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# Naturally formed epitaxial diamond crystals in rubies

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## Abstract

Materials inspired by nature comprise a running theme of modern science. Among the crystals that can be formed, diamond is perhaps most emblematic. In the conventional thinking, natural diamonds form only under high-pressure and high-temperature conditions. Here we show a new, natural form of diamond crystals of high quality that are epitaxial with their ruby substrate. Diamonds in rubies are rare; heteroepitaxial diamonds are twice as unexpected. Epitaxy suggests that the natural diamonds in the rubies were formed after ruby crystallization in a thermodynamically diamond stable region. This striking natural control over diamond epitaxy suggests a general strategy by which to form naturally-inspired, gem-quality crystals.

*Keywords:* Diamond; Epitaxy; Raman spectroscopy; Transmission electron microscopy

## 1. Introduction

Diamond-based electronics, optics and biosensors [1–3] require high-quality diamond crystals, such as epitaxially grown thin films. Heteroepitaxial diamond films on non-diamond substrates grown under low pressure and low temperature (diamond-metastable) conditions have attracted significant interest [4,5]. However, compared with natural diamonds, the synthetic diamond films by heteroepitaxy often show small crystals in sizes less than 0.5 μm [6–8] and the crystals suffer from many crystalline defects.

Ruby inclusions formed in diamonds were uncommonly reported [9]. As the singular case, diamonds were discovered in Vietnam ruby gems [10,11] as needle inclusions. The needle inclusions are large enough to be directly observed under an optical microscope (see the inset of Fig. 1a), and their dimension is about 0.6–1.4 mm long and 3–10 μm wide. Natural diamonds are commonly known to crystallize from volatile (C–H–O) rich fluids [12], or alkali-rich mantle fluids [13,14] at pressures of 5–6 GPa and temperatures in the range of 900–1400 °C [15]. This is well beyond ruby formation conditions (~0.2–1.05 GPa and 500–750 °C depending on geological locations) [16,17]. However, it is not reasonable to suppose that these diamonds were pre-formed in the needle inclusions and trapped before the crystallization of the ruby host, as natural diamond gem deposits are not known in the geologic area of Vietnam.

## 2. Experimental

To clarify the nature of the diamonds in the Vietnam ruby, we carefully characterized the diamond structure/morphology and the inclusion chemistry using transmission electron microscopy (TEM), confocal Raman microscopy, and optical microscopy. For TEM analysis, a thin cross-section of the needle inclusions was prepared using the focused ion beam (FIB) method. During the sample preparation, the positions of the inclusions in the ruby were accurately determined by laser marking with an optical microscope.

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## 3. Results and discussion

Fig. 1a shows a microscopy picture of the internal structure of the needle inclusion obtained at the enclosed rectangular region indicated in the inset. The width of the inclusion is about 3.0±0.5 μm. Four different minerals were found in the inclusion labeled M-1, M-2, M-3 and M-4. We note that mineral M-1 has a trapezoidal cross-section of ~1.0 μm sitting on the ruby host with a flat interface (as indicated by a black dotted line), which is unlike other interfaces in the inclusion. The crystal structures and chemical compositions of the four minerals were determined by high-resolution TEM (HRTEM), energy-dispersive X-ray spectrometry (EDS), and electron energy-loss spectroscopy (EELS); these data are summarized in Table 1 (see Supplementary data, Figs. S1, S2 and S3). The presence of Fe, Ni and Cr in the fluid inclusion is significant because both Fe and Ni are well known catalysts [18,19] for diamond growth and Cr is a good carbon solvent [19]. EELS analysis was performed to identify the bonding structure of the carbon mineral M-1 with the energy resolution of 0.8 eV. Fig. 1b compares one of the carbon K-edge electron energy-loss spectra obtained from mineral M-1 with that of a graphite particle. Unlike the alternative possibility of graphite, which has both π* peak (285 eV) and σ* peak, the observed pure σ* peak without π* states in the spectra obtained from mineral M-1 confirms carbon $sp^3$ bonding. This is characteristic of diamonds, as diamonds have only the σ* peak (290 eV) [20].

Table 1
Crystal structures and chemical compositions of the needle inclusion consisting of four minerals labeled M-1, M-2, M-3 and M-4

| Minerals | Crystal structures | Chemical compositions (at.%) |
|---|---|---|
| Ruby | Single crystal | Al: 39.9, O: 59.9, Cr: <0.2 |
| Mineral M-1 | Single diamond crystal | C: 100 |
| Mineral M-2 | Single $TiO_{1+x}$ crystal | Ti: 48.9, O: 51.1 |
| Mineral M-3 | Amorphous or nanocrystalline $AlO_x$ | Al: 49.7, O: 50.2, Cr: <0.1 |
| Mineral M-4 | $Fe_2O_3$ nanocrystals + amorphous Fe–Cr–Ni–F oxide | Fe: 49.6, O: 32.2, Cr: 8.8, Ni: 6.3, F: 3.1 |

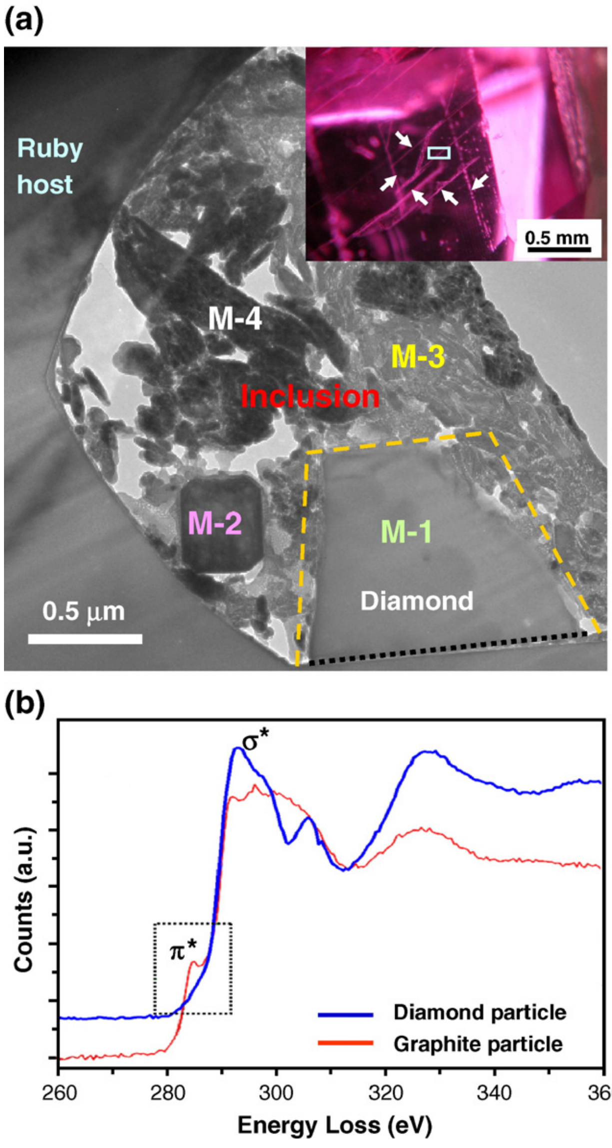

Fig. 1. Needle inclusions in a Vietnam ruby. The optical microscopy image in the inset shows the pinkish red Vietnam ruby and the needle inclusions (indicated by arrows). (a) A cross-sectional TEM image, which shows the internal structure of a needle inclusion in the Vietnam ruby. The inclusion consists of four minerals (M-1, M-2, M-3 and M-4). The black dotted line indicates the flat interface between the ruby host and the mineral particle M-1. (b) The carbon K-edge electron energy-loss spectra taken from the carbon mineral M-1. Compared to graphite, the carbon mineral M-1 shows only the σ* peak (290 eV) indicating $sp^3$ bonding and diamond structure.

The epitaxial relation of this diamond to the ruby substrate was another notable observation. Fig. 2a shows a TEM image of the flat interface between the ruby host and the diamond crystal. Ruby crystals have a hexagonal corundum structure. A selected area electron diffraction (SAED) pattern, taken from the ruby host, indicates that the ruby in the picture is oriented with the (0001) plane of the hexagonal structure parallel to the interface (Fig. 2b). Fig. 2c and d shows an SAED pattern and an HRTEM image, respectively, taken from the diamond particle. Both show a single crystal with the cubic diamond structure. Atomic distances, precisely measured by the SAED and nano-area electron diffraction (NED) pattern [21], also verify that the diamond has an *Fd3m* cubic structure. The crystallographic relation between the diamond crystal and the ruby matrix indicates that natural diamond grew in the {111} orientation (or (1$\bar{1}$1) according to the index of the diffraction pattern) on the ruby (0001) basal plane with an in-plane relationship of diamond [011]//ruby [1010]. It must be pointed out that this orientation relationship is exactly the same as for epitaxially grown synthetic diamonds on a sapphire substrate [22], which has the same crystal structure as the ruby. The (0001) plane of the ruby is hexagonal, which matches the symmetry of the diamond {111} lattice planes. The mismatch between the (0001) plane of the ruby and the {111} diamond planes is also small, 6% at ambient pressure and temperature. Low mismatch is a condition for heteroepitaxial growth.