

Studies of Nano-crystals at High Pressures-A Brief Guideline

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ABSTRACT

Nanoparticles are known to have distinct properties than their bulk counterparts. Besides, metastable or even amorphous phases of bulk materials with new properties can be synthesized in nanosize form. Both the understanding of nanomaterials properties and the synthesis of new phases of nanomaterials can be undertaken with the help of the application of static high pressures. High pressure techniques allow a precise control of interatomic distances in materials which is an invaluable way to investigate many fundamental and unique properties of nanoparticles. Furthermore, studies of nanocrystals at high pressures can lead to the synthesis of new nanomaterials since many high-pressure phases of bulk materials can be metastably recovered at ambient conditions after a high-pressure treatment of nanomaterials. In this work, we will review some of the capabilities of high pressure studies to understand nanoparticle properties and to create new nanomaterials by providing some examples. We will also present some of the most recent advances in the study of nanomaterials at high pressures.

I INTRODUCTION

Nanomaterials are materials with a length scale between 1 nm and 100 nm. They include 2D materials (nanolayers or monolayers like graphene), 1D materials (nanotubes and nanowires) and 0D materials (nanocrystals and quantum dots) but also 3D materials with framework structures with nanocages (fullerites, zeolites and clathrates). The different chemical properties of nanomaterials compared to bulk materials are related to the high surface/volume ratio of nanomaterials which results in a high surface energy which can be comparable to the volume energy. The different physical properties of nanomaterials compared to bulk materials are related to the occurrence of confinement of particles and quasiparticles in nanomaterials, like electron or phonon confinement. Therefore, the different properties of nanomaterials with respect to bulk materials depend very much on the system (surface energy of a certain crystal or amorphous structure, mean-free paths, scattering or coherent lengths) and it has been shown that many nanomaterials with sizes above 50 nm have properties similar to bulk materials. In general it can be stated that most nanomaterials display different chemical properties than bulk materials below 50 nm while most nanomaterials display different physical properties than bulk materials below 20 nm.

Nanomaterials are extremely sensitive to interactions with the environment due to the large number of atoms at their external or internal (porous) surfaces; therefore, the physical and chemical properties of nanomaterials can be very different from bulk materials and are highly dependent on the size, impurity or defect concentration and surface passivation. Furthermore, the high surface energy of nanomaterials opens

new paths for chemistry of new phases not available in bulk materials.

II PRESSURE EFFECTS

Pressure, like temperature, is an important thermodynamic parameter which allows an increase of matter density by reducing volume. The reduction of volume leads to an overall decrease of interatomic and intermolecular distances that allows exploring in detail atomic and molecular interactions. It is well known that changes in physical properties with increasing temperature are due to both volume changes (expansion at high temperatures) and phonon interactions (higher phonon energies available and higher population at high temperatures). However, changes in physical properties with increasing pressure are only due to volume changes; therefore, pressure is a more clean variable than temperature in order to explore the change in properties. Consequently, studies of materials at high pressures can provide a deep understanding of the materials properties at ambient conditions in order to design materials with improved properties.

III RESULTS AND DISCUSSION

The values of pressures in laboratory which can be applied to materials (10^6 bar) exceeds by three orders of magnitude the changes in temperature which can be applied to materials (10^3 K). Therefore, application of high pressures can induce changes in the free energy of materials that exceed those of the strongest chemical bonds present at

ambient pressure (>10 eV) thus leading to phase transitions which can result in new phases of materials (many of them recoverable at ambient conditions) with new properties. The most common example is diamond, a meta-stable phase of carbon at ambient conditions which can be obtained by pressurizing graphite at high temperatures. In this respect, it is noteworthy to mention that pressure can completely redistribute electronic densities and change the nature of the chemical bonds thus leading to profound changes in materials, like converting insulators into metals and soft chemical bonds into stiff bonds. Therefore, the Periodic Table of Elements gets a new dimension at high pressures since elements under compression develop redefined affinities, electronegativity and reactivity.

On the other hand, studies of materials at high pressures are very important for technological applications. For instance, the determination of the lattice parameters or the phonons of a material at high pressures allows the estimation of the tensile or compressive strain suffered by thin layers in a number of devices. Similarly, the determination of the stability of a phase of a certain material at high pressures is important to foresee the conditions of applications of that material under tensile or compressive strains.

The studies of nanomaterials at high pressures date back to 1967 [1] but gained a renewed interest in the last two decades. Among the studies of nanomaterials at high pressures we can distinguish between those corresponding to physical and chemical properties.

Physical properties can be subdivided into structural and mechanical properties, vibration properties, optical properties, transport properties and thermal properties. In particular, structural properties have shown different lattice parameters and bulk modulus of nanomaterials than in bulk materials and different phase transformations and phase transformation pressures in nanomaterials than in bulk materials [2, 3]. Vibration properties have shown abnormal effects due to internal and external compensation of pressures in nanocrystals and phonon confinement effects [4]. Finally, optical properties have shown electron and hole confinement effects [4] and enhancement of photoluminescence in some nanomaterials.

IV CONCLUSION

Studies of chemical properties at high pressures in nanomaterials have shown many synthesis routes of new nanomaterials. In particular, it has been shown the transformation of nanomaterials either by collapse of open framework structures [5] or due to phase transformations (crystal-crystal, crystal-

amorphous, amorphous-amorphous). Chemical reactions between nanomaterials have been observed like polymerization of fullerenes or nanomaterials [6]. Finally, the interaction between the nanomaterial and the pressure-transmitting medium in high-pressure studies has been observed to lead to intercalation of the medium in nanostructures or nanocages [7], or to chemical reactivity of nanomaterials and the medium, which depends on surface passivation of nanomaterials. Finally, it must be highlighted that new experimental techniques are being developed in the last years which open new and exciting possibilities to study nanomaterials at high pressures [8-10]

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