Origin of high pressure phase transition in the $Ln_2Ti_2O_7$ (Ln = La, Nd, Pr) Carply- Galy phases.

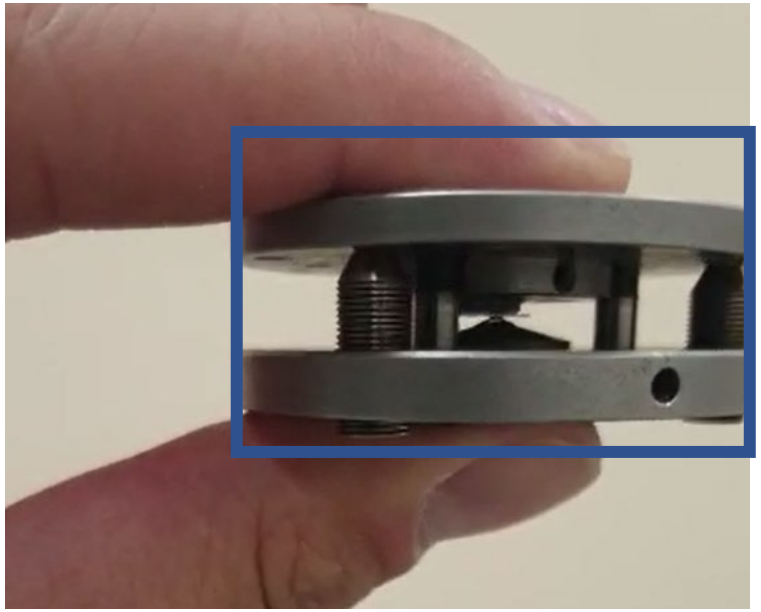
A.G. Asadov[1,2,3], A.I. Mammadov[2], D.P. Kozlenko[1], R.Z. Mehdiyeva[2], S.E. Kichanov[1], E.V. Lukin[1]

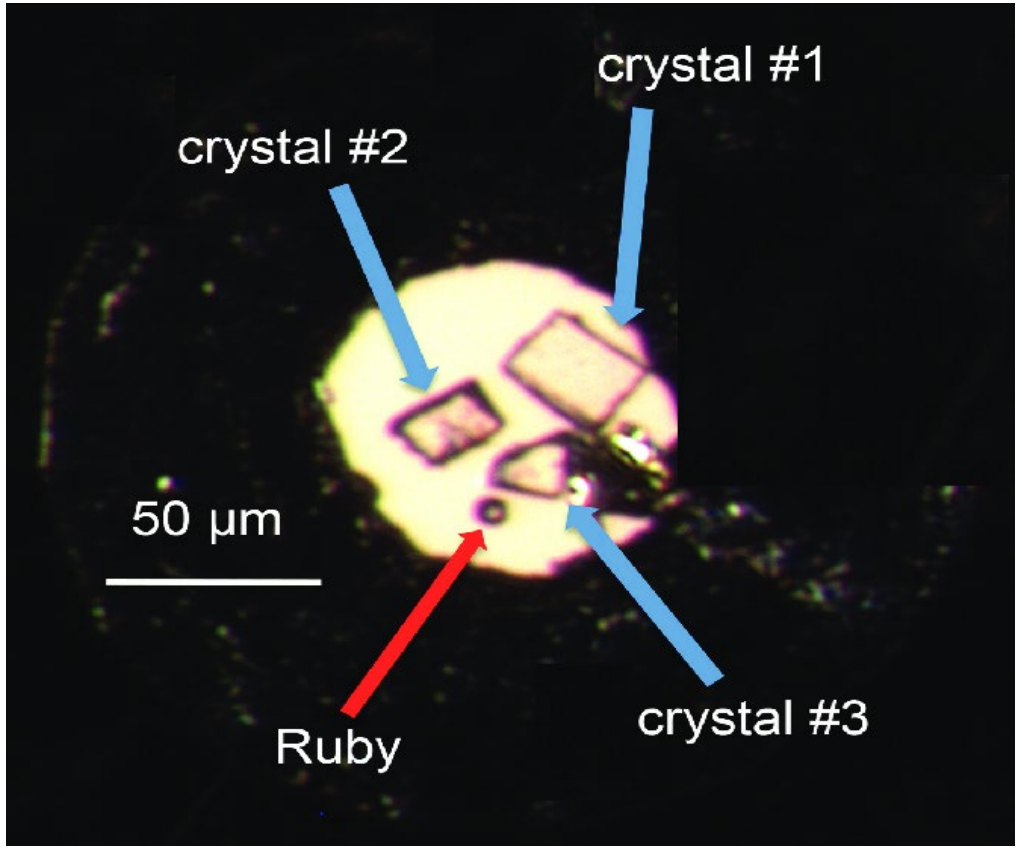
[1] Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia.
[2] Institute of Physics, Azerbaijan National Academy of Sciences, Baku AZ-1143, Azerbaijan.
[3]Khazar University, AZ1096, Baku, Azerbaijan.

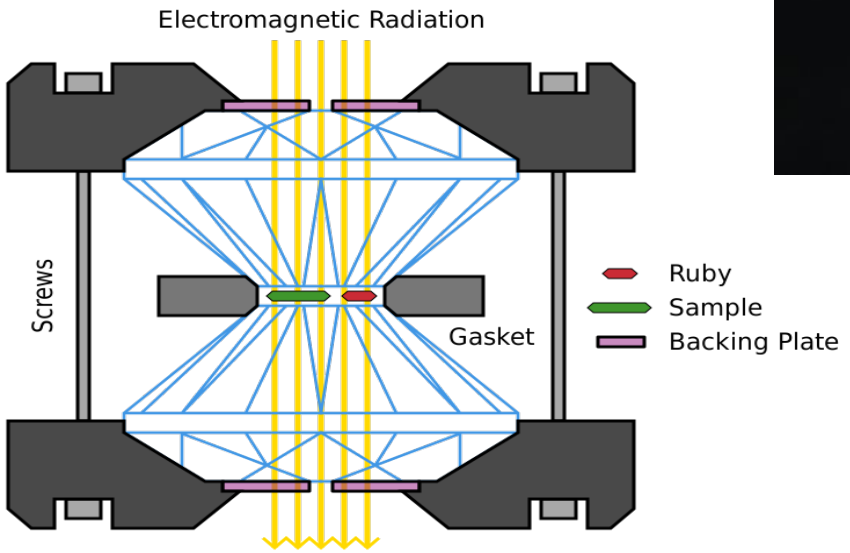
Speaker : Asif Asadov

Anniversary Seminar of the Laboratory of Neutron Physics,
Dedicated to the 110th Anniversary of the Birth of F.L.Shapiro

The Boehler-Almax Plate type diamond anvil cell

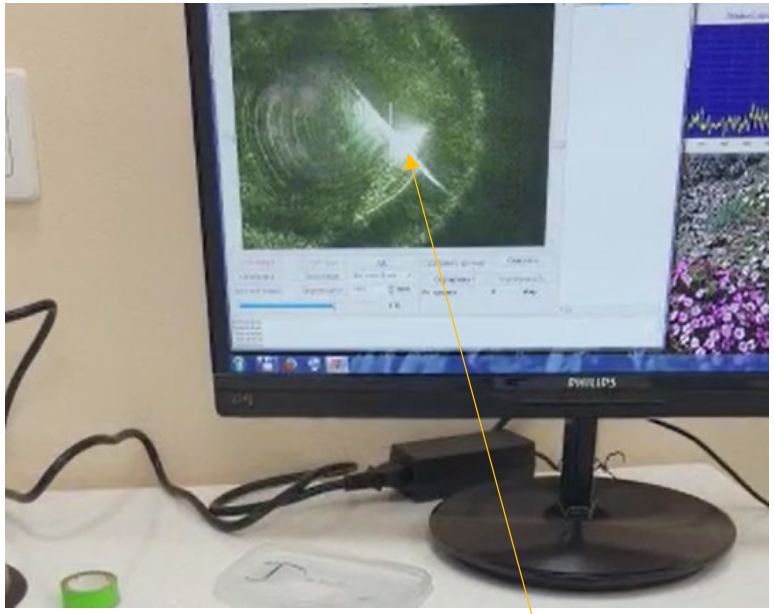




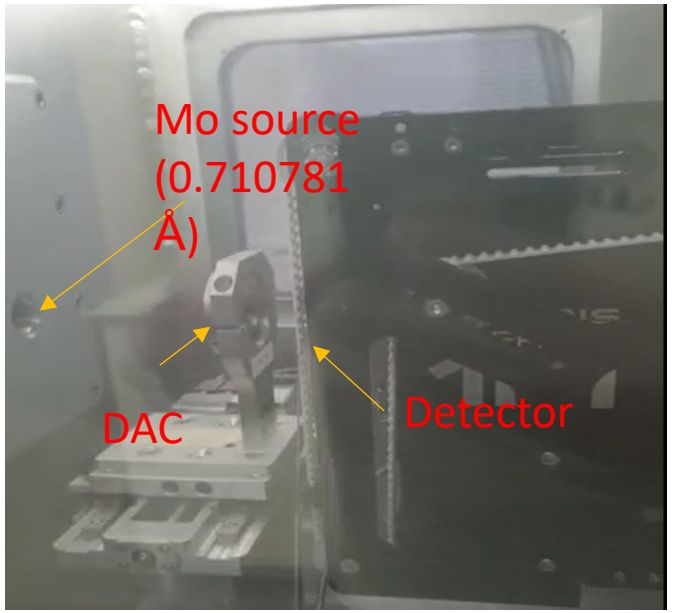


Schematic representation of DAC

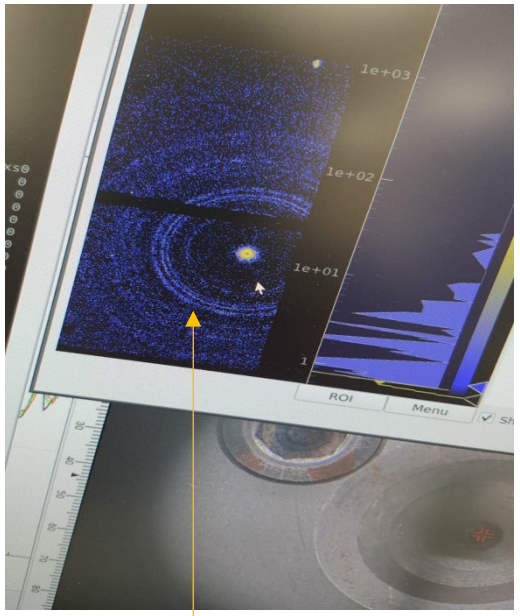
Installation To Xeuss3.0 X-ray diffractometer



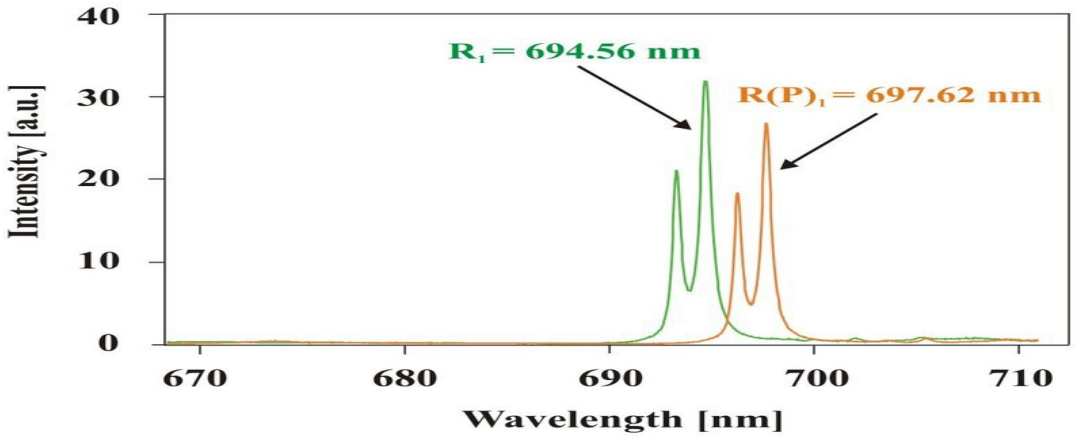
Pressure mesurements with Ruby balls



DAC in Vacuum chamber



Debye – Scherrer rings



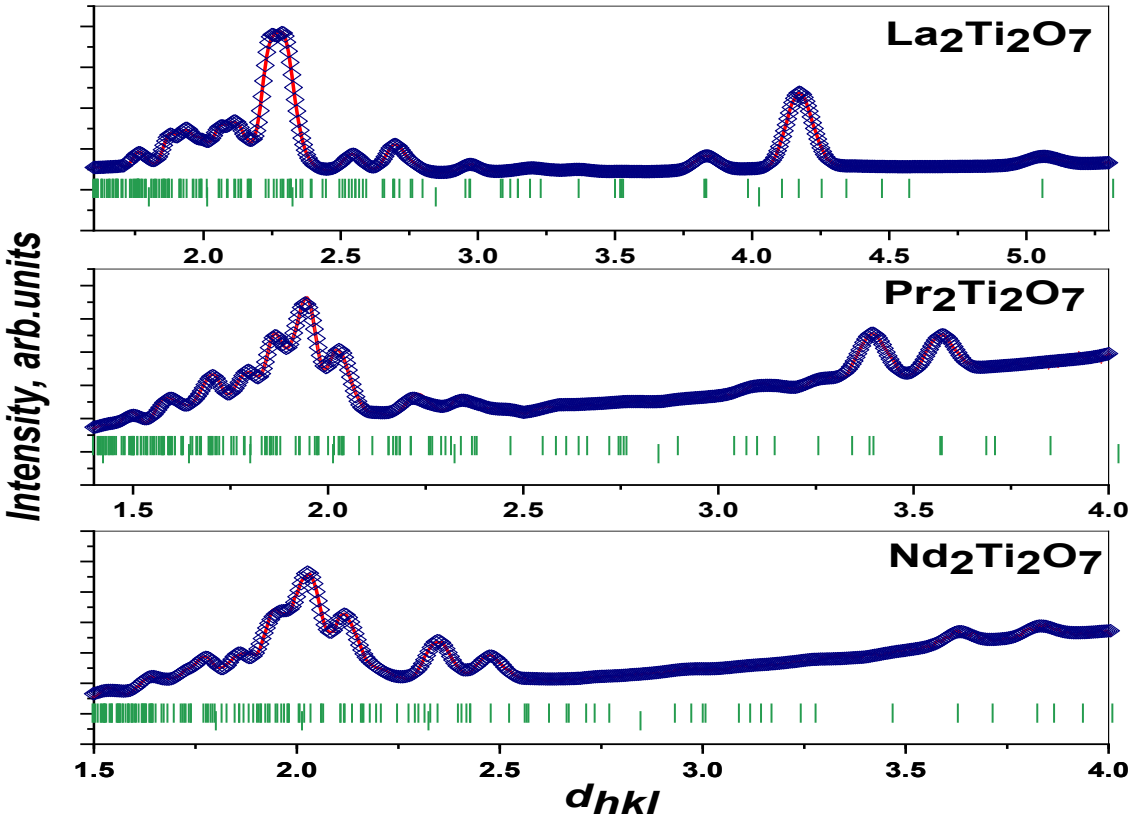
$$P(\text{Mbar}) = \frac{a}{b}\left\{\left[\left(1+\frac{\Delta\lambda}{\lambda_0}\right)^{b}\right]-1\right\},$$

a and ***b*** are quasihydrostatic pressure

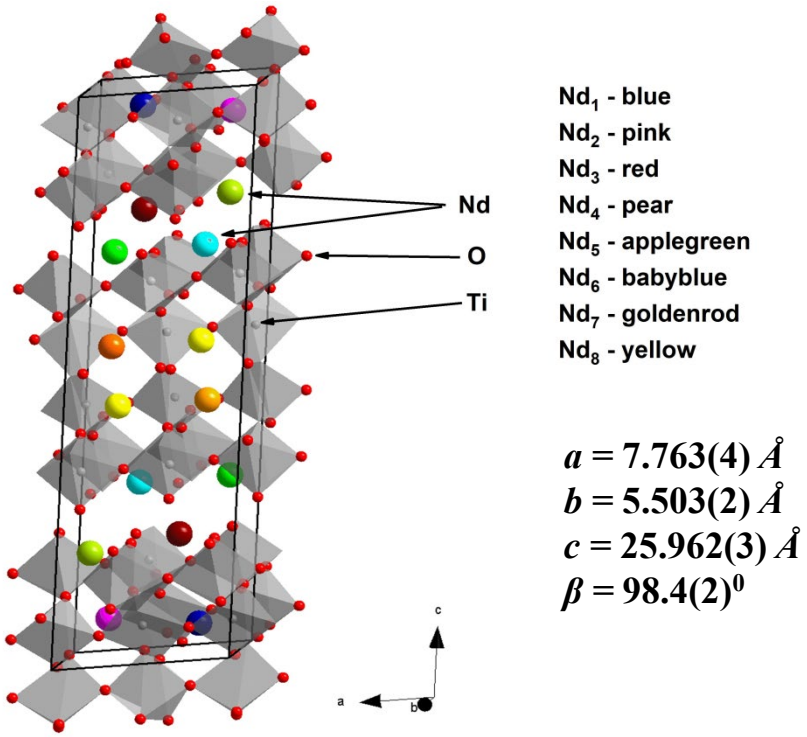
Discussions.

Neutron diffraction

- Neutron diffraction of ReTO confirms that, the sample posses to perovskite-like layered (PL) structure with TiO_6 octahedras at ambient condition with $P2_1$ space group symmetry (monoclinic).

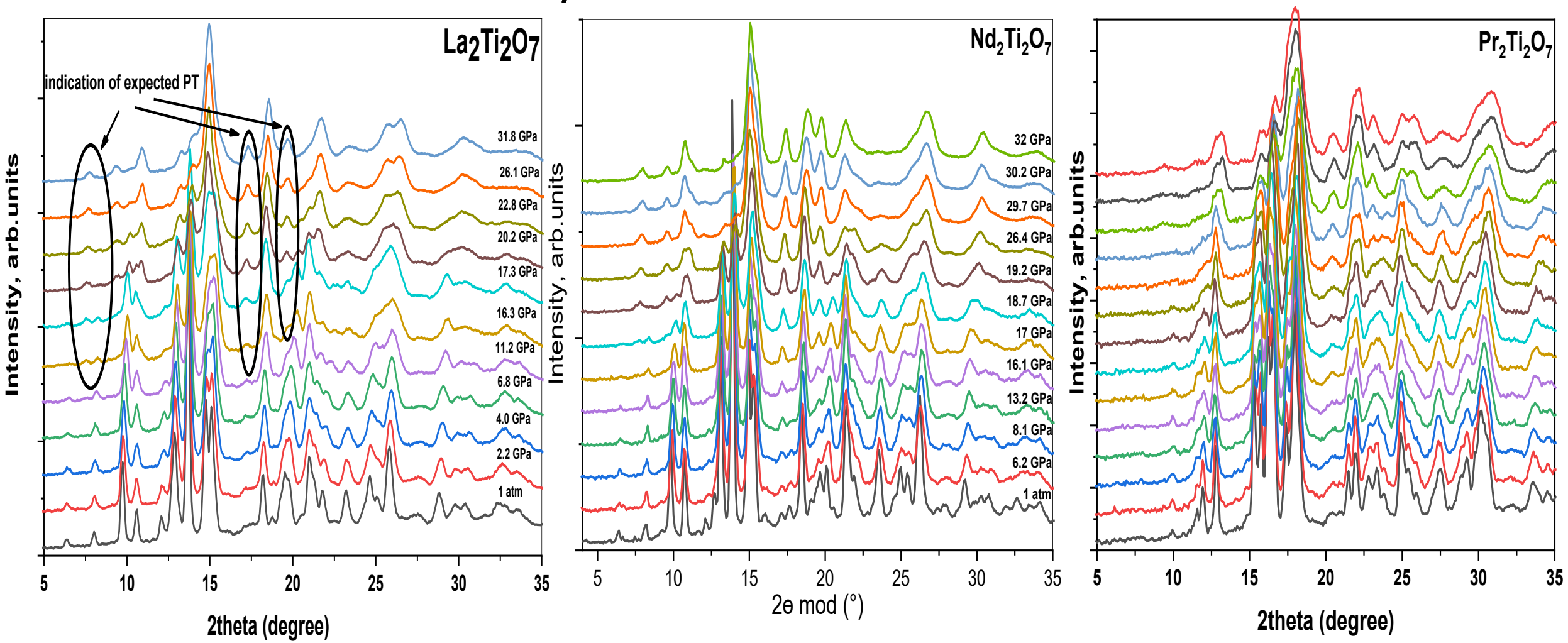


Reitveld refined (FULLPROF) Neutron diffraction data (high intensity mode) of ReTO.



The $P2_1$ monoclinic structure of NTO at ambient condition

XRD pattern of NTO from 1 atm to 30.2Gpa measured by Xeuss3.0 diffractometer



The X-ray diffraction patterns of $Re_2Ti_2O_7$ at selected pressures and processed by the Rietveld method. circles shows the new peak formation due to increasing pressure

Pressure effect on Crystal

- Pressure induced changes in cell parameters and volume from 0 Gpa to 30.2 Gpa from up to bottom a, b, c, beta, volume respectively. Vertical bar line determine phase transition at 19.2 GPa.

$k_a = 0.0009\ GPa^{-1}$

$k_b = 0.0008\ GPa^{-1}$ *before phase transition*

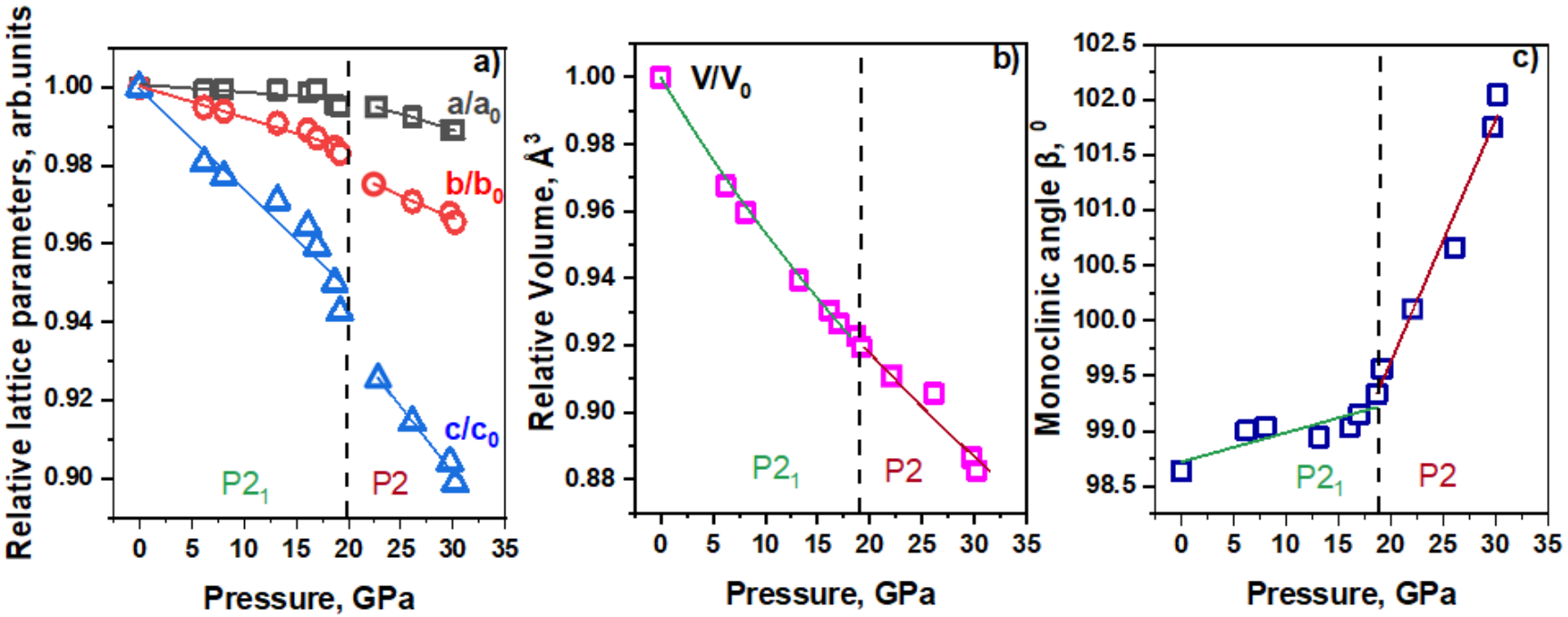
$k_c = 0.0026\ GPa^{-1}$

Compressibility

$k_a = 0.00084\ GPa^{-1}$

$k_b = 0.0015\ GPa^{-1}$ *after phase transition*

$k_c = 0.0040 GPa^{-1}$



The Birch – Murnaghan fitting used for P – V relation with the **B' = 4.0(5)** and bulk modulus.

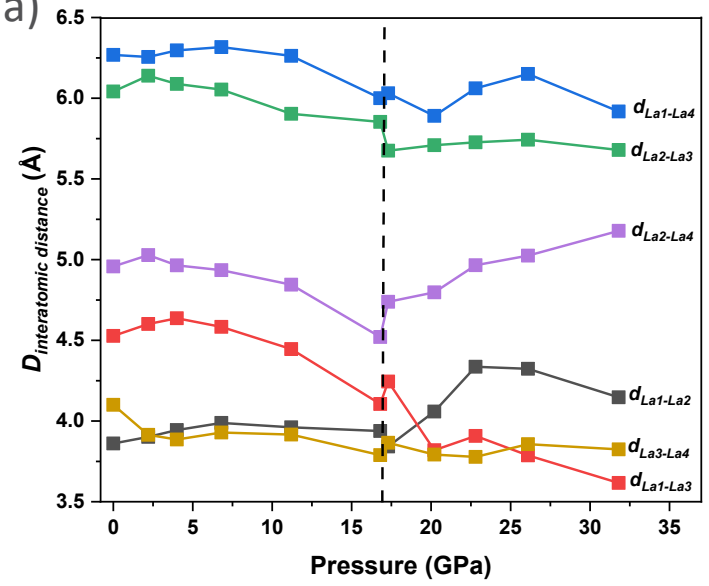
Low pressure: B_0=191.2(1) GPa.

High pressure: B_0=202.2(3) GPa.

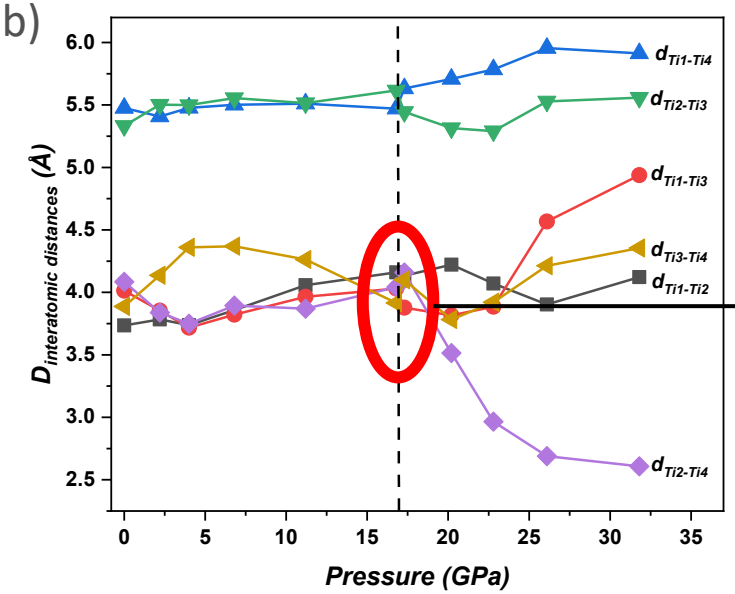
$$P = \frac{3}{2}B_0\left(x^{-\frac{7}{3}} - x^{-\frac{5}{3}}\right)\left[1 + \frac{3}{4}(B' - 4)\left(x^{-\frac{2}{3}} - 1\right)\right]$$

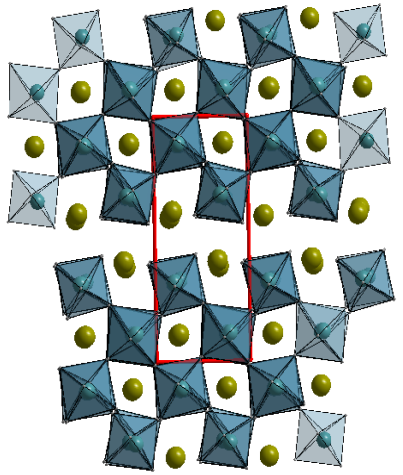
Mechanism of Phase transition.

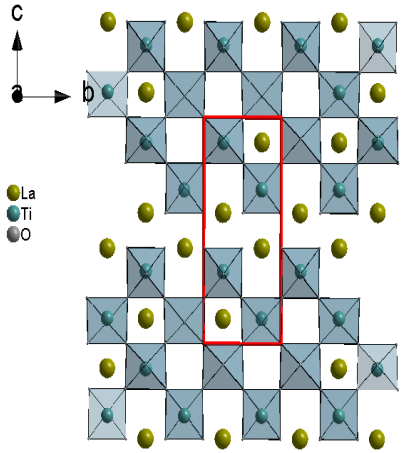
a)



b)







Calculated interatomic distances for Nd and Ti atoms indicate that at high pressures the distance between Ti atoms tends to become same, which create square form of Ti plane

c)

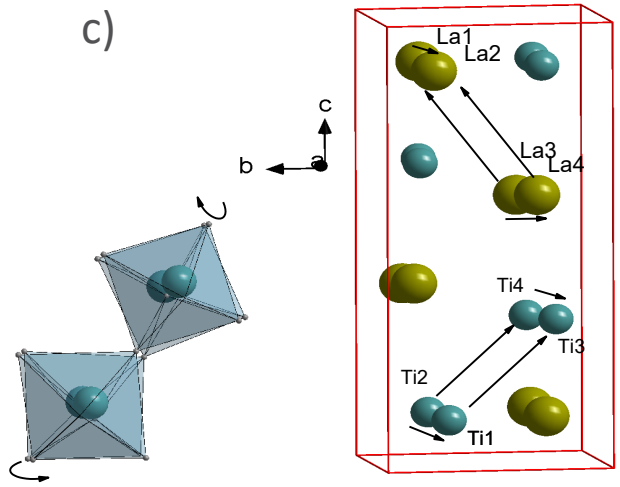
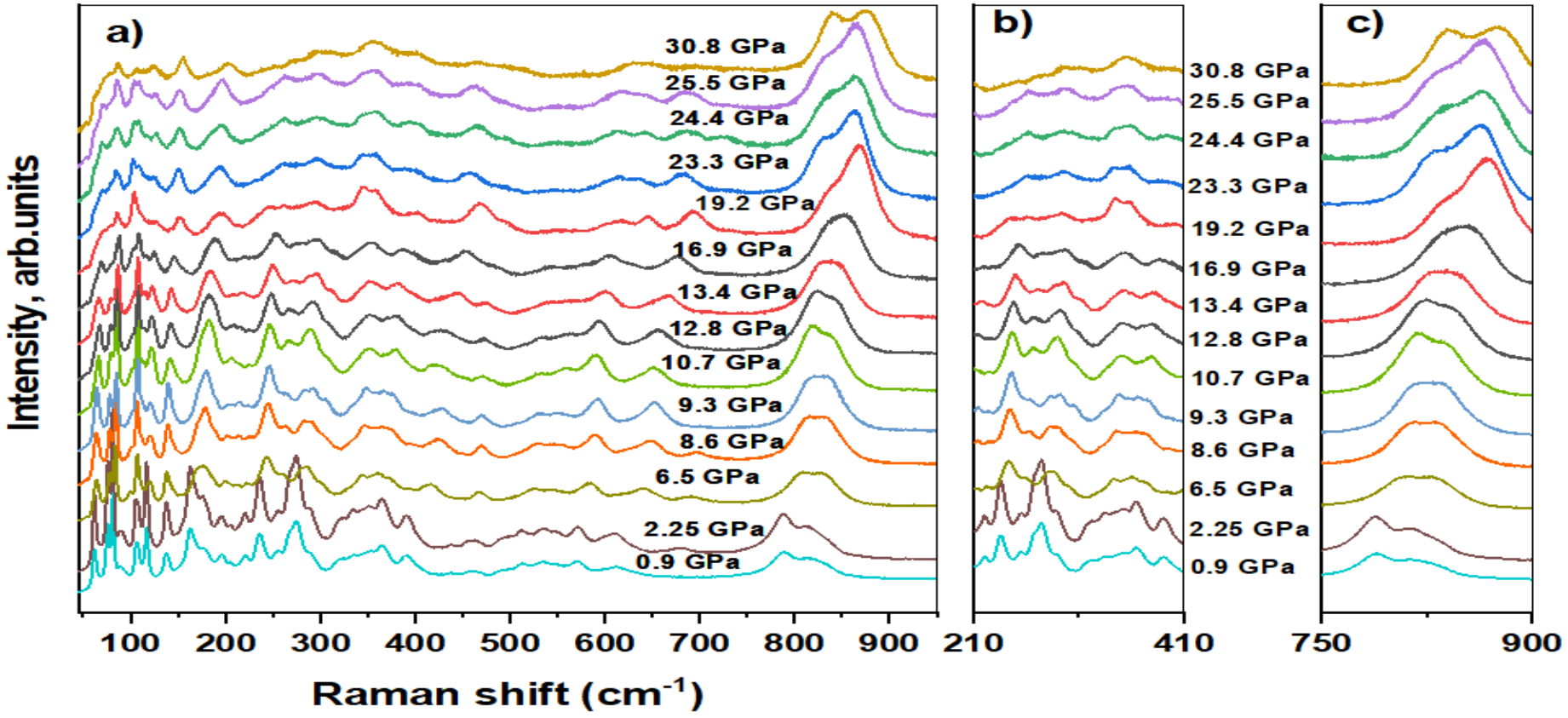


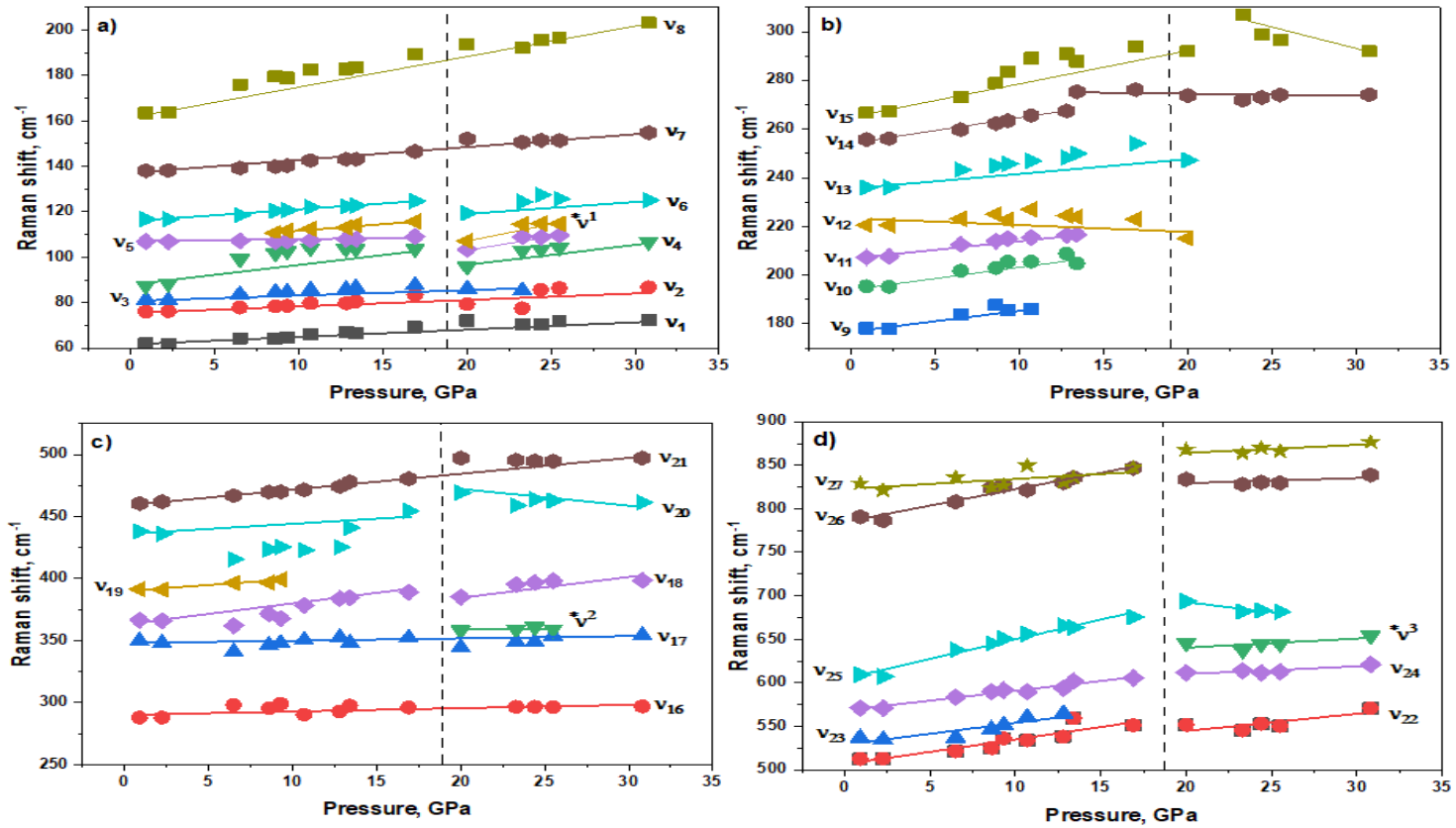
Figure a illustrates the interatomic distances of La atoms within the crystalline structure of La2Ti2O7 under varying pressure conditions. Concurrently, Figure b depicts the interatomic distances of four distinct Ti atoms (Ti1, Ti2, Ti3, and Ti4) within the same sample at a pressure of 17.0 GPa. Remarkably, at this specific pressure, the interatomic distances among Ti atoms converge to a **uniform length**, forming a distinctive quadratic arrangement. This observation suggests a significant structural transformation in the La2Ti2O7 compound under high-pressure conditions, indicative of a pronounced effect on the spatial arrangement of Ti atoms within the crystal lattice.

High-Pressure effect on Raman Spectra



Both high pressure experiments for Raman and XRD made by DAC with 4:1 methanol-ethanol medium.

High-Pressure effect on Raman Spectra



Shifts of Raman modes are linearly fitted and all modes show increasing tendency by increasing pressure except v_{20} (O-Ti-O, Eg asymmetric stretch of TiO_6) *and* v_{25} (A1g, O-Ti-O symmetric stretch). Vertical bar line determine phase transition at 19.2 GPa.

Results

The present research findings suggest the occurrence of anomalous changes in the refinement results obtained from the fullprof software in this study, particularly with respect to the cell parameters and volume dependence pressure. Specifically, the compound $Nd_2Ti_2O_7$ exhibits: Three orthorhombic modifications **Pna21, Cmcm, and Cmc2$_1$** and four monoclinic modifications**: P2, Pm, P2/m, and P2$_1$**

1) The refinement analysis indicates that the initial structure corresponds to the **P2$_1$ (4)** monoclinic space group, but at a pressure above:
2) **P_{LTO}=17.3GPa, P_{NTO}= 18.7 GPa, P_{PTO}=13.8GPa** peak broadening and the emergence of new peaks occur and new phase form.

The present results provide evidence that the formation of new peaks may be attributed to:

3) A phase transition to the **P2 (3)** monoclinic phase or **Pna2$_1$ (33)** and **P2$_1$/m (11)** (paraelectric)
4) The latest findings suggest that the orthorhombic **Cmc2$_1$** phase can also be assigned to the new phase.

Such a transition may be linked to:

1. The formation of a monoclinic superstructure **(P2)** or
2. The displacement of Nd^{3+} along the *b*-axis, as well as the tilting of TiO_6 octahedrons.

Both Raman and XRD results prove the results.

Aim of the Research.

Rare earth titanium oxides are popular by their high Curie temperature (T_c > 1400^0C) and as a piezoelectric material with high coercive field (E_g>45 kV/cm). Because of this characters this materials are at the focus of **automation and aerospace industries**. This kind of materials undergo phase transition at very high temperature ($T_{transition}$> 900^0C)

Our research aims to investigate the decreased transition temperature of $Re_2Ti_2O_7$ and its potential applications in modern technologies and research areas. Additionally, the study of the crystal behavior under extreme conditions using various experimental and theoretical methods. This research may provide valuable insights into the properties and behavior of rare earth titanium oxides, and inform the development of new and improved materials.

THANK YOU FOR YOUR ATTENTION!!!