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Application of rocking-scan method to detect the low-content diamonds in a complex mixture

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ABSTRACT

A method for detecting large-size diamonds with low content in a complex mixture was described. Phase identification via conventional X-ray diffraction method is unsuitable because of the large-size and low-content characteristics of the diamonds. Thus, we proposed a convenient approach (i.e., rocking scan) for assessing the presence of low-content diamonds in a complex mixture. A thorough rocking scan of the (111), (220), and (311) planes revealed the presence of low-content diamonds prepared by reducing dense carbon dioxide with alkali metals. This procedure can be successfully applied to several standard mixture samples prepared by mixing α-SiO_2, α-Al_2O_3, graphite, and pure diamond powders, which are commercially available. We estimated that the detection limit was at or below the 0.1 wt% level by using the proposed method under the current condition. This method is straightforward, routinized, and may be specifically developed to satisfy the requirements of public and private institutions for a rapid identification of other mixture phases, of which the large-size and low-content characteristics do not allow an instant phase identification by conventional X-ray diffraction methods.

1. Introduction

Diamond is a material with uniquely attractive electronic, structural, and optical properties that are ideal for a wide range of applications, including abrasives, tool coatings, bearing surfaces, microelectronics, optics, and corrosion protection [1–4]. Diamonds are commercially grown using high pressure and high temperature (HPHT) [5] and chemical vapor deposition (CVD) for thin films [6]. Chen synthesized large-size diamond crystals by reducing dense carbon dioxide with alkali metals (Na, K, and Li) in a stainless steel autoclave at a temperatures range of 400 °C to 600 °C [7–9]. However, the reactions were accompanied by large amounts of by-products that were difficult to separate, such as α-SiO_2, α-Al_2O_3, and graphite. Moreover, the size of the diamond particles reached micron level (10–510 μm).

Several analytical techniques (e.g., Raman spectroscopy and X-ray diffraction) have been utilized to substantiate the identification of diamond powders. X-ray powder diffraction (XRD) is a versatile and non-destructive analytical method for the identification and quantitative determination of crystalline phases in powder and solid samples. As such, XRD is used as a conventional diamond analysis method that is universally accepted. X-ray powder diffractometers typically use the Bragg-Brentano geometry. The θ-θ geometry is the most common. A specimen should ideally contain numerous small, equiaxed, and randomly oriented grains. The grain size of the powders should be ≤50 μm. In a powder or a polycrystalline material, the grains are generally randomly oriented, and some grains are oriented in a favorable direction to the x-ray beam, thereby facilitating diffraction from a specific set of lattice planes. If the grains in the specimen are excessively large or very few, then some of the reflections in the XRD pattern may be anomalously intense or absent. The missing reflections in a diffraction pattern are missing not because they are forbidden by the structure factor but because the grains are not oriented in the correct way such that diffraction could occur from these planes. In a multi-component system, the limit of detectability of the minor phase in a major phase is unsatisfactory below 5% [10]. Thus, the large-size samples with low contents are unsuitable for qualitative analysis by conventional X-ray powder diffraction method, suggesting that identifying large-size diamond crystals synthesized by the reduction of dense carbon dioxide with alkali metals is an intricate process.

The preferred orientation in a thin film can be analyzed by measuring the rocking curve measurement. In this work, we aimed to establish a method (rocking curve scan) for identifying large-size samples with low contents by using conventional XRD technique.

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2. Materials and method

2.1. Materials

All reagents were of analytical grade, purchased from Shanghai Chemical Company, and used as received without further purification.

2.2. Synthesis of diamond

The diamond synthesis process was similar to that described in a previous report [8].The reaction was performed in a stainless steel autoclave (10 mL), in which a sufficient amount of solid CO_2, which was freshly made from high-purity CO_2 gas (99%), was placed in an autoclave to ensure that the CO_2 was in supercritical states at high temperatures. A typical reaction used 8.0 g of CO_2 and 2.0 g of metallic Na, in which CO_2 was in excess for the oxidation of metallic Na. The products were sequentially washed with absolute ethanol, 2.0 mol/L aqueous HCl, and aqueous $HClO_4$ (70 wt%) at 180 °C. The products were characterized without further complex purification. The final powder was dried in an oven.

2.3. X-ray powder diffraction

The XRD data were recorded using an X'Pert PRO diffractometer (Panalytical Co., Ltd., Netherlands) equipped with a 1D detector and $CuK_{\alpha 1}$ radiation (λ = 1.54056 Å; generator setting: 40 kV and 40 mA). Variable divergent slit and antiscattering slit were used of 1°. Nickel filter was used in the secondary beam path. To obtain a rocking curve scan, an omega scan is first performed, as shown in Fig. 1a. The 2θ angle was fixed at the Bragg angle of the corresponding reflection. A rocking curve scan was then acquired by varying the angle ω while keeping the 2θ angle fixed. In the next step, on the basis of the ω positions in the rocking curve, the offset angles were calculated ($\alpha = \omega - \theta$), and θ-θ scans (20°–100° 2θ) were collected to confirm the phase identification by the offset angular correction, as shown in Fig. 1b.

2.4. Standard mixture samples

To confirm the feasibility of the method and the detection limit of the diamond under the current condition, standard mixture samples were prepared by mixing commercially available pure diamond, α-SiO_2, α-Al_2O_3, and graphite powders. Table 1 shows the commercial powders used in making the mixture samples. The XRD patterns of the standard mixture samples were in accordance with JCPDS 06-0675, JCPDS 46-1045, JCPDS 10-0173, and JCPDS23-0064. The α-SiO_2, α-Al_2O_3, and graphite powders were mixed at a weight ratio of 8:1:1 and passed through a 500-mesh sieve prior to characterization. The diamond powder was passed through 150- and 500-mesh sieves. The four reference samples containing the corresponding amounts of diamond were mixed as listed in Table 2.

Table 1
Commercial powders used to prepare the standard mixture samples of known compositions.

Compositions	Grain size [μm]	JCPDS
Diamond	25–100	06-0675
α-SiO_2	< 25	46-1045
α-Al_2O_3	< 25	10-0173
Graphite	< 25	23-0064

Table 2
Standard mixture samples with different diamond contents.

Samples	Diamond content [wt%]
S1	0.8
S2	0.6
S3	0.1
S4	0.08

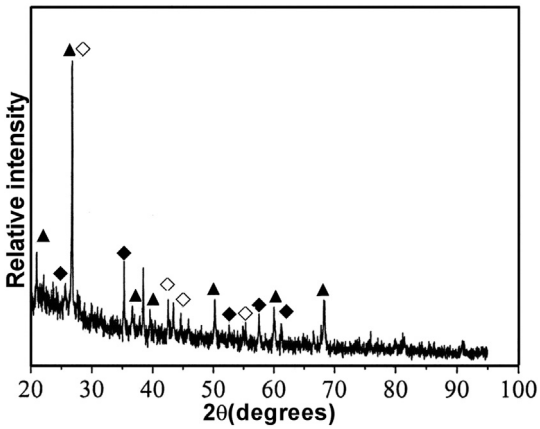

Fig. 2. X-ray diffraction pattern of the samples produced in the solid CO_2 system after treatment. α-SiO_2 marked by ▲, graphite by ◇, and α-Al_2O_3 by ◆.

3. Results and discussion

Fig. 2 shows the XRD pattern of the product synthesized by the solid CO_2 in this study. This product may be a mixture of several phases. It contained characteristic reflection peaks that corresponded to α-SiO_2 (JCPDS 46-1045). A peak appeared at 26.2°, which indicated the formation of graphite. Other observed peaks were assigned to α-Al_2O_3

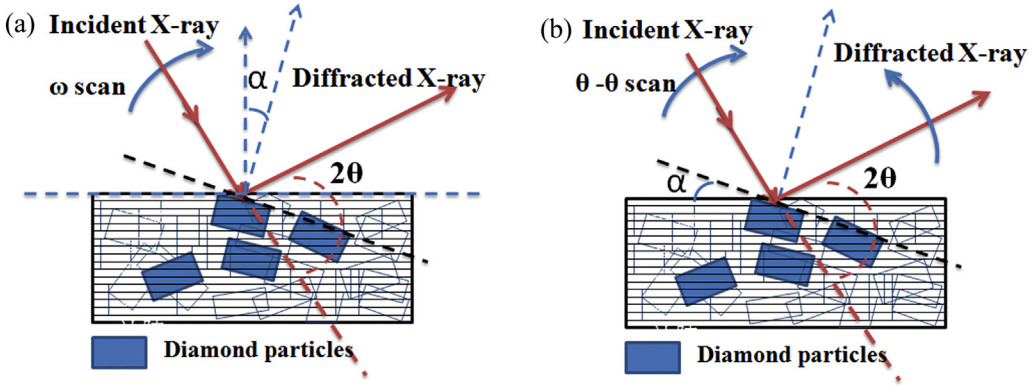

Fig. 1. Schematic of the rocking curve (a) and θ-θ (b) measurement.