Critical Pressure for Weakening of Size-induced Stiffness in Si$_3$N$_4$ and CeO$_2$ Nanocrystals and the Resulting Mechanism

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Nanocrystalline materials with particle sizes of 1-100 nm are of current interest because they display novel physical and chemical properties that may differ from those of their corresponding bulk materials [1]. The structural stability of nanocrystalline material is of particular interest, especially when related to first-order transformations, because of its relevance to many research areas, including the engineering of materials with enhanced mechanical properties [2]. Previous high-pressure studies indicated a correlation between increasing transition pressure and decreasing particle size, or vice versa. These nanocrystals exhibit a higher bulk modulus than their bulk counterparts. However, recent investigations demonstrate that the compressibilities of materials with a large stability range of pressures (i.e. they do not undergo first-order transformations) do not change with particle size. In order to explore the potential mechanism and connection between these two types of compression behaviors, we selected recently synthesized cubic-spinel structure Si$_3$N$_4$ and cubic CeO$_2$ nanocrystals. The samples were studied by using a Diamond Anvil Cell together with high-resolution synchrotron radiation. Our results indicate that the particle size effect on compressibility becomes insignificant above a critical pressure for the two nanocrystals.

As shown in Figure 1, the compressibility of spinel Si$_3$N$_4$ nanocrystals increases when the pressure is raised above ~40 GPa [3]. Si$_3$N$_4$ nanocrystals initially exhibit an extremely high bulk modulus of 685(45) GPa. But, above 40 GPa, the bulk modulus is reduced to 415(10) GPa. Thus, a critical pressure of ~40 GPa was determined that signifies the onset of size-induced weakening of elastic stiffness in nanocrystalline Si$_3$N$_4$. The same pressure-induced phenomenon was observed in CeO$_2$ nanocrystals (Figure 2) [4]. The pressure induced weakening effect takes place at ~20 GPa. The bulk modulus was reduced to 230(10) GPa from 328 (12) GPa. Enhanced surface energy contributions to the shell layers of nano-particles and the resulting effect on the corresponding large d-spacing planes are used to easily explain the increased bulk modulus below the critical pressure, but the pressure induced weakening effect still remains unclear.

![Fig 1: The EOS curves fitted from the volumetric data obtained at pressures below and above 40 GPa, respectively. Note: data obtained previously and at decompression in this study are also presented for comparison.](image1)

![Fig 2: Room temperature equation-of-state data for bulk and nanocrystalline CeO$_2$.](image2)
In order to explore such a novel pressure-induced phenomenon, we combined the bulk pressure standard platinum and CeO$_2$ nanocrystals to compare the pressure induced growth of particle size [4]. As shown in Figure 3, comparison of line broadenings of x-ray diffraction peaks of platinum standard and CeO$_2$ indicates that a significant growth of particle size in CeO$_2$ appears at a pressure of ~20 GPa. Thus, it is concluded that the weakening of elastic stiffness is due to a pressure-induced growth of particle size. This study provided a reasonable explanation for the existing irreconcilable compression behaviors of different nanocrystals.

![Graphs showing FWHM vs Pressure for Platinum and CeO$_2$ Nanocrystals](image)

Fig 3: Comparison of the FWHM of x-ray of 111 diffraction peaks between platinum standard and CeO$_2$ nanocrystals under pressures.

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