IN SITU DIFFRACTION EXPERIMENTS AT VEPP-3 BEAMLINES No.2 AND No.6

Alexander N. Shmakov

Boreskov Institute of Catalysis SB RAS, Novosibirsk

Zakhar S. Vinokurov
Alexander G. Selyutin
Dmitry V. Krasnikov
Alexey S. Arakcheev
Margarete Yu. Kameneva
Konstantin E. Kuper

SFR-2016

Synchrotron and Free Electron Laser Radiation:
Generation and Application SFR-2016
Novosibirsk, July 4-7, 2016

SSTRC Beamlines

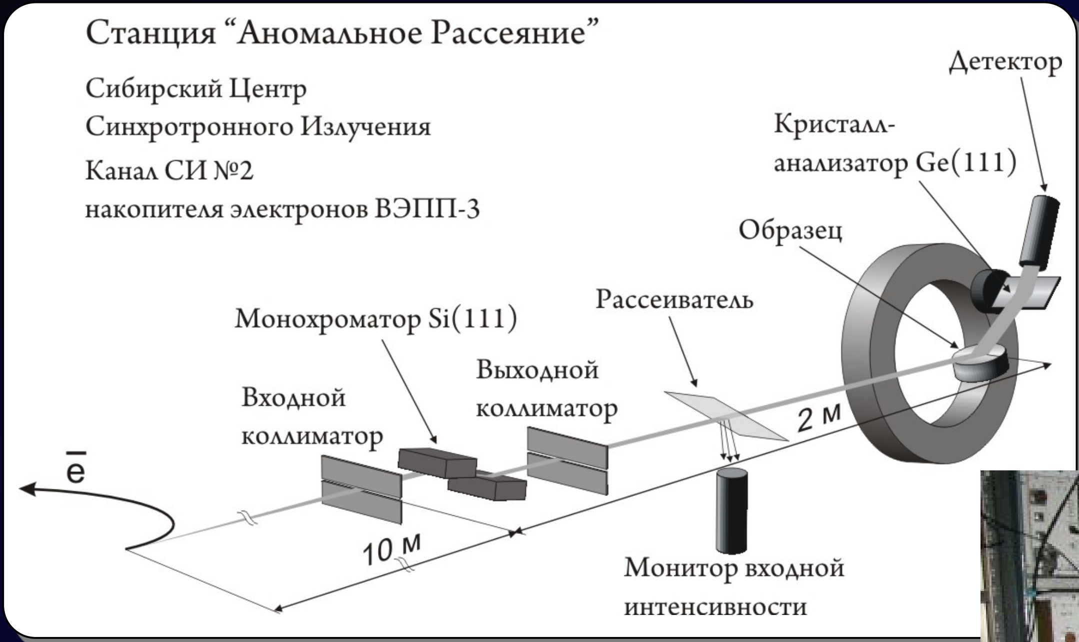
VEPP-3 SR source

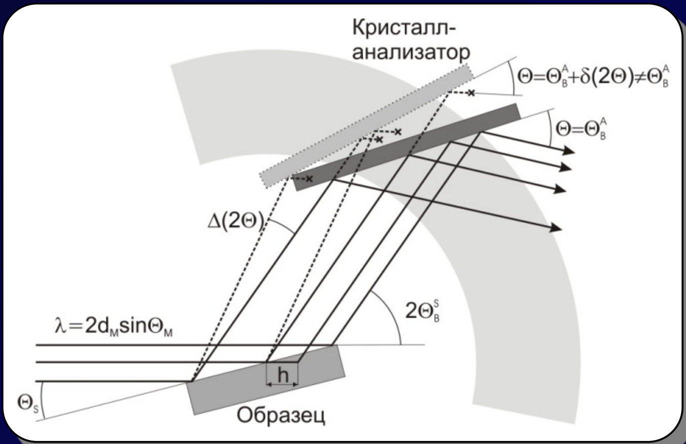
- LIGA technology and X-ray Lithography
- "Explosion": Submicrosecond Diagnostics
- Anomalous Scattering (Beamline No.2)
- Local and Scanning X-ray Fluorescent Element Analysis
- Diffractometry in Hard X-rays
- X-ray Microscopy and Microtomography
- Diffraction “Movie" (time-resolved diffractometry) and Small Angle Scattering
- Time-resolved Luminescence
- Precision Diffractometry (Beamline No.6)
- EXAFS Spectroscopy
- Metrology and EXAFS Spectroscopy in the Soft X-ray Range

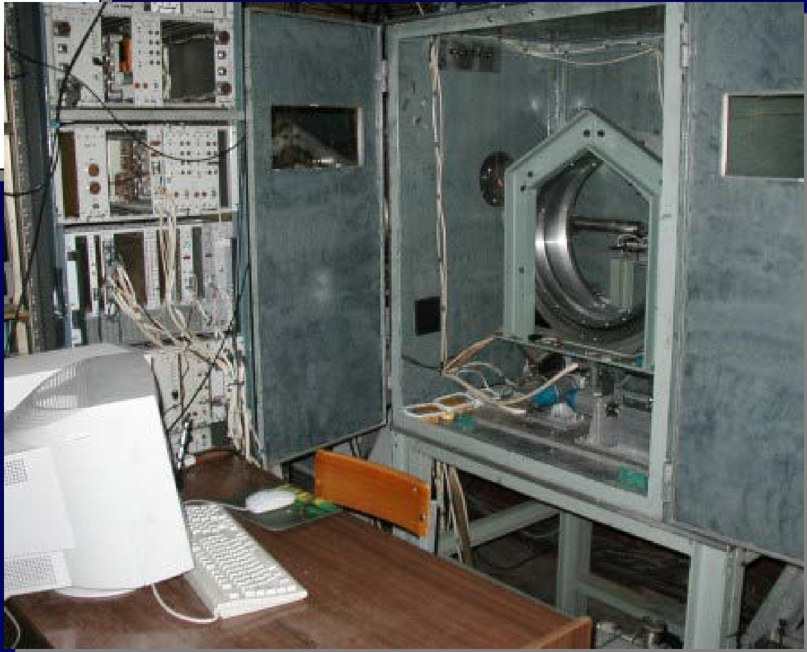
VEPP-4 SR source

- COSMOS – Detector Diagnostics
- “Detonation”: Submicrosecond Diagnostics
- Hard X-ray microscopy and Fluorescence Element Analysis (diffraction)
- High Precision X-ray Diffractometry
- SAXS
- High Pressure Diffractometry

“Anomalous Scattering” Beamline





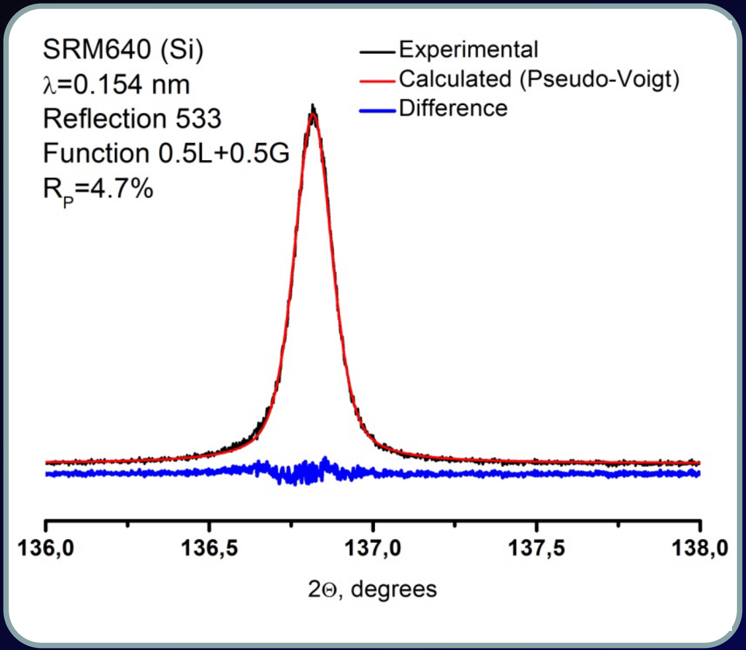


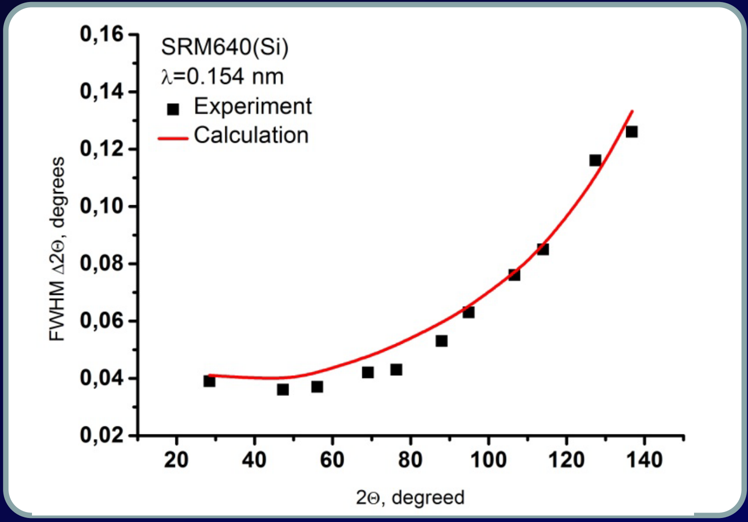
X-ray Diffraction Techniques Available on “Anomalous Scattering” Beamline

1. High Angular Resolution
2. Resonant Scattering
3. Grazing Incidence Diffraction
4. Radial Electron Density
   Distribution Functions
5. Long *d* Diffraction

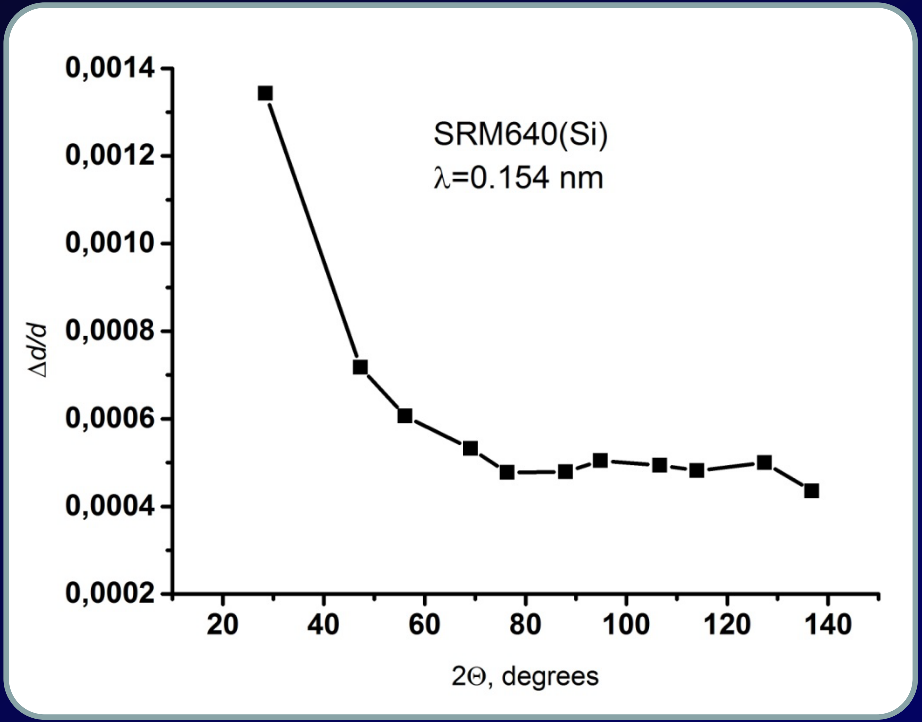
“Anomalous Scattering” Beamline

High Angular Resolution





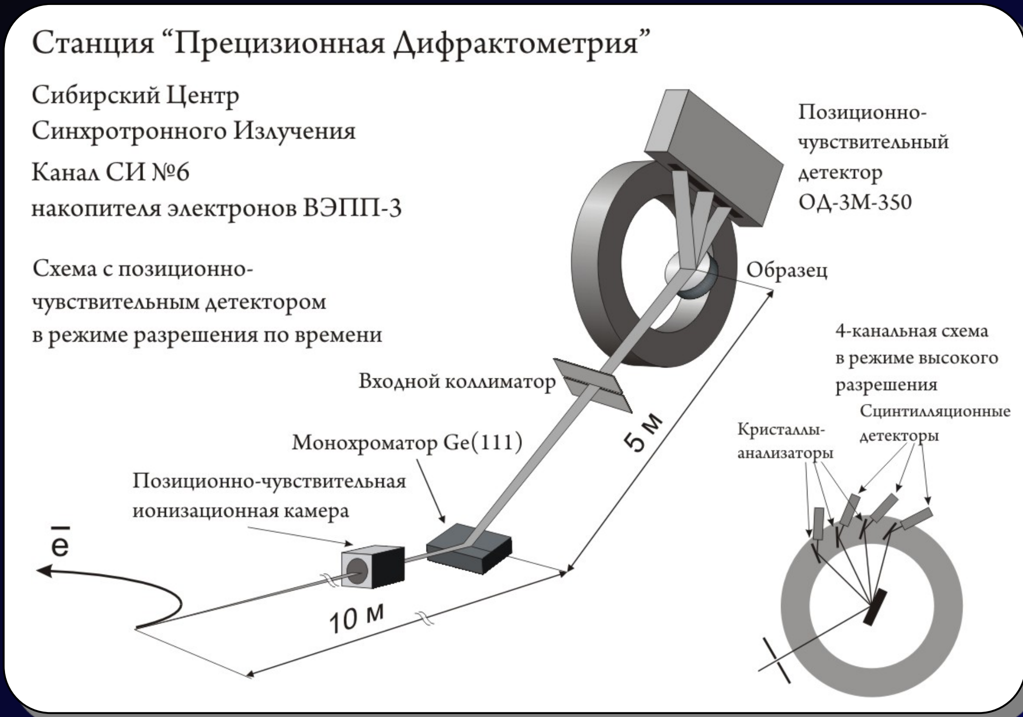
Resolution vs Diffraction angle

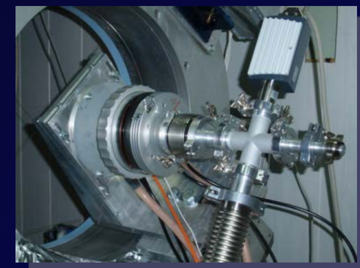


$$\Delta d/d = \Delta\Theta \, \mathrm{ctg}\Theta;$$

$$\Theta \sim 70°, \; \Delta\Theta \sim 0.07 \Rightarrow \Delta d/d \sim 5 \cdot 10^{-4}$$

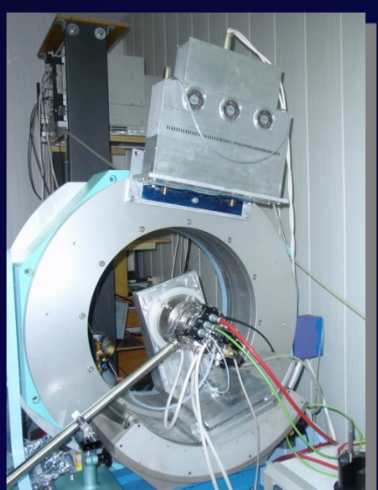
“Precision Diffractometry” Beamline





HTK-2000 X-ray High Temperature Chamber

XRK-900 Reactor Chamber

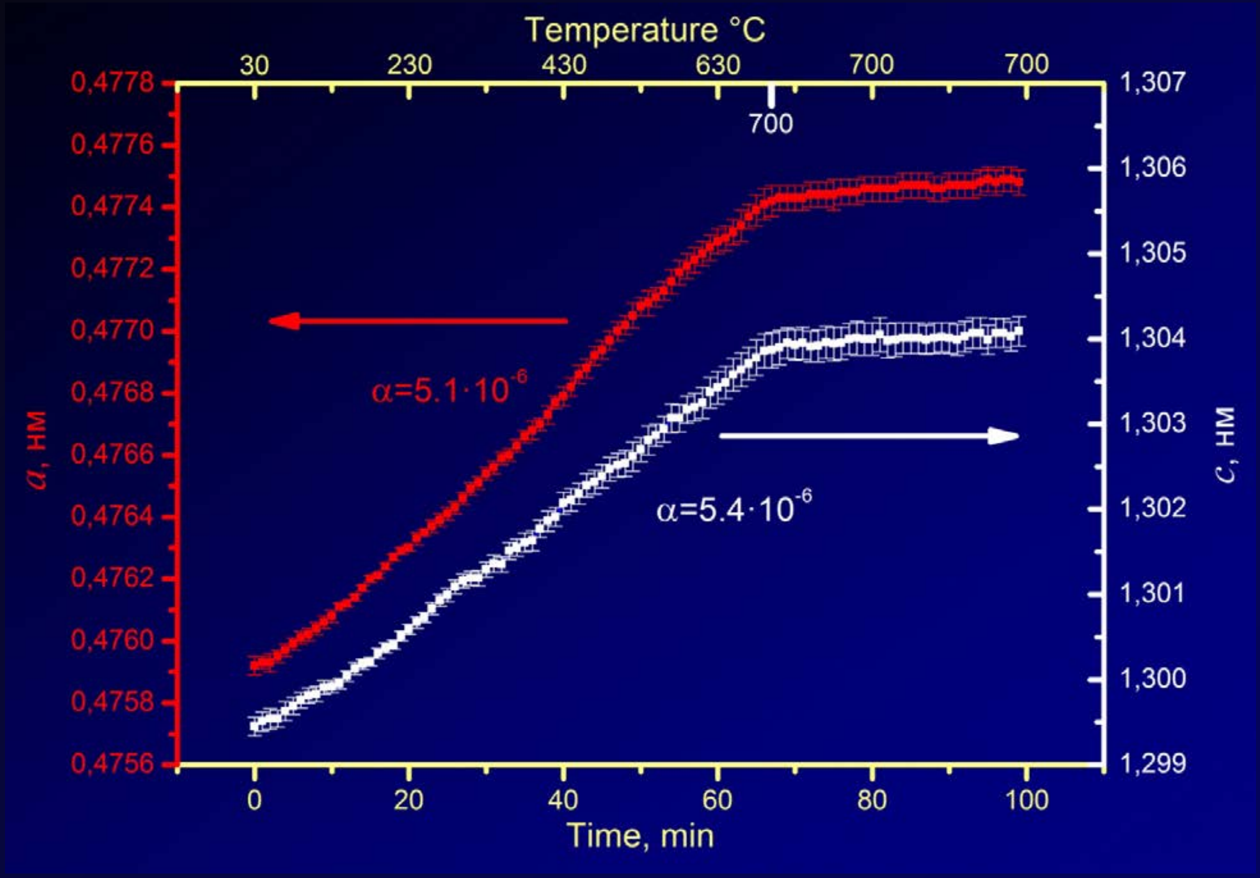


X-ray Diffraction Techniques Available on “Precision Diffractometry” Beamline

Time resolved diffractometry in non-ambient temperature conditions and reaction media with moderate time resolution (>1 sec)

“Precision Diffractometry” Beamline

SRM676 (Corundum) Heating from Room to 700°C



Temperature linearity of heater
and thermal expansion coefficients of corundum

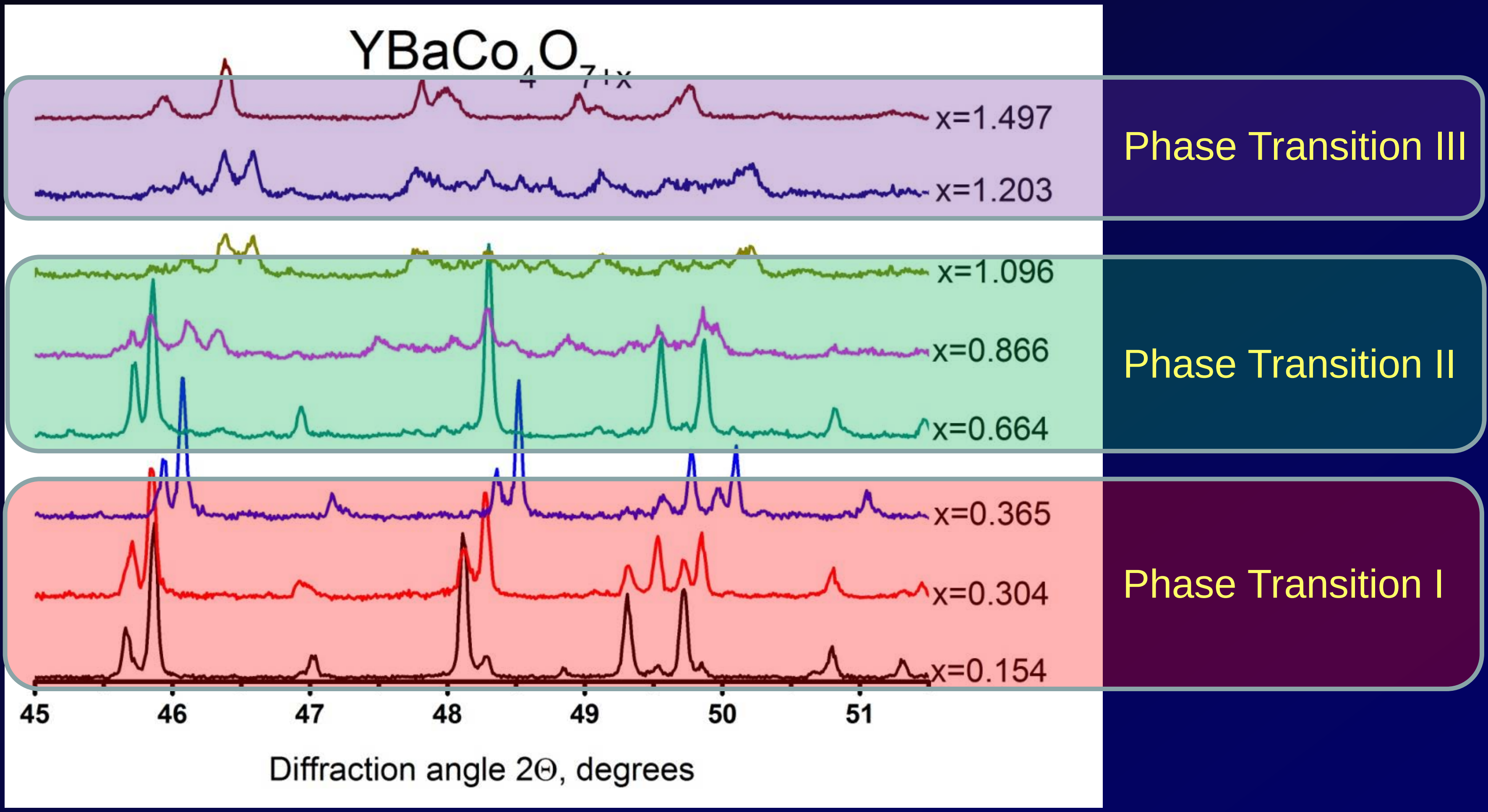
Equipment of the Beamline:

- 3-channel Gas mixture preparation system based on flow-mass controllers;
- Quadrupole Mass-Spectrometer for Gas mixture contvposition analysis at input and output of the reactor

“Anomalous Scattering” Beamline Activity

High Angular Resolution

Materials for Oxygen Accumulation and Storage

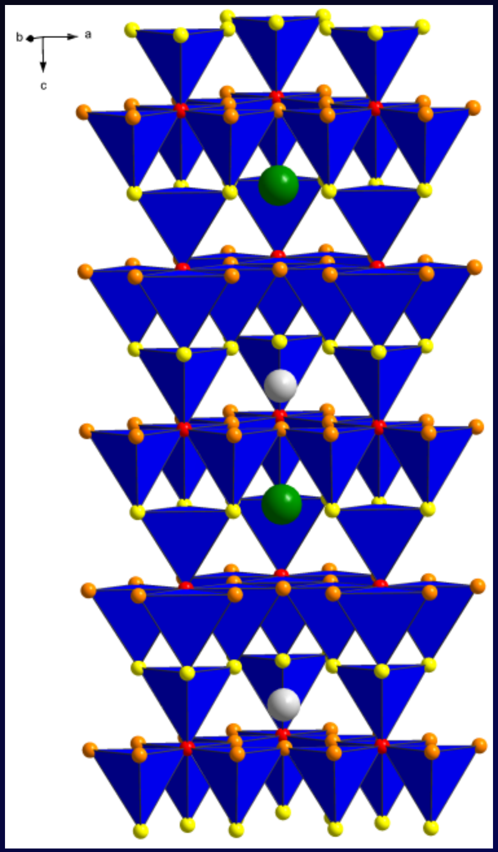


Series of XRD Patterns with different oxygen stoichiometry

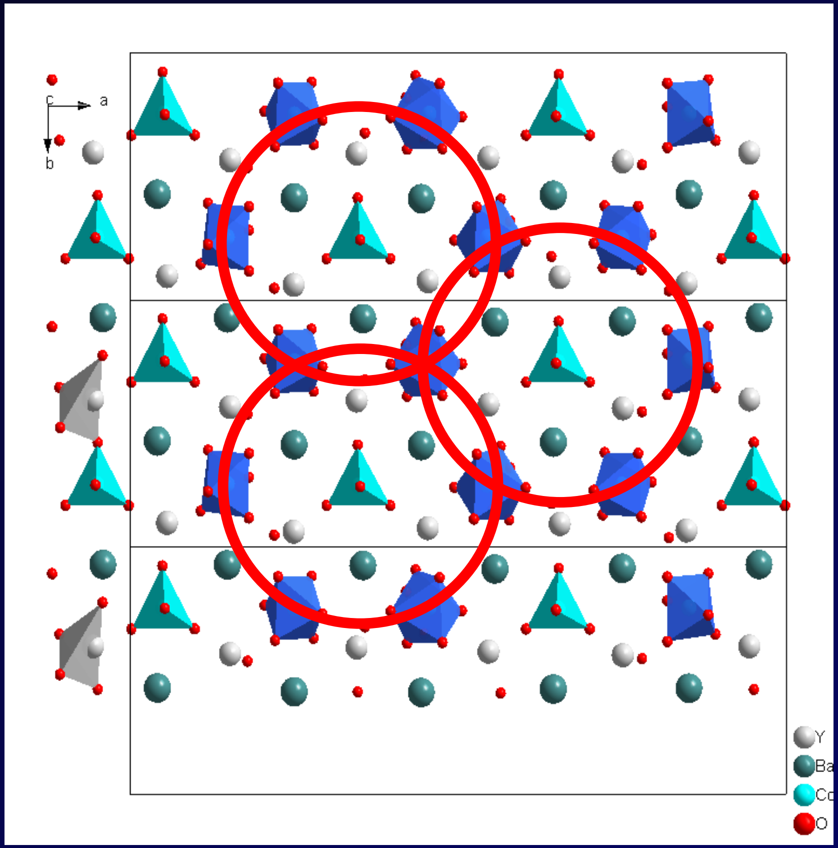
"Anomalous Scattering" Beamline Activity

High Angular Resolution

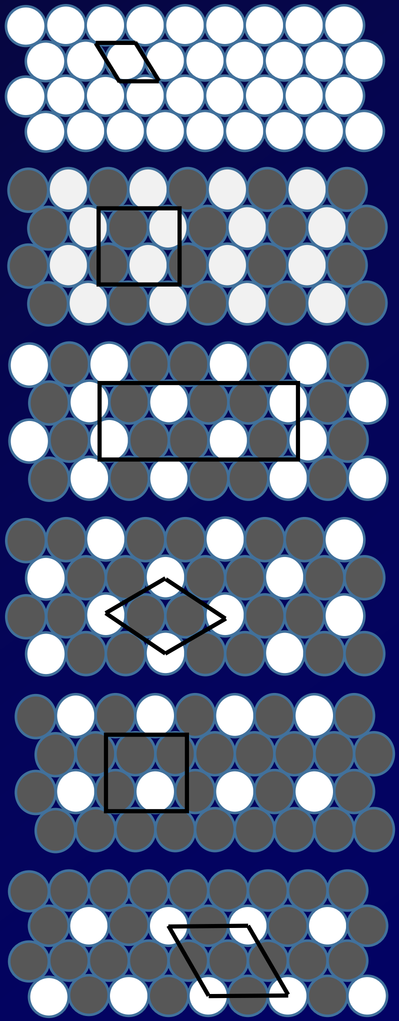
Oxygen Accumulation and Storage



Parent Structure
$YBaCo_4O_7$



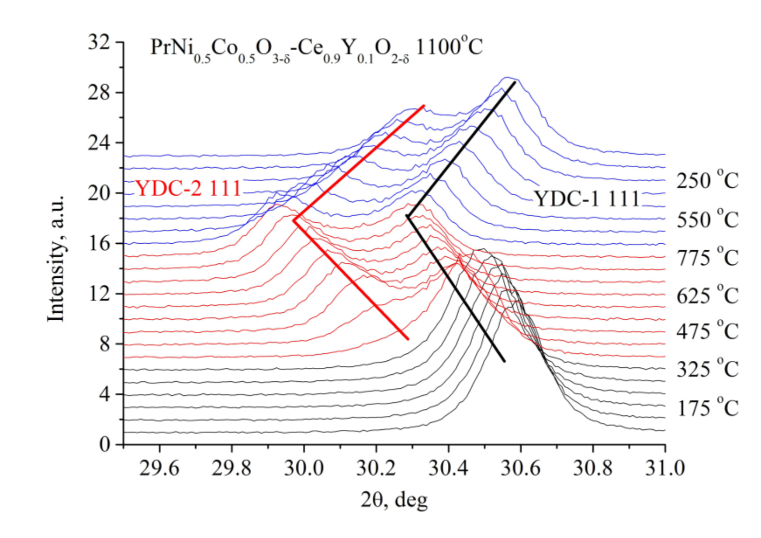
Ordering of Oxygen Saturated Co Polyhedra at Stoichiometry
$YBaCo_4O_{8.2}$ (x=1.2)



Model of Arrangement of Insaturated and Saturated Co Polyhedra

"Precision Diffractometry" Beamline Activity

Perovskite-like Oxides Crystal Structure Relaxation Caused by Oxygen Loss

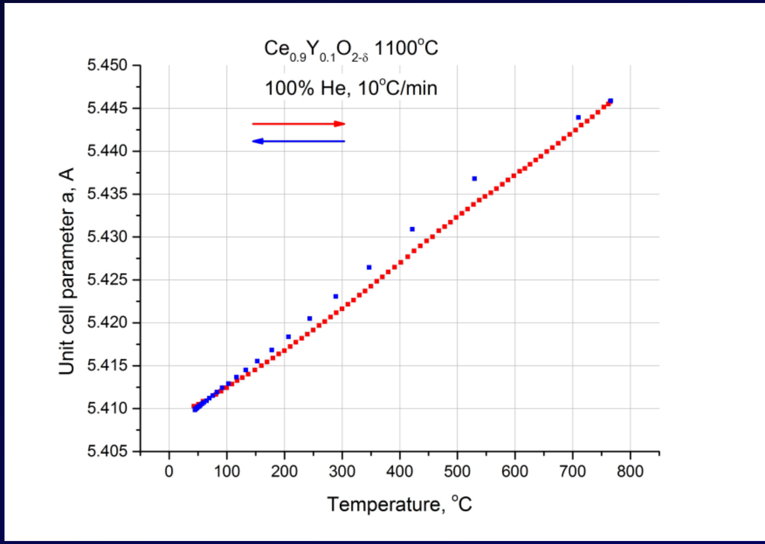


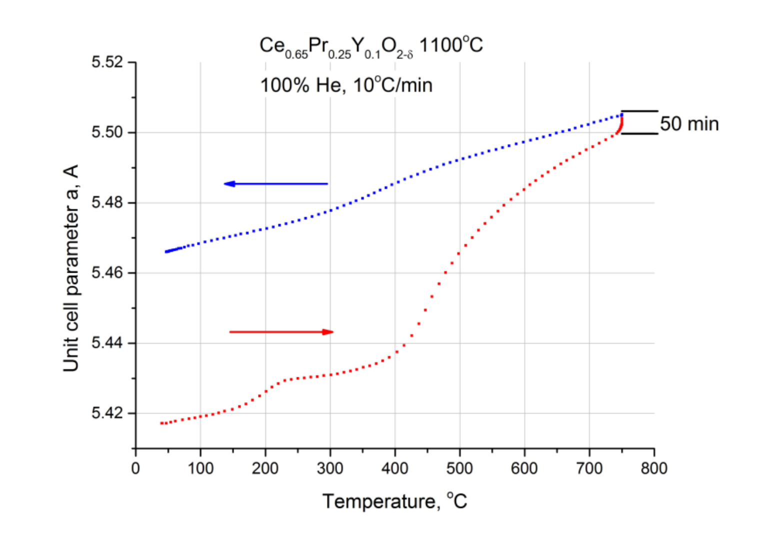
$PrNi_{0.5}Co_{0.5}O_{3-\delta}$ − $Ce_{0.9}Y_{0.1}O_{2-\delta}$ Composite Material heated in 100%He.

Decomposition on two phases with different oxygen content is observed.

$Ce_{0.9}Y_{0.1}O_{2-\delta}$ and $Ce_{0.65}Pr_{0.25}Y_{0.1}O_{2-\delta}$ Composite Materials heated in 100%He.

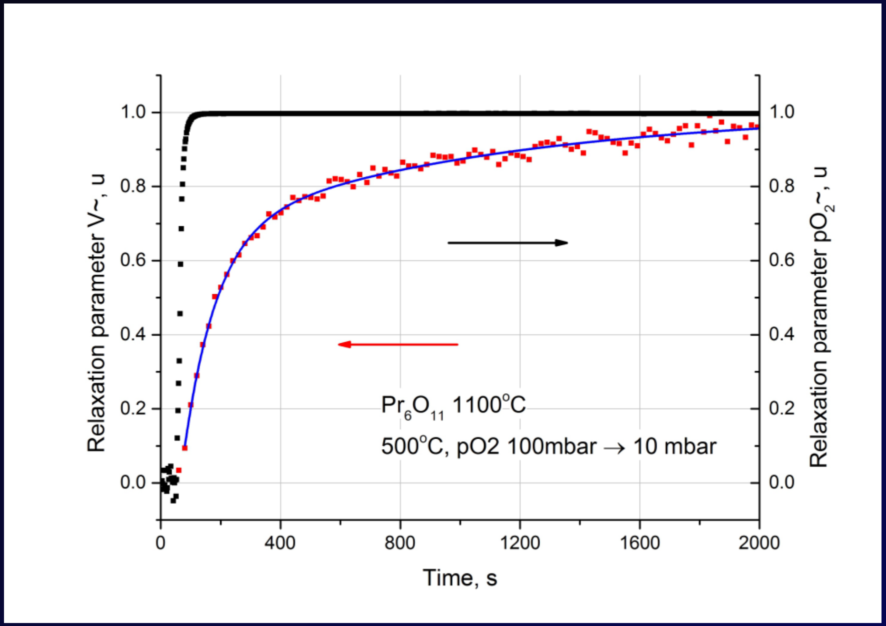
Insertion of Pr highly increases oxygen mobility in this material

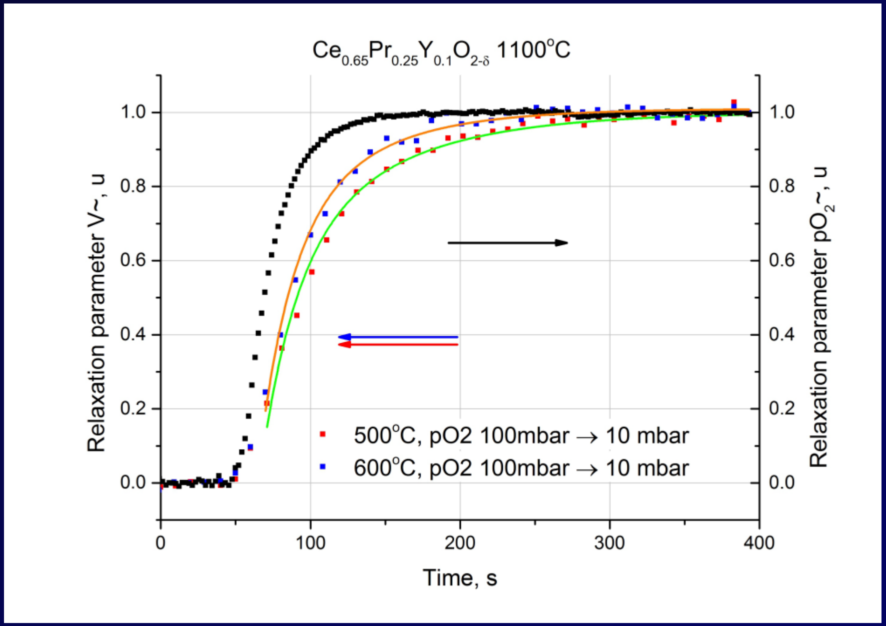




“Precision Diffractometry” Beamline Activity

Perovskite-like Oxides Crystal Structure Relaxation Caused by Oxygen Loss





Pr_6O_{11}

D_{chem} ~ $5.5 \cdot 10^{-7}$ cm/s
K_{chem} ~ $5.0 \cdot 10^{-4}$ cm/s

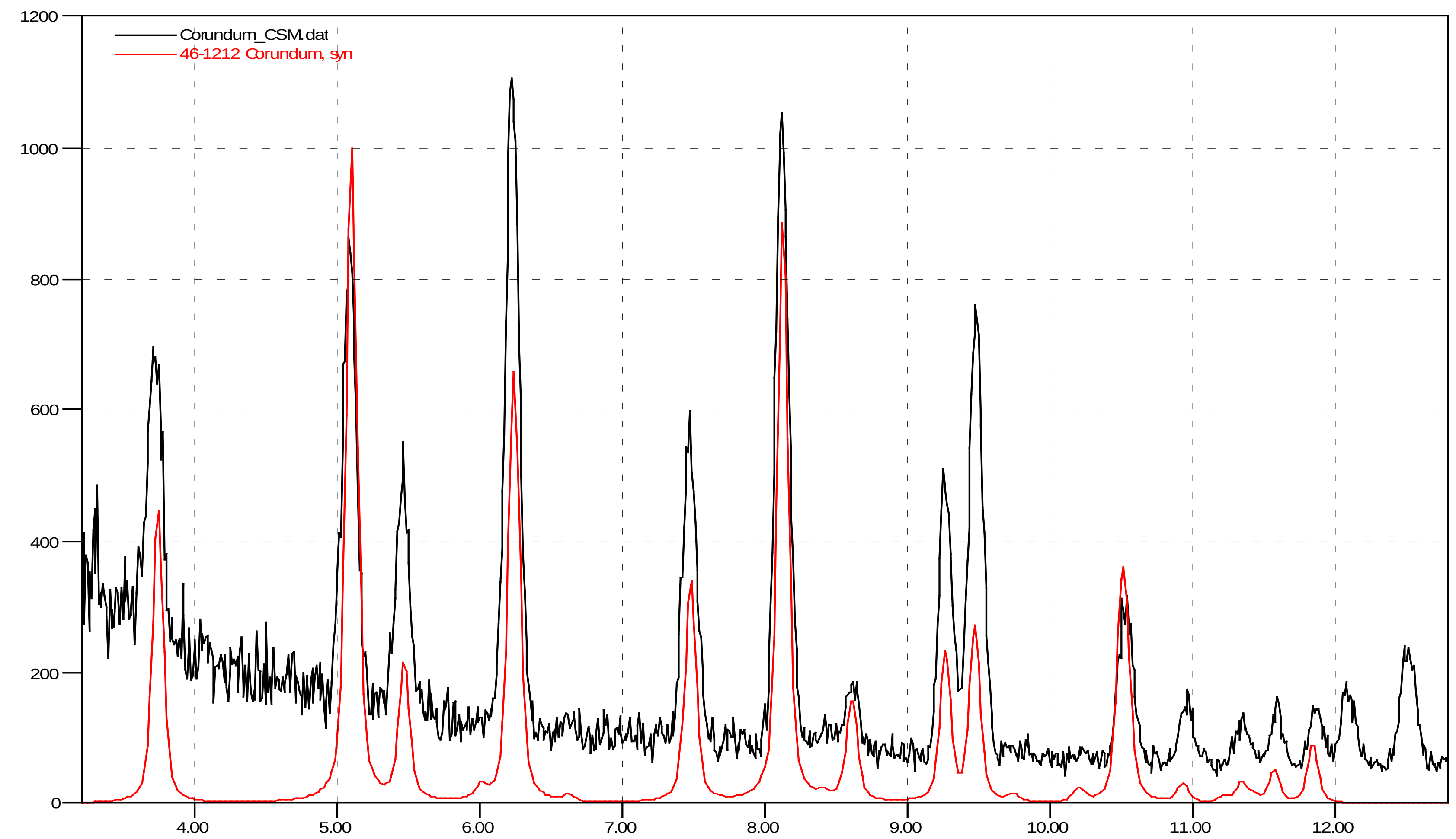
$Ce_{0.65}Pr_{0.25}Y_{0.1}O_{2-\delta}$

K_{chem} ~ $1.3 \cdot 10^{-4}$ cm/s

Unit cell volume relaxation

High Energy X-ray Diffraction at VEPP-4

Test Experiments on the Possibility of HE XRD at 54.6 keV

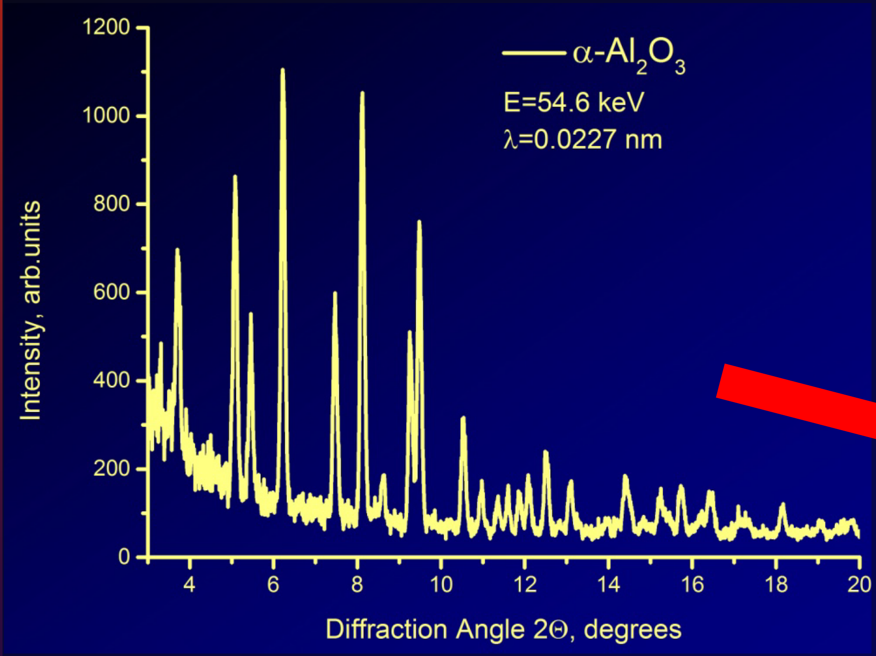


Experimental and calculated XRD patterns of SRM676 (corundum) at E=54.6 keV (λ=0.0227 nm)

High Energy X-ray Diffraction at VEPP-4

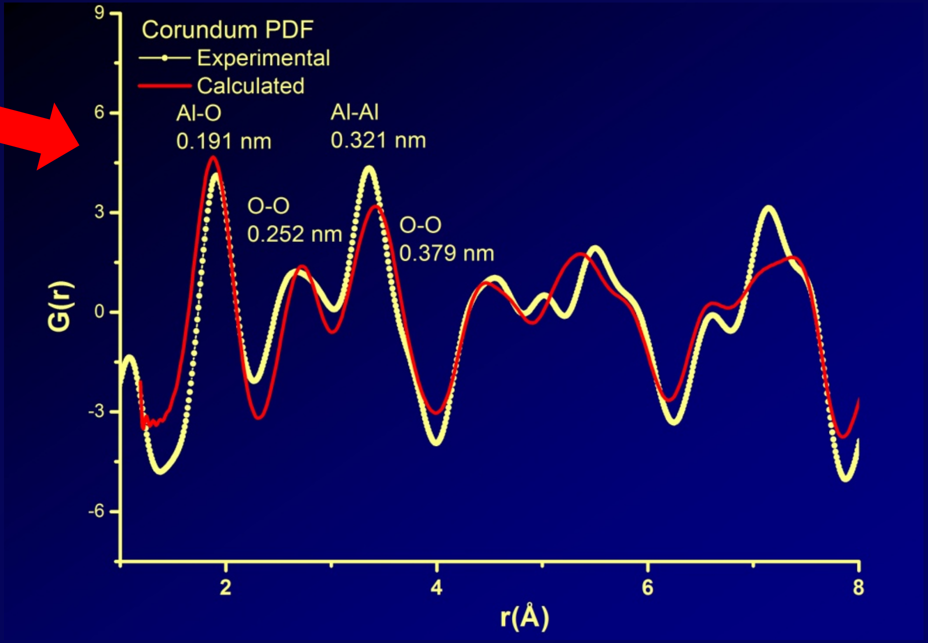
Test Experiments on the Possibility of HE XRD at 54.6 keV

Calculation of Pair Distribution Function of α-Al_2O_3 from HE XRD Pattern



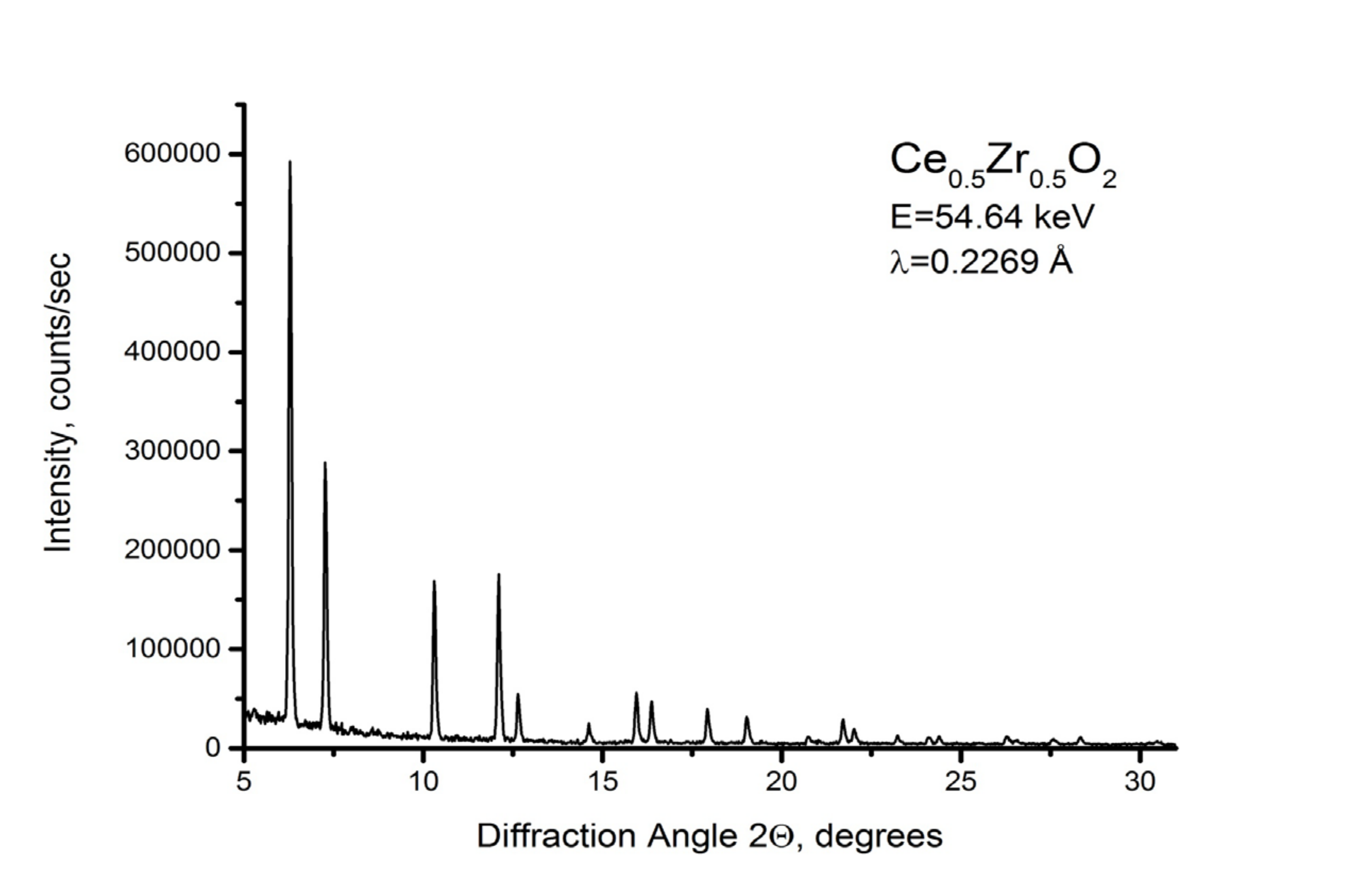
Experimental α-Al_2O_3 HE XRD Pattern

Calculated α-Al_2O_3 PDF



High Energy X-ray Diffraction at VEPP-4

Test Experiments on the Possibility of HE XRD at 54.6 keV



High Energy X-ray Diffraction at VEPP-4

Advantages and Disadvantages of High Energy XRD

Advantages:

- Debye Cone Contraction – most of structural information is confined within narrow angular range close to small angle region
- High Penetration Ability – allows to study objects placed inside different devices, i.e. electrochemical cells, high pressure autoclaves, etc.
- Wide Range of Scattering Vectors $4\pi\sin\Theta/\lambda$, up to 1000 nm^{-1} – application of Pair Distribution Function method to poorly organized and high dispersive materials, such as catalysts
- Resonant Scattering for Heavy Elements – selectivity for Pt, Au which are important for catalytic application

Disadvantages:

- Debye Cone Contraction – poor angular resolution
- High Penetration Ability – large sample volume needed