Институт физики металлов имени М. Н. Михеева
Уральского отделения Российской академии наук

МЕХАНИЗМ ВОССТАНОВЛЕНИЯ МЕТАЛЛОВ ИЗ ОКСИДОВ И СУЛЬФИДОВ ПРИ ДЕФОРМАЦИИ ПРИ ИНТЕНСИВНЫХ БАРОДЕФОРМАЦИЯХ

RECOVERY OF METALS FROM OXIDES AND SULFIDES UNDER HIGH PRESSURE DEFORMATION

Пилюгин В.П.,[a] **Анчаров А.И., Соловьева Ю.В.,**[a,b] **Толмачёв Т.П.,**[a] **Гижевский Б.А.**[a]

Pilyugin V.P.,[a] **Ancharov A.I.,**
Solov'eva Yu.V.,[b] **Tolmachev T.P.**[a] **, Gizhevskii B.A.**[a]

[a]*M.N. Mikheev Institute of Metal Physics of the Ural Branch of the RAS,*
S. Kovalevskoy st. 18, Yekaterinburg, 620990, Russia, e-mail: pilyugin@imp.uran.ru

[b]*Tomsk State University of Arcitecture and building,*
pl. Solyanay, 2, Tomsk, 634053, Russia

ЗНЧ-17

Типы связи в оксидах и сульфидах металлов обуславливают их высокую температуру плавления, малую пластичность, низкие электро- и теплопроводность.
Сильная направленная связь затрудняет образование и движение дислокаций в полях напряжений. Давление блокирует появление трещин. Механизм образования и перемещения точечных дефектов.

Оксиды *d*- металлов: ионная и ионно-ковалентная, ковалентно-полярная
Сульфиды *d*- и *f*-металлов: металлическая и ионно-ковалентная связь

Types of bonds in metal oxides and sulfides are cause their high melting point, low ductility, low electrical and thermal conductivity. Strong directional bond hinders the formation and movement of dislocations in the stress. Pressure inhibits the cracking. The mechanism of formation and movement of point defects.

Oxides of d- metals: ion and ion-covalent, polar covalent bonds
Sulfides of d- and f-metals: metal and ion-covalent bonds

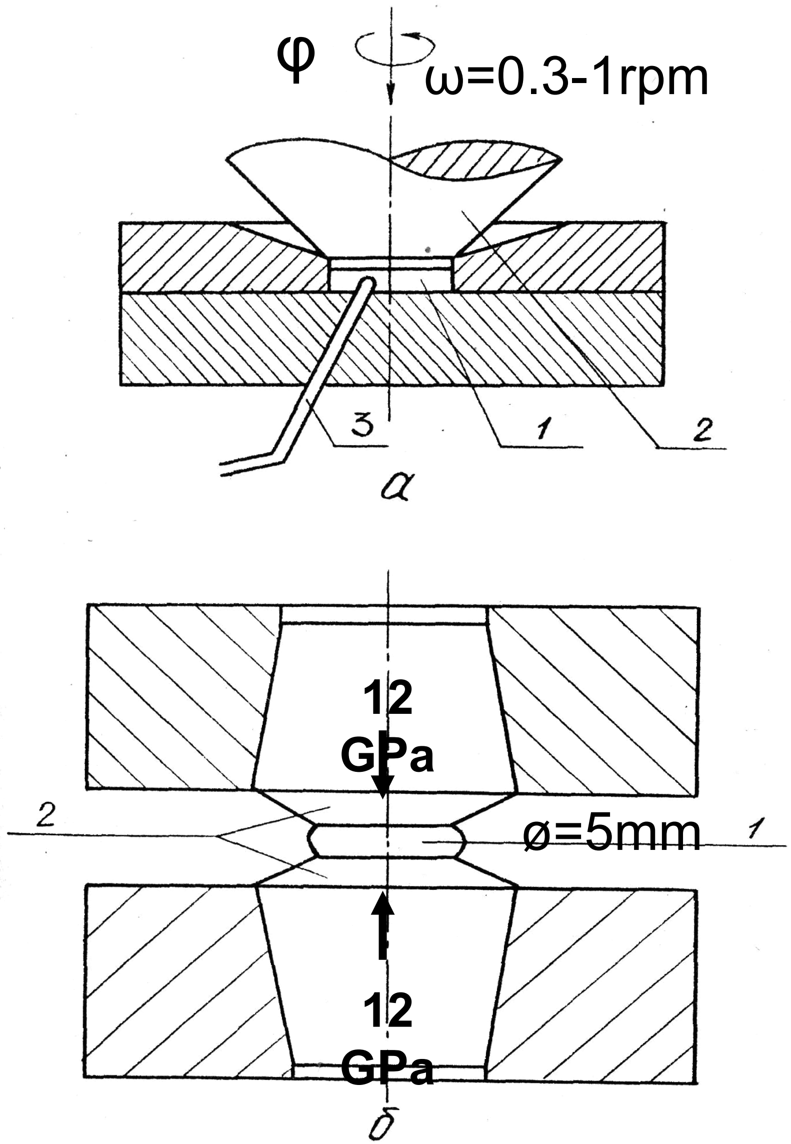
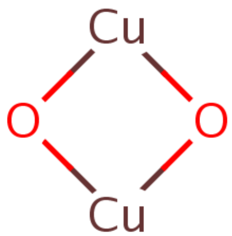
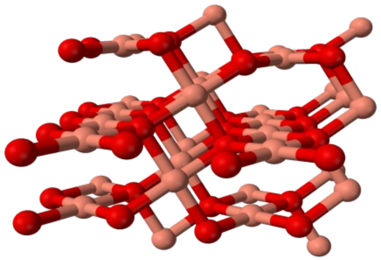


Схема кручения под давлением – сдвиг под давлением

High pressure torsion – shear under pressure

- 1 – образец
- 2 – наковальни (сплав ВК6 -WC-Co, c-NB или «скелетон» - наноалмазы+Si)
- 3 – термопара
- 1 – sample
- 2 – anvil (alloy VK6 -WC-Co, c-NB or "skeleton" - nanodiamonds+Si)
- 3 - thermocouple

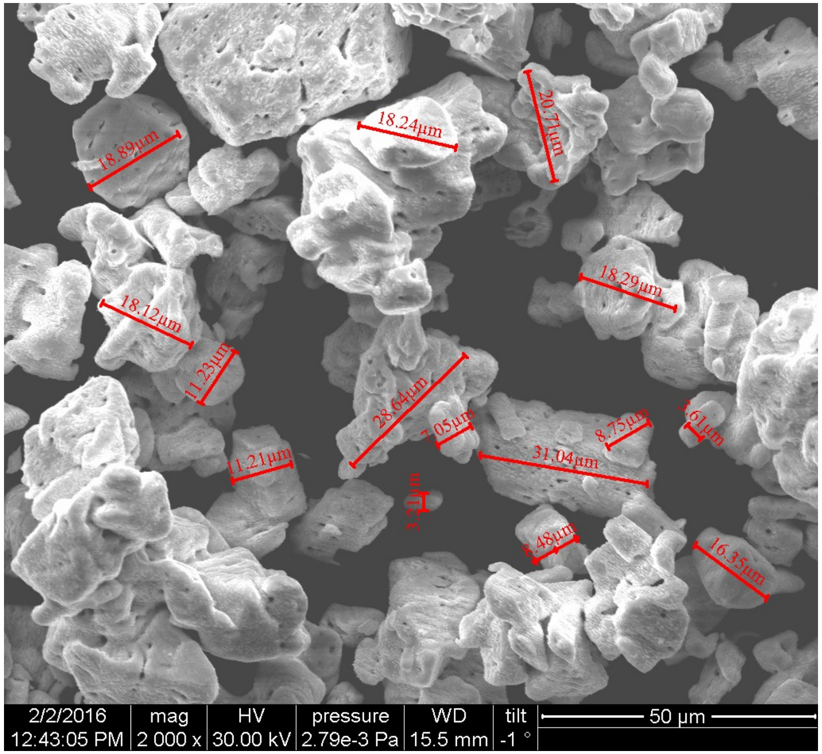




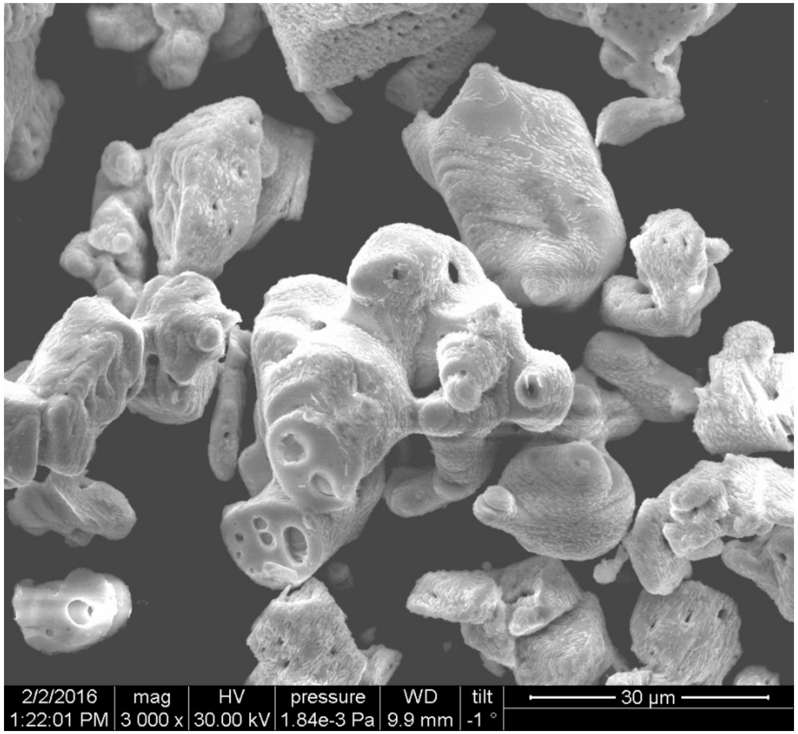
CuO

Окси́д ме́ди (II) CuO- основный оксид двухвалентной меди. Кристаллы чёрного цвета, в обычных условиях довольно устойчивые, моноклинная сингония

PbO

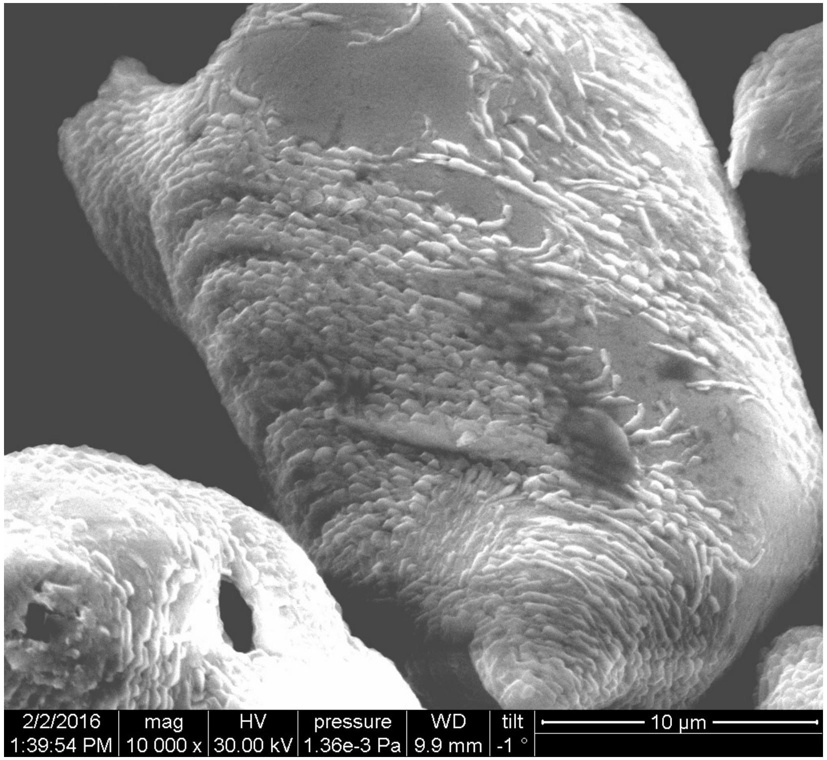


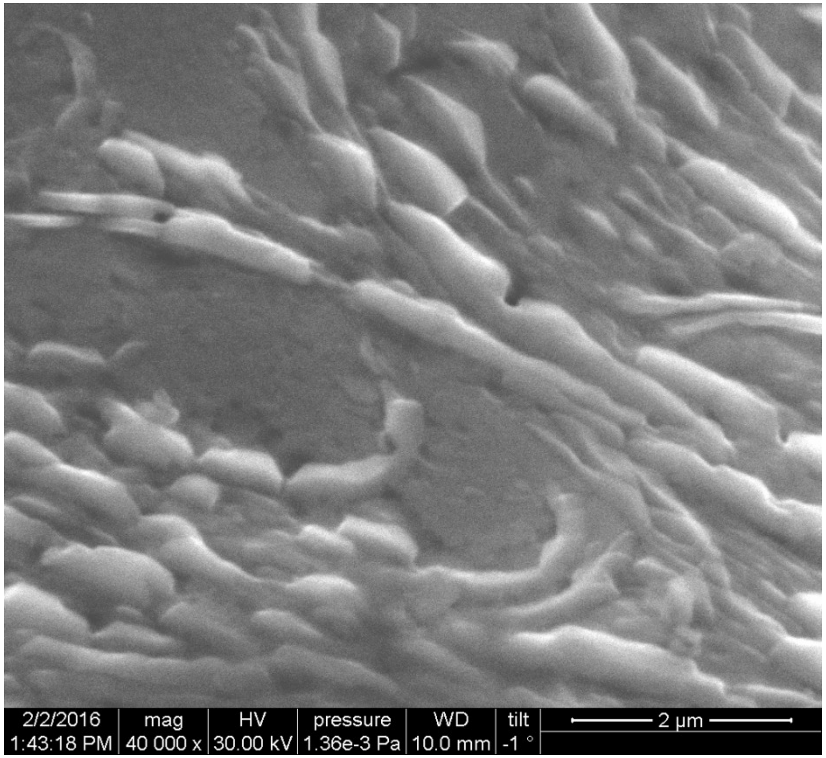
18.89µm
18.24µm
20.71µm
18.29µm
18.12µm
11.23µm
28.64µm
7.05µm
8.75µm
3.61µm
11.21µm
31.04µm
3.71µm
8.48µm
16.35µm
2/2/2016 12:43:05 PM
mag 2 000 x
HV 30.00 kV
pressure 2.79e-3 Pa
WD 15.5 mm
tilt -1 °
50 µm



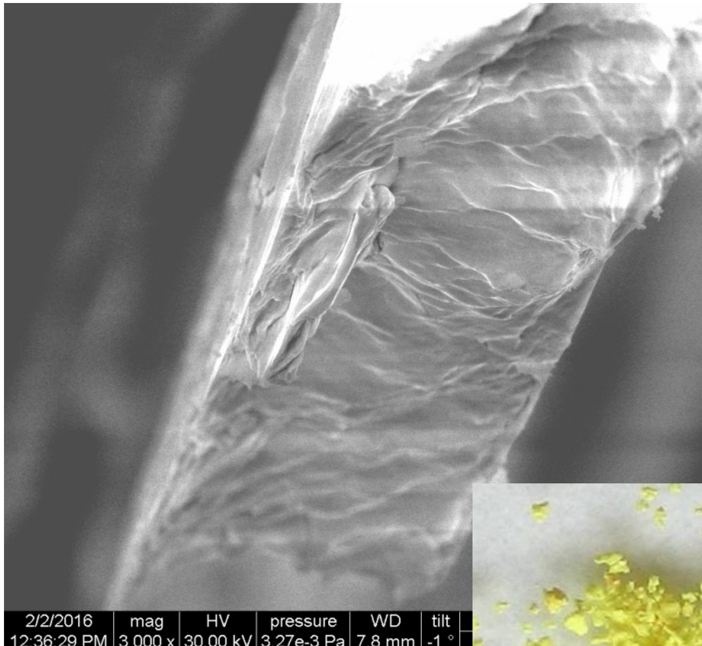
2/2/2016 1:22:01 PM
mag 3 000 x
HV 30.00 kV
pressure 1.84e-3 Pa
WD 9.9 mm
tilt -1 °
30 µm

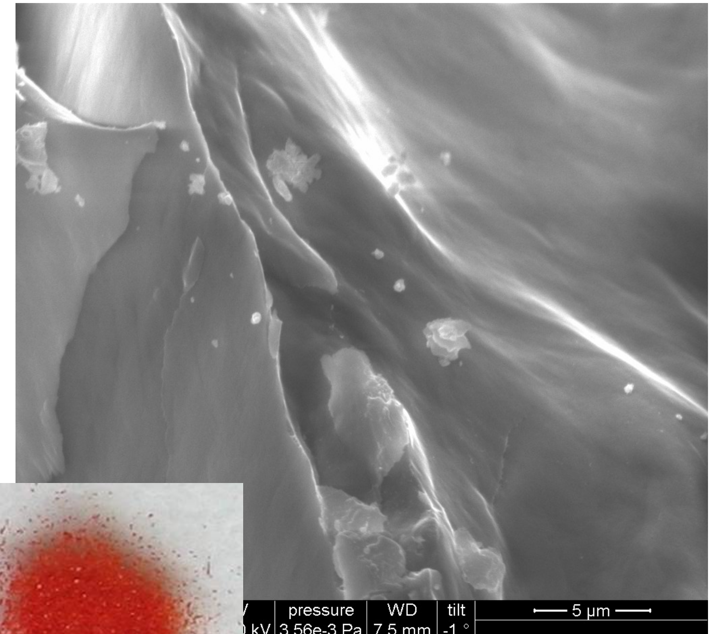
PbO(II), массикот (жёлтый)





Fractures PbO after pressing to with shear



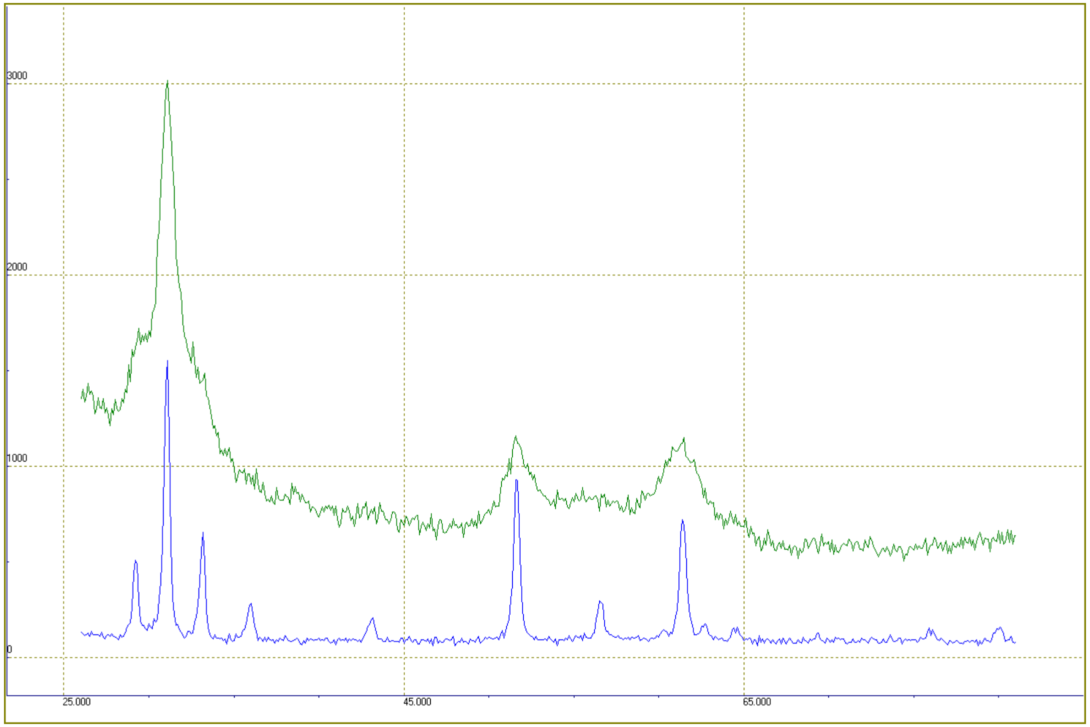


Resistant to
temperature 489 ° C

β-PbO (II), massicot (yellow), the orthorhombic system
proceeds under compression and deformation in α- PbO (II), glёt (red)
tetragonal.
With further deformation is reduced to metallic
metal conductive state.
deformation mechanism.
Lowering the temperature reduces the kinetics of the reduction to the metal

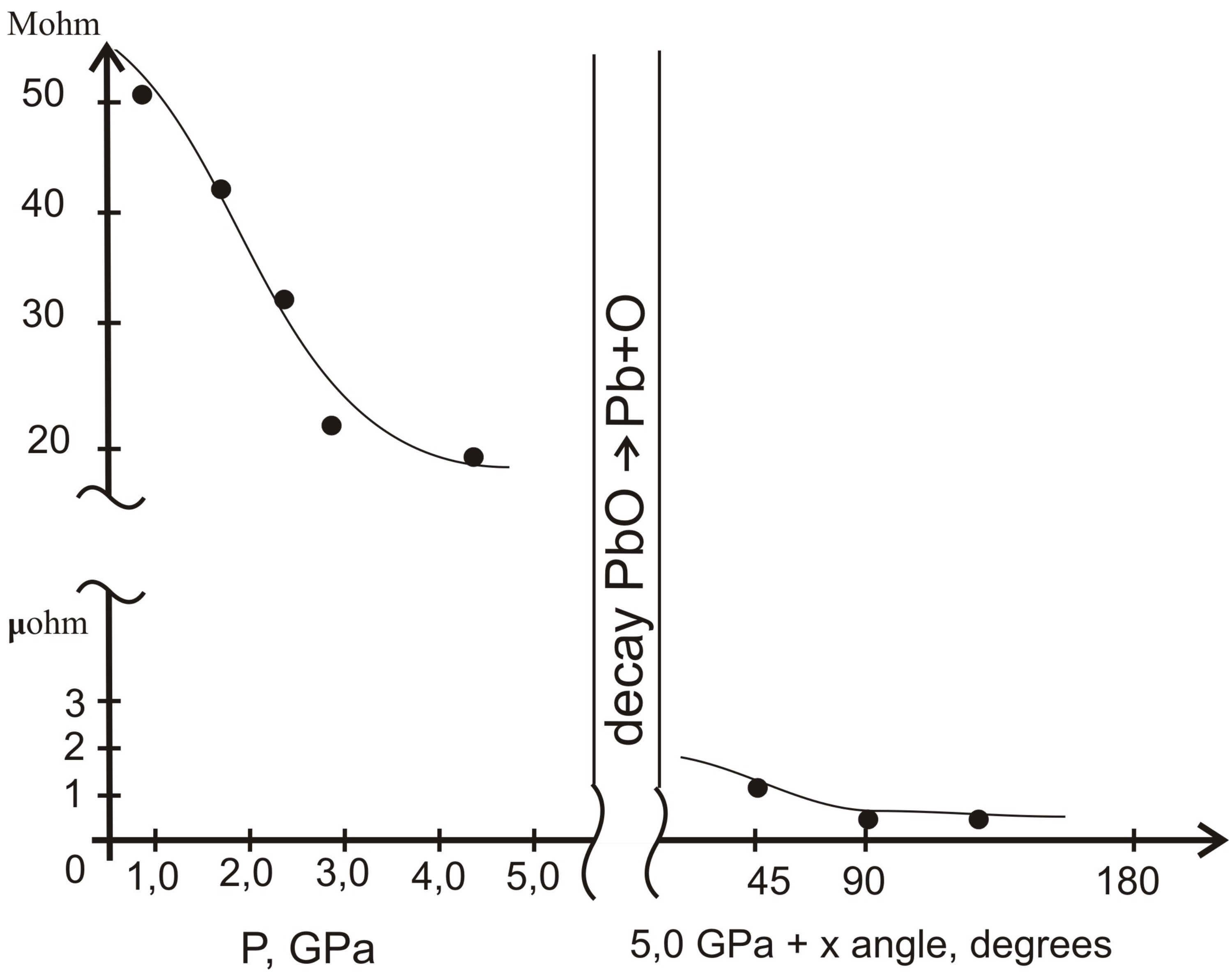
CdS

X-ray diffraction pattern of
bottom - powder,
at the top - "black" after the sample P = 4 GPa, ω = 0.3ob / min, φ = 60 °



Cadmium sulfide - sphalerite (zinc blende) and wurtzite. It has a yellowish color Mohs hardness is 3.8.

Electrical resistance PbO in situ under pressure and high pressure torsion



Compound	-ΔH (кJ/mol)	Compound	-ΔH (кJ/mol)
AgO_2	31,1	Ag_2S	32,8
CuO	162	Fe_2O_3	822
FeO	264	SiO_2	909,5
MgO	601	Al_2O_3	1676

Some decomposition reaction synthesis proceed by explosive (PVC, chromic anhydride, bismuth oxide)

Criterion of oxides metallization during deformation under pressure

The oxides and sulphides:

CuO, Cu_2O, PbO, NiO, CdO, TiO, MgO, Al_2O_3, CdS, ZnS

The criterion is the recovery value of the enthalpy of the compound:

CuO - 162 (кJ/mol)

PbO - 217 (кJ/mol)

border enthalpy

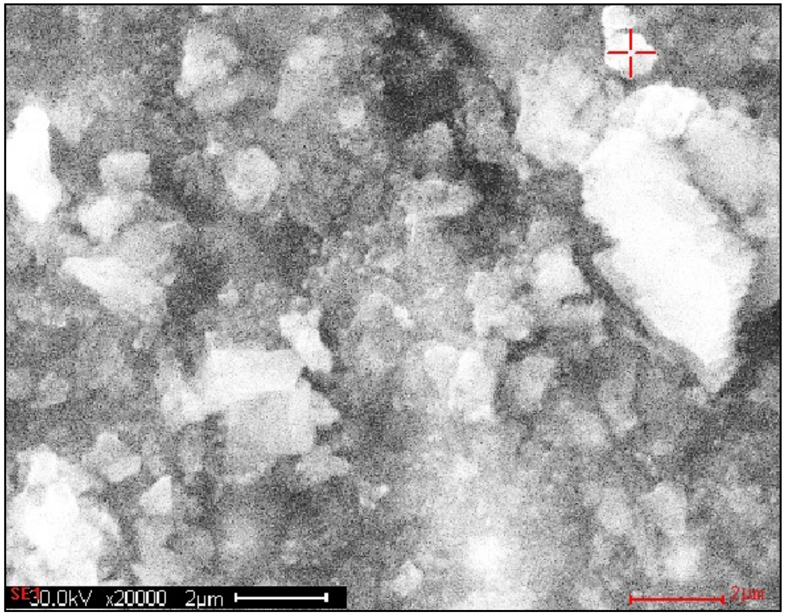
TiO - 526 (кJ/mol)

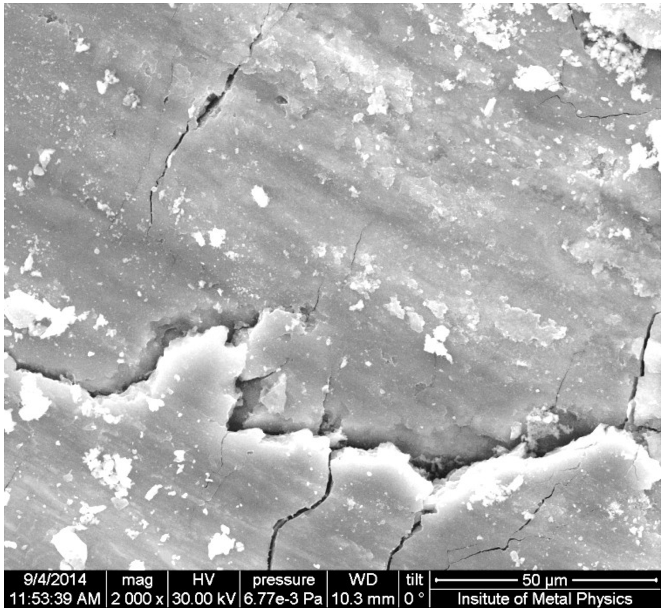
ZrO_2

Al_2O_3

with a covalent bond and diamond lattice

Si

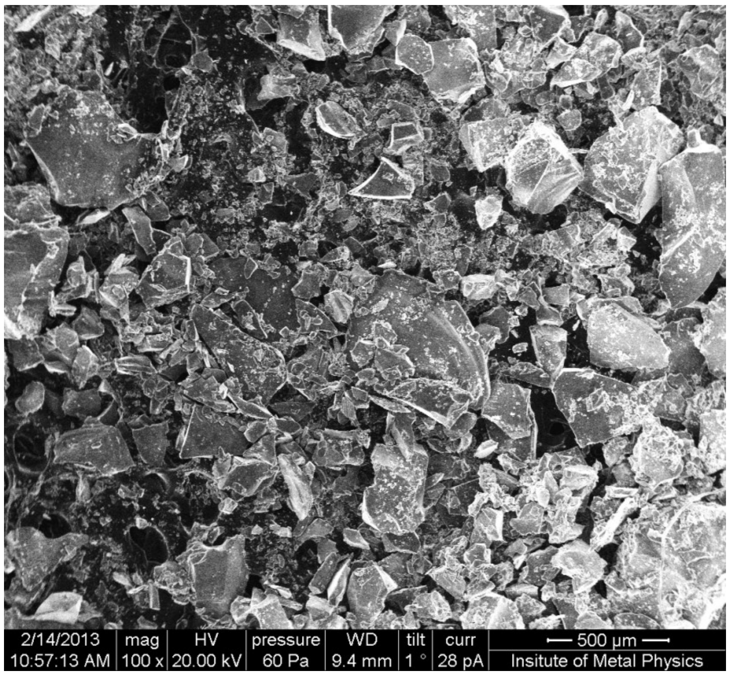

SEI 30.0kV x20000 2µm
2µm

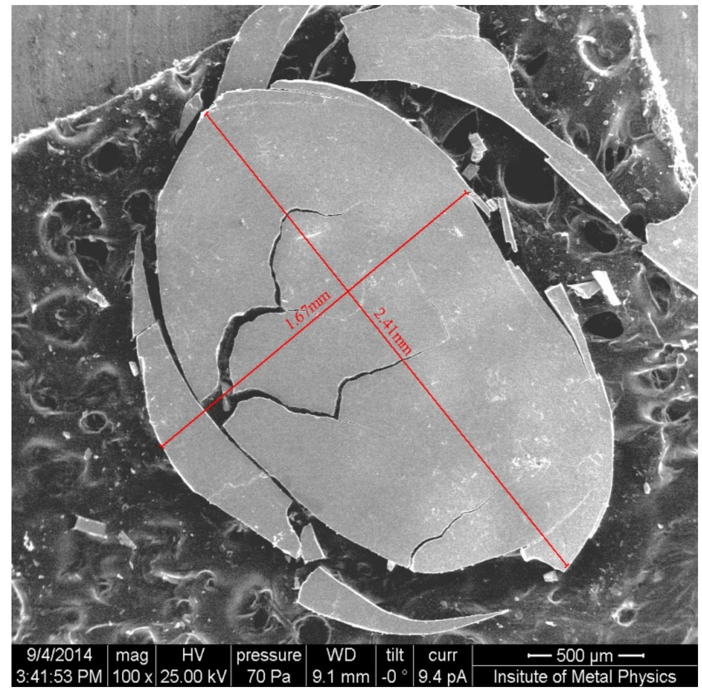

9/4/2014
11:53:39 AM
mag
2 000 x
HV
30.00 kV
pressure
6.77e-3 Pa
WD
10.3 mm
tilt
0 °
50 µm
Insitute of Metal Physics

SiO_2

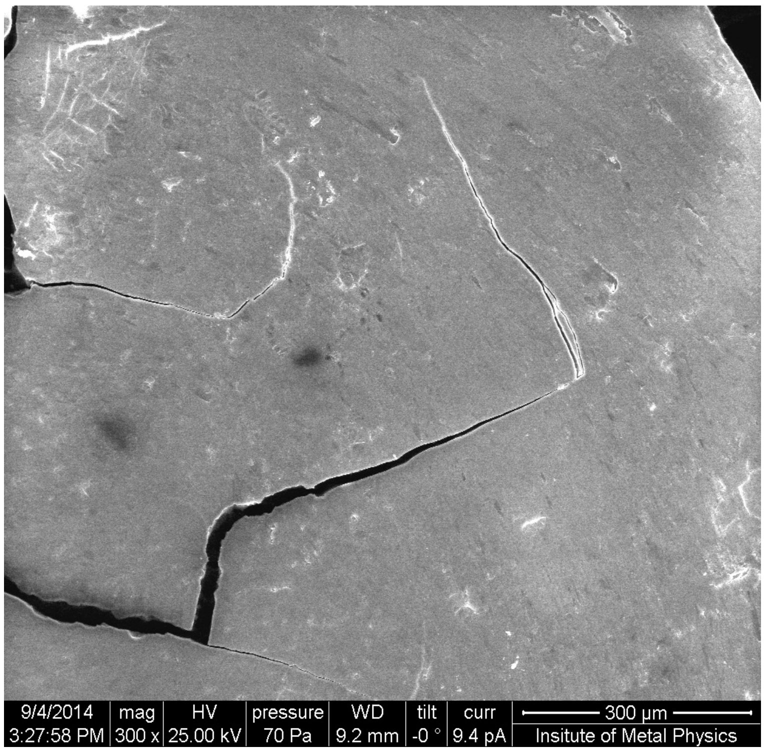
in crystalline and amorphous (glass)

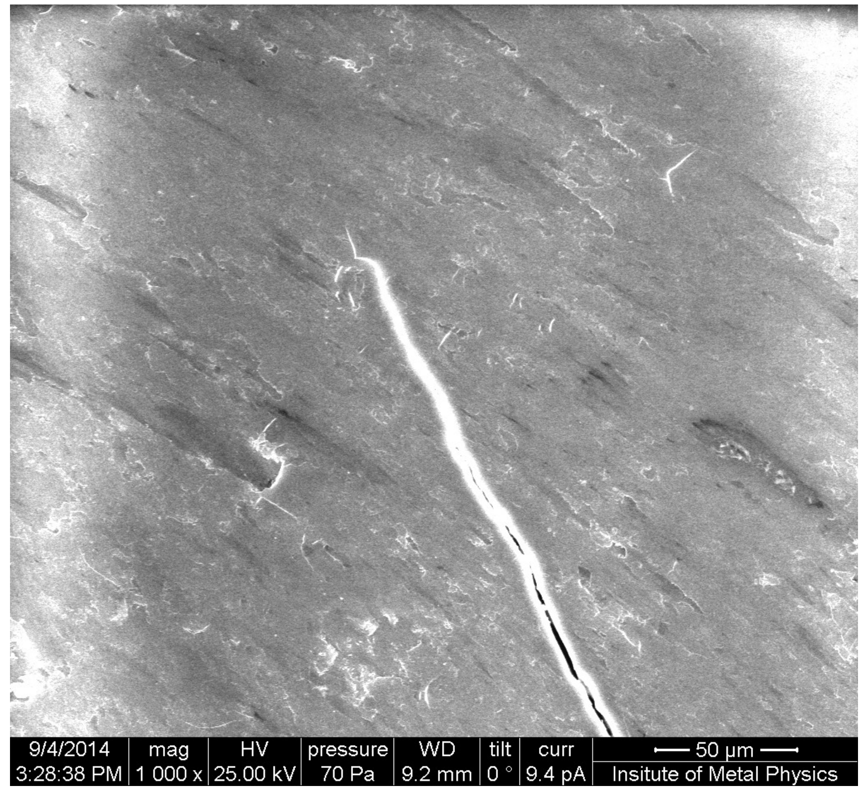
SiO_2- glass (amorphous)



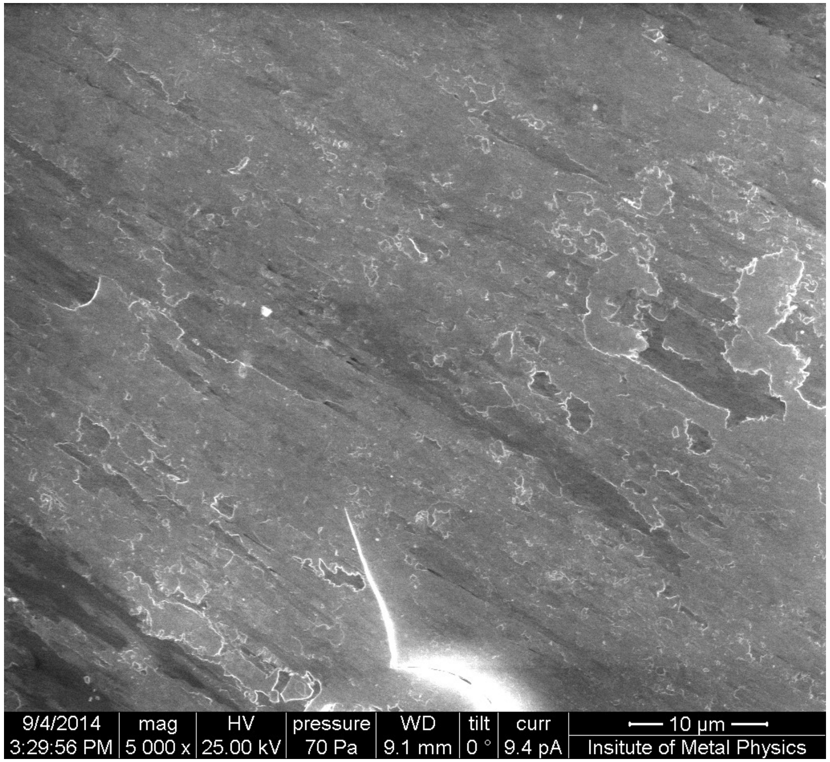


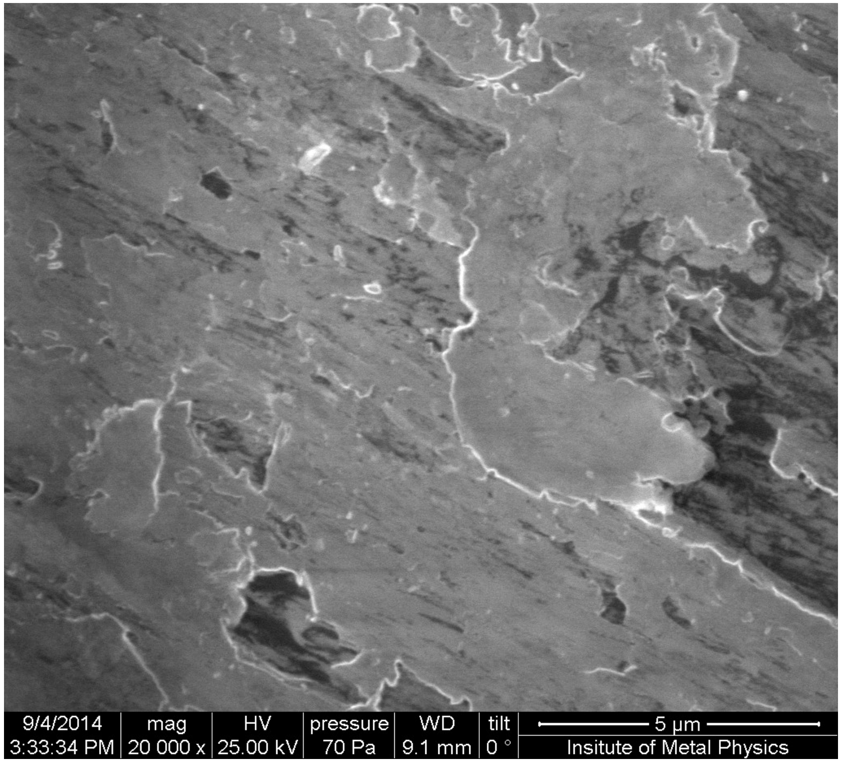
The microstructure of pressed glass powder. The pressure was 12 GPa, the deformation was relatively small (0.4-0.7), but "giant" for glass



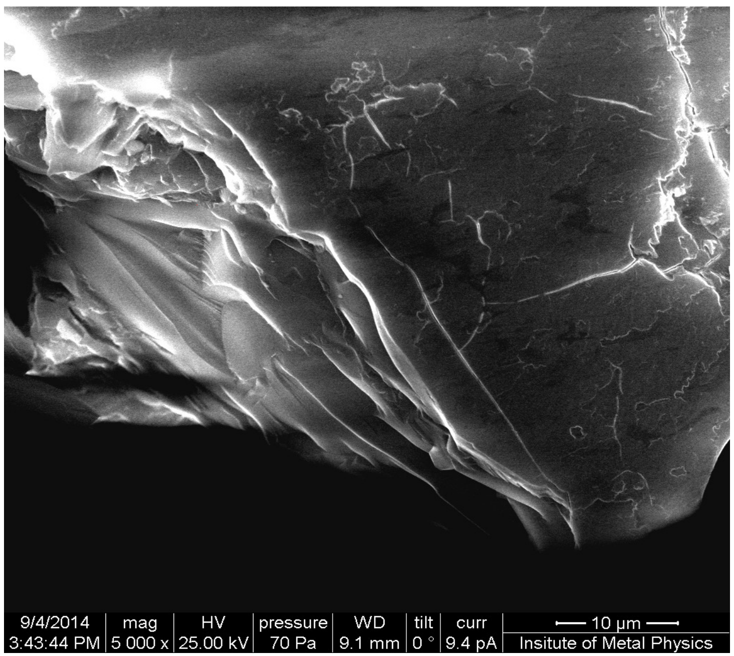


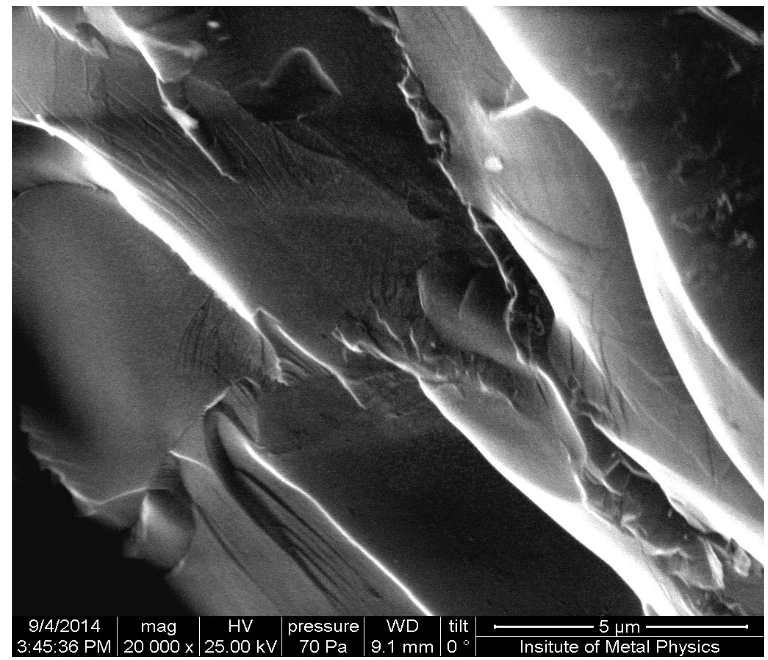
Microstructure of glass processed by strong compression. Particle section boundaries are inherited



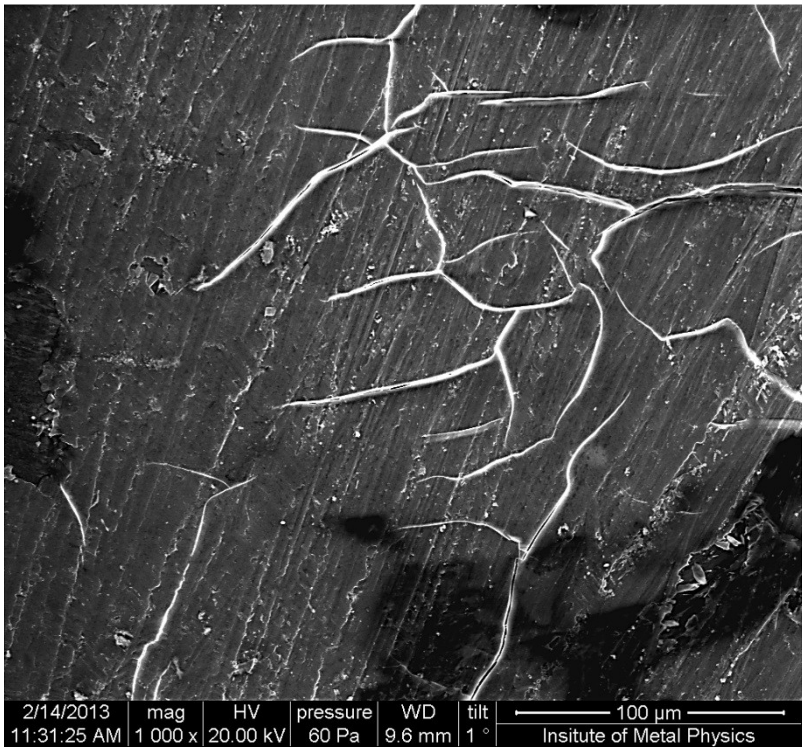


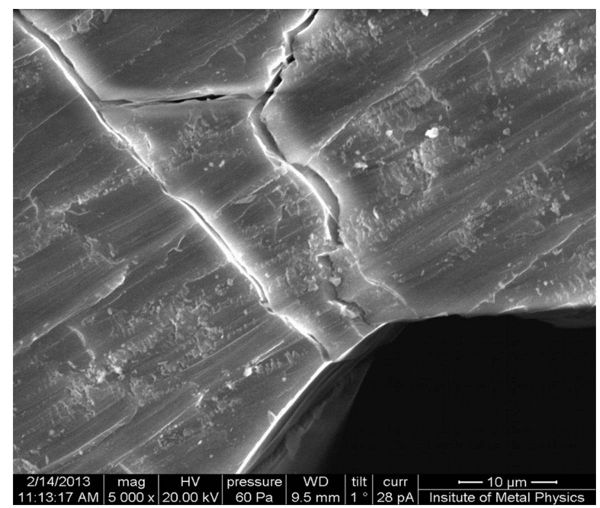
Cleavages of glass pressed by high pressure arisen after the subsequent unloading





The cracks in the pressed glass after unloading

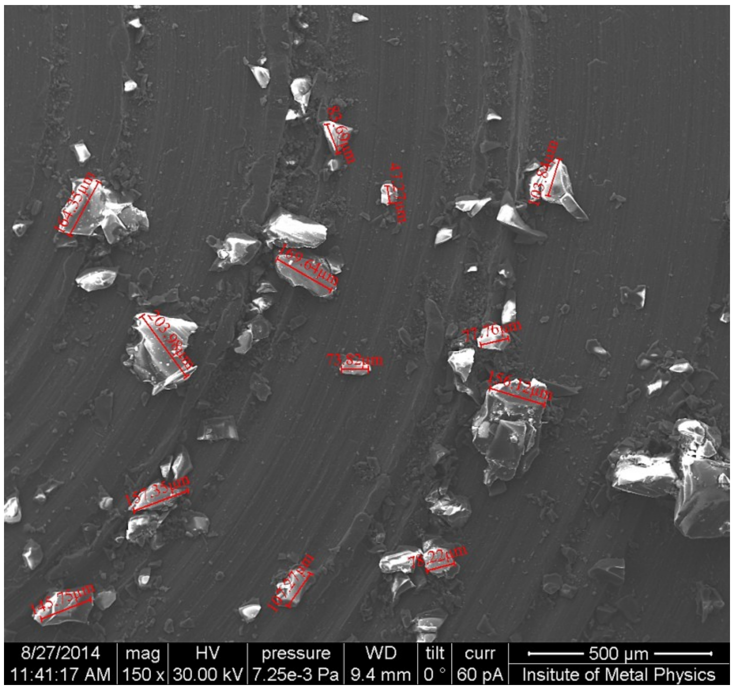


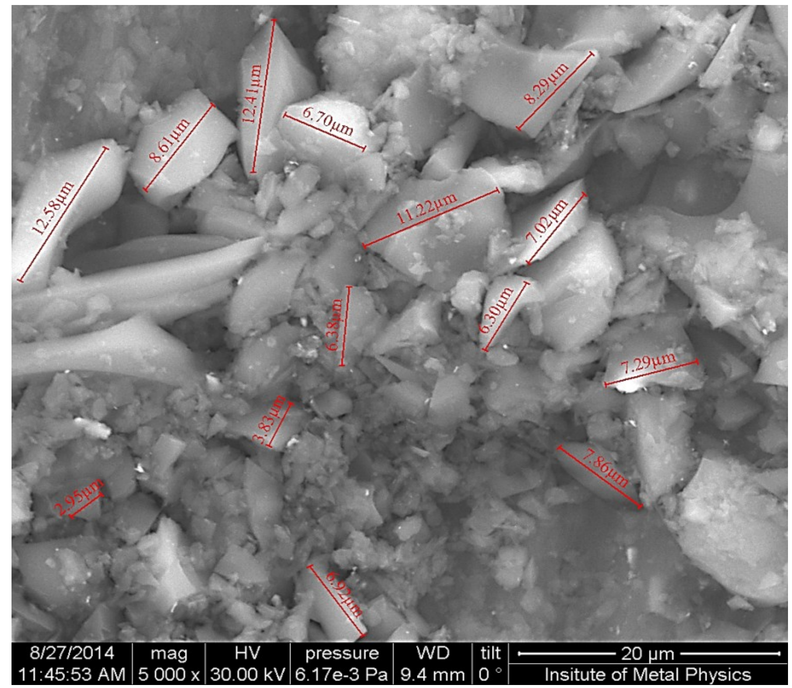


Quartz glass

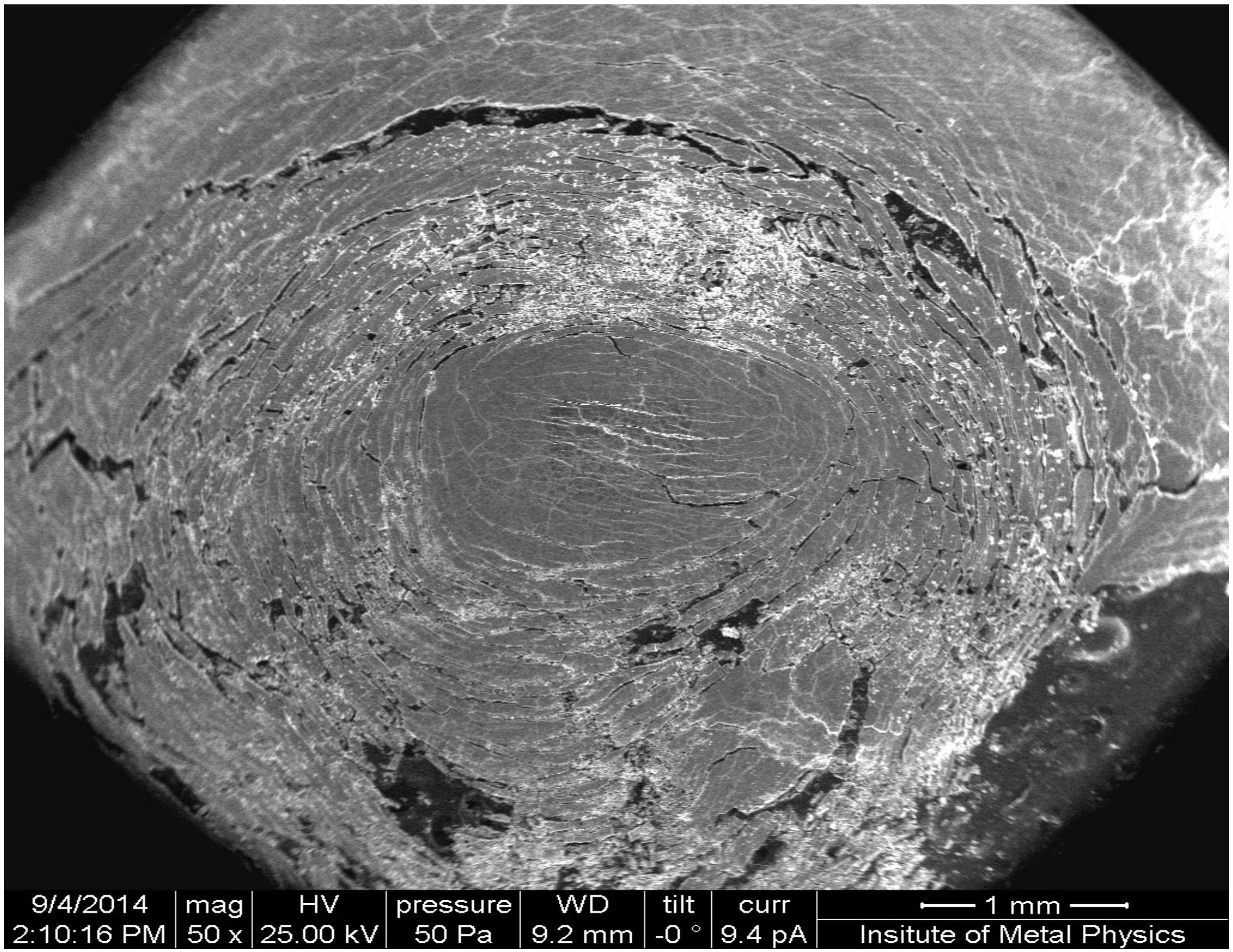
SiO_2

Quartz particles

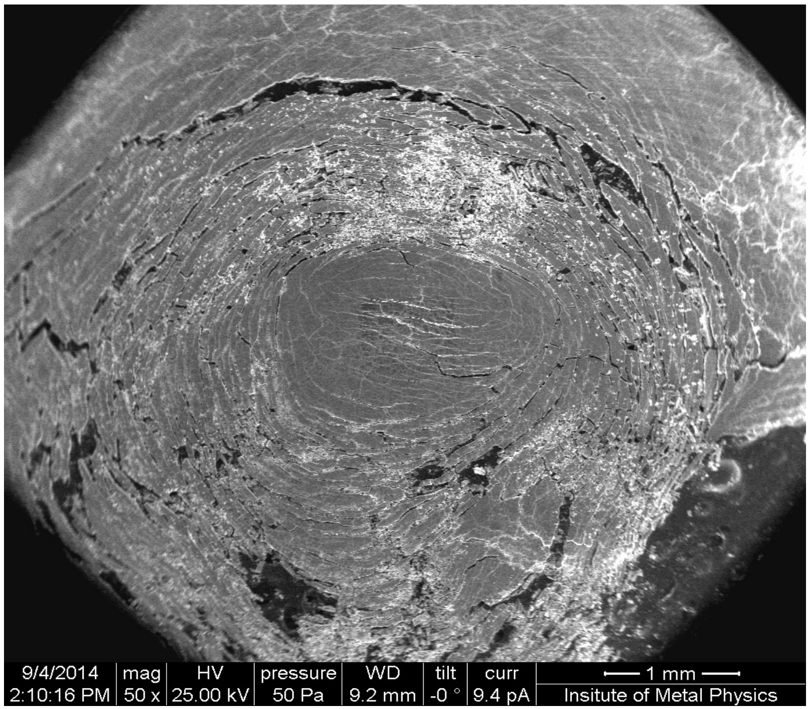


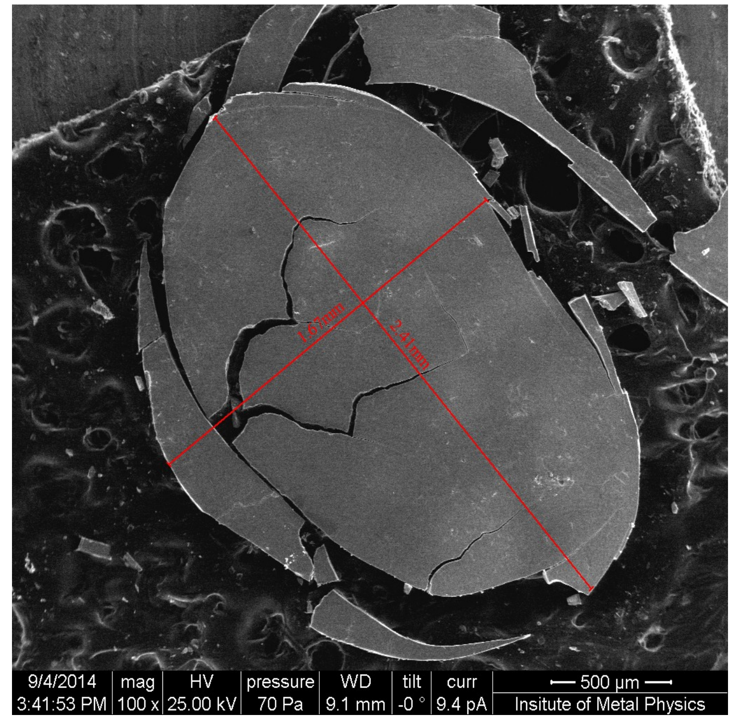


Pressed quartz SiO2 - the initial state of the crystal structure of the powder

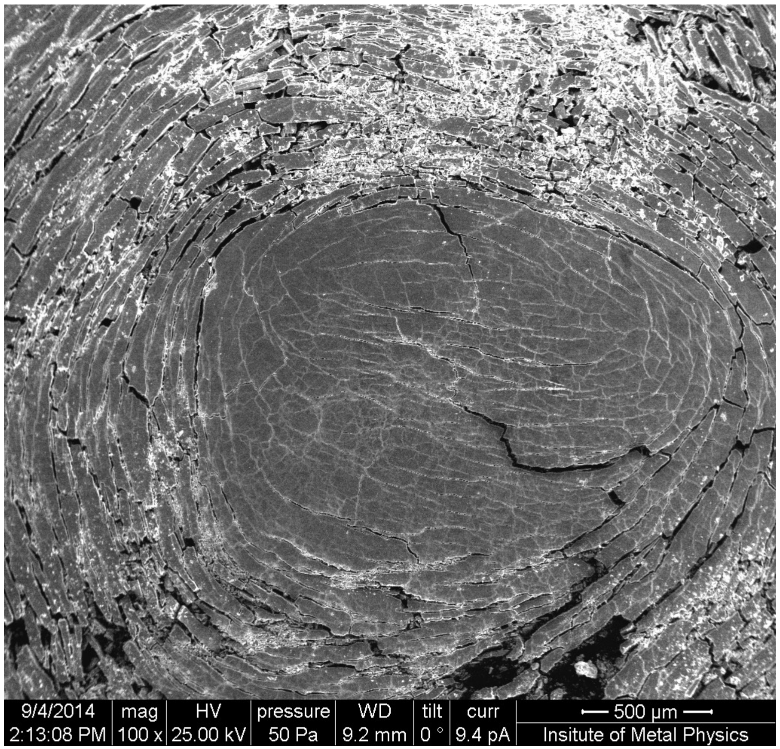


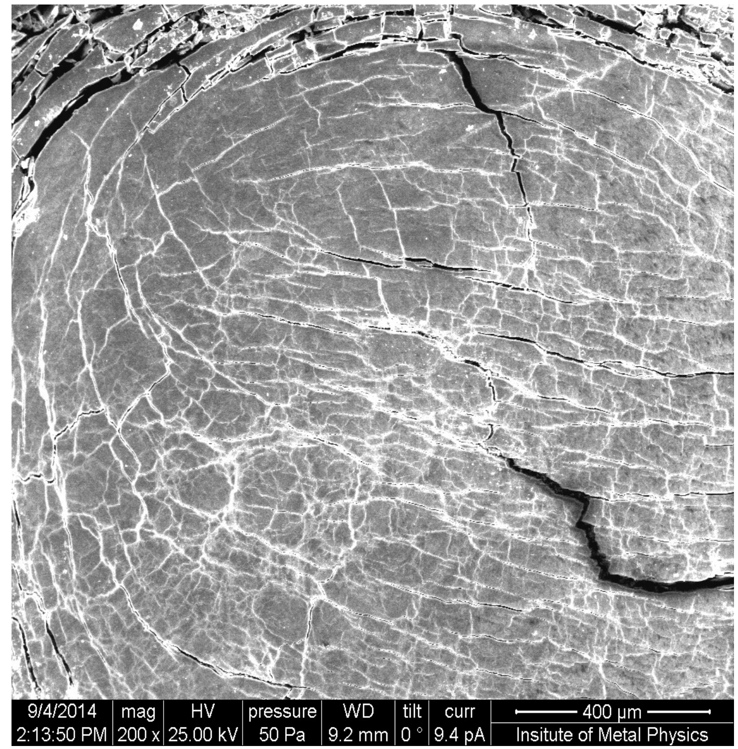
Various microstructural states of quartz and glass. Initially close powder state and identical processing conditions





Quartz SiO_2


9/4/2014 2:13:08 PM
mag 100 x
HV 25.00 kV
pressure 50 Pa
WD 9.2 mm
tilt 0 °
curr 9.4 pA
500 µm
Insitute of Metal Physics


9/4/2014 2:13:50 PM
mag 200 x
HV 25.00 kV
pressure 50 Pa
WD 9.2 mm
tilt 0 °
curr 9.4 pA
400 µm
Insitute of Metal Physics

Where this occurs?

Подкаменная Тунгуска
Podkamennay Tunguska

Lake Chebarkul. Chelyabinsk

Meteor crater Arizone

- At depths of 360-400 km first phase transitions from olivine to spinel are occures. Coesite SiO_2 t ≥ 300 C°, P = 1,5 GPa, artificial analogue of coesite was synthesized in 1953 by the American chemist Coesite (1915-1973). And in 1960, Eugene Shoemaker found the mineral in the quartz-bearing rocks in meteorite crater in Arizona. It was later approved as a mineral. Coesite stable in the pressure range of 28 - 95.5 kbar.
- At a depths of 650-700 km there is the second region of phase transitions. Stishovite – t ≥ 1200 C°, 12 GPa

- The principle possibility of a significant deformation of brittle materials (metal- and semimetal oxides and sulfides) at high pressure. Required superimposed pressure must have a value no less than the initial microhardness of the material values.

- Oxides and sulfides decomposition by shear under high pressure poses the problem of experimental determination of decay of silicon, aluminum and titanium oxides under high pressure and establishes a possible determination of their potential as the primary source of oxygen in the atmosphere of the planet. It is source metal deposits - tin, mercury, copper and others.

Результаты и выводы

- **При давлениях в диапазоне ГПа (верхняя и нижняя мантия Земли) при наличии сдвиговых напряжений (полосы сброса и локализации, разрушение и залечивание) происходит разрыв химсвязи у оксидов и сульфидов. Механизм - в градиенте напряжений существует направленное движение точечных дефектов (преимущественно вакансий в область меньшего сжатия), что является механизмом разделения атомов металла и окислителя.**

- **Существует пороговая скорость эффекта восстановления (разложения), для некоторых оксидов процесс идёт взрывным путём,**

Для оксидов с высокими значениями энтальпии (химически активных металлов) достичь и преодолеть динамическое равновесие «восстановление-окисление» можно только при экстремально высоких скоростях деформирования, при которых вкачиваемая энергия сопоставима с энергией связи решётки.

1. At pressures in the GPa range (lower and upper mantle) in the presence of shear stress (band reset and localization, fracture and healing) there is a gap of chemical bonds of oxides and sulphides. The stress gradient, there is directed movement of point defects (mainly vacancies in the area of the smaller grip), which is the mechanism of separation of metal atoms and oxidizer

2. There is a threshold speed of the recovery effect (decomposition), for a number of oxides, the process goes through explosive

3. For oxides with high values of enthalpy (reactive metals) to achieve and overcome dynamic equilibrium "reduction-oxidation" is possible only at extremely high deformation rates in which the power supply is comparable to the binding energy of the lattice.

Thank you for attention