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Characterization of synthetic diamonds by EPR and X-ray diffraction techniques

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Electron paramagnetic resonance (EPR) spectroscopy and X-ray diffraction (XRD) studies were carried out on synthetic diamonds prepared using nickel, invar and monel as the catalyst solvents at high temperature and high pressure. Nitrogen and nickel were found to be the main impurities present in these specimens. α-Quartz and copper phases were also observed in some cases. The width of EPR hyperfine lines of nitrogen atoms was found to depend on the catalyst solvents used in the synthesis. These studies show that EPR and XRD techniques yield complementary results about the defects/impurities present in synthetic diamonds.

1. Introduction

Synthetic diamonds are superhard materials of great industrial importance. Since the first successful synthesis of diamond in the laboratory at high pressure and high temperature by Bundy *et al.* [1], this material has been extensively studied [2-5]. A large number of catalyst solvents have been used for synthesizing diamonds [2]. In the process of synthesis, part of the catalyst is incorporated in the body of the crystals and essentially behaves like an impurity. The electrical, optical and other properties of diamonds are very sensitive to these small amounts of impurities. It is interesting to investigate the impurities in diamonds synthesized with different catalyst solvents and compare the results. Most of the catalyst solvents used are known to give paramagnetic centres and, therefore, electron paramagnetic resonance (EPR) spectroscopy is well suited for investigating such paramagnetic defects and trace impurities present in the diamonds [3, 6]. Some of these impurities segregate into separate phases. For the structural characterization of these phases, powder X-ray diffraction (XRD) is suitable. We have studied a number of diamonds synthesized by employing EPR spectroscopy and XRD techniques. Results of these investigations are reported here.

2. Experimental procedure

Diamond crystals were synthesized in our laboratory at high temperature and high pressure using three catalyst solvents, namely nickel, invar (66% iron, 34% nickel) and monel (70% nickel, 30% copper). Details of the synthesis of these diamonds have already been published elsewhere [7]. For the sake of convenience these diamonds will be referred to as groups A, B, and C, respectively. Several samples belonging to these groups were investigated. For comparison, commercially available synthetic diamond obtained from General Electric (USA) (Grade MBG 660) and labelled as Group D was also studied.

EPR spectra were recorded by using an X-band, reflection type EPR spectrometer (Varian, model E-112) by modulating the magnetic field at 100 kHz. Line widths were checked as a function of modulation amplitude. Any possible microwave frequency saturation was also checked by varying the klystron output, during which no change was observed in EPR line contours. Temperature variations of the samples were achieved using Varian variable temperature accessory E-257.

Modern powder X-ray diffractometry is normally used for structural characterization of the specimen containing several crystalline phases. In case a crystalline phase is present in small concentrations and not detectable by diffractometry, it is worthwhile to employ photographic powder X-ray diffraction techniques with long exposure time. Therefore, we have used both these powder XRD techniques. A Debye-Scherrer camera of radius 57.3 mm using filtered CuK_α radiation from an X-ray generator operated at a rating of 35 kV and 12 mA was used to record X-ray diffraction patterns. An exposure time of about 15 h was used for all the specimens. All the X-ray diffractograms were recorded on a Siemens D-500 X-ray diffractometer.

3. Results and discussion

3.1. Results of electron paramagnetic resonance measurements

A typical EPR spectrum of a synthetic diamond specimen observed at room temperature is shown in Fig. 1. It consists of a broad asymmetrical signal on which a weak and narrow line is superimposed on the high field side. The line width of this broad signal was more than 2000 G. The g-value of this line was 3.00. These features may be due to different transition metal impurities present in dispersed form in these crystals. Similar observations have been reported earlier by Huggins and Cannon [8]. The other narrow and weak line was amplified. It was found to consist of three isotropic lines having a g-value of 2.0025 as shown in Fig. 2. We assign this signal to isolated nitrogen atoms

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Figure 1 EPR spectrum of a typical diamond powder observed at room temperature.

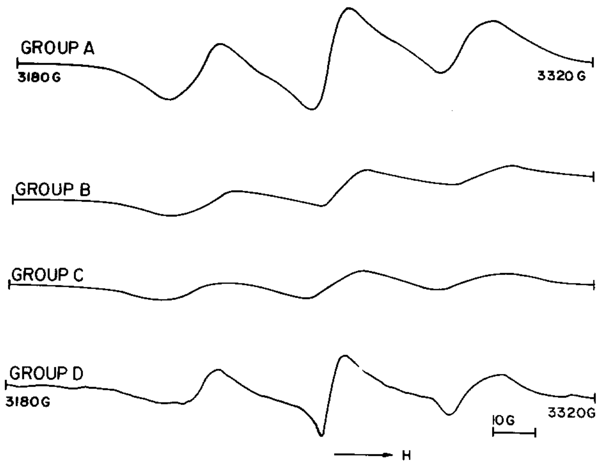

Figure 2 Hyperfine lines due to nitrogen atoms ($s = \frac{1}{2}$, $I = 1$) in diamonds of different groups.

in view of the discussion that follows. It is well known that nitrogen is the most prominent impurity in natural diamonds and it has been extensively studied [9, 10]. When nitrogen atoms are dispersed throughout the crystal they occupy isolated substitutional lattice sites. Nitrogen being a group V atom, it behaves like a donor in the diamond lattice and introduces a deep level in the band gap at about 2.2 eV below the conduction band edge [9]. The donor electron on the substitutional nitrogen atom is unpaired and therefore becomes a paramagnetic centre which can be detected by spin resonance. Its signal consists of three lines because of the hyperfine interaction of the unpaired electron with the nitrogen nucleus, having a nuclear spin $I = 1$ [9]. We have also investigated a large number of natural diamond crystals of type 1b and observed nitrogen signals in all of them [11]. The g-value of the central line observed with natural crystals was found to be the same as that given by synthetic diamond specimens. Moreover, nitrogen is practically the only element with a nuclear spin 1 which is likely to be present in diamond crystals and to give a three-line ($2I + 1$) hyperfine spectrum. Therefore we attribute this three-line signal (Fig. 2) to the atomically dispersed nitrogen impurity [9, 11]. Table I lists g values and line widths of the different spectral lines observed in different samples.

The width of the nitrogen line in natural diamond crystals was about 1 G [9, 11]. In the synthetic diamonds investigated by us it varied from 6 to 13 G (Table I). The large width in these samples may be due to the presence of different transition metal impurities. These impurities are expected to modify the magnetic field strengths at nitrogen sites and thus resulting in an inhomogeneous broadening of the signal [6, 12]. In samples of group D which were obtained from General Electric, the width of the nitrogen centre was found to be minimal (6 G). This shows that the ferromagnetic impurities in group D samples are present only in small quantities. Line widths for samples of group A are of the same order of magnitude as for the samples of group D. However, the line width is considerably more for samples of groups B and C which were synthesized with invar and monel, respectively, catalyst–solvent. This comparison clearly shows that invar and monel catalysts although they promote the growth of diamonds, lead to significant contamination of the product.

In samples of group C, a well defined broad and intense signal was also obtained along with the three weak, hyperfine lines reported above. A typical spectrum obtained for this group of samples is shown in Fig. 3. The width of this line was nearly 800 G and it has a g-value of 2.2. We assign this broad line to copper ions [6] because monel (copper–nickel alloy) was used for its synthesis. We shall discuss the presence of copper in this type of diamonds along with XRD data in the next section.

At liquid nitrogen temperature, one extra EPR line was obtained along with other signals in all samples of groups A, B, C and D. This was a narrow signal having a width of about 7 G and a g-value of 2.031. Some typical spectra for samples of different groups are shown in Fig. 4. We assign this signal to nickel ions present as impurities in these specimens. As will be reported in the next section, XRD results show the presence of an Ni_xC ($x > 4$) phase in all samples. However, in samples of group C, the nickel signal was considerably weak. In order to confirm its presence in this group of samples, we recorded the EPR spectrum of a number of specimens selected from separate batches synthesized under identical conditions. The weak signal due to nickel ions was observed in all of these samples. A similar EPR signal due to nickel impurities in synthetic diamonds was reported earlier by Loubser and Van Ryneveld [13].

TABLE I EPR parameters of different centres in synthetic diamonds

Group	Room temperature		Liquid nitrogen temperature			
	Signal due to nitrogen		Signal due to nitrogen		Signal due to nickel	
	Line width*	g-value	Line width*	g-value	Line width*	g-value
A	8.0	2.0029	10.0	2.0028	8.0	2.0316
B	12.0	2.0030	12.0	2.0028	7.0	2.0315
C	13.0	2.0026	15.0	2.0026	7.5	2.0314
D	6.0	2.0025	7.5	2.0025	7.0	2.0316

*Peak-to-peak line width, (G).

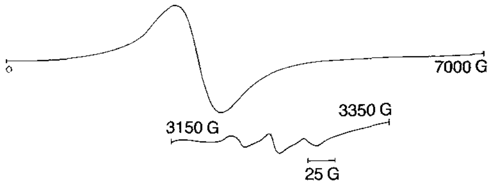

Figure 3 Broad EPR signal along with three hyperfine lines (amplified) observed in diamond of group C.

3.2. Results of X-ray diffraction studies

Figs. 5a–d show typical Debye–Scherrer powder patterns obtained for synthetic diamonds belong to goups A, B, C and D, respectively. In addition to the main phase i.e. diamond, small quantities of other phases were also observed. These are: Ni_xC ($x > 4$), Cu and SiO_2 (α-quartz). Ni_xC ($x > 4$) was found to be present in all specimens. The strong diffraction lines of Ni_xC observable at lower values of the Bragg angle overlap with the corresponding diffraction lines of diamond, particularly those due to (1 1 1) and (2 2 0) reflections. The most striking evidence of the presence of an Ni_xC phase in samples of different groups comes from the presence of (2 0 0) and (2 2 2) reflections, which are forbidden reflections for diamond. Table II gives crystallographic data about the phases detected from the Debye–Scherrer patterns shown in Fig. 5.

It may be mentioned that some of the diffraction lines in Fig. 5c (for specimens of group C) appear to be due to copper metal. The strongest XRD lines of copper are expected at the following *d*-values 0.2088, 0.1808 and 0.1278 nm. These lines can be clearly observed not only in the Debye–Scherrer photographs (Fig. 5c) but also in X-ray diffractograms. Fig. 6 shows a typical diffractogram of sample C. Well resolved peaks due to (1 1 1), (2 0 0) and (2 2 0) planes are clearly seen. The EPR spectra of these diamonds do show the presence of isolated copper ions as mentioned above; copper carbide is a possible material. No EPR spectrum due to conduction electrons of copper metal was observed. The comparison of the results of XRD and EPR studies shows that these specimens perhaps contain larger quantities of metallic copper and traces of copper carbide. The EPR spectroscopy is quite sensitive to the presence of copper carbide, but cannot easily record a signal due to copper metal because of relaxation effects [6]. The XRD experiments record the presence of copper metal due to its higher concentration and do not detect copper carbide as it is present in very small quantities.

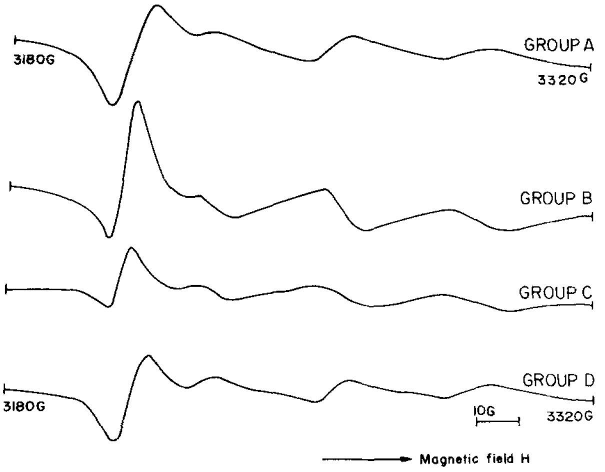

Figure 4 EPR signals due to nickel and nitrogen impurities in diamonds observed at 77 K.

Giardini and Tydings [14] studied the diamond growth employing the metal catalyst–solvent process at high temperatures and high pressures in detail. Their studies were aimed at understanding the growth mechanism. They suggest that in the case of a metal catalyst–solvent process, carbon dissolves in the metal solvent and a state of supersaturation is reached. The thermodynamic instability of this solution initiates precipitation followed by crystallization of precipitated carbon into diamond. In the present study XRD results have shown the presence of Ni_xC, $x > 4$. The formation of this compound might have taken place at high temperature and high pressure in the diamond stable region of the pressure–temperature (P–T) diagram. These were essentially intermediate phases which lead to the growth of diamond crystals.

In addition to Ni_xC, α-quartz (SiO_2) has also been detected in the specimens of group B and C. It may be mentioned that SiO_2 is commonly observed in natural diamonds as an impurity phase [15]. Silicon can be present as an impurity in the metal alloys which were

TABLE II Results of the analysis of powder XRD patterns for synthetic diamonds.

Crystalline phase	Prominent lines		Specimens in which present*
	d-value (nm)	Diffracting planes	
Ni_xC, $x > 4$	0.177	(2 0 0)	A(w), B(w), C(m), D(w)
	0.102	(2 2 2)	A(w), B(w), C(w), D(0)
	0.079	(1 3 3)	A(w), B(w), C(m), D(w)
Cu	0.208	(1 1 1)	A(0), B(0), C(s), D(0)
	0.180	(2 0 0)	A(0), B(0), C(m), D(0)
	0.127	(2 2 0)	A(0), B(0), C(w), D(0)
	0.108	(3 1 1)	A(0), B(0), C(w), D(0)
α-quartz	0.334	(1 0 1)	A(0), B(w), C(w), D(0)
	0.245	(1 1 0)	A(0), B(w), C(w), D(0)
	0.230	(1 0 2)	A(0), B(w), C(w), D(0)
	0.181	(1 1 2)	A(0), B(w), C(w), D(0)
	0.153	(2 1 1)	A(0), B(w), C(w), D(0)

*First letter, group to which the specimen belongs. Brackets, visual intensity of the diffraction line as follows: s = strong; m = medium; w = weak; 0 = absence of the diffraction line in question. Radiation used: CuK_α.

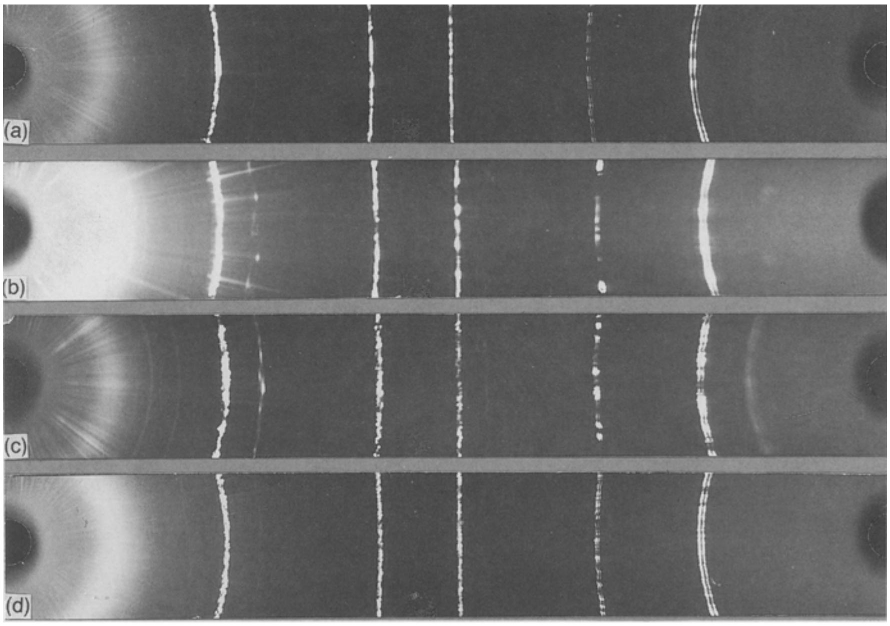

Figure 5 Debye–Scherrer patterns for samples of groups (a) A, (b) B (c) C and (d) D.

used as catalyst–solvents. Due to oxidation of silicon at high pressures and high temperature, some quantities of SiO_2 could be formed.

4. Conclusions

In the present investigations we have combined for the first time two powerful techniques, namely EPR and XRD, for the study of minor phases resulting from the catalyst solvent used in the laboratory synthesis of diamonds. These investigations show the presence of nickel carbide and nitrogen impurities in all samples. Traces of copper metal and copper carbide were observed in diamonds synthesized by using monel as the catalyst solvent. It has also been shown that the widths of EPR lines of nitrogen present in the specimens are quite sensitive to the nature of the catalysts employed in the synthesis experiments.

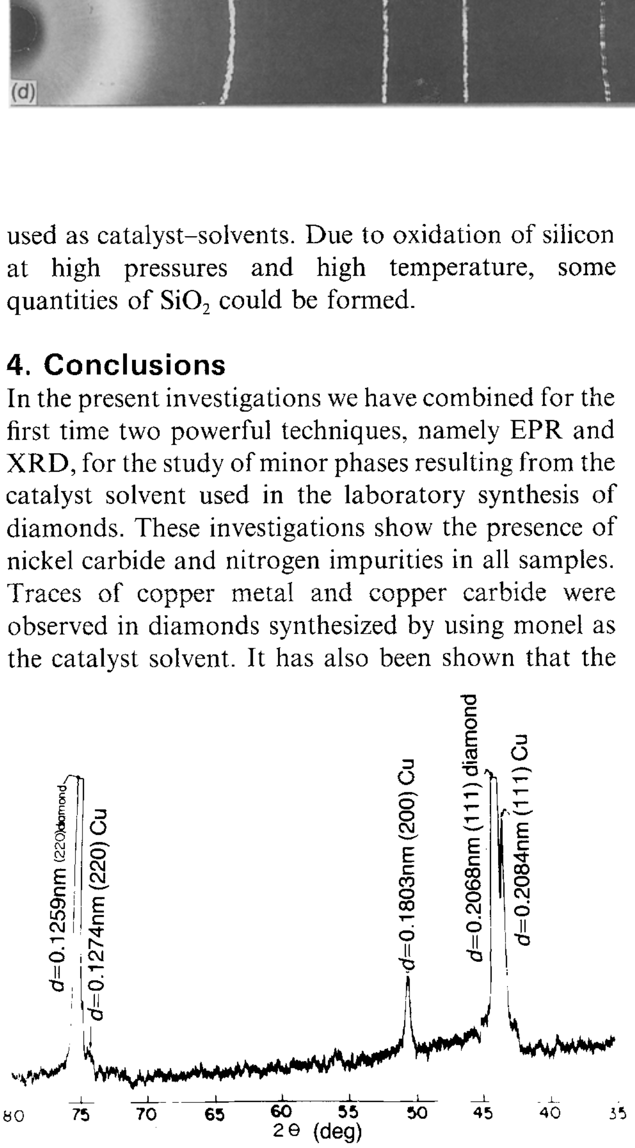

Figure 6 X-ray diffractogram of group C specimen using CuK_α as the incident X-ray beam.

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