

## JOINT ABSTRACT OF THE LECTURES 1 – 3 BY L. DUBROVINSKY

### High Pressure Chemical Crystallography: Methodology and Applications for Oxides, Nitrides, Halides, Hydrides, and Carbides

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High-pressure studies have had an enormous impact on fundamental physics, chemistry, and especially Earth and planetary sciences. Modern science and technology rely on the fundamental knowledge of matter provided by crystallographic studies. Chemical crystallography, a well-established discipline, is based on single-crystal X-ray diffraction (SCXRD) analysis, which enables structure determination and chemical characterization. Until recently, determining structures using SCXRD in a diamond anvil cell (DAC) at high pressures beyond 15 GPa was challenging. SCXRD analysis was considered inapplicable to materials synthesized at high pressures in a laser-heated (LH) DAC, as the products of chemical reactions are typically multiphase mixtures of microcrystalline solids. About a decade ago, our group pioneered an approach to SCXRD data collection and analysis for the products of chemical reactions in LH-DACs that led to the discovery of new materials with unique properties. However, it required certain training, crystal-chemical intuition, and experience. Since then, we have designed and built new instrumentation to enable sophisticated in situ experiments in-house and at synchrotron radiation facilities, and created powerful software (the Domain Auto Finder (DAFi) program) for studies of multiphase polycrystalline and microcrystalline (powder) materials. Our efforts have pushed the range of static pressures achievable in DACs up to 1 TPa and enabled single-crystal X-ray diffraction experiments under such extreme conditions. Structural studies at simultaneous high pressures of over ~200 GPa and temperatures of several thousand degrees have also become possible. This has led to remarkable findings in solid-state physics, mineral physics, and chemistry under extreme conditions, including the discovery of numerous, often unpredictable materials and insight into possible physical phenomena underlying their formation, chemical bonding, and properties.

The series of three lectures will cover (1) methodological aspects of the diamond anvil cell technique (diamond anvils; DACs preparation; pressure measurements; laser heating in DACs; SCXRD in DACs; analysis of diffraction data collected in DACs), (2) high-pressure oxides chemistry (effects of pressure on chemical composition and crystal chemistry of oxides; changes in structural types with compression on the example of dioxides; access to metastable states of oxides under pressure on the example of silica; novel high-pressure chemistry of iron oxides; effects of spin state on crystal chemistry of transition metal oxides; structure-properties relations in high-pressure oxide phases; variation of oxygen oxidation state and its significance for past and present of Earth), and (3) synthesis and properties of novel nitrides, halides, and carbides (why and how nitrides, halides, hydrides, and carbides should be synthesized under pressure; enhanced stability of polyanions under high pressures; how accurately theory predicts chemical composition and structures of high-pressure phases; fantastic crystal chemistry as a reason for fantastic properties; extremely incompressible and hard nitrides; unexpected possible origin of organic matter in the Universe; hopes and disappointments in the search for high-temperature superconductivity).

## **Application of high-pressure spectroscopy in the study of radiative recombination processes in semiconductor structures and transition metals/rare earth ions doped materials**

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High hydrostatic pressure generated in diamond anvil cell (DAC) is an efficient experimental tool allowing to obtain a lot of data that are difficult or not possible to get by other methods. In particular, it can be used to verify mechanisms of light emission in semiconductor structures and materials doped with optically active centers.

The application of hydrostatic pressure on direct bandgap semiconductors leads to an increase of the bandgap, and therefore to a regular blue shift of the photoluminescence (PL) energy. The linear change of the PL energy is generally referred to as the pressure coefficient  $dE_{PL}/dp$ . However, not always  $dE_{PL}/dp = dE_G/dp$ . There exist some phenomena that influence  $dE_{PL}/dp$  and also light emission properties and efficiency. They are the presence of localized donor states, conduction band filling and non-parabolicity effects, or built-in electric fields in polar structures, e.g. in nitride (In,Al,Ga)N and oxide (Zn,Mg)O semiconductors.

In the case of materials doped with optically active centers (which are mainly dielectrics or semiconductors doped with transition metals or rare earth ions), one of the most important issues in a deep understanding of PL mechanisms is to determine the location of dopant energy levels with respect to the valence and conduction bands of the host crystal, and a detailed investigation of the involved energy transfer processes. Since the application of pressure affects both the strength of the crystal field experienced by the dopant ion and the energy structure of the crystal matrix, high-pressure spectroscopy is very well suited for these purposes.

A short overview will be given on the studies of these phenomena conducted by the Group of High-Pressure Spectroscopy at IP PAS.

## Counterintuitive Volume-Pressure Relations

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It is a well-known paradigm of physics that the volume of any one phase is reduced by increasing pressure. In other words, the monotonic compression of one phase, defined as  $\beta = -(1/V)(dV/dp)|_{T=\text{constant}}$ , must be positive [1]. Sometimes the compression measurements can be confusing, due to some phenomena distorting the results. The negative-compressibility condition does not necessarily apply to the compounds undergoing chemical reactions [2]; when the compound changes its composition, for example, due to the sorption [3,4,5]; or when new phases are nucleated under high-temperature high-pressure conditions [6]. Most recently we found an example of the low-density preference for a high-pressure phase of a chemical compound [7], which challenges the assumption that high-pressure phases must be more dense than the low-pressure ones [1].

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## Quantum Crystallography of Crystals under Pressure

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In this communication, I will present what quantum crystallography is and give examples of testing crystals/minerals using various quantum crystallography methods. This includes quantitative experimental studies of electron density distributions in crystals, and applications of Hirshfeld Atom Refinement to structures with high hydrogen atom content. I will show how to improve the quality of the final refinement results of both X-ray data (single crystal and powder), but also electron diffraction data and other related methods, and how to obtain the local structure of crystals in the case of disorder.