

Neutron characterization of aluminium nitride nanotubes

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The results of experiments carried out at the ILL neutron facilities in Grenoble on nanotubes of aluminium nitride synthesized through a DC arc plasma process are presented. We discuss the phonon generalized density of states $G(\omega)$ of the nanotubes in comparison with bulk AlN. $G(\omega)$ for the bulk features two main bands at low (about 30 meV) and high (about 80 meV) frequencies. Both bands are completely smeared out in the nanomaterial indicating a broad distribution of force constants induced by structural disorder. Apart from the smearing out of the vibrational bands, we observe enhanced intensities at low frequencies ($\omega < 10$ meV) as usually found in disordered systems. Two additional bands at 12 and 17 meV hint at pure aluminium regions within the nanomaterial. The observed changes in the microscopic dynamics must lead to appreciable differences in the thermal and transport properties of the nanotubes with respect to the bulk material. Powder diffraction experiments show sharp lines from crystalline regions superimposed on a high and rather unstructured background.

Keywords: Neutron diffraction; Aluminium nitride; Nanotubes; Nanoparticles

1. Introduction

Aluminium nitride is a wide band-gap semiconductor ($E_g = 6.2$ eV) with very good optical and piezoelectric properties. It has very high thermal conductivity ($k = 2$ W/cm K, i.e. 5–6 times larger than Al_2O_3) and is one of the best ceramic materials with very low thermal expansion coefficient ($\Delta a/a = 4.2 \times 10^{-6}/\text{K}$ and $\Delta c/c = 5.3 \times 10^{-6}/\text{K}$) and high electrical resistivity. It is highly resistant to chemical reactions and melts at 3700°C at atmospheric pressure. A wide range of work function values has been reported for AlN (from 3.9 to 5.35 eV). In addition to being a good dielectric material (dielectric constant $\epsilon = 4.8$), it is also optically transparent to visible light and exhibits attractive piezoelectric properties (suitable for surface acoustic wave device applications) and yields a potential candidate for the realization of UV light sensors.

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The methods for its synthesis are common to most nanophase materials:

- inert gas phase condensation;
- plasma synthesis;
- laser ablation;
- laser pyrolysis;
- sol-gel synthesis;
- electrochemical etching; and
- ball milling

Nanotubes of aluminium nitride have been synthesized by thermal arc plasma process and characterized by various techniques [1,2]. These nanotubes have a large size distribution that is typical of the high temperature plasma synthesis process. The tubes were analysed both by transmission electron microscopy and scanning tunneling microscopy and were found to form in typically two size ranges: (a) larger tubes of diameter 25–30 nm and lengths of ~ 700 nm and (b) smaller tubes of 2–3 nm with length scales of ~ 700 nm. X-ray diffraction analysis of these samples revealed the material possessing a rare metastable cubic phase (zinc blend structure). Fourier transform infrared spectroscopy studies showed that the vibration modes were pushed more towards higher wavenumbers in the mid-infrared as compared to the bulk aluminium nitride. The smaller tubes have helicoidal structure and the bigger ones have hollow tubular structure [2]. Although the bulk AlN has a large band-gap of 6.2 eV, the corresponding nanotubes have a much lower band-gap varying with the tube diameter (right from metallic behaviour to semiconducting behaviour of 5.1 eV). The structure and phonon spectrum of bulk aluminium nitride is known from the literature and rather well understood on theoretical grounds [3]. The phonon density of states strongly resembles that of SiC, another wide band-gap semiconductor. In contrast to the case of bulk AlN, so far AlN nanotubes are rather less studied. The lack of theoretical understanding makes it difficult to predict the related physical properties. Nanotubes have many interesting applications, including those based on particle channeling through micro and nanostructures [4,5]. AlN nanotubes are potential candidates for applications as gas sensors. We explore the catalytic properties of AlN nanotubes through experimental measurement of neutron diffraction.

2. Experimental details

Powder samples of AlN have been measured on the time-of-flight instruments IN4 (thermal neutrons with an incoming energy of $E_i = 25$ meV and an elastic resolution of 0.9 meV) as well as IN6 (cold neutrons with an incoming energy $E_i = 4.8$ meV and an elastic energy resolution of 0.3 meV). Both instruments were used in the up-scattering mode (neutron energy gain) with IN6 time focussing in the inelastic region. The very high-energy end of the spectrum has equally been investigated with the Be—filter instrument IN1-BeF in down-scattering mode.

Apart from the bulk (commercial powder), we studied two nanomaterial samples, one consisting of nanotubes and the other of more spherically shaped nanoparticles [1,2]. It turns out (see figure 1) that the microscopic dynamics is very similar for both types of nanomaterial. Special care was taken to avoid contamination of the sample with water. In the case of IN4, we used sealed Al containers. For IN6 and IN1-BeF the samples were wrapped in Al-foil and heated to 400 K under dynamic vacuum. The time-of-flight data were corrected for container scattering and detector efficiency and then converted to a generalized, i.e.

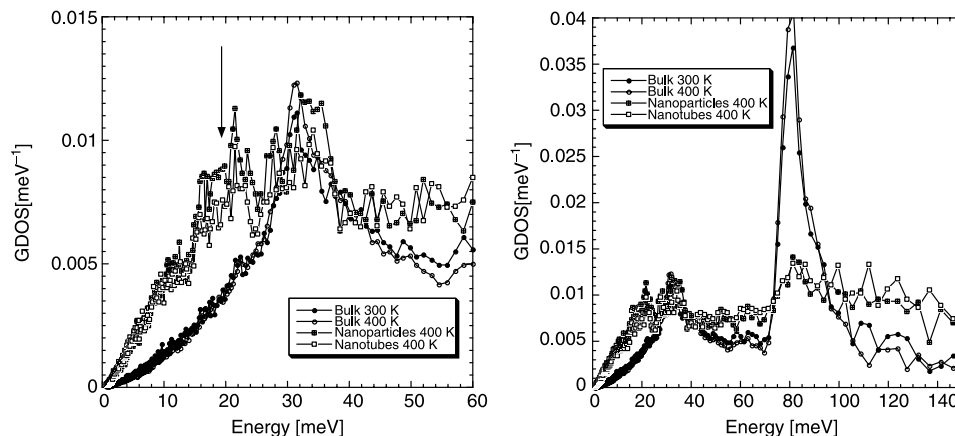


Figure 1. Generalized densities of states $G(\omega)$ as obtained on the instrument IN6 for AlN bulk, nanotubes and nanoparticles. The low-frequency region is shown to the left the total spectrum to the right. The AlN bulk powder has been measured both at room temperature and 400 K. All samples were in dynamic vacuum to avoid water contamination.

neutron scattering power weighted, density of states $G(\omega)$ using the incoherent approximation [6]. Comparison of IN4 and IN6 data shows good agreement within the respective resolution limits demonstrating the validity of the incoherent approximation. Due to better statistics of the IN6 data, we will not present the IN4 results in detail here. In the case of the Be-filter the measured data correspond to a particular cut through $Q-\omega$ space. Apart from coherence effects the recorded intensities for high energies and low temperatures ($\hbar\omega \gg kT$) correspond to the generalized density of states.

Diffraction data were taken on the instrument D20 using the wavelength of 1.3 Å in high-resolution mode.

3. Experimental results

The $G(\omega)$ obtained for bulk AlN on IN6 (figure 1) and IN1-BeF (figure 2) agrees nicely with published data [3]. It consists mainly of two bands centered around 30 and 80 meV. The higher band is split as best visible on the IN1-BeF data due to the better resolution at these high energies. Please note that the generalized density of states is dominated by the vibrational contributions of nitrogen due to the several times larger scattering power.

The clear structuring into bands observed in the bulk is neither present in the nanoparticles nor in the nanotubes. Peaks around 30 and 80 meV still remain but they are extremely weak as observed both on IN6 and IN1-BeF. There is a new low-frequency band centered on about 17 meV clearly visible in the IN6 spectra (figure 1). The bulk still shows a pure Debye behaviour ($G(\omega)$ proportional to ω^2) in this region. In addition to this band, there is a large enhancement of $G(\omega)$ down to the lowest frequencies. This enhancement is so pronounced that no Debye-region can be identified for the nanomaterial within the used experimental resolution.

The extra band at 17 meV resembles that observed in bulk aluminium and thus can be attributed to regions within the sample that are composed of pure aluminium. In fact, the nanomaterial does not possess the ideal bulk stoichiometry but features a net excess of Al as obtained from atomic probe characterization.

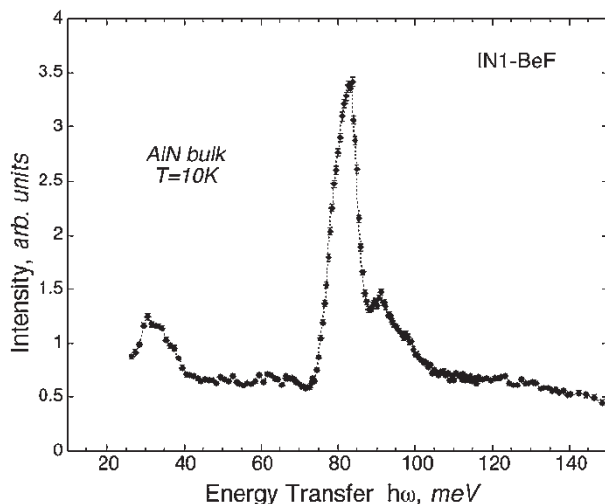


Figure 2. Spectrum measured for bulk AlN on IN1-BeF. The agreement with the IN6 measurement (figure 1) is very good. Due to the better resolution at high energies the fine structure of the 80 meV band is resolved.

The fact that the two main bands of bulk AlN are completely smeared out in the nanomaterial can only be explained by a very large distribution of force constants or mass defects. This distribution must be created by structural disorder. Structural disorder can equally explain the extra intensity at very low frequencies as observed in nearly all the structural glasses.

The structural disorder deduced from the inelastic spectra contrasts with the sharp peaks observed in the elastic data (figure 3). Sharp peaks indicate well-ordered crystalline regions. Compared to the bulk there are extra peaks indicating a mixture of hexagonal and cubic phases in the nanomaterial. The intensity of the peaks in the powder spectra is very weak

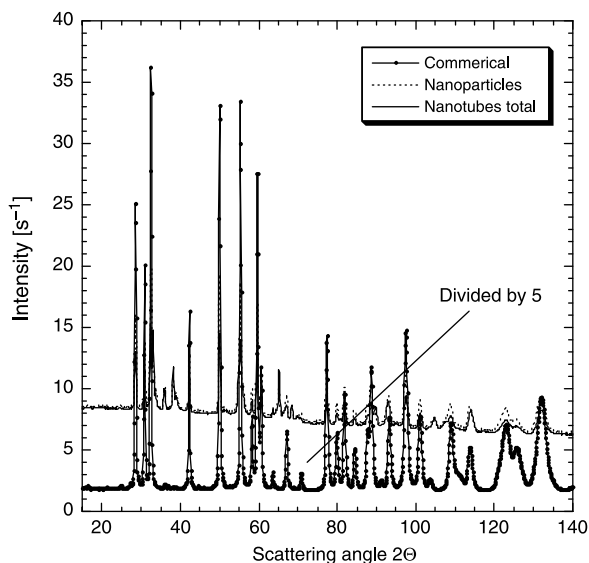


Figure 3. Powder diffraction pattern as obtained on the instrument D20 at 5 K. The intensities of the commercial sample have been scaled down by a factor 5.

compared to the bulk sample. At least part of this difference can be attributed to the smaller amount of nanomaterial in the beam. Strikingly the peaks in the nanomaterial are equally very weak when compared to the background. The experiments on IN6 clearly show that the background, i.e. the intensity observed between peaks in the elastic channel, is to be attributed to scattering from the sample. A respectively higher background therefore accompanies the weaker peaks in the nanomaterial. This background has no apparent structure that would allow us to identify it with an amorphous structure factor. The small monotonous drop of the intensity could be explained by a Debye–Waller factor associated with local disorder scattering. If attributed purely to incoherent scattering from hydrogen then this background requires a few percent of H-contamination of the nanomaterial based on the assumption that the bulk AlN is hydrogen free. Such a small contamination would be insufficient to explain the drastic changes in the inelastic spectra.

4. Conclusions

The inelastic neutron data clearly show that AlN produced as nanomaterial differs strongly from the bulk at the atomic level. These differences become most pronounced in the vibrational density of states. All physical properties depending on the distribution of phonon frequencies must experience these differences. This holds in particular for specific heat and heat transport. The large smearing of vibrational frequencies mirrors the broader distribution of interatomic forces and/or mass defects and ensuing change in dispersion relations. The interatomic forces are linked to the bonds and thus to the electronic states of the material, which in consequence should be equally appreciably different from the bulk.

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