

Diamond thermal expansion measurement using transmitted X-ray back-diffraction

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The linear thermal expansion coefficient of diamond has been measured using forward-diffracted profiles in X-ray backscattering. This experimental technique is presented as an alternative way of measuring thermal expansion coefficients of solids in the high-resolution Bragg backscattering geometry without the intrinsic difficulty of detecting the reflected beam. The temperature dependence of the lattice parameter is obtained from the high sensitivity of the transmitted profiles to the Bragg angle variation with temperature. The large angular width of the backscattering profiles allows the application of this technique to mosaic crystals with high resolution. As an application of this technique the thermal expansion coefficient of a synthetic type-Ib diamond (110) single crystal was measured from 10 to 300 K. Extremely low values (of the order of $1 \times 10^{-7} \pm 5 \times 10^{-7}$) for the linear thermal expansion coefficient in the temperature range from 30 to 90 K are in good agreement with other reported measurements.

Keywords: X-ray back-diffraction; diamond single crystal; linear thermal expansion coefficient; low temperature.

1. Introduction

Precise determination of the lattice parameter and linear thermal expansion coefficients (α) as a function of temperature are of importance for a number of studies of the crystalline state. Interest covers a wide range of subjects from the study of fundamental properties of solids to the tailoring of new materials with zero thermal expansion (ZTE). As an example, the intermetallic compound YbGaGe shows negligible volume change between 100 and 400 K and points to being a suitable material with reduced strain or internal stress for applications in systems subjected to large temperature fluctuations as in space applications and thermomechanical actuators (Salvador *et al.*, 2003). Normally materials expand upon heating although, more rare, some materials expand upon cooling. In a microscopic view the temperature variation of the lattice parameters and the linear thermal expansion are related to anharmonic terms in the ionic interaction energy. The unusual behavior of materials having negative thermal expansion (NTE) can be related to geometrical or electronic processes as in the cooperative rotation of the oxide tetrahedra in ZrW₂O₈ (Mary *et al.*, 1996) or the internal charge transfer of Yb ions in the YbGaGe compound (Salvador *et al.*, 2003). X-ray techniques are unique for probing lattice parameter and anisotropic lattice parameter variations complementing conventional techniques such as high-pressure ultrasonic experiments, capacitance dilatometers and others.

In particular, synchrotron radiation with its particular properties, such as high flux, energy tunability and high collimation, allows the development of new techniques for measuring lattice parameters with high precision using the high-resolution regime of Bragg backscattering (Wille *et al.*, 2002; Munakata & Okazaki, 2004; Hu *et al.*, 2003). This technique allows high-resolution lattice parameter measurements in different crystallographic directions.

A particular area of interest lies in tetrahedrally bonded solids. Calculations in terms of lattice dynamics have shown the existence of NTE at low temperatures in Si, Ge, CdTe and GaAs, confirmed by measurements (Barron *et al.*, 1980; Soma, 1977; Xu *et al.*, 1991). *Ab initio* calculations explain this behavior by a negative Grüneisen parameter of the transverse acoustic mode of phonons (Xu *et al.*, 1991). An important application of these properties has been the X-ray optics developments for third-generation synchrotron radiation sources. The zero and negative thermal expansion of silicon at liquid-nitrogen temperatures was a successful solution as an optical element with crystalline perfection to the extremely high thermal power of its insertion devices.

Among the tetrahedrally bonded solids, diamond, with its high X-ray transparency, high thermal conductivity and low α coefficient, is attracting particular attention for use as an optical element for beamlines of synchrotron radiation and the forthcoming fourth-generation sources. Applications range from X-ray monochromators for high-brilliance

synchrotron sources (Freund *et al.*, 2001; Pal'yanov *et al.*, 2000; Takiya *et al.*, 1999), filters and vacuum windows for coherence preservation, phase plates for polarization transformation (Giles *et al.*, 1994, 1995), anvil cells for high-pressure experiments, and recent developments are pointing towards solid-state radiation detectors (Tanaka *et al.*, 2001). The present and future needs of synthetic diamond samples were discussed in connection with X-ray source requirements in a recent workshop at the European Synchrotron Radiation Facility (ESRF) in Grenoble (Härtwig, 2004). Concerning diamond intrinsic properties it is not clear as to whether the thermal expansion coefficient of diamond has a negative value at low temperature (Biernacki & Scheffler, 1989; Haruna *et al.*, 1992; Pavone *et al.*, 1993; Reeber & Wang, 1996; Saotome *et al.*, 1998; Sato *et al.*, 2002; Xu *et al.*, 1991). Theoretically, high-purity diamond single crystals cannot have a negative value (Pavone *et al.*, 1993; Xu *et al.*, 1991). However, measurements with X-rays by the Bond method in a diamond single crystal, which was supposed to be an almost perfect and high-purity crystal (Sato *et al.*, 2002), show a tendency to a negative value for α between 30 K and 90 K.

This paper shows an alternative and simple technique for precise thermal expansion measurements based on the high-resolution back-diffraction geometry, and as an application we determine the low-temperature values of the thermal expansion coefficient of diamond. It is well known that the energy resolution is a function of the scattering angle and the highest resolution is obtained when the Bragg angle is close to 90° (Munakata & Okasaki, 2004). The experimental difficulty of this type of measurement lies in the detection of the reflected beam which involves the need of semi-transparent detectors (Wille *et al.*, 2002) or the need of very long distances between sample and detector (Hu *et al.*, 2003). Here the lattice parameter variation with temperature is measured by recording the forward-diffracted profile at a back-diffraction regime that is possible for a certain range of semi-transparent samples at X-ray energies (Giles & Cusatis, 1991). In this configuration the forward-diffracted beam is directly measured at the detector collecting the transmitted beam. The energy of the incoming beam is tuned by a pre-monochromator to satisfy the back-diffraction condition, and further monochromated by a four-crystal monochromator for increasing the energy resolution of the beam to about ten times the energy bandwidth of the measured crystal diffraction. In this way the high sensitivity to the lattice parameter variation and the high-energy resolution of the forward-diffracted profiles can be used for the determination of the thermal expansion coefficient α for a variety of crystals. Furthermore, the wide angular range in back-diffraction allows mosaic crystals (with mosaicities of the order of the enlarged back-diffraction Darwin widths) to be measured without significant loss of resolution (Hashizume & Nakahata, 1988).

It is worth noting that the back-diffraction technique has been recently applied to the study of the influence of isotopic composition in the lattice parameters of Si (Wille *et al.*, 2002) and Ge (Hu *et al.*, 2003) and also for the lattice parameter determination of Al_2O_3 (Lucht *et al.*, 2003). Nevertheless, all these measurements involve the experimental difficulties of detecting the back-diffracted beam (h-beam). The proposed technique can easily be adapted to any high-resolution X-ray diffraction beamline.

2. Experiment

The experiment was performed at the high-resolution single-crystal diffraction beamline (XRD2) at the Brazilian National Synchrotron Light Laboratory (LNLS). The incident beam was tuned at an energy of about 9.8 keV by a channel-cut Si(111) pre-monochromator to satisfy the back-diffraction condition for the (440) reflection of a diamond single crystal. Also, a four-crystal Si(220) monochromator [4C monochromator, made of two channel-cut crystals in the (+, -, -, +) configuration] was inserted to further reduce the energy bandwidth ($\Delta\lambda/\lambda = 8 \times 10^{-5}$), compatible with the energy bandwidth of the diamond (440). The experimental set-up is schematically shown in Fig. 1. The 4C monochromator was thermomechanical stable, assured by the use of a robust double-axis diffractometer made of one solid piece of cast iron and positioned in the vertical scattering geometry. With the insertion of these optical devices the vertical divergence was 3×10^{-5} rad and the horizontal divergence, limited by the slits, was 2×10^{-4} rad.

The temperature control of the diamond single crystal was achieved using a closed-cycle He cryostat installed in the Huber six-circle diffractometer of the beamline. The back-scattering condition was obtained by tuning the incident energy, controlling the temperature of the sample and allowing the rotation of the crystal in the vertical and horizontal scattering planes by putting the χ axis perpendicular to the θ axis ($\chi = 90^\circ$). The forward-diffracted beam (O-beam) was detected using a scintillator detector. The back-diffracted beam was also measured using a second scintillator detector on the 2θ arm of the diffractometer set at a scattering angle close to but smaller than 180° or, alternatively, by inserting an ionization chamber (IC) before the diffractometer. Measure-

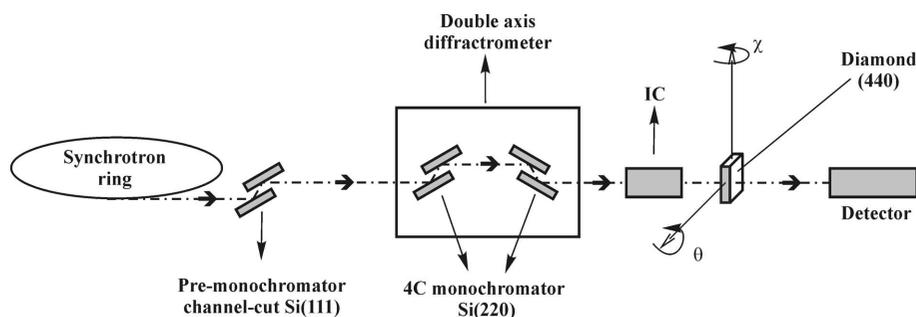


Figure 1 Schematic set-up for precise thermal expansion determination using transmitted X-ray back-diffraction at the XRD2 beamline at the LNLS.

ments of the O-beam back-diffraction profiles at Bragg angles close to 89.5° (in the vertical and horizontal scattering plane) of the diamond (440) reflection were recorded at temperatures varying from 10 to 300 K. Thermal stability of the sample during data collection was of the order of 0.1 K and the temperature accuracy of the sample was estimated to be better than 2 K.

The diamond (110) single crystal used in this experiment was a 1 mm-thick plate. This sample is transparent but a little yellowish in visible light, characteristic of the type-Ib diamonds. This was verified by the infrared spectra where the absorption line at 1130 cm^{-1} was observed (Sumiya *et al.*, 1997). This single crystal was also structurally characterized by X-ray Berg-Barret topography (Tanner, 1976) and with rocking-curve measurements using a triple-axis arrangement and using a small spot scan at different surface points. These measurements have shown that the crystalline quality was limited to $\Delta d/d \simeq 3 \times 10^{-3}$, probably due to the presence of multiple sector growths and growth striations visible through X-ray topography.

Usual X-ray techniques for precise thermal expansion measurements are based on a precise determination of the lattice parameter d at different temperatures. The resolution is limited by the crystalline quality $\Delta d/d$ of the sample which is of the order of 10^{-7} or 10^{-8} only for perfect crystals as obtained in Si and Ge. Available synthetic or natural diamond single crystals do not have the same degree of quality and the overall effect of defects is to broaden the diffraction profile and limit the resolution of the lattice parameter determination. Nevertheless, in the extreme condition of X-ray diffraction close to the backscattering regime the broadening of the rocking curve due to mosaicity is considerably reduced as a consequence of the enlargement of the diffraction profile at this diffraction regime. As a consequence, the diffraction

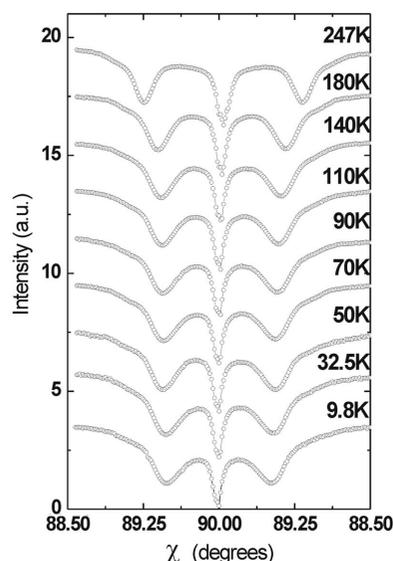


Figure 2
Diamond X-ray back-diffraction profiles rocking the χ angle (horizontal scattering plane) for the temperature range from 10 K to 250 K.

profiles maintain high sensitivity to the lattice parameter variation with temperature even in the case of mosaic crystals. Consequently, good resolution linear thermal expansion measurements are obtained even if the precise lattice parameter is not obtained.

3. Results

Several sets of back-diffraction profiles (O-beam) from the diamond (440) planes rocking the χ angle (horizontal scattering plane) and θ angle (vertical scattering plane) were recorded as a function of temperature varying from 10 K to 300 K for an incident energy, determining a Bragg angle close to 89.5° . Typical sets of profiles are shown in Fig. 2. Multiple-beam diffraction can also be seen in Fig. 2, exactly at 90° for all profiles. The multiple scattering was more evident in the θ profiles than in the χ profiles because the beam divergence in the vertical scattering plane (3×10^{-5} rad) was smaller than in the horizontal scattering plane (2×10^{-4} rad). Multiple-beam diffraction at this configuration is a six-beam case involving the planes (400) and (040), (422) and $(02\bar{2})$ coupled with the (440) plane in back-diffraction (Sutter *et al.*, 2001). The Bragg-angle variation with temperature is clearly seen by the variation of the minimum of the O-beam profile at different temperatures. Fig. 3(a) shows a θ scan where O-beam and h-beam diffraction profiles are overlapped. It is clearly seen that the maximum of the back-diffracted profile is at the same position as the minimum of the forward-diffracted profile. Fig. 3(b) shows a dynamical theory calculation verifying that this is indeed predicted by theory. Therefore, the evaluation of the Bragg-angle change is easily performed by measuring the

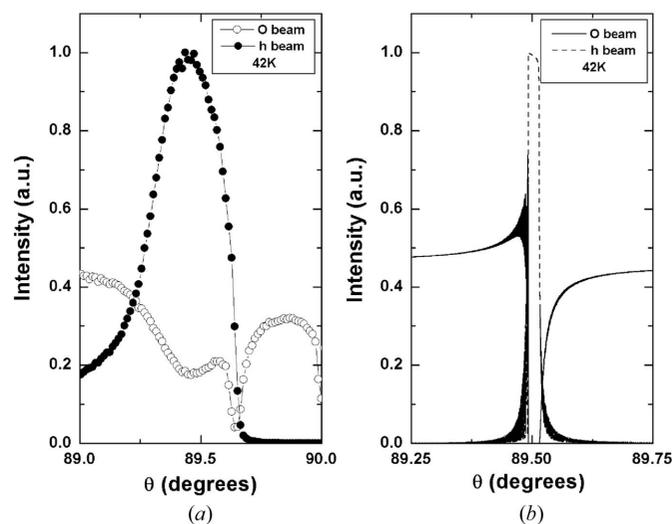


Figure 3
(a) Forward-diffracted (O-beam) and back-diffracted (h-beam) profiles of diamond measured in the vertical scattering plane at a Bragg angle of 89.5° . The angular position of the back-diffracted maximum corresponds to the forward-diffracted minimum of the profile. (b) This feature can be seen in profiles calculated by X-ray dynamical theory for a monochromatic beam. The larger width of the experimental profiles is due to the convolution with the energy and angular spreads of the incoming beam.

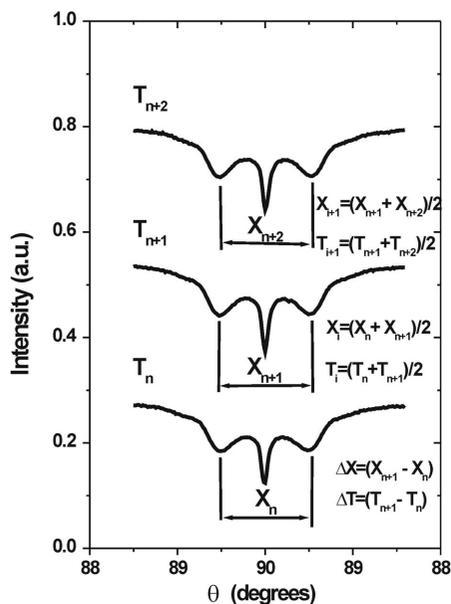


Figure 4
Methodology used to find the linear thermal expansion coefficient (α) of diamond in the Bragg backscattering geometry.

angular positions of the minimum of the (440) and ($\bar{4}\bar{4}0$) diffraction profiles occurring at the Bragg angles θ and $\pi - \theta$.

To find the α coefficient a differentiative procedure was used. By differentiating the general form of Bragg's law, the result is the following expression (Cusatis *et al.*, 1996),

$$\alpha = \frac{\Delta d}{d \Delta T} = - \frac{\Delta X}{\Delta T \tan(X)}, \quad (1)$$

where $\Delta d/d$ is the relative lattice parameter variation, X is the diffraction angle (θ or χ), ΔX is the variation of the diffraction angle ($\Delta\theta$ or $\Delta\chi$) and ΔT is the temperature variation.

The diffracted angle X was obtained from the average of two consecutive data sets of the diffraction profile data, *i.e.* $X = (X_n + X_{n+1})/2$ (Fig. 4) for two consecutive temperatures T_n and T_{n+1} . The same average procedure is used for the temperature, *i.e.* $T = (T_n + T_{n+1})/2$.

The variation of the diffraction angle ΔX is found from the difference $\Delta X = X_n - X_{n+1}$. The same procedure is used to find the temperature variation $\Delta T = T_n - T_{n+1}$.

With these parameters obtained from the measurements shown in Fig. 2, the linear thermal expansion coefficient was found using (1). The results are shown in Fig. 5 together with other results found in the recent literature for high-purity synthetic IIa diamond single crystals (Sato *et al.*, 2002), Ib synthetic diamond single crystals (Haruna *et al.*, 1992) and an unidentified type of diamond (Reeber & Wang, 1996). The present results show a linear thermal expansion coefficient for this type of diamond (Ib) very close to zero at temperatures between 30 K and 90 K, as can be seen in Fig. 5. Certainly the availability of a better quality diamond crystal sample would also justify a more precise determination of its lattice parameter.

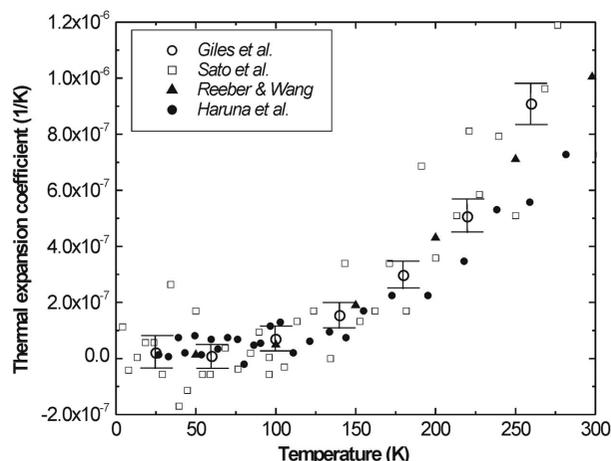


Figure 5
Linear thermal expansion coefficient (α) obtained in the present work compared with other results found in the recent literature. Values for α between 30 K and 90 K are of the order of 1×10^{-7} , compatible with published results.

4. Discussion and conclusion

X-ray back-diffraction profiles of the forward-diffracted beam were used to determine the thermal expansion coefficient (α) of diamond through the high sensitivity of the back-diffraction profiles as a function of temperature from 10 K to 300 K. This determination was obtained by measuring the temperature variation of the interplanar distance of the (440) reflection. It is worth noticing that it is desirable to repeat this measurement in some interesting crystallographic directions such as the cubic lattice axis [211] where an enhanced α coefficient could be obtained by taking into account the phonon modes predicted for this lattice axis in this temperature range (Xu *et al.*, 1991). The high sensitivity to the lattice parameter variation and high-energy resolution with increased tolerance to mosaic spreads show that X-ray back-diffraction can be used to determine the α coefficient for a variety of mosaic crystals as was the case for the available synthetic Ib diamond single crystals measured in this work.

Finally, the present results show that the X-ray back-diffraction in the forward-diffraction configuration can be used as an efficient alternative technique to determine the α coefficient of solids at low temperatures releasing the stringent requirement of good crystalline quality. Furthermore, the technique allows measurements in different crystallographic directions by selecting the appropriate reflection tuned at the backscattering geometry. Measurements can be performed using asymmetric reflections also and crystal thicknesses can be selected to allow small absorption of the forward-diffracted beam. The experimental set-up can be easily adapted in existing high-resolution X-ray diffraction synchrotron radiation beamlines.

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