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**NEUTRON-SCATTERING STUDIES OF NITRIDE, OXIDE, AND PHOSPHATE
CERAMICS AND THEIR RELATIONSHIP WITH MOLECULAR-DYNAMICS
SIMULATIONS OF HIGH-TEMPERATURE PROPERTIES***

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NEUTRON-SCATTERING STUDIES OF NITRIDE, OXIDE, AND PHOSPHATE CERAMICS AND THEIR RELATIONSHIP WITH MOLECULAR-DYNAMICS SIMULATIONS OF HIGH- TEMPERATURE PROPERTIES

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1. Introduction

At room temperature the tensile strength of typical steels varies from 1 to 1.4 GPa, which is two to three times of the flexure strength of the toughest sintered ceramics like silicon nitride or silicon carbide. Therefore, there is little incentive to develop strong ceramic materials for applications under ambient conditions. However, at 1100°C metals soften and become useless, yet the strength of ceramics is essentially unchanged. Moreover, at high temperatures ceramics in general have higher hardness, lower density, lower thermal expansion, and better corrosion and oxidation resistance than metals. Hence advanced ceramics are the major contenders for high-temperature applications. Currently, the strength and reliability of nitride and carbide ceramics are not sufficient to meet the demands of high-tech applications such as heat engines. A large R & D effort is needed to advance the field of ceramic science and engineering.

The strength of ceramics depends on both the nature of atomic bonding such as covalency versus ionicity and the microstructure such as flaws and stress within the materials. The length scale of these influential factors ranges from 0.1 to 5000 nm, thus presenting a challenge to experimentalists for a complete, quantitative characterization. The method of neutron scattering provides distinct advantages:

- Neutrons probe directly the vibrating nuclei and the unpaired electrons through nuclear and magnetic scattering, respectively. Phonon measurements are not restricted by selection rules;
- Neutrons penetrate into the bulk of matter typically of dimensions in centimeters;
- The scattered intensities afford a direct comparison with molecular-dynamics (MD) simulations or model calculations;
- The technique is nondestructive. Experiments can be carried out *in situ* under conditions emulating certain processing conditions; and
- Measurements can be made to be more element specific by using isotopic substitution or tuning to nuclear resonance of selected nuclei.

As a result of densification, alloying, transformation toughening, and/or composite reinforcement, practical ceramics inherently contain defects, noncrystalline impurity phases, anisotropies, and inhomogeneities. Neutron diffraction yields information about the atomic organization (crystal structures) and the location of residual strains in the final products. Small-angle scattering enables the measurements of microstructure such as pore/particle distribution over a matrix, phase separated precipitates of size up to about 500 nm. The density profile 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. The phonon density of states (PDOS) obtained from neutron spectroscopy permits a direct measurement of the underlying atomistic dynamics. Structural information alone is not sufficient to model the force fields for atomic interactions and the excited states. A comparison of the observed PDOS with that from MD simulations is essential to the validation of inter-particle potentials.

In this paper, we present the neutron-scattering results of several important nitride oxide, and phosphate ceramics and point out the connections between the neutron data and computer simulations towards to the goal of designing high-temperature materials.

2. The $\text{SiO}_2\text{-Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$ 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. Silicon nitride has been at

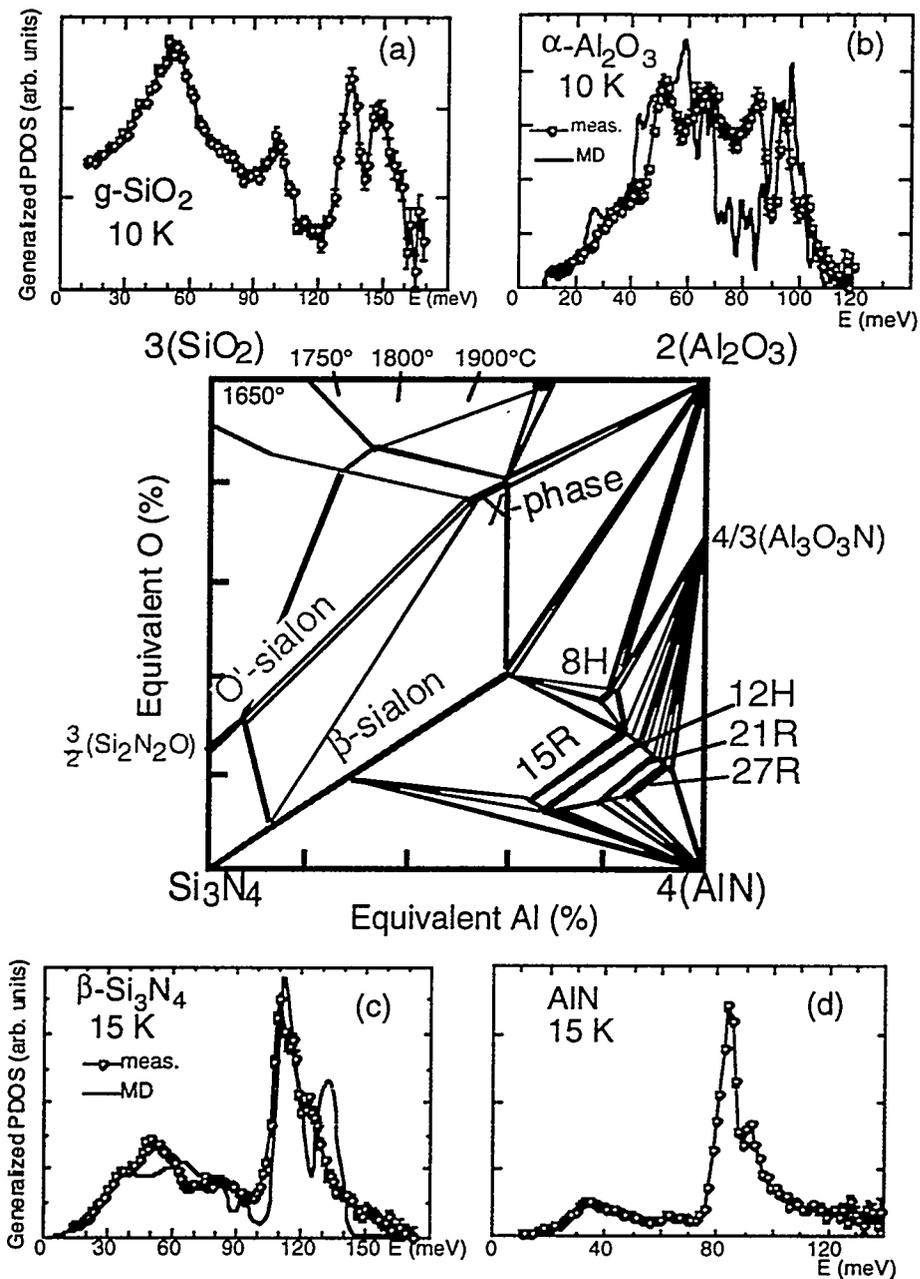


Figure 1. (Central panel) The phase diagram of the $\text{SiO}_2\text{-Si}_3\text{N}_4\text{-AlN-Al}_2\text{O}_3$ system. (after [1]) The observed and MD simulated generalized (neutron-weighted) phonon densities of states of (a) $g\text{-SiO}_2$, (b) $\alpha\text{-Al}_2\text{O}_3$, (c) $\beta\text{-Si}_3\text{N}_4$, and (d) AlN . The lines connecting the data points are guides to the eye.

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. Aluminum nitride is an electronic ceramics which features, among other desirable properties, good dielectric strength and outstanding thermal conductivity. Corundum (α -Alumina) is well-established as a technologically useful ceramic. The high melting point, excellent electrical resistivity and high hardness make this substance attractive for applications ranging from wear-resistant and electrically insulating components to biomedical implants. The solid solution of the SiO_2 - Si_3N_4 - AlN - Al_2O_3 system, as shown in Fig. 1, contains a variety of new phases some of which may represent new ceramic alloys offering combined merits of their parent materials.[1] Currently, knowledge regarding the atomic structures and thermophysical behavior of these solution phases is far from complete. In order to facilitate the prediction of materials properties over different phase regions, the structure and dynamics of the parent phases must first be determined by experiments and successfully modeled by simulations.

The observed PDOS of monolithic vitreous SiO_2 and crystalline Si_3N_4 , AlN and Al_2O_3 are shown in Fig. 1(a)-(d). The neutron inelastic experiments were performed using a time-of-flight chopper spectrometer at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Details of the experimental procedure were given elsewhere.[2] The MD simulations were carried out by Kalia and co-workers at Louisiana State University.[3, 4] MD simulations of the structure and dynamics of vitreous and crystalline phases of silica have been undertaken by many authors, including those presented new results in this Proceedings. A preliminary MD simulation and a lattice-dynamics calculation of the phonon spectrum of AlN have been carried out.[5] Among these four parent materials, the investigation of the microscopic properties of Si_3N_4 by computer simulations has progressed to a new level of sophistication recently. Following the confirmation the structural and dynamics of crystalline and amorphous Si_3N_4 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_3N_4 ceramics by large-scale simulations with parallel computers.[6-8] It appears that the accumulative experience from experimental and MD investigations of these parent ceramics has paved the way for studying the ceramic alloys in the SiO_2 - Si_3N_4 - AlN - Al_2O_3 system, which is a step closer to tailoring and predicting materials properties for technological applications.

In the SiO₂-rich region of the phase diagram (Fig. 1) the readiness of forming liquid and glassy phases and lower temperatures facilitates the binding of Si₃N₄-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. The determination of crystal phases, the microstructures, and the phonon densities of states is an important first experimental step. Currently, the X-phase of approximate composition of Si₃Al₆O₁₂N₂ formed near the liquid-phase region has not been well characterized.[9] The O'-sialons, Si_{2-x}Al_xO_{1+x}N_{2-x} (0 < x < 0.2), are isostructural to Si₂N₂O whose structure is not as robust as Si₃N₄. [10] Other better known crystalline phases include Al₃O₃N and a number of polytypoid phases which are structurally related to the wurtzite-type structure of AlN. The β-sialons, Si_{6-z}Al_zO_zN_{8-z} (0 < z < 4), are isostructural to β-Si₃N₄. They retain many of the desirable properties of Si₃N₄ and the alloying provides a better handle in the fabrication of useful ceramic components.[1, 11]

3. Si_{6-z}Al_zO_zN_{8-z} (0 ≤ z ≤ 6) Including β-Sialons

Sialon ceramics as structural materials are usually densified by hot pressing or hot isostatic pressing methods. Recently, reaction-sintered β-sialon ceramics have been fabricated using aqueous slurries by a slip-casting technique.[12] Such a technique has an obvious advantage, namely, the capability of forming relatively complex shapes by using inexpensive plaster molds. The fabrication process, mechanical properties, and crystal structures of this slip-cast materials, Si_{6-z}Al_zO_zN_{8-z} (0 ≤ z ≤ 6), have been reported.[2, 12, 13] Here we present the results of a neutron-scattering measurement of the PDOS.

Fig. 2 shows the observed PDOS of selective Si_{6-z}Al_zO_zN_{8-z} (0 ≤ z ≤ 6) ceramics and a pure β-Si₃N₄ powder. The spectra of β-sialons (0 ≤ z ≤ 4) show a one-phonon DOS extending to ~170 meV with two broad bands centered at about 50 and 115 meV. The low-energy region (< 40 meV) involves mainly the lattice vibrations of the tetrahedra network. The 50-meV and 115-meV bands may be assigned to bending and stretching of the Si(Al)-N(O) bonds, respectively. The DOS of the z = 0 ceramic resembles closely that of the Si₃N₄ powder[3] excepting the somewhat sharper features in the powder sample. This probably reflects a larger strain distribution over the crystalline grains in the ceramic sample resulted from the sintering process. As Si and N are replaced by Al and O in the z ≥ 1 samples, the

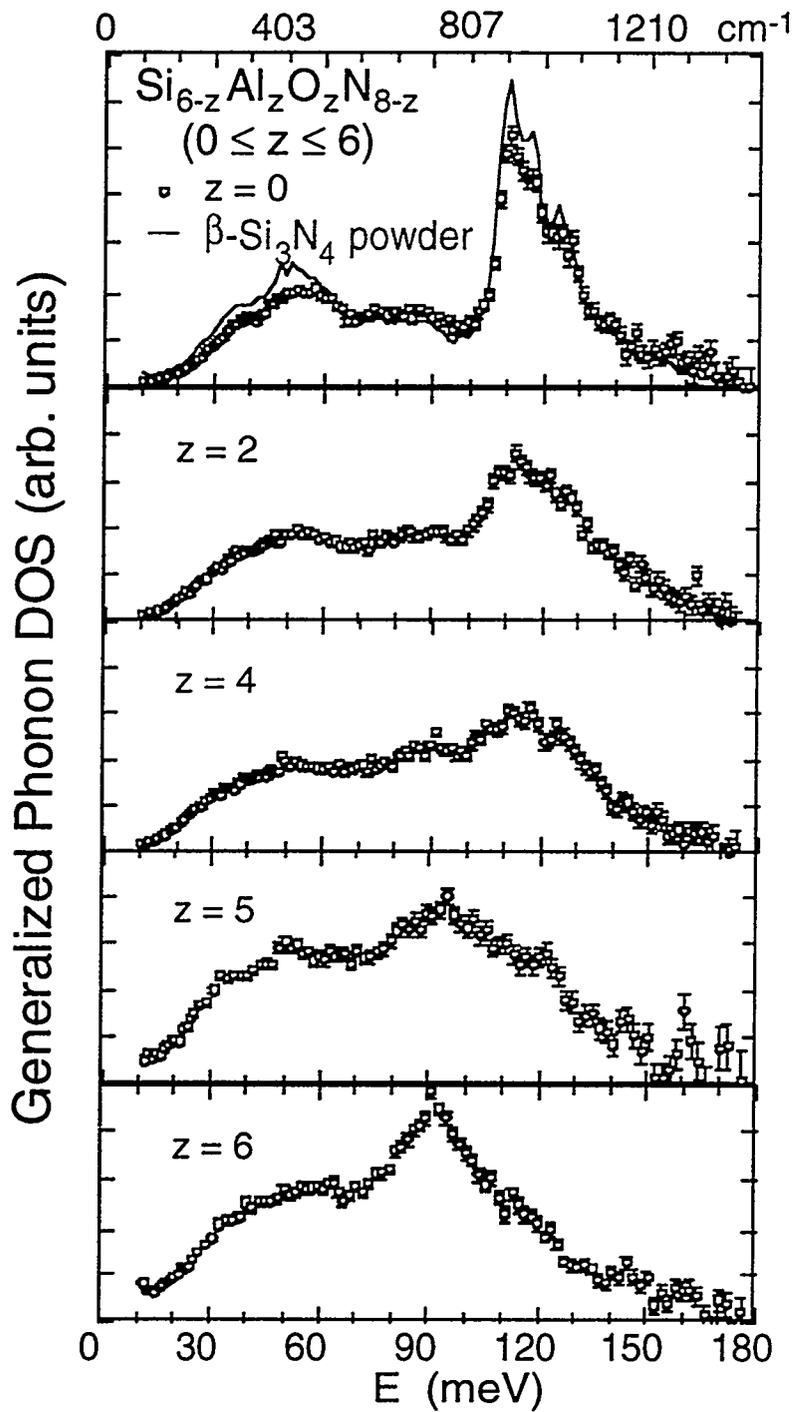


Fig. 2 The observed generalized (neutron-weighted) phonon densities of states of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ for $z = 0, 2, 4, 5$ and 6 .

two vibrational bands broaden and the phonon densities in the 60-90 meV and 130-150 meV regions increase progressively. A slight increase of density below ~30 meV as increasing z can also be seen. Thus the atomic dynamics shows a distinct response to the bonding environment due to chemical disorder over a wide range of vibrational frequencies.

$\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ does not form single-phase materials for $z > 4$. Instead, complex multiple crystalline phases were observed.[13] Only a minute portion (~6%) of β' -sialon phase remains in $\text{SiAl}_5\text{O}_5\text{N}_3$. The predominant phase in the $z = 5$ sample is $\alpha\text{-Al}_2\text{O}_3$. The predominant phase in the $z = 6$ sample was identified as the cubic phase $\text{Al}_3\text{O}_3\text{N}$ having the same structure as Al_2MgO_4 . This explains the drastic difference between the PDOS of the $z \leq 4$ and the $z = 5 - 6$ materials. In fact, the PDOS of the $z = 6$ sample resembles a superposition of the PDOS of $\alpha\text{-Al}_2\text{O}_3$ and AlN . Given the existence of data on the crystal structures, phonons, and mechanical properties of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ ($0 \leq z \leq 6$) ceramics, it is of interest to extend the MD simulations of Si_3N_4 to this system and calculate the high-temperature properties.

4. Rare-Earth Phosphate and Alumina Ceramic Composites

In order to meet the demands of diverse technological applications, ceramists develop composite materials so as to take advantage of the complementary properties of different components. The capability of computer assisted design of composites based on data of the individual components and knowledge of the interfaces is very important, otherwise designers are confronted with a vast range of compositions over which the properties cannot be optimized solely based on chemical insights in the starting materials. Recently, two-phase composites consisting of rare-earth orthophosphates and alumina were found to be machinable, and alumina fibers coated with rare-earth phosphates were superior to bare fibers in the prevention of fiber puncture.[14] These phenomena are thought to be related to the relatively weak interfaces between alumina and phosphates.

We have recently carried out a systematic study of the magnetic and phonon properties of RPO_4 compounds ($\text{R} = \text{La, Ce, Nd, Tb, Dy, Ho, Er, Tm, Yb}$ and Lu).[15] In particular, the phonon dispersion curves along major symmetry directions and the PDOS of LuPO_4 were measured by neutron scattering using single-crystal and powder samples, respectively.[16, 17] The phonon data were analyzed by a lattice dynamics shell model. Figs. 3 and 4 display the measured and calculated phonon spectra of LuPO_4 . The lattice specific heat from the model

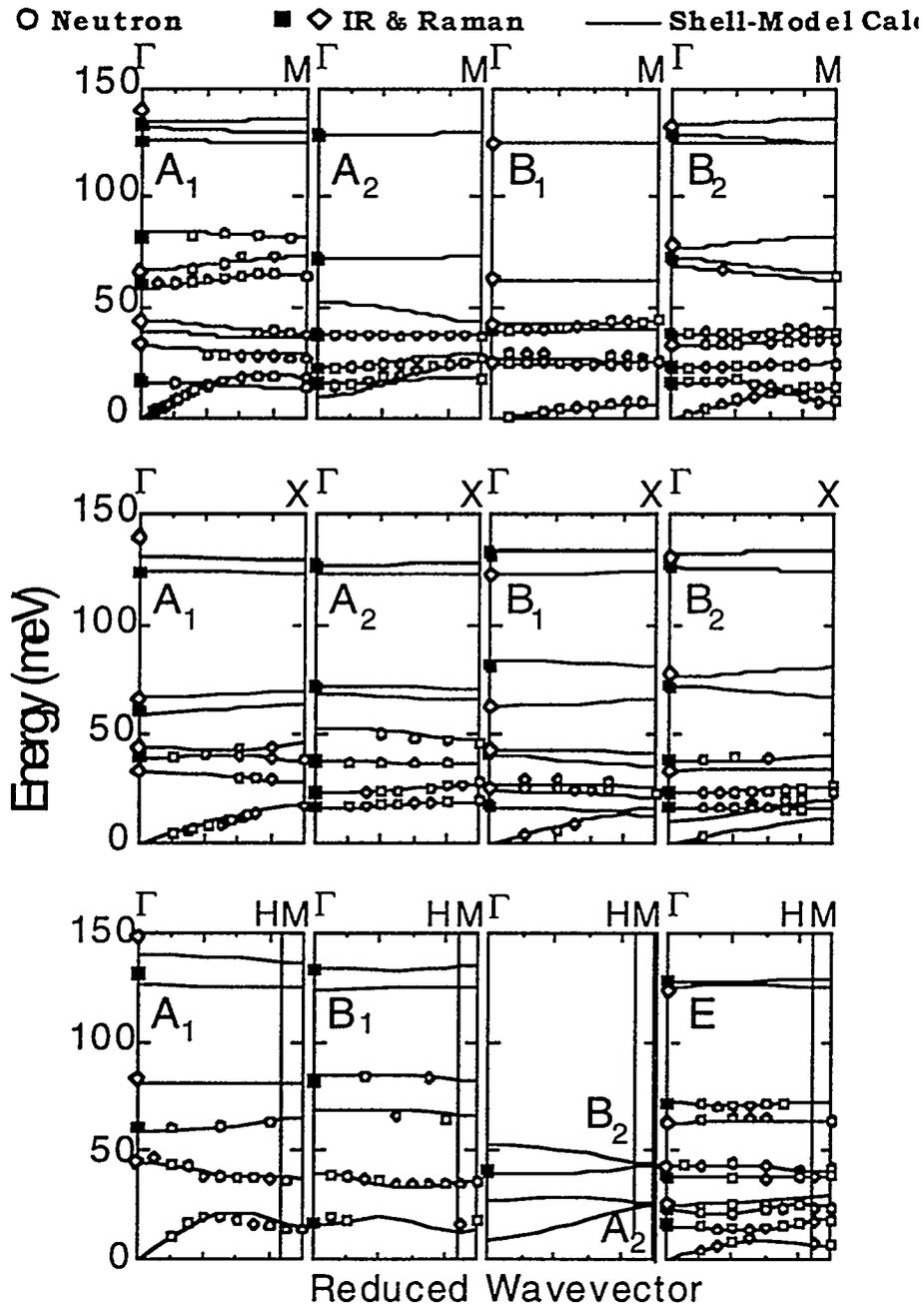


Fig. 3 The measured and observed phonon dispersion curves of LuPO_4 at 15 K. The phonon branches along various symmetry directions in the body-centered tetragonal Brillouin zone of zircon-type are labeled according to group theoretical analysis.[16, 17]

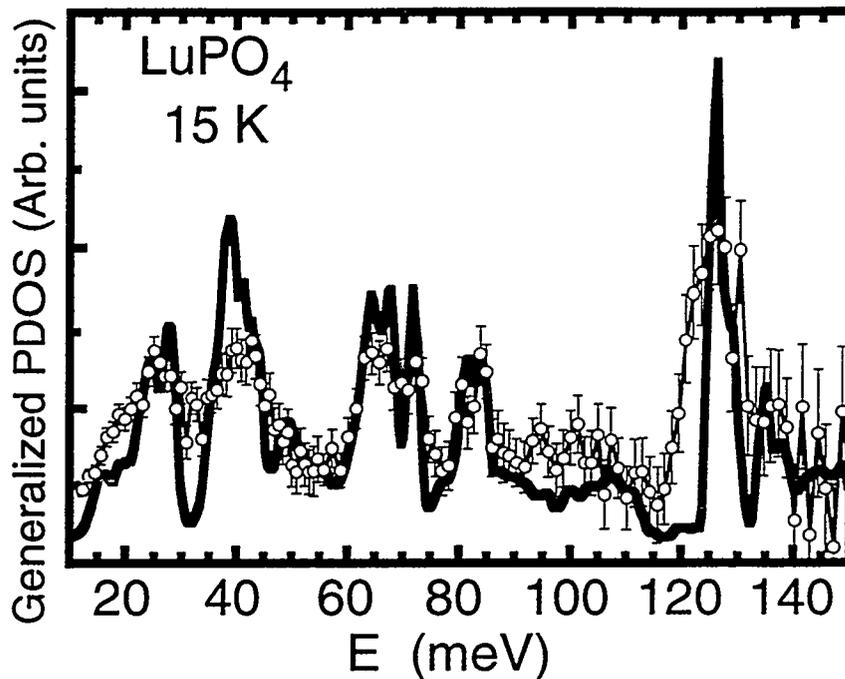


Fig. 4 The observed (symbols) and calculated (line) generalized (neutron weighted) phonon density of states of LuPO_4 .

calculations agrees very well with the experimental values in the literature.[16]

An atomistic simulation of the $\text{RPO}_4\text{-Al}_2\text{O}_3$ composites can, in principle, be carried out using the structural and dynamic information of alumina and LuPO_4 based on the neutron data and an adjustable interfacial interaction scheme. Because of the high melting points ($\sim 2000^\circ\text{C}$ for RPO_4 and 2051°C for $\alpha\text{-Al}_2\text{O}_3$) and the chemical inertness, this ceramic composite system is expected to exhibit many attractive properties at high temperatures.

5. Summary

Fundamental microscopic properties, such as crystal structures and phonon density of states obtained from neutron-scattering experiments are the key information for large-scale molecular dynamics simulations of realistic materials properties. The joint neutron and MD study of Si_3N_4 ceramic is an important step for the eventual prediction of high-temperature behavior. We have presented the phonon results from neutron measurements of important monolithic ceramics SiO_2 , Si_3N_4 , AlN , $\alpha\text{-Al}_2\text{O}_3$, and LuPO_4 as well as ceramic alloys of $\text{Si}_{6-z}\text{Al}_2\text{O}_z\text{N}_{8-z}$ ($0 \leq z \leq 6$). These

data are useful for further computer simulations of high-temperature properties of β -sialons and $\text{RPO}_4\text{-Al}_2\text{O}_3$ composites.

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