4-1.Purple amethyst : Coloration by photonic carbon nano-structures

ROCKS

AND

MINERALS

Purple amethyst: Coloration by photonic carbon nano-structures

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Abstract

Nano-scale carbon fibers were identified in purple amethyst from Amethysta mine in Brazil, using transmission electron microscopy. This study reveals that the abundant spherical carbon particles are presented in purple regions. The purple portion contained relatively high carbon (0.485 wt%). High resolution TEM showed micro morphology of carbon particles, such as single-walled carbon tubes and onion like structures of 3 - 4 nm in diameter. The nano-scale single-walled carbon particles form an onion like skin structure of graphite with a spacing of 0.34 nm lattice images. TEM observations of purple amethyst revealed carbon particles that are arranged in a randomly oriented array with the spacing wavelength of purple light. The solid carbon particles act as holes. The nano-structures are interpreted to form a photonic material with the wavelength of purple light. This is a first observation of photonic carbon particles in purple amethyst.

Key Words: Purple amethyst, Coloration, Photonic carbon, Nano-structures, HRTEM.

INTRODUCTION

Quartz occurs usually colorless, however crystals are often colored in yellow, grey-brown to black, pink and purple varieties. The colored forms are termed citron, smoky quartz, rose quartz, and amethyst respectively. The cause of these colors has not been well documented. Trace amounts of Ge, Al, Li, Fe, Mg, Ca, Na, and K may occur in solid solution, as well as solid and fluid inclusions in quartz (Frondel 1945). The nano-fibers of pink fibrous crystals within massive rose quartz are related to dumortierite (Goreva et al. 2001; Ma et al. 2002). Other workers have suggested that the color of rose quartz is due to internal charge transfer between $Fe^{2+} + Ti^{4+} \rightarrow Fe^{3+} + Ti^{3+}$ (Smith et al. 1978).

The purple color of amethyst has been attributed to trace Fe^{3+}. Amethyst is often decolorized by heating to 290 ℃, and at 550 - 560 ℃ yellow-brown color may develop on cooling. Bleached quartz may be colored purple again by irradiation. The wavelength of visible ray ranges 3.8×10^{-7} - 7.8×10^{-7} m, from violet to red. The wavelength of purple light (bluish violet) ranges 380 - 430 nm, which is the shortest visible ray with strong refraction.

In this paper we report the characteristics of nano-scale carbon particles found in Brazilian amethyst: the nano-structures are interpreted to form a photonic crystal with dimensions of the wavelength of purple light. We found also single-walled carbon, nano-tubes and rings 3 - 4 nm diameter in natural purple amethyst which are similar to synthesized nano-tubes which are important for light wave fiber production. Carbon nano-tubes exhibit several technologically important characteristics. Previously, detailed TEM studies of carbon nano-tubes for electronics application have been reported on natural soot and heated structure (Collins and Avouris 2000). For comparison, detailed TEM studies of carbon in true amethyst have been very limited to date.

EXPERIMENTAL PROCEDURES

Samples

Amethyst crystals within cavities of basalt flows were collected from the Amethyst mine, Amethysta, southern Brazil (Fig. 1A). The purple coloration is always strong at the point of the amethyst where the crystal is softer and more porous (Fig. 1B). Small, mm-scale cavities are dispersed in colored areas of the crystals.

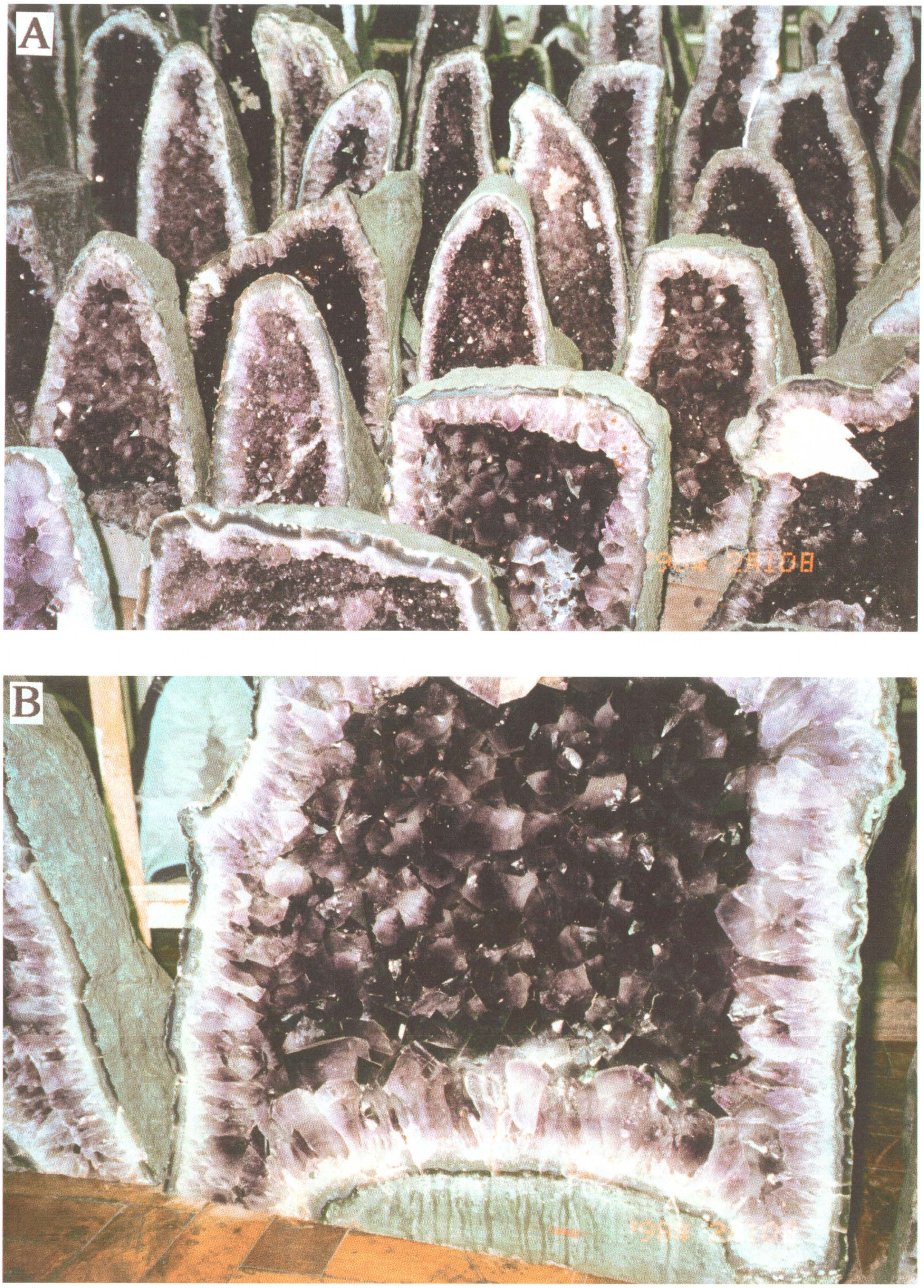

Figure 1 Photographs of purple amethyst collected from Amethysta mine, Brazil.

Transmission electron microscopy

Crushed sample was observed by transmission electron microscopy (TEM) (JEOL JEM 2000EX) under 200 kV accelerating voltage. Automatic gas chromatographic elemental analyzer (CE instruments NA 2500-NCS) was used for elemental analysis of carbon, nitrogen, and sulfur contents in amethyst crystals. X-ray powder diffraction analysis (Rigaku Rinto 1200) of the sample using Cu Kα radiation showed that the mineral phases present in the purple portions are mainly quartz. Iron oxide minerals and graphite were not detected by XRD in either purple or uncolored parts of the amethyst crystals.

RESULTS

The elemental analyses of 3 amethyst quartz grains indicated relatively high carbon content (0.485 wt%) with trace of nitrogen (0.023 wt%) and sulfur (0.016 wt%). This analytical result supports the presence of graphite in amethyst quartz (Table 1).

Table 1 Chemical composition of amethyst quartz collected from Amethysta mine, Brazil, using automatic gas chromatographic elemental analyzer. The data indicated relatively high carbon content, supporting the presence of graphite in amethyst quartz.

Samples	N	C	S
1	0.025	0.482	0.017
2	0.022	0.469	0.017
3	0.022	0.503	0.015
Ave.	0.023	0.485	0.016

(wt%)

Low-resolution TEM studies reveal aggregation of particulate material to consist of multi-walled spherical nano-carbon particles of 30 - 50 nm in diameter (Fig. 2). The carbon particles with randomly oriented basic structural units forming onion-type structures with several condensation units. The aligned layer structures can be seen. Some parts are arranged as ordered chips with high density (Fig. 2 arrows).

High resolution TEM clearly showed the presence of abundant nano-scale carbon fibers in the quartz (Fig. 3). Two types of nano-carbon particles were found by high resolution TEM: the first one with an onion skin structure (Figs. 2 - 4); and another one with single-walled carbon tubes and ring carbon structures randomly oriented (Fig. 5).

The aggregation of graphite carbon shows a basic structural unit with a spacing of 0.34 nm (002). The typical onion like skin structure is 20 - 150 nm in diameter, characterized by 0.34 nm lattice images (Fig. 4). The single-walled carbon fibers are 3 - 4 nm in diameter. The most well crystallized onion like skin structure with 150 nm in diameters is graphite crystals grown in the quartz (Fig. 4). Typical single-walled carbon nano-tubes and rings appear to stick to each other to form ribbon type structures (Fig. 5). The cross sections of the rings and the tubes are seen where the axis is aligned along the viewing direction. Electron microscopic observations have also revealed the growth processes of graphite structure through ribbon type with a spacing of 0.34 nm lattice images (Fig. 5 right corner). The graphite seems to grow from precursors of single-walled carbon nano-ring and tube with 3 - 4 nm in diameter (Fig. 5) to onion like skin structure (Fig. 3). Well-crystallized carbon particles are shown in Fig. 4 showing 0.34 nm lattice images indicating the hkl (002) reflection of graphite. Both types are densely packed in the purple point of the crystals suggesting strong light refraction. Assemblies of hollow graphitic spheres occur in the most brilliant amethyst.

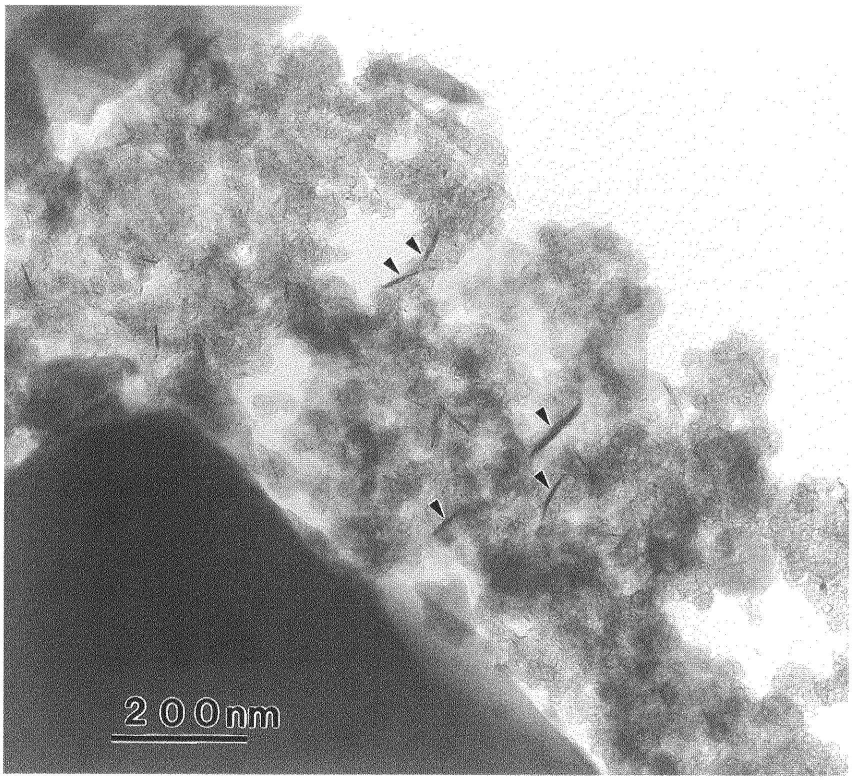

Figure 2 TEM micrograph of aggregation of graphite in amethyst shows primitive stage of graphite crystallization.

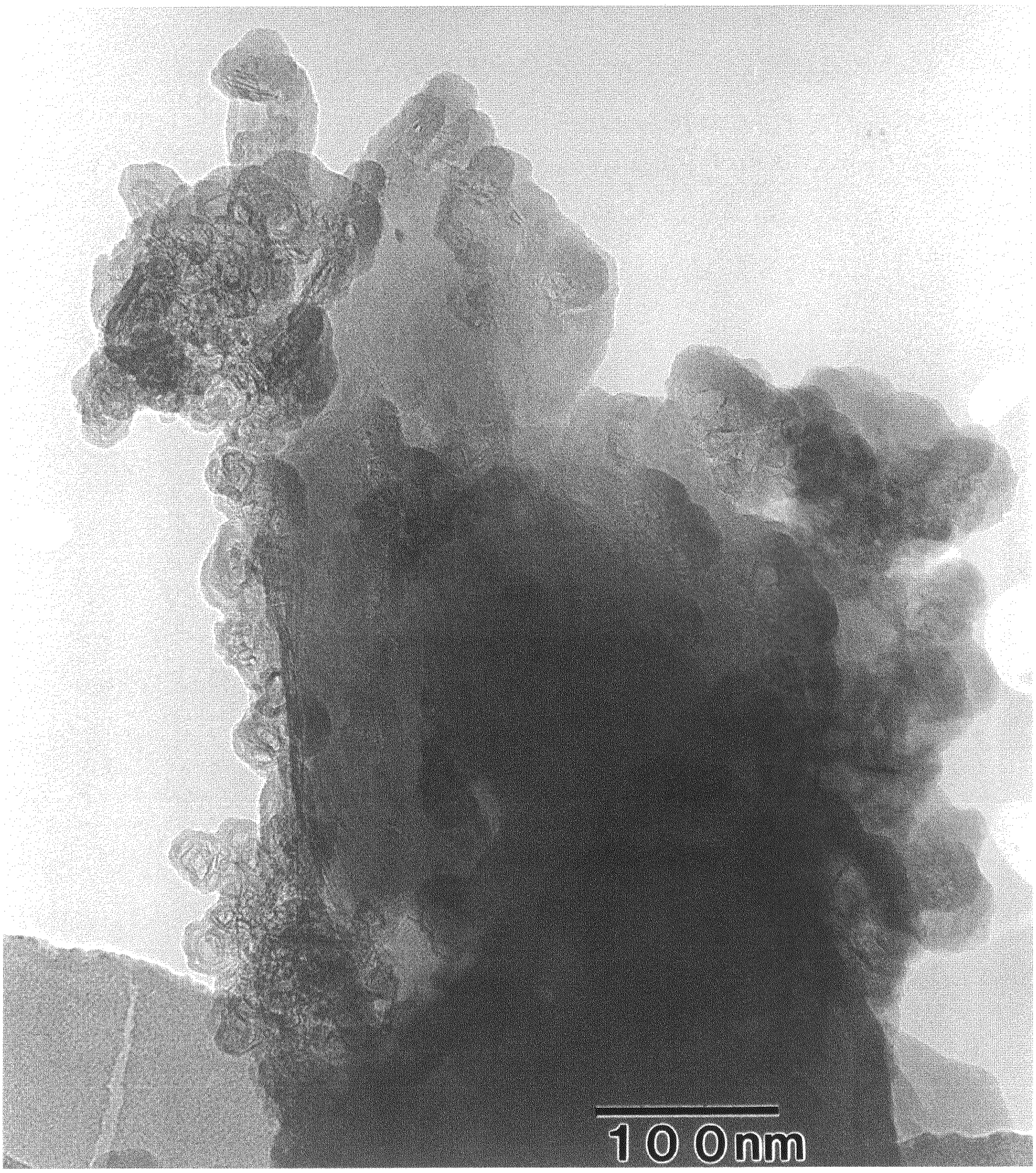

Figure 3 TEM micrograph shows onion like graphite at the purple point in amethyst quartz.

Figure 4 HRTEM micrograph shows carbon nano-structure in amethyst quartz. Lattice images show 0.34 nm spacing of graphite.

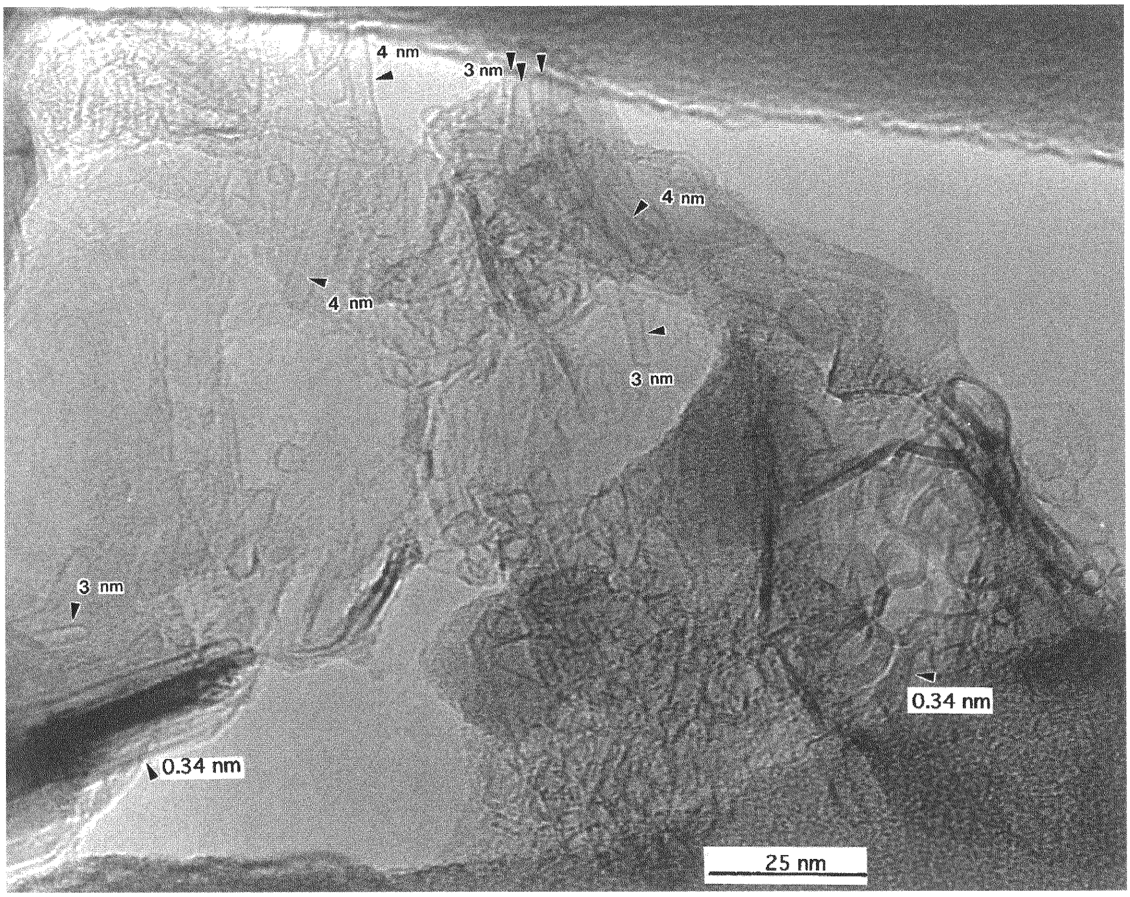

Figure 5 HRTEM micrograph of single-walled ring and nano-tube carbon, associated with ribbon structure with 0.34 nm spacing of graphite. Rings and tubes with 3-4 nm in diameter (arrows) appear to stick to each other grow to ribbon typed structure (right bottom).

DISCUSSION

Carbon in quartz

Quartz forms in rock cavities where it precipitates from warm silica-saturated aqueous solutions flowing through the cavities (McAthur et al. 1993; Eckert 1997; Leveille et al. 2000). Icosahedral cage formed of fragmental, curved sheets of polymerized SiO_4 tetrahedral may serve as nucleus certes for non-crystalline silicates, or spherical phyllosilicates, when P and N ions are present in enough amounts (Sudo 2000; Ren et al. 1998). Puddephatt et al. (1998) have found in many cases of warm, hot, fluids that mobilize SiO_2 and gold, that graphite is formed when hot fluids contain a component of carbon monoxide, CO. As this fluid cools, 2CO reacts to CO_2 and carbon.

Carbon is a major player in the evolutionary scheme of the universe because of its abundance and its ability to form complex species (Tazaki 1993, 1994; Tazaki and Dissanayake 1997; Takasu and Tazaki 1994). Typical structure of carbon particles critically depends on condensation conditions such as total pressures, temperature, and H or O partial pressures. Hexagonal onion-like texture is the most stable form of carbon during graphite crystallization. High resolution of carbon in spectra of ESCA can discriminate various ratios of carbon chemical bindings of COO (6.6 %), C-O (6.8 %), C-C (20.8 %), and graphite (65.8 %) from Sri Lanka. Both organic (3.0 %) and inorganic (5.8 %) carbon, such as Fe_3C and SiC are present in the sample (Tazaki and Dissanayake 1997). The synthesis of massive arrays of mono dispersed carbon nano-tubes that are self-oriented on patterned porous silicon and planar silicon substrates is reported by Kong et al. (1998) and Fan et al. (1999). The well-oriented nano-tube can be used as electron field emission arrays. Saito and Matsumoto (1998) produced a new form of graphitic nano-cages, rectangular parallel pipes or cubes, by arc evaporation of carbon with alkaline-earth metals calcium or strontium. The cubes contain 5 to 20 layers of multi walled graphitic carbon with a spacing of 0.34 nm. Carbon nano-tubes aligned over areas up to several square centimeters were grown on nickel-coated glass below 666 ℃, plasma-enhanced hot filament chemical vapor deposition (Ren et al. 1998; Pendry 1999).

Photonic carbon

Opals are valued as gemstones because of their bright iridescent colors, which change as a function of the viewing angle. This iridescence is due to the interference of light that is scattered by a photonic crystal or a regular dielectric structure with feature sizes of the light's wavelength. Natural opals consist of a regular three-dimensional (3D) crystalline array of colloidal silica spheres several hundred nm in size (Eckert 1997; Van Blaaderen 1998). Assemblies of hollow graphitic spheres show brilliant opalescence. At higher resolution the regularity of the assembly gives rise to strong interaction with visible light (Pendry 1999). These new materials, often referred to somewhat imprecisely as <photonic materials>, have in common the property of strong interaction with light.

Some novel new research has focused on the empty spaces in lattices. New compounds composed of ordered arrays of large holes have been prepared: synthesis procedure can be <tuned> to create arrays of holes, termed photonic crystals, from several angstroms to hundreds of nanometers is size. TiO_2 crystals shimmer like opals due to arrays of nanometer-sized holes.

In this study, natural amethyst consists of quartz and graphite crystalline array of random oriented spheres, tubes, and rings with 3 - 4 nm in size, due to arrays of nm-sized holes of bright iridescent colors of bluish violet. Porous carbon particles are 3D periodic on the scale of optical wavelengths are made by a synthesis route resembling the geological formation of natural opal. Porous silica opal crystals were sintered to form an interface through which the silica was removed after infiltration with carbon precursor (Eckert 1997; Zakhidov et al. 1998; Pendry 1999). The graphite sheets of ordered carbon atoms are themselves ordered with the symmetry of the dissolved face-centered cubic colloidal crystal array. They also used various chemical-vaporized deposition methods to fill the lattice voids with carbon. With a propylene-nitrogen blend, they synthesized graphite structures. The group points out that one of the products, termed cubic graphite, actually contains a new phase of carbon. The structure, which is reminiscent of carbon "onion" forms on the outer surface of the SiO_2 spheres and consists of graphite stacks governed by the silica spheres (Takasu and Tazaki 1994; Tazaki 1994; Fan et al. 1999; Sano et al. 2001).

Single-walled carbon to onion like structure

Meyer et al. (2000), Sano et al. (2001), and Ouyang et al. (2001) synthesized single-walled carbon nano-tubes (SWNTs) by chemical vapor deposition of methane on the patterned substrates. Many of the synthesized nano-tubes are perfect, individual SWNTs with diameters of 1 - 3 nm and length of up to tens of micron meter. The rings appear to be fully closed as opposed to open coils, as ring-openings. The average diameter of the rings was 540 nm whereas the nano-tube length was 800 nm (Sano et al. 2001).

In this study we found single-walled rings and tubes with 3 - 4 nm in diameter and onion like skin structure (20 - 150 nm in diameter) in amethyst which is the almost the same size as synthetic examples. Terrones et al. (2000) shows the coalescence of single-walled carbon nano-tubes by in situ irradiation and heating in a high resolution TEM and consider in detail the possible atomistic mechanisms leading to the merger. The three tubes coalesce into a more circular cross section.

Nano-structured materials may help reduce the size, weight and power requirements of productions of nano-technology (Roukes 2001). Tang et al. (2001) reported the observation of 1D superconductivity in single-walled 4 Å carbon nano-tube, fabricated by pyrolyzing tripro-pylamine in the channels of zeolite crystals.

This synthesis method could also have applications in natural colored amethyst. Graphite particles in amethyst cause the bright bluish violet colors visible to the eye. Electron micrograph shows that this nm size carbon material derives its optical properties from an array of nm-sized voids. Precursor carbon material or poorly crystallized carbon formed during a transient thermal event. To the author's knowledge, natural nano-carbon structure in amethyst has not been reported before.

IMPLICATIONS AND CONCLUSIONS

Here we report the discovery of solid nano-carbon graphite in a natural amethyst. The precursor single-walled carbon crystallized to onion like skin structure of graphite particles in the soft part of purple amethyst. The aggregated graphite particle structures are governed by the silica structures. The late crystal growth is purple-colored with graphite inclusions. We conclude that the purple color is due to these silica graphite structures.

REFERENCES

Collins, P. G. and Avouris, P. (2000) Nano-tubes for electronics. *Scientific American*, December, **283**, 62-69.

Eckert, A. W. (1997) The world of opals. John Wiley & Sons. Inc.Toront, 447p.

Fan, M. G., Chapline, M. G., Franklin, N. R. and Dai, H. (1999) Self-oriented regular arrays of carbon nano-tubes and their field emission properties. *Science*, **283**, 512-514.

Frondel, C. (1945) History of the quartz oscillator-plate industry. *American Mineralogist*, **30**, 205-213.

Goreva, J. F., Ma, C. and Rossman, R. (2001) Fibrous nano inclusion massive rose quartz; The origin of rose coloration. *American Mineralogist*, **86**, 466-472.

Kong, J., Soh, H. T., Cassell, A. M. and Dai, H. (1998) Synthesis of individual single walled carbon nano-tubes on patterned silicon wafers. *Nature*, **395**, 878-881.

Leveille, R. J., Fyfe, W. S. and Longstaffe, F. J. (2000) Geomicrobiology of carbonate-silicate microbialites from Hawaiian basaltic sea caves. *Chemical Geology*, **169**, 339-355.

Ma, C., Goreva, J. S. and Rossman, G. R. (2002) Fibrous nano-inclusions in massive rose quartz: HRTEM and AEM investigations. *American Mineralogist*, **87**, 269-276.

McAthur, J. R., Jennings, E. A., Kissin, S. A. and Sherlock, R. L. (1993) Stable-isotope, fluid-inclusion, and mineralogical studies relating to the genesis of amethyst, Thunder Bay Amethyst Mine, Ontario. *Canadian Journal of Earth Sciences*, **30**, 1955-1969.

Meyer, R. R., Sloan, J., Dunin-Borkowski, R. J., et al. (2000) Discrete atom imaging of one-dimensional crystals formed within single-walled carbon nano-tubes. *Science*, **289**, 1324-1326.

Ouyang, M., Huang, J. L., Cheung, C. L. and Lieber, C.M. (2001) Energy gaps in "Metallic" single-walled carbon nano-tubes. *Science*, **292**, 702-705.

Pendry, J. (1999) Playing tricks with light. *Science*, **285**, 1689-1688.

Puddephatt, R. J., Zhou, S. and Fyfe W. S. (1998) Transport of gold in high temperature, low pressure, gas phases with Cl_2, CO, H_2S: A clue to gold mobilization from the lower crust. In R.B. Bhappu and R.J. Harden (Eds) Gold forum on technology and practices-World Gold 89. Society for Mining, Metallurgy, and Exploration, Inc. Littleton, Colorado, 1989, 124-130.

Ren, Z. F., Huang, Z. P., Xu, J. W. and Provencio, P. N. (1998) Synthesis of large arrays of well-aligned carbon nano-tubes on glass. *Science*, **282**, 1105-1107.

Roukes, M. (2001) Plenty of room, indeed. *Scientific American*, **284**, 42-49.

Saito, Y. and Matsumoto, T. (1998) Carbon nano-cages created as cubes. *Nature*, **392**, 237.

Sano, M., Kamino, A., Okamura, J. and Shinkai, S. (2001) Ring closure of carbon nano-tubes. *Science*, **293**, 1299-1300.

Smith, G., Vance, E. R., Hasan, Z., Edgar, A. and Runciman, W. A. (1978) A change transfer mechanism for the colour of rose quartz. *Physica Status Solidi*, **(A) 46**, K135-K140.

Sudo, T. (2000) Geometrical approach to the structure of nano-crystalline silica precipitates. *Structureal Chemistry*, **11**, 15-17.

Takasu, A. and Tazaki, K. (1994) Elemental color map analysis of graphite from Sri Lanka. *Earth Science (Chikyu Kagaku)*, **48**, 16-19.

Tang, Z. K., Zhang, L., Wang, N. et al. (2001) Superconductivity in 4 angstrom single-walled carbon nano-tubes. *Science*, **292**, 2462-2465.

Tazaki, K. (1993) Process of formation of bacterial iron and carbon minerals. *Science Rep. Kanazawa Univ.*, **38**, 59-77.

Tazaki, K. (1994) Observation of carbon by electron microtechniques. *Earth Science*, **48**, 395-411.

Tazaki, K. and Dissanayake, C. B. (1997) Transformation of carbon to graphite. In Gupta, A.K., and Kerrich, R., Ed., The dynamic geosphere. National Academy of Sciences, India Allahabad. 152-164.

Terrones, M. T., Terrones, H., Banhart, F., Charlier, J. C. and Ajayan, P. M. (2000) Coalescenve of single-walled carbon nanotube. *Science*, **288**, 1226-1229.

Zakhidov, A. A., Baughman, R. H., Iqbal, Z., Cui, C., Khayrullin, I., Dantas, S. D., Marti, J. and Ralchenko, V. G. (1998) Carbon structures with three-dimensional periodicity at optical wavelengths. *Science*, **282**, 897-901.

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