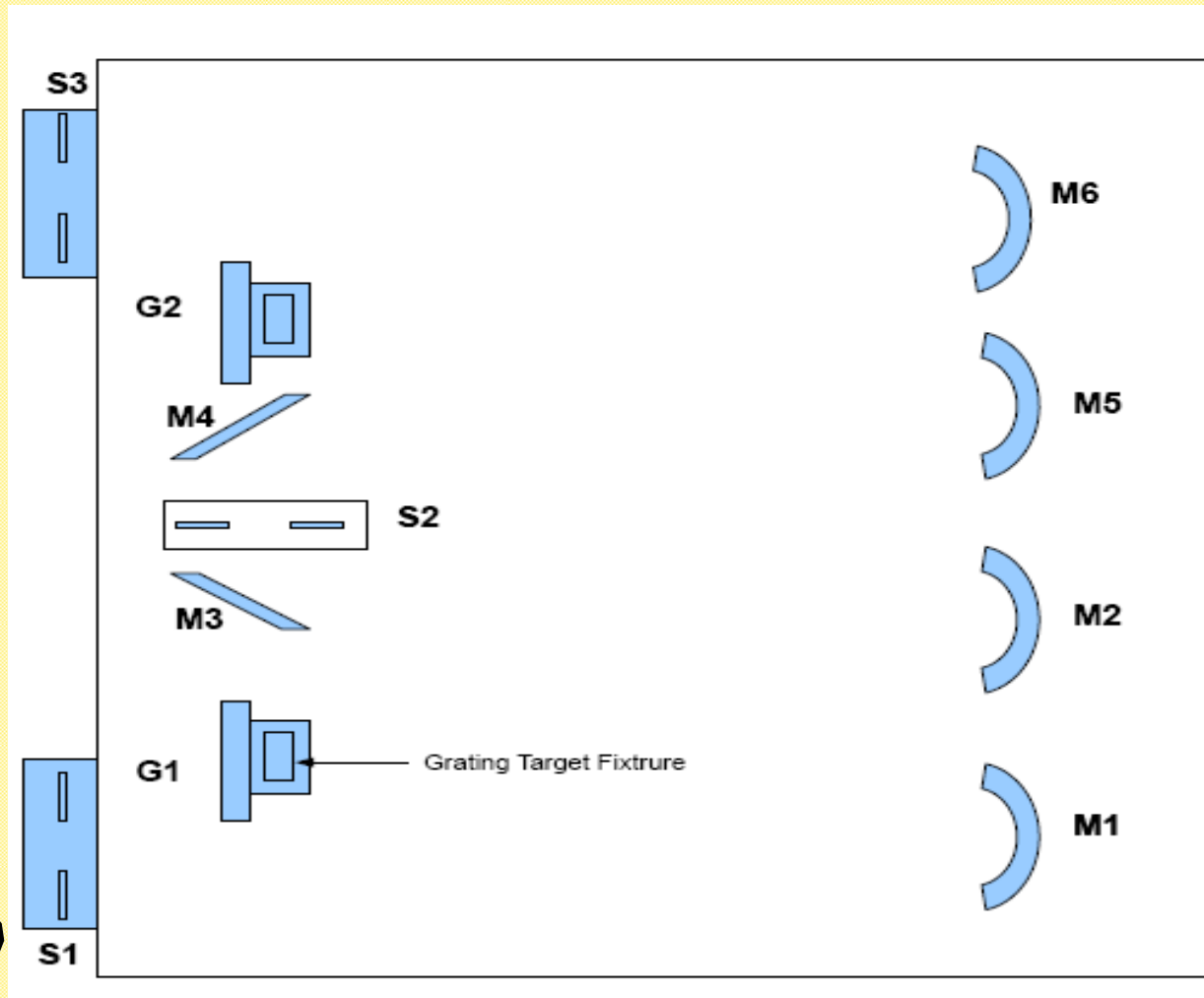
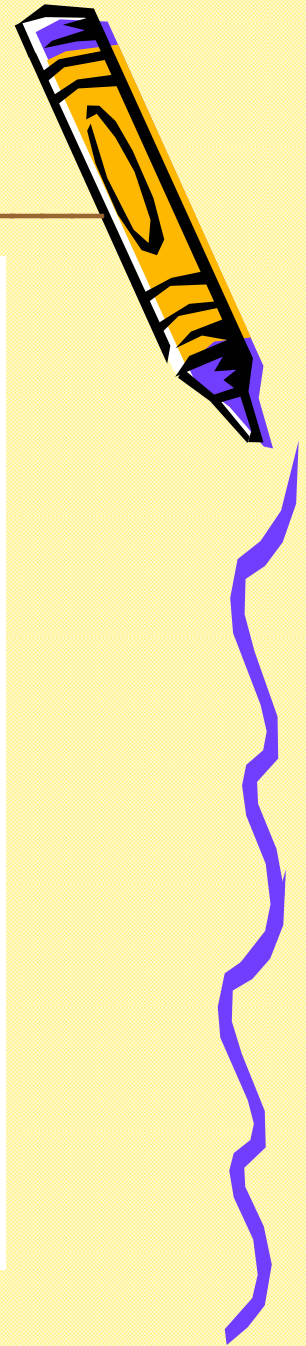
- Structural changes that alter the crystal symmetry often have a significant effect on the Raman spectrum
- Raman scattering is very sensitive which can detect low-concentration impurity phases, which might be missed out by other techniques (XRD)
- Its simple and sophisticated requiring no sample preparation, it can be used for the detailed study of solids, liquids & gases
- Raman scattering technique works faster than other techniques in the identification of a sample



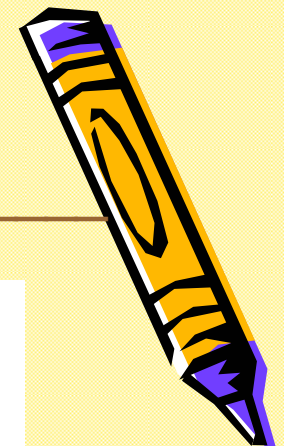
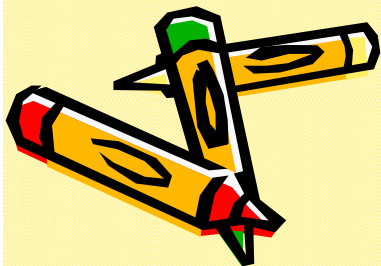
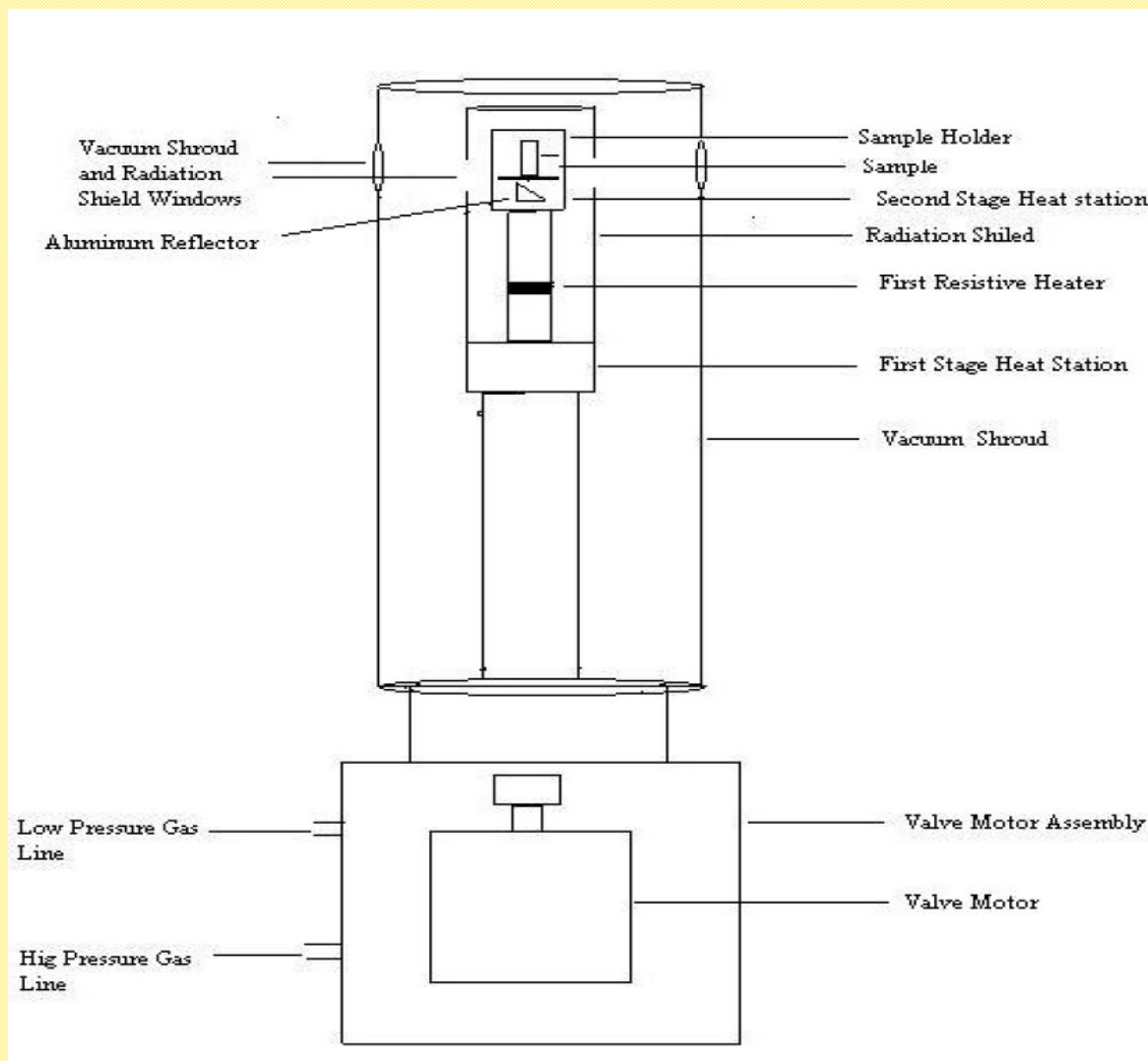
Typical Experimental Set-up



Typical Experimental Set-up

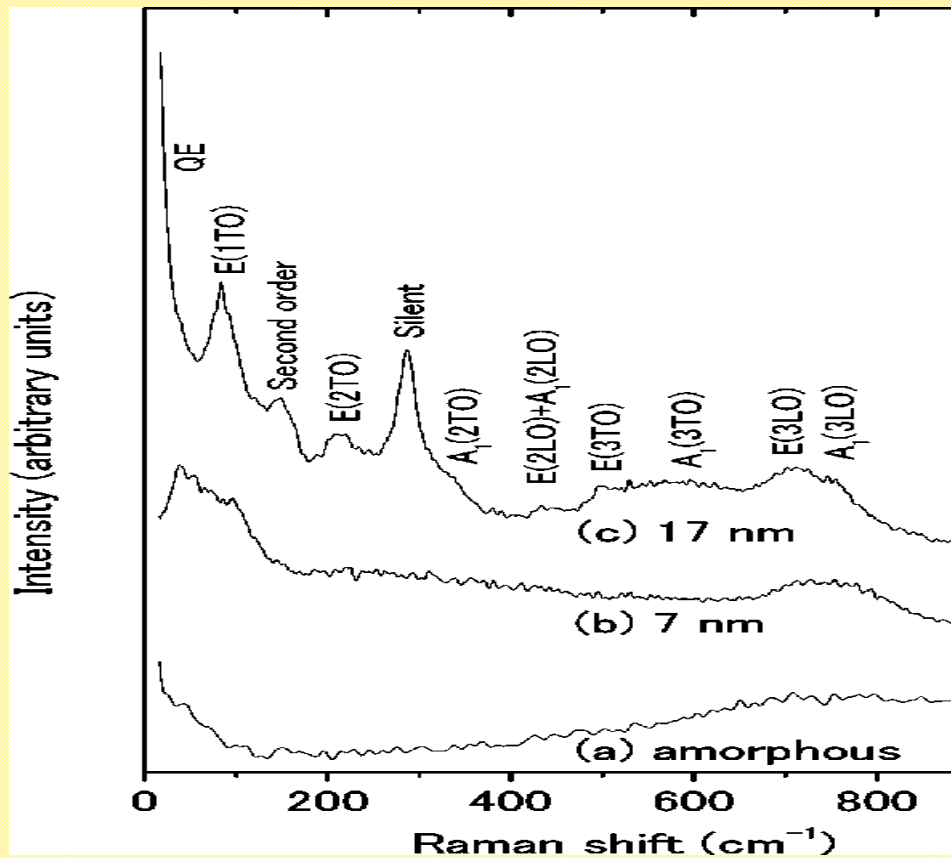


Cryostat

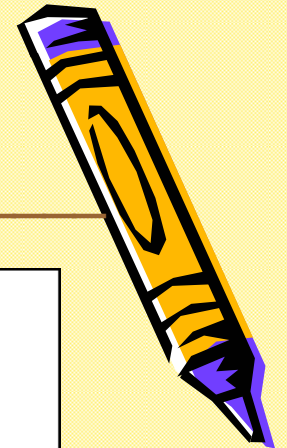


Size-induced Phase Transitions PbTiO_3 Ferroelectrics

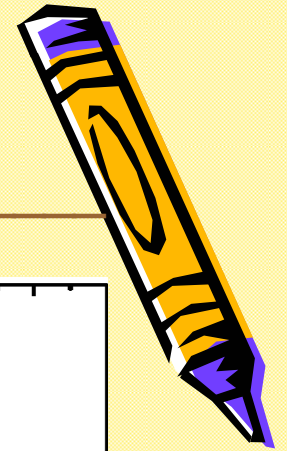
17-nm particles are in tetragonal phase at room temperature and 7-nm particles are neither in tetragonal nor in amorphous



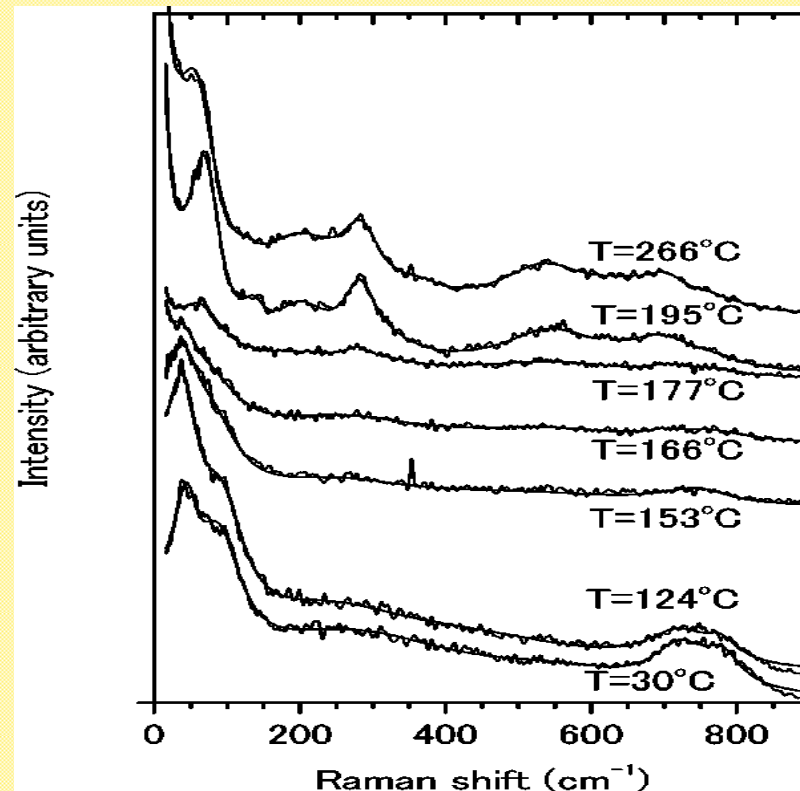
Fu, D., Suzuki, H., and Ishikawa, K., Phys. Rev. B 62, 5, 3125 (2000)



Phase Transition of 7-nm PT Nanocrystals



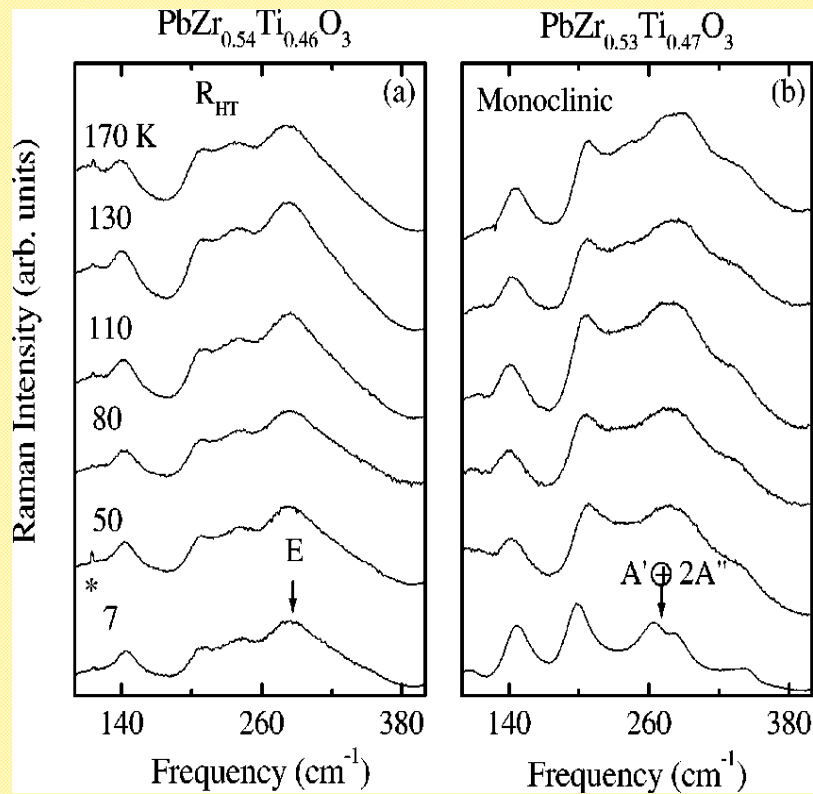
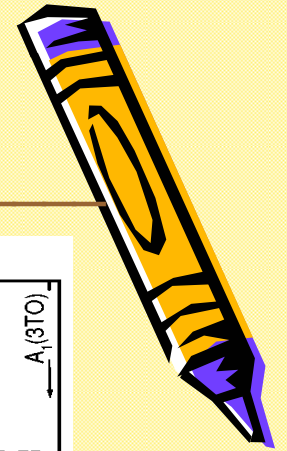
With the increase in temperature spectra above 200 cm^{-1} varies slightly. The intensity of the lowest mode (mode 1 at 50 cm^{-1}) is much larger than that of its neighbour (mode 2 at 100 cm^{-1}). As the heating progresses, the spectra become weak enough and in the vicinity of temperature 166°C these modes appear to degenerate, which consequences that around this temperature (T_c^0 -T) a phase transition takes place and the new phase is identified to be tetragonal phase



Fu, D., Suzuki, H., and Ishikawa, K., Phys. Rev. B 62, 5, 3125 (2000)

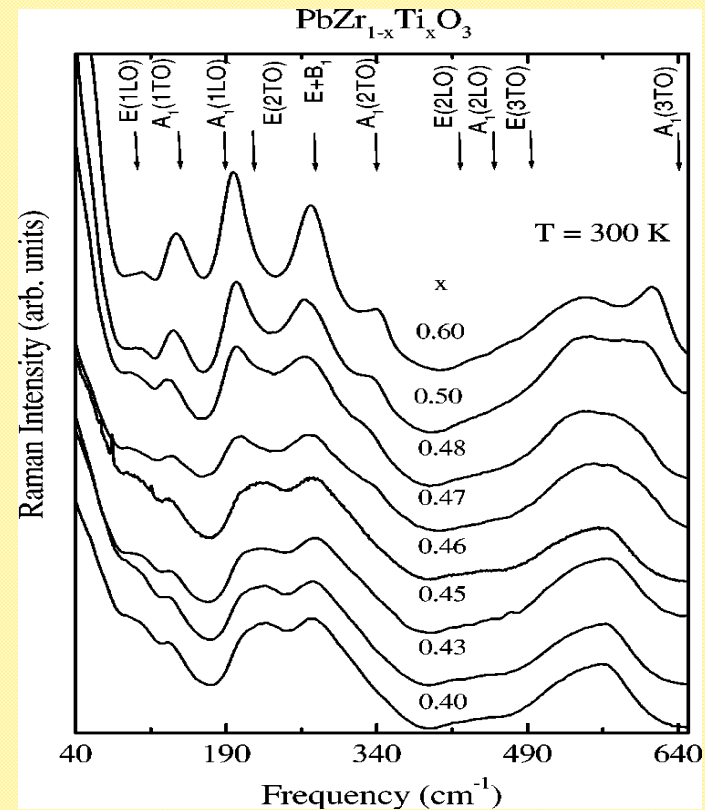
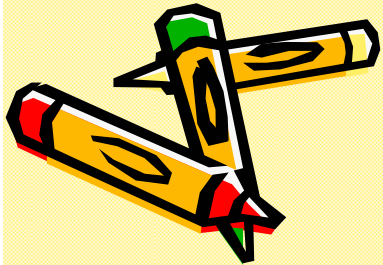


Ti-Substituted Phase Transitions in PbZrO_3



No Phase Transition in the observed temperature range

Souza, A. G., Filho, et al. Phys. Rev. B, 66, 132107 (2002)

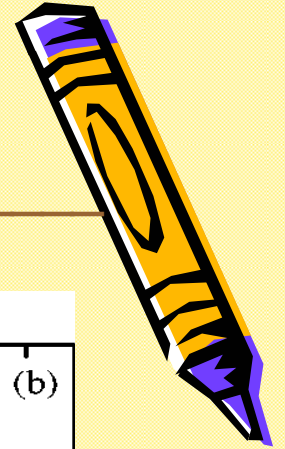


Coexistence of monoclinic and tetragonal Phases and broadening the bands at $x \approx 0.48$

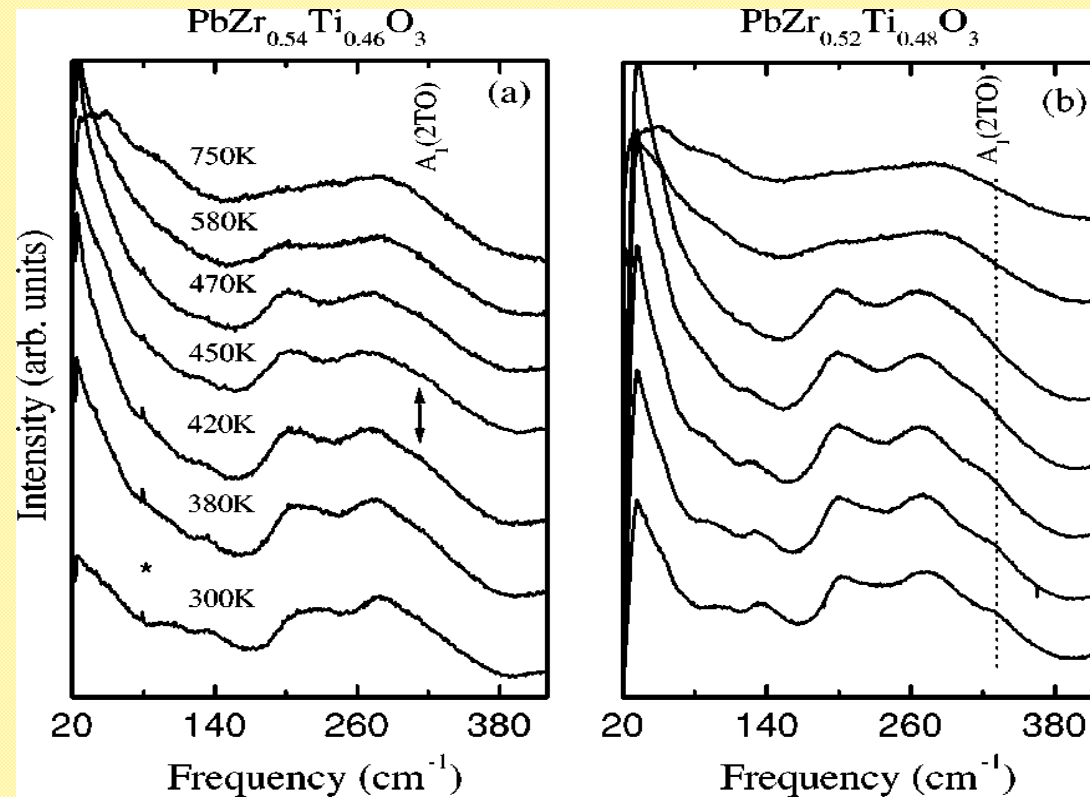
Burns, G. and Scott, B. A., Phys. Rev. B 7, 3088 (1973)



Ti-Substituted Phase Transitions in PbZrO_3



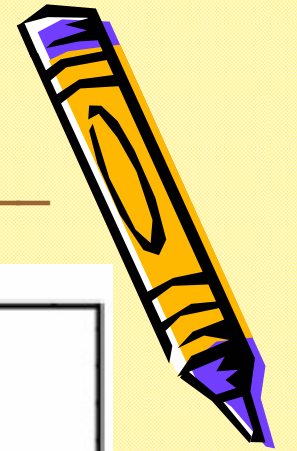
$A_1(2TO)$ mode for all spectra in the temperature range $300 \leq T \leq 470\text{K}$ which indicates no evidence of phase transition for this composition. At $T = 450\text{K}$ for $x = 0.46$ and $x = 0.48$ both the Raman spectra are in tetragonal phase



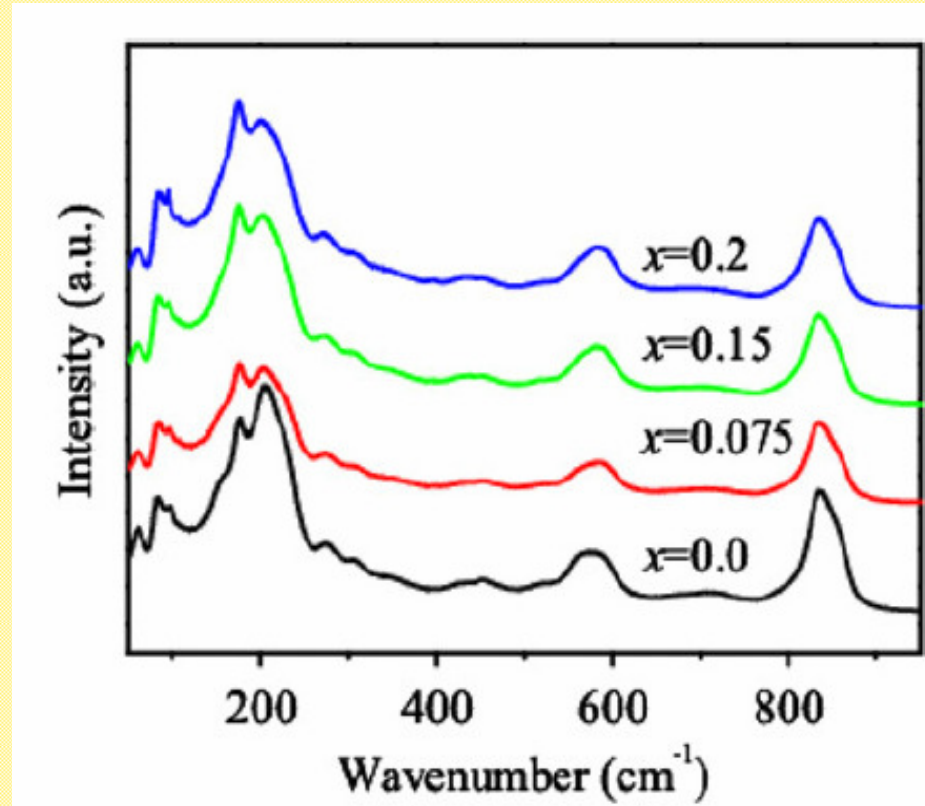
Souza, A. G., Filho, et al. Phys. Rev. B, **66**, 132107 (2002)



Raman Spectra of La-doped $\text{SrBi}_2\text{Nb}_2\text{O}_9$



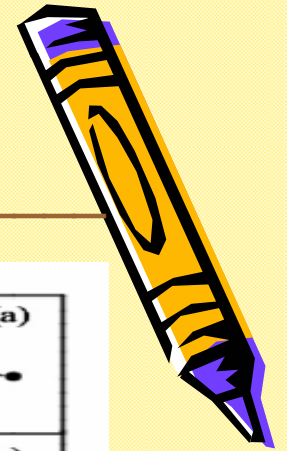
Raman bands around 61, 98, 176, 206, 575 and 835 cm^{-1} are very intense



Liu, G. Z., et al.; J. Phys. D: Appl. Phys. 40, 7817-7820(2007)

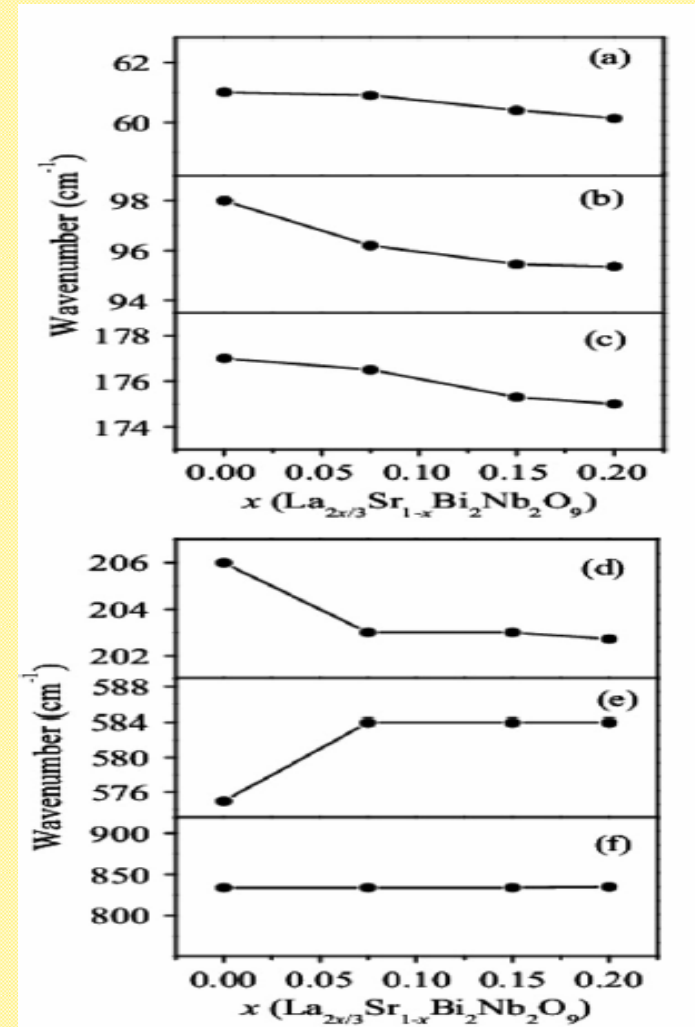


Raman Spectra of La-doped $\text{SrBi}_2\text{Nb}_2\text{O}_9$



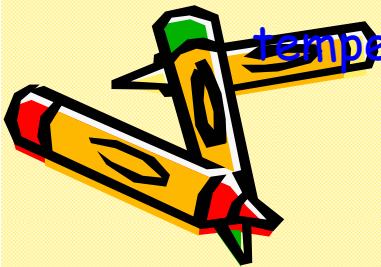
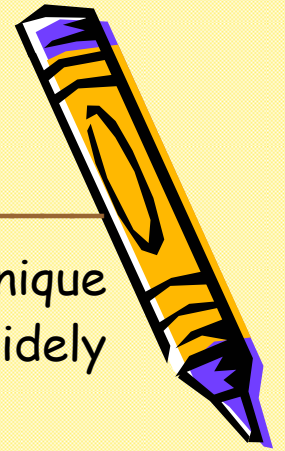
The Raman shift takes place due to

- The heavier mass of La
- For mode 575 cm^{-1} with the La-content relaxation of the bonds in the Bi_2O_2
- La-substitution causes weakening the chemical stability of Bi_2O_2 layers damages the original functions of Bi_2O_2 layers as electron insulation and electron reservoirs



Summary

- Raman spectroscopy is a powerful, non-destructive technique based on inelastic scattering of monochromatic light and widely be used to study solid, liquid and gaseous samples
- The presence of any kind of doping element gives rise to new Raman bands that are very useful for the characterization of purity, crystallite size etc in different samples
- The relative intensities of Raman bands depend upon the photon energy of the laser source
- Raman spectroscopy can also provide very useful information about the phase transitions caused by particles size, temperature, pressure or by other external physical parameters



THANK YOU



QUESTIONS?

