Journal of Quantitative Spectroscopy & Radiative Transfer 194 (2017) 1–6

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Mid-infrared optical properties of pyrolytic boron nitride in the 390–1050 °C temperature range using spectral emissivity measurements

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ARTICLE INFO

Article history:
Received 11 January 2017
Received in revised form
10 February 2017
Accepted 11 February 2017
Available online 1 March 2017

Keywords:
Boron nitride
Emissivity
Mid-infrared
Optical phonons
Dielectric constants
Effective medium approximation

ABSTRACT

This paper shows a systematic experimental and theoretical study on the temperature dependence of the infrared optical properties of pyrolytic boron nitride (pBN), from 390 to 1050 °C for wavelengths between 4 and 16 μm. The temperature dependence of these properties has never been analyzed before. The measured emissivity spectra were fitted to a dielectric function model and an effective medium approximation. The phonon frequencies and dielectric constants agreed well with room temperature experimental values from the literature, as well as with *ab initio* and first principles calculations. In addition, the phonon frequencies of the perpendicular mode and the dielectric constants of the parallel mode showed an appreciable parabolic temperature dependence, which justifies the interest of more theoretical efforts in order to explain this behavior. Finally, the results of this work demonstrate that thermal emission spectroscopy allows obtaining the values of the optical and dielectric parameters of impure ceramic materials in a simple manner as a function of temperature.

1. Introduction

Boron nitride shows four polymorphic variants whose special properties make this compound suitable for a large number of technological applications [1–4]. The hexagonal form (h-BN) is the most common phase and the one that shows the most unique electronic and optical properties. It is a very good electrical insulator, has great chemical stability and oxidation resistance, low thermal conductivity and can withstand extreme temperature conditions. Due to these properties, it is widely used in microelectronic devices, nuclear energy, X-ray lithography, lubrication, vacuum technology or high-performance oxidation-resistant coatings for metals and graphene up to 1100 °C in an oxidizing atmosphere [5–10]. Recently, the discovery of several new features has increased its interest. Firstly, the achievement of h-BN nanotubes with this simple hexagonal structure [11]. Secondly, its lasing capacity at a wavelength of 210 nm, which shows great potential for optoelectronic applications in the ultraviolet range [12]. Thirdly, its very good optical selectivity (infrared emitter and visible reflector) has made it a good candidate for coating heat shields of solar probes [13]. Finally, the presence of two phonon bands in the mid-infrared can be exploited to tune its optical properties by coupling them to plasmon polaritons from graphene or from a metal grating [14–16].

Hexagonal BN crystallizes in the $P6_3/mmc$ space group with four atoms in the unit cell and with the following irreducible representation of the phonon modes at the Brillouin zone center: $\Gamma_{vib} = A_{2u}(IR) + E_{1u}(IR) + 2E_{2g}(Raman) + 2B_{1g}(silent)$. This h-BN polymorphic modification consists of sp^2-bonded 2D layers [1]. Within each layer the atoms are bound by strong covalent bonds, whereas the layers are held together by weak Van der Waals forces. Since 1950, a continued effort has been made for the characterization of the physical properties of this compound. In particular, the optical properties of h-BN were studied by means of a large number of experimental techniques, mainly for wavenumbers above 3000 cm^{-1}, using single crystals, polycrystals and thin films deposited on different substrates (see for example references in [7]). First principles and *ab initio* calculations were made using different theories and approximations in order to analyze the experimental results. However, infrared and Raman spectroscopic experimental data that characterize the optical properties in the mid-infrared range or that allow obtaining the

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http://dx.doi.org/10.1016/j.jqsrt.2017.02.016
0022-4073/

energies of the phonons at the Γ-point of the Brillouin zone are scarce [17–24]. The same scarcity occurs with respect to the number of publications that give theoretical values of the dielectric constants and the frequencies of the Γ-point phonons based on *ab initio* calculations [25–30]. Moreover, some discrepancies may be found among data from the literature, mainly in the parallel components of the static and high frequency dielectric constants, but also in some of the IR active phonon frequencies [17,19–21,24]. These discrepancies are also observed between experimental and theoretical values [25–30].

In this paper, we report an experimental study on the emissivity spectra of pyrolytic boron nitride (pBN), as well as its optical constants, Γ phonon frequencies and dielectric properties (high-frequency and static dielectric constants) obtained by thermal emission spectroscopy. The theoretical interpretation of the experimental results is carried out by using a four-parameter dielectric function model as well as a Kramers–Kronig analysis. In addition to the basic interest of these measurements for the analysis of the discrepancies indicated above, this material shows promising properties in the mid-infrared range that make it attractive for many applications. As noted above, pBN may be an appropriate candidate for the main thermal protection system of the Solar Probe Plus (NASA) [10,31] or, from a broader viewpoint, as a high temperature passive thermal controller. Besides, tunable infrared absorption has also been achieved with a h-BN metamaterial, and it is known that numerical simulations for these applications require accurate values of the temperature-dependent dielectric function [32]. In order to implement these possible applications, it is necessary to expand the scarce number of published data on the temperature dependence of its optical properties [31,33,34]. The paper also presents the first study on the temperature dependence of the optical constants, Γ phonon frequencies and dielectric properties (high-frequency and static dielectric constants) of pBN samples.

2. Experimental

The pBN sample studied in this paper consisted of a 1 mm thick square plate of hexagonal BN deposited on a graphite substrate by pyrolysis of precursor gases at 1800 °C [35]. The route employed ensures good homogeneity and high purity, since it does not involve binding phases. The composition and microstructure of the sample were characterized by chemical analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The X-ray diffractogram (shown in Fig. 1) and the SEM images are in complete agreement with those of a previous sample [24]. The sample density was measured to be 2.03 g/cm^3, a value 11% lower than the single-crystal value. The surface roughness parameters, measured with a conventional profilometer, are R_a = 0.90 μm, R_q = 1.08 μm, R_z = 4.35 μm and R_t = 5.15 μm.

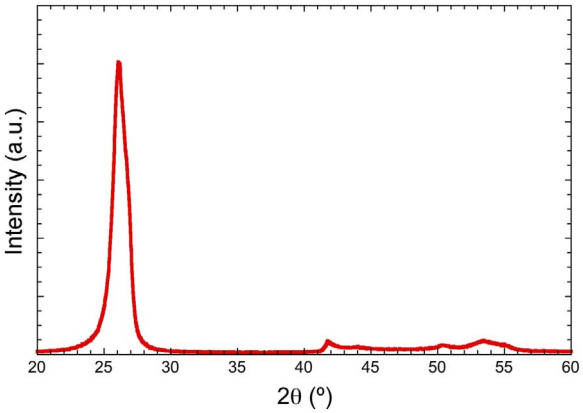

Fig. 1. X-ray diffractogram of the sample, taken with Cu-K_α radiation.

The emissivity measurements were made with a radiometer which has been described in the literature [36]. The sample chamber was purged with dry air in order to avoid CO_2 and water absorption. The sample was heated with a CO_2 laser (λ = 10.6 μm), which allows reaching temperatures beyond 1000 °C. The sample thermal emission was collected with a Fourier transform infrared spectrometer calibrated by a black-body. The emissivity was then determined in the whole spectrum by comparison of the sample and black-body signals through the following formula:

$$E = \frac{FT(I_S - I_{RT})}{FT(I_{BB} - I_{RT})} \times \frac{P_{BB} - P_{RT}}{P_S - P_{RT}} E_{BB} \quad (1)$$

where *FT* means Fourier transform; I_S, I_{BB} and I_{RT} are the interferograms recorded for the sample, black-body and room temperature background of the apparatus; P_S, P_{BB} and P_{RT} are the Planck functions calculated at the temperatures of the sample, black-body and apparatus; and E_{BB} is the emissivity of the black-body.

The temperature of the sample was determined at the Christiansen point (λ_{Chris}), a wavelength at which ceramic materials behave like a black-body (E=1). This point does not depend on temperature and is thus used as a common non-contact method for surface temperature measurement in ceramic materials [37]. In this paper, it was determined by a room-temperature diffuse reflectance measurement using an integrating sphere, with a value of λ_{Chris} = 6.0 μm.

3. Results and discussion

The X-ray diffractogram of Fig. 1 confirms the polycrystalline nature of the material, with no preferential orientation of the crystallites. It also reveals, together with the results from SEM microscopy, the presence of a small amount of graphite, which originates in the deposition process and has been found in similar samples in the literature [38]. The size of the graphite inclusions was observed to be smaller than the wavelength range of interest in this paper, which justifies the choice of the theoretical models for the interpretation of the data.

The emissivity spectrum of pBN was measured in the 390–1050 °C temperature range and for wavelengths between 4 and 16 μm. The wavelength range of study was limited by the onset of transmittance at both extremes, which makes the emissivity of the material to fall abruptly to 0. The maximum temperature was chosen to avoid any possible oxidation, while the minimum temperature chosen was the lowest one that ensured an acceptable signal-to-noise ratio in the selected spectral range. The emissivity spectra for three temperatures are shown in Fig. 2.

The spectra show two *reststrahlen* bands at 6–8 and 12–14 μm, corresponding to the two infrared active phonons of h-BN. These spectra show a great similarity to those observed by reflectance measurements at room temperature [17,24] and with the only emissivity spectrum found in the literature [34]. No experimental data in the infrared was found for single crystals. However, there are slight differences between the measured spectrum on polycrystalline samples [17] or highly oriented ones (hopBN) [24] with the measured spectrum in this paper. Group theory predicts that the observation of each phonon requires a determined direction of polarization ($\vec{E} \| c$ and $\vec{E} \perp c$). This occurs for hopBN samples but not for pBN, for which, as shown in Fig. 2, both phonons are observed in a near-normal measurement without polarization. This behavior is associated, as mentioned before, with the presence of