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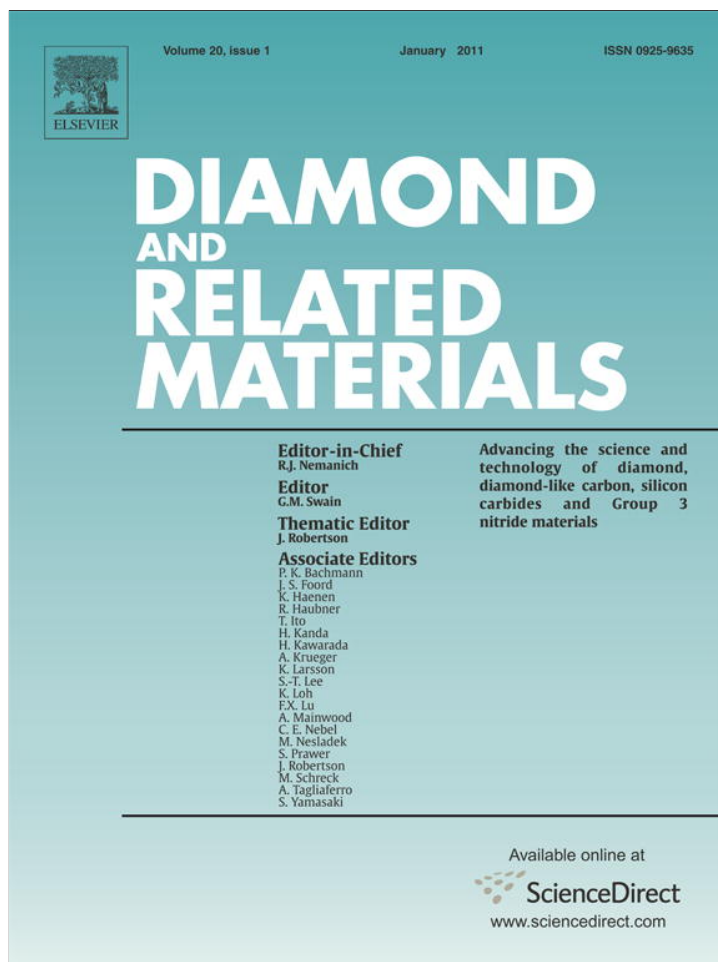


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First-principles, UV Raman, X-ray diffraction and TEM study of the structure and lattice dynamics of the diamond–lonsdaleite system

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ABSTRACT

We report the results of the study of the polycrystalline powder of the diamond–lonsdaleite system by X-ray diffractometry, transmission electron microscopy and UV Raman spectroscopy. The measured data of structural parameters are in good agreement with *ab initio* calculations. We show that the Raman spectrum is proportional to the phonon density of states of the diamond–lonsdaleite system.

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1. Introduction

There has been an increasing interest to the synthesis of superhard carbon materials in the recent decades. Lonsdaleite or hexagonal diamond [1] is one of such carbon materials, the hardness of which is 58% higher than cubic diamond according to theoretical prediction [2]. Cubic diamond with 3 C structure (space group $Fd\bar{3}m$) and lonsdaleite with 2 H structure (space group $P6_3/mmc$) are the end member diamond polytype structures. These diamond polytype structures differ only in the stacking sequences of identical puckered hexagonal carbon layers containing only sp^3 -type bonds of carbon. These identical carbon layers lie parallel to the cubic 3 C (111) and the hexagonal 2 H (001) planes.

The lonsdaleite structure is often seen in the diffraction pattern of diamond as the effect of stacking faults. The recursive description in layered crystals was originally developed in the work [3] and called DIFFaX program. The modification of this program, allowing all instrumental, structural and microstructural parameters to be refined using the available diffraction data, was proposed in the work [4] and called DIFFaX+. The random stacking can be described in terms of the probability matrix α , which determines the probability that layers in the diamond crystal will stack in cubic diamond sequence. Thus $\alpha = 0$ corresponds to pure lonsdaleite, and $\alpha = 1$ corresponds to pure diamond. This layered structure was called the diamond–lonsdaleite system.

The hexagonal diamond has been synthesized in the laboratory under conditions of static pressure > 12 GPa and temperature > 1300 K

[1]. It was found [5] that lonsdaleite might be obtained under pressure of 5.5–12 GPa with shear deformation and at temperature of 1070–1600 K.

The previous Raman study of lonsdaleite (see [6] and references there) did not allow assigning the Raman bands to lonsdaleite unambiguously.

In this paper, we studied the polycrystalline powder of the diamond–lonsdaleite system by means of X-ray diffraction, transmission electron microscopy (TEM) and UV Raman spectroscopy and compared the measured data with the calculated ones from first principles. Results of this study pave the way for development of materials with unique properties.

2. The experimental and theoretical techniques

The polycrystalline powder of the diamond–lonsdaleite system was synthesized from the natural purified well-crystallized graphite (from Zavalye deposit). The experiments were carried out using toroid-type apparatus calibrated by resistance jumps in the Bi (2.5, 2.7, 7.7 GPa) and Sn (9.5 GPa) reference metals at phase transitions. The temperature graduation of the apparatus was performed using Pt/Pt-10% Rh thermocouples. The graphite was heated with AC current flowing through a heater and graphite. The experiments were carried out at high pressures of 7–9 GPa and high temperatures of 1170–1470 K. The polycrystalline powder of the diamond–lonsdaleite system was separated from specimens by oxygenating of unconverted graphite by the $HClO_4$ acid during 25–40 h.

TEM studies were carried out using a JEM-2010 high-resolution transmission electron microscope. The X-ray diffraction patterns were obtained using ARL X'TRA apparatus with Si (Li) semiconductor detector and Cu $K\alpha$ -radiation.

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The UV Raman spectra were excited with the frequency-doubled line at 257 nm (WaveTrain, Spectra-Physics) of an Ar-laser (BeamLok 2065–7s, Spectra-Physics) and detected with the TRIAX-552 spectrometer (Horiba), the “razor-edge” filters (Semrock) and the CCD camera Spec-10:2KBUV (Princeton Instruments). UV Raman offers stronger sp^3 -type carbon signal due to resonant enhancement and lower level of the photoluminescence background that provides a relatively easy identification of the diamond–lonsdaleite system. The power of laser radiation was ≤ 1 mW to avoid overheating of the sample. The spectral resolution of the spectrometer was 3 cm^{-1} . The calibration of the spectrometer was performed with the lines of mercury lamp and checked on the 1332.5 cm^{-1} diamond peak.

The first-principle calculations were performed within the density-functional perturbation theory using the ultrasoft pseudopotentials, the local density approximation, the linear response and the Quantum Espresso simulation package [7]. We used plane wave energy cutoffs of 800 eV and 3200 eV for the kinetic energy and the charge density, respectively, together with a $(8 \times 8 \times 8)$ Monkhorst-Pack (MP) grid. The hexagonal cell and the atom positions were relaxed in order to obtain forces and pressures lower than 10^{-4} eV/\AA and $2 \times 10^{-3}\text{ GPa}$, respectively. In these approximations the parameter of the diamond relaxed unit cell was 3.5419 \AA and the frequency of the optical phonon was 1336 cm^{-1} . The convergence of the calculated results was investigated in dependence of the different MP grids and the energy cutoffs.

3. Results and discussion

The TEM image of crystal of the diamond–lonsdaleite system (Fig. 1a) shows its layered structure. The electron diffraction pattern (Fig. 1b) corresponds to the image shown in Fig. 1a. The letters *d* and *l* denote spots related to the lattices of diamond and lonsdaleite, respectively. Traditional orientation relationship for diamond and lonsdaleite is fulfilled: $(111)_d \parallel (001)_l$.

In distinction from the diamond reflections one can see streaked lonsdaleite reflections in Fig. 1b that may be due to that lonsdaleite layers are thinner than diamond layers. Hence, our diamond–lonsdaleite system has layered structure with thin layers of lonsdaleite and thicker diamond layers.

Fig. 2 shows the X-ray diffraction pattern of the polycrystalline powder of the diamond–lonsdaleite system. The most intensive diffraction peak of 100 lonsdaleite is distinctly seen in Fig. 2. The other lonsdaleite reflections superimpose on diamond reflections. The full profile analysis (Rietveld refinement) shows 51.4% of lonsdaleite and 48.6% of diamond that is in accordance with the calculated profile with $\alpha \approx 0.5$ (Fig. 2 in [3]). The small amount of graphite (peak 002) and an unknown phase (peak near graphite 002 peak) are also present in our sample.

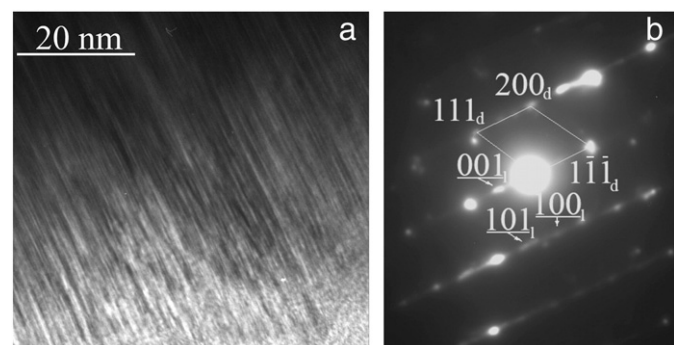


Fig. 1. a) TEM image of crystal of the diamond–lonsdaleite system and b) electron diffraction pattern corresponding to the image shown in Fig. 1a. The letters *d* and *l* denote spots related to the lattices of diamond and lonsdaleite, respectively.

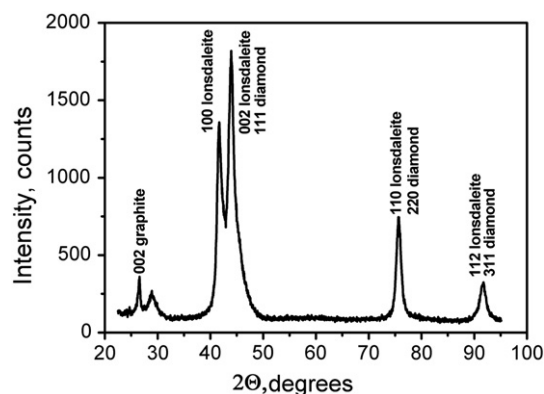


Fig. 2. The X-ray diffraction pattern of a polycrystalline powder of the diamond–lonsdaleite system.

The structural parameters obtained by Rietveld refinement of XRD data are in good agreement with the first-principles calculations (Table 1). It should be noted that the bond length d_1 perpendicular to layers is higher than the bond length d_2 in layers. Earlier the first-principles calculations of lonsdaleite were performed assuming the equal bond lengths d_1 and d_2 [8]. This assumption is inconsistent with our X-ray data and the *ab-initio* relaxed structure of lonsdaleite (Table 1). The calculated frequencies of optical modes are given in Table 2. Only the A_{1g} , E_{1g} and E_{2g} modes are the Raman active [8]. As in other crystals of the wurtzite structure, the frequency of double-degenerated mode E_{1g} is higher than that of A_{1g} . This is due to that in the E_{1g} mode the atoms of the short bond d_2 are moved oppositely in the (001) plane, whereas in the A_{1g} mode the atoms are displaced oppositely along the long bond d_1 . The ratio of the squares of the susceptibilities of the Raman modes are $1(A_{1g}):0.1(E_{1g}):0.1(E_{2g})$. Hence, the A_{1g} mode at 1280 cm^{-1} is expected to be the most intense line in the Raman spectrum of lonsdaleite.

The intense lines at 1340 and 1590 cm^{-1} , a narrow line at 867 cm^{-1} and a number of weak broad bands are seen in the Raman spectrum of our sample (Fig. 3). The 1590 cm^{-1} line may be attributed to graphite, which can also be seen in the X-ray diffraction pattern. The 867 cm^{-1} line was also observed in the graphite spectrum in [9]. We assign the 1340 cm^{-1} line to diamond, that is present in the sample, according to the TEM and X-ray diffraction data. A shift of the diamond line from 1332.5 cm^{-1} to 1340 cm^{-1} , as well as of the graphite line from 1582 cm^{-1} to 1590 cm^{-1} , may be due to a presence of strain between layers in the diamond–lonsdaleite system. The absence of narrow Raman lines that could be assigned to lonsdaleite may be due to small dimensions of crystallites in our sample that follows from the TEM and X-ray diffraction data. In this case the Raman spectrum can be proportional to phonon density of states (PDOS) of the diamond–lonsdaleite system. A comparison of the calculated PDOS with the Raman spectrum shows (Fig. 3) that the PDOS peaks correlate with the positions of the weak broad bands at $670, 990, 1120, 1225$ and 1306 (the shoulder) cm^{-1} . These bands are absent in the Raman spectra of nanodiamond and nanocrystalline graphite. We conclude that the

Table 1

The experimental and calculated structural parameters of lonsdaleite. d_1 and d_2 are the C–C bond lengths along [001] and in (001) plane, respectively. α_1 is the angle between the bonds d_1 and d_2 . α_2 is the angle between the bonds d_2 in (001) plane.

Parameters	a, Å	c, Å	d_1 , Å	d_2 , Å	α_1 , deg	α_2 , deg
Rietveld refinement	2.505	4.159	1.5679	1.5342	109.485	109.454
Calculated	2.4906	4.1477	1.5526	1.5295	109.925	109.014

Table 2
Calculated frequencies of optical modes of lonsdaleite in Γ point of Brillouin zone.

Modes	E_{2u}	B_{1u}	E_{2g}	B_{2g}	A_{1g}	E_{1g}
Frequency, cm^{-1}	524	1055	1221	1252	1280	1338

Raman observation of these modes is an indicator of the presence of lonsdaleite in our samples.

4. Summary

In conclusion, TEM analysis has shown that the polycrystalline powder of the diamond–lonsdaleite system produced has layered structure with very thin stacking layers of diamond and lonsdaleite. Analysis of the powder X-ray diffraction pattern of our sample has shown that the number of layers of diamond and lonsdaleite is approximately equal. The calculated frequencies and intensities of Raman active modes in the Γ point of Brillouin zone do not agree with the observed Raman spectra. We have shown that the Raman spectrum is proportional to the phonon density of states in diamond–lonsdaleite system.

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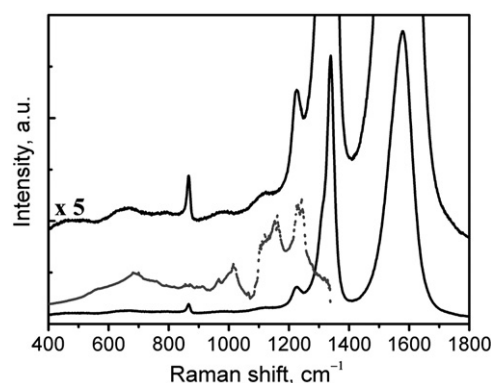


Fig. 3. Raman spectra of polycrystalline powder of the diamond–lonsdaleite system (solid lines); calculated phonon density of states (dashed line).

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