

Application of Powder Diffraction Methods to the Analysis of Short- and Long-range Atomic Order in Nanocrystalline Diamond and SiC: the Concept of the Apparent Lattice Parameter (*alp*)

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Abstract. Two methods of analysis of powder diffraction patterns of diamond and SiC nanocrystals of different grain size are presented: (1) examination of changes of the lattice parameters ("*apparent lattice parameter*", *alp*) with the diffraction vector Q , which refers to Bragg scattering, and (2), examination of inter-atomic distances based on the analysis of the atomic Pair Distribution Function, PDF. Application of these methods based on theoretical diffraction patterns computed for models of nanocrystals having either a perfect, uniform crystal lattice or a core-shell structure constituting a two-phase system was studied. The models are defined by the lattice parameter of the grain core, thickness of the surface shell and the magnitude and the strain field distribution in the shell. X-ray and neutron diffraction data of nanocrystalline SiC and diamond powders of grain diameters from 4 nm up to micrometer range were analyzed. The effects of the internal pressure and strain at the grain surface on the structure, based on the experimentally determined dependence of the *alp* values on the Q -vector, and changes of the inter-atomic distances with the grain size determined experimentally by the atomic Pair Distribution Function (PDF) analysis are discussed. The experimental results lend strong support to the concept of a two-phase, core and the surface shell structure of nanocrystalline diamond and SiC.

Introduction

In polycrystals with micrometer size grains, the surface contains an insignificant fraction of the total number of atoms and its effect on the overall properties of the material can be ignored. The situation is different for small, nano-size particles where, due to the size, a considerable fraction of the atoms is located at the surface, i.e. where some of their neighbors are missing. Such a situation always leads to changes in the lengths of inter-atomic bonds of the surface atoms relative to those in the bulk. To date, no specific experimental methods have been developed for the structural analysis of the surface of nanocrystals and therefore information on the arrangement of atoms at the surface of nanograins is very limited. This work presents analyses the applicability of powder diffraction techniques for elucidation of the atomic structure of nanocrystals, particularly at the surface shell.

In a number of publications detailing changes in the physical properties of nanocrystals related to their size [1 - 9] the dependencies reported are often related to the lattice parameters which, for very small crystals, appear to be a size dependent property of the material. A dependence of the lattice parameters on the grain size have been reported for a variety of nanomaterials, like metals (Au [10, 11], Al [12], Cu [13]), semiconductors (CdSe [14], GaN [15]), ionic crystals (NaCl, KCl, NaBr, LiF [16], Y₂O₃ [17]), and others (e.g. Se [18]). Those results are often attributed to the presence of an "internal pressure" caused by surface stresses [19 - 28]. The stresses are located at the surface and a quantitative evaluation and description of this property of nanocrystals would require precise determination of the inter-atomic distances in the grain interior and the surface.