

**The Trend of Neutron-Scattering Studies of Hard Materials\***

C.-K. Loong

Intense Pulsed Neutron Source Division  
Argonne National Laboratory, Argonne, Illinois 60439, U. S. A.

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Corresponding author:  
Chun Loong  
IPNS, Bldg. 360  
Argonne National laboratory  
9700 S. Cass Ave  
Argonne, IL 60439-4814  
U. S. A.  
Tel: 708-252-5596  
FAX: 708-252-4163  
Email: loong@anlpns.pns.anl.gov

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# The Trend of Neutron-Scattering Studies of Hard Materials

C.-K. Loong\*

*Institute of Materials Structure Science  
High Energy Accelerator Research Organization,  
Tsukuba, Ibaraki 305, Japan  
and*

*Intense Pulsed Neutron Source Division  
Argonne National Laboratory, Argonne IL 60439 U. S. A.*

## I. Introduction

Future high-tech applications will undoubtedly demand materials for carrying out complex tasks under stringent or adverse conditions. One of the important goals in materials design is to be able to introduce specific desirable properties in the components at an early stage during fabrication and to predict the performance of the final product. This approach requires a database of atomic-level structures and response of a variety of key materials and sophisticated algorithms for large-scale computations. Slow (cold to epithermal) neutrons probe the organization and dynamic response of atomic nuclei and electrons in a substance (bulk and low-dimensional) thereby providing a valuable means for a microscopic interpretation of materials properties. For decades neutron technologists and instrument scientists have striven to improve the neutron sources and instrumentation for condensed-matter research. In this International Workshop of the JHF Projects and the N-Arena, I wish to comment on the trend of instrument development, using some recent studies of hard materials as an example.

The requirement for high strength at high temperatures has led to intense studies of nitride- and carbide-based ceramics. Additional incentives include the lower density, lower thermal expansion, and better corrosion and oxidation resistance of ceramics as compared to metals. However, the current strength and reliability of nitride and carbide ceramics are not sufficient to replace the metallic counterparts such as heat engine components. The knowledge of atomic short-to-long range ordering, the microstructure of the crystalline grains and intergranular phases as well as the dynamic response of atoms to applied force and temperature fields is an important prerequisite for the realization of wide-spread high-temperature applications of ceramics. The goal of neutron-scattering methodology is to provide the best means for high-resolution characterization of these

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\* E-mail: [ckloong@anl.gov](mailto:ckloong@anl.gov), Web Site: <http://www.anl.gov>

properties over a wide range of length and time scales ( 0.1 - 1000 nm and  $10^{-8}$  -  $10^{-13}$  sec). Obviously, many different kinds of instruments have to be developed in parallel with the advancement of neutron sources.

## II. The Present

Presently, neutron diffraction is widely used to probe the atomic and spin organization. Multiple phrasal analyses of crystal structures are now routinely applied. Partial structure factors of atom-atom correlations in liquids and amorphous materials can be obtained from measurements of specimens with selective isotopic substitution. The penetration power of neutrons in most materials provides the opportunity of surveying the interior of large (~centimeters) samples. As the resolution of the diffractometers improves, various intrinsic properties such as crystalline or magnetic domain size, microstrains, defects or faults, and residual strains can be measured. Small-angle scattering enables the measurements of microstructure such as pore/particle distribution over a matrix, phase separated precipitates (and the magnetic analogs) of size up to about 500 nm. Larger-scale structures up to  $\mu\text{m}$  in ceramics can be investigated from the analysis of the multiple-scattering profiles. The atomic or magnetization density variation and mass transport across an interface can be studied by neutron reflectometry. Atomic vibrations (phonons) are the principal excitations responsible for the thermodynamic behavior of insulating or semiconducting ceramics. Quasielastic and inelastic scattering obtained from neutron spectroscopy permit a direct measurement of the underlying atomistic or spin dynamics. Detailed information regarding the atomic motion in a crystalline or disordered system can be obtained through joint analysis of the measured dynamic structure factors,  $S(\mathbf{Q}, E)$  where  $\mathbf{Q}$  and  $E$  are the neutron wavevector and energy transfer, respectively, and molecular-dynamics (MD) simulations, lattice-dynamics modeling, or calculations of the dynamic correlation functions.

In the following some aspects of the above techniques are illustrated by recent studies of the  $\text{SiO}_2$ - $\text{Si}_3\text{N}_4$ - $\text{AlN}$ - $\text{Al}_2\text{O}_3$  system. Silica is one of the most widely used and studied ceramics.

Nevertheless, the structure and dynamics of many of the high-pressure crystalline phases as well as the amorphous phase of silica are still not well understood. A full measurement of the  $S(\mathbf{Q}, E)$  of amorphous silica was realized by pulsed-source chopper spectroscopy, elucidating the short-to-medium range order structure.<sup>1</sup> Recently, more detailed neutron measurements and theoretical

studies have thrown new light on the nature of low-energy boson-peak and acoustic-phonon-like excitations in vitreous silica.<sup>2, 3</sup>

Silicon nitride has been at the forefront of research for high-temperature, high-strength materials. The combination of low thermal expansion and high strength results in superb thermal-shock resistance, and the strong covalent bonding between the atoms gives rise to high resistance to mechanical deformation and chemical corrosion. The crystal structures and phonon excitation spectra of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  powders were determined by neutron diffraction and inelastic scattering, respectively.<sup>4</sup> The neutron data were compared favorably with the results MD simulations which also reproduced correctly the bulk modulus and lattice specific heat.

Aluminum nitride is an electronic ceramic which exhibits high electrical resistivity, good dielectric strength, a thermal expansion coefficient closely matching that of silicon, non-toxicity and outstanding thermal conductivity. These properties make AlN ideal for microelectronic substrate applications. Furthermore, densified AlN has high strength, high thermal stability and corrosion resistance. Therefore, it can potentially be used under extreme conditions. Recently, the phonon density of states (DOS) of AlN was determined by time-of-flight neutron spectroscopy using a polycrystalline sample.<sup>5, 6</sup> A rigid-ion model was applied to the interpretation of the data. After optimization, the model provided a satisfactory description of the neutron results as well as the Raman and IR data, sound-velocity measurements and the lattice specific heat. The partial and total DOS and the phonon dispersion curves along major symmetry directions of the Brillouin zone were calculated, and the contribution of phonons to the Debye behavior of the low-temperature thermal conductivity was compared with other ceramics of diamond-like structures.

Transitions of various crystalline phases of alumina occur over a wide range of temperatures (~300-1200°C). Depending on the chemical routes in synthesis, heat-treatment temperatures, atmospheric conditions and other factors, these intermediate phases, collectively referred to as transition aluminas, often coexist metastably in a gel or powder. Porous aluminas are widely used as catalytic supports for noble metals in various chemical processes and automobile-emission control. The effect of rare-earth dopant on transformations of the  $\gamma \rightarrow \theta \rightarrow \alpha$  phases in fine alumina powders under vacuum was investigated by *in situ* neutron diffraction from 500 to 1300°C.<sup>7</sup> Addition of 1 mol% of La in  $\text{Al}_2\text{O}_3$  was found to be effective in the retardation of the  $\alpha$ -phase formation temperature from ~1125°C for pure alumina to ~1250°C.

Automotive catalytic powders of the  $\text{CuO-Al}_2\text{O}_3$  system, designated for NO removal under lean-burn engine conditions, were investigated by diffraction and small-angle scattering<sup>8</sup> for the purpose of determining the microstructural evolution, phase transitions and thermal durability of the catalysts. A sequence of  $\gamma\text{-Al}_2\text{O}_3 + \text{CuO}$  to  $\gamma$ -phase  $(\text{Cu}, \text{Al})_2\text{O}_3$  solid solution to  $\alpha\text{-Al}_2\text{O}_3 + \text{CuAl}_2\text{O}_4$  transformations were identified with the corresponding heat-treatment temperatures. The evolution from the almost mass-fractal-like aggregate of crystalline particles with micro- and mesoporosity to a random packing of coarsened, solid particles was observed. These observations, as considered in conjunction with results from nitrogen adsorption isotherm, ESR and NO removal measurements, indicate that the low-temperature phases and the fractal-like aggregate are important to the high efficiency of NO conversion.<sup>9</sup>

The high melting point, excellent electrical resistivity and high hardness of corundum ( $\alpha\text{-Al}_2\text{O}_3$ ) make it attractive for applications ranging from wear-resistant and electrically insulating components to biomedical implants. The phonon DOS was investigated by neutron-scattering and MD simulations using an optimized ES+ model.<sup>10</sup>

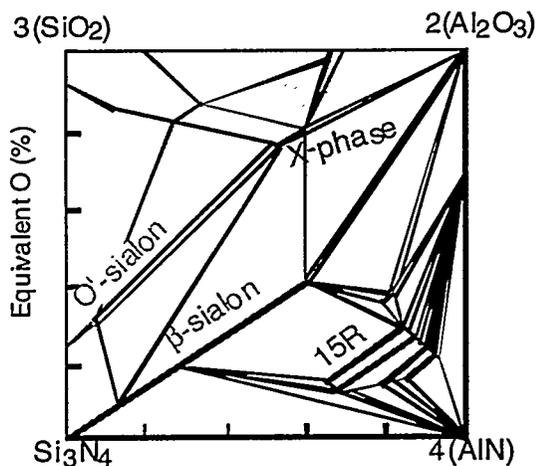


Figure 1. The phase diagram of the  $\text{SiO}_2\text{-Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$  system.

### III. The Future

The accumulative experience from experimental and MD investigations of the parent ceramics has paved the way for studying the ceramic alloys in the  $\text{SiO}_2\text{-Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$  system, as shown in Fig. 1. The alloy system contains a variety of new phases some of which may represent new

ceramics offering combined merits of their parent materials. Currently, knowledge regarding the atomic structures and thermophysical behavior of these solution phases is far from complete. In the SiO<sub>2</sub>-rich region of the phase diagram, the readiness of forming liquid and glassy phases and lower temperatures facilitates the binding of Si<sub>3</sub>N<sub>4</sub>-based crystalline grains to form dense green bodies. However, the presence of intergranular glass residues is known to degrade the modulus of rupture at high temperatures. So far only a correlation between the crystal structures and phonon spectra with the strength of Si<sub>6-2z</sub>Al<sub>2z</sub>O<sub>2z</sub>N<sub>8-2z</sub> (0 ≤ z ≤ 6) including β-sialons (see Fig. 1) was investigated by neutron scattering and mechanical-property measurements.<sup>11-13</sup> Currently, the X-phase of approximate composition of Si<sub>3</sub>Al<sub>6</sub>O<sub>12</sub>N<sub>2</sub> formed near the liquid-phase region has not been well characterized. The O'-sialons, Si<sub>2-x</sub>Al<sub>x</sub>O<sub>1+x</sub>N<sub>2-x</sub> (0 < x < 0.2), are isostructural to Si<sub>2</sub>N<sub>2</sub>O whose structure is not as robust as Si<sub>3</sub>N<sub>4</sub>. Other crystalline phases of AlONs including Al<sub>3</sub>O<sub>3</sub>N and a number of polytypoid phases which are structurally related to the wurtzite-type structure of AlN have not been fully explored by neutron and MD studies.

The observed phonon DOS from neutron spectroscopy is essential to the validation of interatomic potentials employed by MD simulations. Once the reliability of the interparticle potentials for the key substances is verified by comparing with the static structure, atomic dynamics, and other macroscopic thermal and mechanical behavior, new composite materials with tailored properties may be “fabricated” by computer-aided simulations.<sup>14</sup> For example, following the confirmation of the structural and dynamics of crystalline and amorphous Si<sub>3</sub>N<sub>4</sub> with neutron results as well as elastic and thermodynamic data, Kalia, Vashishta and co-workers have extended the MD studies to sintering and fracture dynamics of Si<sub>3</sub>N<sub>4</sub> ceramics by large-scale simulations with parallel computers.<sup>15-17</sup> Recently, the oxidation dynamics of nanophase aluminum clusters was investigated by MD simulations.<sup>10</sup> This in turn gives rise to new predictions of materials properties to be examined experimentally.

The next-generation neutron sources like the JHF N-Arena are expected to provide a neutron flux increase of 4-8 times of that of the ISIS facility which is currently the most powerful spallation source. Neutron-scattering studies at these new sources will throw new light on important issues such as fracture dynamics and chemical reactions in materials. However, the sufficiency of intensity is still a concern in kinetic studies of pin-point locations within a sample. New flux-

conserving, Q-space focusing devices have to be designed and tested. Accommodating sample environments to allow extreme conditions or concurrent multiple probes have to be adapted. More efficient and reliable detector arrays have to be developed. Sophisticated data acquisition and visualization hardware and software have to be implemented. In order to achieve these goals, neutron scientists and engineers should collaborate to exchange information, set priorities, share experience and resources in the development of new neutron instruments. This international workshop sets a good example.

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