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Visible emission of single-wall carbon nanotubes formed in micro-channels of zeolite crystals ☆

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Abstract

Emission spectroscopy is performed to study the optical transitions between electronic bands of SWCNs formed in $AlPO_4 - 5$ (AFI) crystal. Strong visible emission is observed under laser light illumination at room temperature. The emission is excited by the light polarized along the *c*-axis and its polarization is also along this direction. On the other hand, non-linear emission is observed under the resonant excitation of the lowest absorption band of SWCNs. The emission is excited by the light polarized along the *c*-axis, but it shows the polarization perpendicular to the *c*-axis. The polarization character is discussed on the basis of the selection rules of the optical transitions predicted by the full line-group symmetry of SWCNs. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Single-wall carbon nanotube (SWCN) is known as a single layer of graphite that is wrapped up into a seamless cylinder. The electronic structure is mainly determined by the diameter, d, and the wrapping angle that are determined by one parameter called the chiral vector, $\mathbf{C} = n\mathbf{a} + m\mathbf{b}$, where n and m are integers, **a** and **b** are unit vectors which specify the locations of two inequivalent carbon atoms in the unit cell. The symbol (n, m) specifies the type of the SWCN and determines whether the SWCN is metallic or semi-conducting

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in the lowest order approximation. SWCNs have attracted considerable interest in basic research and in potential nanotechnology applications.

Recently, the SWCNs of the smallest diameter, $d \sim 0.4$ nm were found in micro-channels of 0.73 nm diameter in Zeolite (IUPAC Cord AFI), $AlPO_4 - 5$ single crystals [1]. They are packed in hexagonal arrays and aligned along the c-axis of the crystal. The diameter of an SWCN is comparable to a similar one found in the innermost shell of the multi-wall CNs [2]. Given the small diameter, the available type of the SWCNs is limited to be $(5,0)$, $(4,2)$ or $(3,3)$. However, the definite identification of the type has not been established. The most probable type of the present SWCNs has been considered to be $(5,0)$.

The single crystals of AFI themselves are elongated hexagonal prisms. They are optically transparent and isotropic up to near ultraviolet [3] but the AFI-SWCN system shows strong polarization anisotropy in optical absorption [4]. The assignment of the corresponding absorption spectra has not been settled. On the other hand, the study on the emission spectroscopy of the system has not been published so far. The objectives of the present work are to try the assignment of the anisotropic absorption spectra from the symmetry consideration of the relevant optical selection rules and to study the correlation with the polarization characteristics of the emission. The full line-group symmetry of SWCNs was used.

2. Absorption spectra

The left panel of Fig. 1 shows optical absorption spectra of the AFI-SWCN system [4]. Since the electronic band gap energy, E_g, of an SWCN is inversely proportional to d [5], the corresponding E_g of the present SWCN is supposed to be around 1 eV. The spectra show strong polarization anisotropy as have been predicted theoretically [6–10].

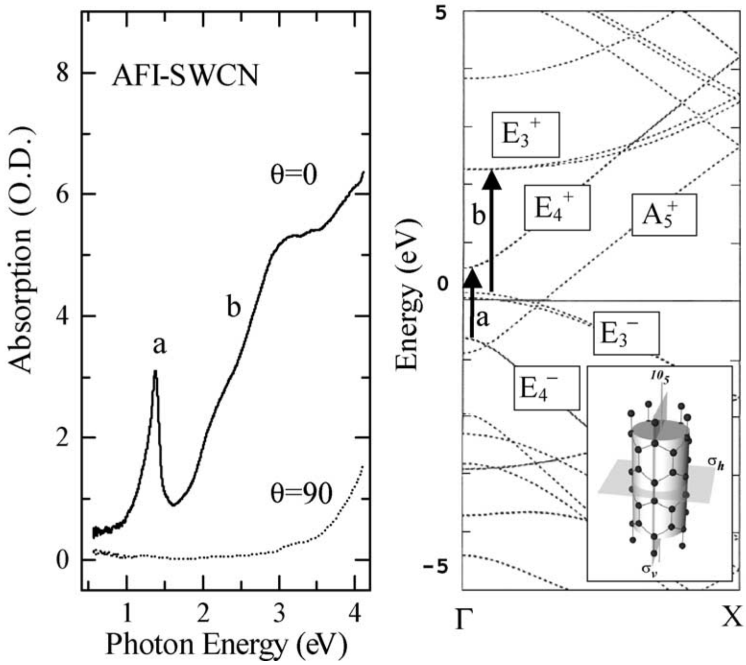

Fig. 1. Left panel: absorption spectra of the AFI-SWCN system. θ represents the angle of the incident light's polarization with respect to the c-axis. Right panel: energy band structure of an SWCN of $(5,0)$ type calculated by LDA method. The symmetry of respective bands is indicated. The notation is explained in the text. a and b show the corresponding dipole allowed transitions of the absorption bands shown in the figure.

The right panel shows the band structure of (5, 0) tube calculated by LDA method. We took account of the modulation in the hybridization caused by the small diameter of the tube [11]. Due to the effects of the curvature of the thin tube, one of the conduction bands is pulled down and it crosses the Fermi level to make the tube metallic. In fact, metallic conduction [12] and also superconducting character [13] have been observed.

The symmetry of the relevant bands at the zone center is identified on the basis of the theory of line-group, $L10_5/mcm$ [14]. In this paper, we confine ourselves to discussing (5, 0) tubes. The structure of (5, 0) tube is shown schematically in the inset.

A shows the non-degenerate even parity band with respect to the vertical mirror reflection, σ_v in the plane parallel to the tube axis. E shows the doubly degenerate bands. The suffix indicates the quantum number of the quasi-angular momentum, M. The parity with respect to the horizontal mirror reflection, σ_h in the plane perpendicular to the tube axis is also given by + for even states and by − for odd ones. According to the line-group symmetry consideration, the electric dipole transitions should be allowed with the polarization $E//c$ in σ_v conserved and σ_h reversed conditions with $\Delta M = 0$. On the other hand, they should be allowed with the polarization $E \perp c$ in σ_v reversed and σ_h conserved conditions with $\Delta M = \pm 1$. Here, magnitude of the wave vector of the light is assumed to be zero. Thus, the absorption structures named "a" and "b" in the left panel are attributed to the transitions with the polarization $E//c$. The corresponding transitions are indicated by arrows in the right panel. According to the usual notation based on the point group, D_{5d}, the corresponding transitions are assigned to $E_{1g} \rightarrow E_{1u}$ and $E_{2g} \rightarrow E_{2u}$. The strong absorption band at 3 eV could not be explained by the transition for (5, 0) tubes.

3. Emission spectra

Fig. 2 shows typical examples of the emission spectra for the AFI-SWCN system. The emission spectra for AFI-TPA crystals without pyrolysis are also shown. The crystals were kept standing vertically on a thin side edge of a slide glass held on a DC-driven *xyz*-translation stage without any support as shown in the upper inset. The emission measurements were performed, avoiding the cracked parts observed as horizontal dark lines.

The lower inset shows a schematic illustration of the experimental setup. θ and ϕ are the angles of the orientation of the polarization of the incident light and that of the analyzer against the c-axis. The spot size of the excitation was about 30 $\mu\phi$. The solid and dotted lines show the emission at $\theta = 0^\circ$ and 90°, respectively. The wavelength of the excitation light is indicated for the respective emission spectra by arrows. The intensity of the emission has linear dependence on the intensity of the excitation light.

The AFI-SWCN crystals showed two types of strong emission of strong polarization anisotropy under the 488 nm excitation. The feature depended on the sample and the location of the excitation spot in the sample. One of them showed fine structures. This emission was observed in a group of samples. In an other group of samples, an additional strong emission peaked around 620 nm was observed, overlapping with the emission mentioned just before. The emission was strongly excited and polarized in $E//c$ direction. To examine the origin of the emission, we measured the emission of the AFI-TPA crystals under similar excitation conditions. As seen in the figure, polarized emission appeared in a similar spectral region but the intensity was very weak. To clarify the characteristic nature of the emission, we also measured emission under the 325 nm excitation. In both systems, similar emission appeared in shorter wavelength region than in the 488 nm excitation. This suggests that the emission observed in this excitation does not originate from the SWCNs. From these data, it is concluded that the strong emission observed in the 488 nm excitation may be characteristic of the AFI-SWCN system. As mentioned before, the emission of AFI-SWCN system depends on the sample quality in general. It seems to be due to the preparation processes of the samples. Useful

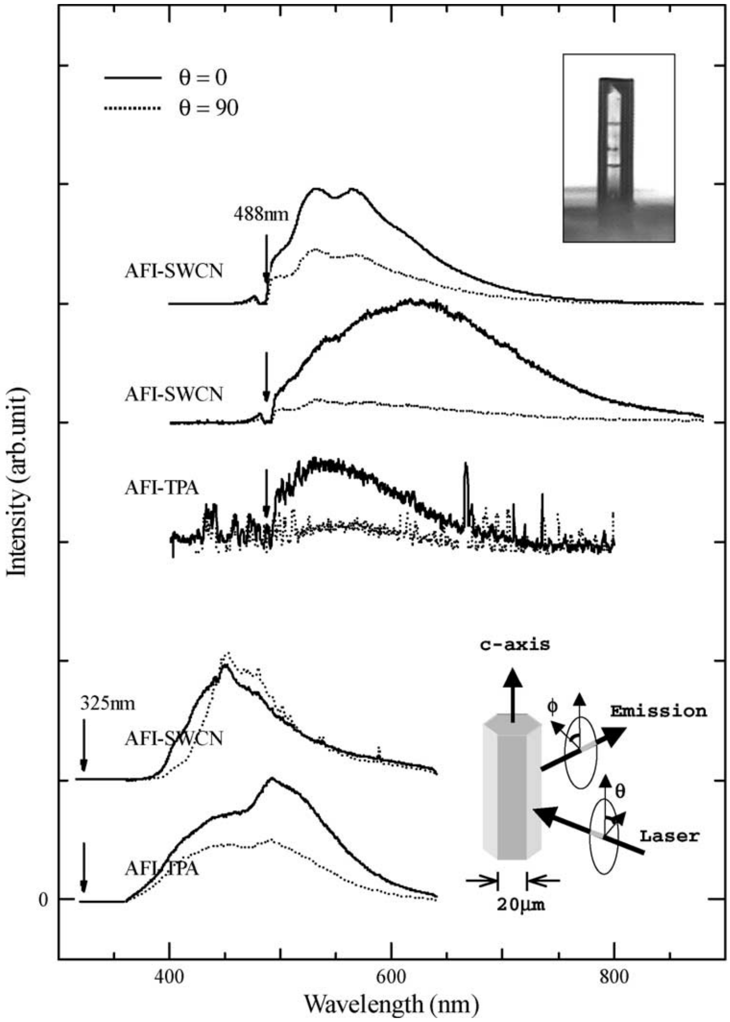

Fig. 2. Emission of AFI-TPA and AFI-SWCN systems. The upper inset shows a microscope image of a sample standing on a thin side edge of a slide glass. The lower inset shows the schematic illustration of the experimental setup. The wavelength of the excitation laser light is shown by ↓. Solid and dotted lines show the spectra in the polarization configuration of $\theta = 0$ and 90, respectively.

means to characterize the sample quality are desired to be found.

For this purpose, we measured the spatial distribution of the characteristic emission of the AFI-SWCN crystals by using a microscope fluorescence tomography. The *Nanofinder* developed by Tokyo Instruments Inc. was used [15]. Figs. 3a and b are the images of the emission under $E//c$ and $E \perp c$ configurations for a sample of relatively high quality. The maximum intensity is normalized in both images but the absolute intensity in $E//c$ at the maximum is much larger than that in $E \perp c$, as seen in Fig. 2. The laser light was perpendicularly focussed on one of six side surfaces of the crystal by a microscope objective lens and the emission was collected by the same lens. The spatial resolution was about 2 μm in these observations. From these images, it is found that the spatial distribution in intensity of the emission depends on the polarization anisotropy

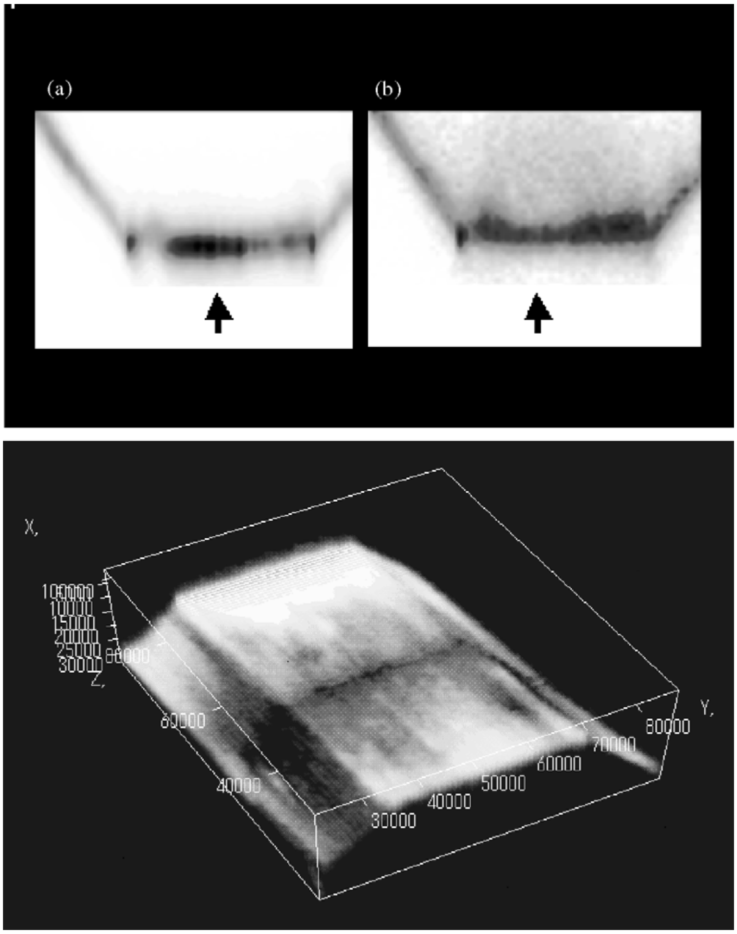

Fig. 3. Spatial distribution of the emission of AFI-SWCN system measured by *Nanofinder*: (a) and (b) show the images from the hexagonal cross section of the crystal at $\theta = 0$ and 90. The direction of the excitation laser light is indicated by an arrow. The lower part shows a bird's-eye-view of the surface region at $\theta = 0$. These figures were reconstructed from a set of two-dimensional intensity distributions recorded by shifting the depth of the focal point of the excitation light stepwise.

of the absorption. However, since the spectrum of the emission is in the spectral region of strong absorption, we have to take account of the re-absorption effects for quantitative discussions. The lower part of Fig. 3 shows an example of three-dimensional tomographic images showing the surface region by the emission under $E//c$. The unit of the scale is nm. The dark line corresponds to one of the cracks of the sample shown in the upper inset of Fig. 2. This suggests that the apparatus will be very useful to characterize the sample quality in nanoscale spatial resolution. Experiments along this line are in progress.

4. Nonlinear emission

In samples of high quality, we found a broad new emission peaked around 750 nm of remarkable non-linearity under the 1064 nm Nd^{+}YAG laser light irradiation. In this case, the peak "*a*" in Fig. 1 is directly excited. Fig. 4 shows an example of the emission spectra. The steep decrease at

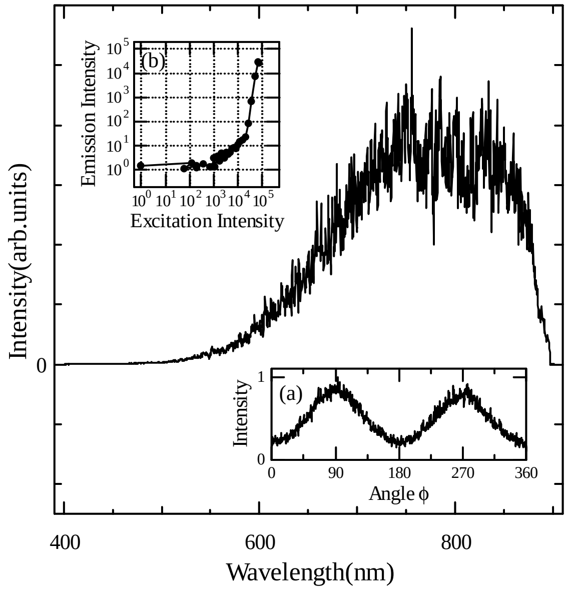

Fig. 4. Non-linear emission spectrum in AFI-SWCN system. The insets show the polarization character (a) and I-dependence in log–log scale (b), respectively.

around 880 nm is due to the drop of the detector's sensitivity.

The emission intensity as a function of ϕ is shown in the inset (a). From this figure, it is clear that the emission is polarized *perpendicularly* with respect to the c-axis. The inset (b) shows the intensity as a function of the intensity of the incident light, I, in log–log scale. A strong threshold is seen at around $5\ \mathrm{kW/cm^2}$ suggesting that some stimulated process is at the origin of the emission.

The peak energy of the emission is about 1.7 eV. It is close to the transition energy between the lowest two unoccupied bands, E_3^+ and E_4^+. According to the selection rules predicted from the line-group $\mathrm{L10_5/mcm}$, the transition is allowed in $E \perp c$, being consistent with the experimental result. Such a transition is predicted to be forbidden in point-group selection rules. The emission light is really up-converted in energy but the intensity does not show quadratic dependence on I. Thus, the origin is not due to the relevant two-photon transition. Some Auger type process would be the origin. Another candidate of the origin of the emission would be some unpolarized emission, such as blackbody radiation. In this case, the emission should be also in $E \perp c$ due to the strong polarized re-absorption of the emission. Under very strong excitation, some samples emit strong SHG light with the sudden diminution of the emission intensity. The study on the origin is in progress.

5. Conclusion

(1) The symmetry of the electronic bands and the relevant optical transitions are examined using the line-group theory assuming the type of the present SWCN is $(5,0)$. It is found that the polarization character of dominant anisotropic absorption bands, a and b in band gap region can be understood on the basis of line-group selection rules. The origin of the absorption band at 3 eV could not be $(5,0)$ tubes.

(2) Various visible emission bands of polarization anisotropy were observed depending on the samples. The origins could not be identified. The effective method for the characterization of the sample is desired. Three-dimensional tomographic technique by *Nanofinder* of nano-scale spatial resolution was found to be promising.

(3) Up-converted non-linear emission was found under the resonant excitation of the lowest absorption band of the SWCNs. The emission was polarized perpendicular to the c-axis. Provisional explanations of the origin were given.

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References

[1] N. Wang, Z.K. Tang, G.D. Li, J.S. Chen, Nature 408 (2000) 50.
[2] L.C. Qin, X. Zhao, K. Hirahara, Y. Miyamoto, Y. Ando, S. Iijima, Nature 408 (2000) 50.
[3] K. Hoffmann, F. Marlow, J. Caro, Zeolites 16 (1996) 281.
[4] Z.K. Tang, Z.M. Li, G.D. Li, N. Wang, H.J. Liu, C.T. Chan, Proceedings of International Symposium on Nanonetwork Materials, Fullerenes, Nanotubes, and Related Systems, ISNM2001, Kamakura, Japan, AIP Conf. Proc. 590 (2001) 125.
[5] M.D. Dresselhaus, R.A. Jishi, G. Dresselhaus, D. Inomata, K. Nakao, R. Saito, Mol. Mater. 4 (1994) 27.
[6] F. Huaxiang, Y. Ling, X. Xide, Solid State Commun. 91 (1994) 191.
[7] H. Ajiki, T. Ando, Physica B 21 (1994) 349.
[8] H. Ajiki, T. Ando, Jpn. J. Appl. Phys. Suppl. 34 (1995) 107.
[9] S. Tasaki, K. Maekawa, T. Yamabe, Phys. Rev. B 57 (1998) 9301.
[10] I. Božović, N. Božović, M. Damnjanović, Phys. Rev. B 62 (2000) 6971.
[11] X. Blase, L.X. Benedict, E.L. Shirley, S.G. Louie, Phys. Rev. Lett. 72 (1994) 1878.
[12] H.D. Sun, Z.K. Tang, J.N. Wang, J. Magn. Magn. Mater. 198/199 (1999) 255.
[13] Z.K. Tang, L. Zhang, N. Wang, X.X. Zhang, G.H. Wen, G.D. Li, J.N. Wang, C.T. Chan, C.P. Sheng, Science 292 (2001) 2462.
[14] I. Božović, M. Vujičić, F. Herbut, J. Phys. A 11 (1978) 2133;
I. Božović, M. Vujičić, F. Herbut, J. Phys. A 14 (1981) 777.
[15] N. Nagasawa, I. Kudryashov, S. Tsuda, Z.K. Tang, Proceedings of International Symposium on Nanonetwork Materials, Fullerenes, Nanotubes, and Related Systems, ISNM2001, Kamakura, Japan, AIP Conf. Proc. 590 (2001) 213.