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Optical, TSL, and OSL Properties of Copper-doped Cesium Bromide Transparent Ceramics Prepared by SPS

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The optical, thermally stimulated luminescence (TSL), and optically stimulated luminescence (OSL) properties of CsBr:Cu transparent ceramics were evaluated. As the photoluminescence properties, two emissions around 460 and 490 nm related to Cu^{+} and Cu^{2+} ions, respectively, were observed under excitation at around 300 nm, and the quantum yield of CsBr:Cu (0.01%) was 17.3%. After X-ray irradiation, all the samples showed a broad TSL and OSL emission band around 400–500 nm. All the samples exhibited good proportionality in the TSL and OSL dose response functions in the dose ranges of 0.01–100 and 1–1000 mGy, respectively.

1. Introduction

Bulk inorganic phosphors have been utilized to measure ionizing radiation, and they are mainly classified into scintillators and storage phosphors.[1] Scintillators convert ionizing radiation such as X- and γ-rays into numerous ultraviolet–visible photons, then the converted photons can be detected by photodetectors such as photodiodes and photomultiplier tubes. Bulk inorganic phosphors have been used in various fields, including security,[2] medical imaging,[3] well logging,[4] astrophysics,[5] and particle physics.[6] On the other hand, storage phosphors temporarily store the incident radiation dose, and then the stored energy can be released by external simulation to emit photons. The photons obtained by the stimulation of heat or light are called thermally stimulated luminescence (TSL) and optically stimulated luminescence (OSL), respectively.[7] Since the TSL and OSL intensities are proportional to the incident radiation dose, storage phosphors are used for personal dose monitoring[8–13] and imaging plates.[14–19]

So far, most research on scintillators and storage phosphors has been on various material forms including single crystals,[20–24] glasses,[25–29] and opaque ceramics.[30–32] In recent years, transparent ceramics have attracted much attention as a new material form.[33–36] When a scintillator or storage phosphor is transparent, luminescence can be detected from not only the surface but also inside the material. Additionally, transparent ceramics generally have a lower

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sintering temperature, higher uniformity of the dopant, and higher mechanical strength than single crystals. In particular, we found that the TSL and OSL properties of transparent ceramics synthesized by spark plasma sintering (SPS) were enhanced in some materials,[37–39] since the SPS was performed in a highly reductive environment, which effectively generates defect centers. However, there are few reports on the TSL and OSL properties of transparent ceramics synthesized by SPS.

In this study, we focused on CsBr, which is a promising host material for storage phosphors because of its effective X-ray absorption.[40,41] According to previous reports, CsBr:Cu crystals show strong OSL emission in the blue to green region.[42,43] However, there are no reports on CsBr:Cu in the transparent ceramic form. Therefore, we synthesized CsBr:Cu transparent ceramics by SPS and investigated their optical, TSL, and OSL properties.

2. Experimental Procedure

CsBr:Cu (0.01, 0.1, and 1%) transparent ceramics were synthesized by SPS using raw powders of CsBr (99.99%, Furuuchi Chemical) and $CuCl_2 \cdot 2H_2O$ (99.99%, Kojundo Chemical Laboratory). These powders were mixed and loaded in a cylindrical graphite die and held between two graphite punches. As shown in Fig. 1, the temperature of the SPS equipment was increased from 20 to 450 °C at a rate of 43 °C/min, then maintained at 450 ºC for 10 min while applying a pressure of 6 MPa. After sintering, the surfaces of samples were mechanically polished with sandpaper.

To evaluate the optical properties of the samples, in-line transmittance spectra were obtained by a spectrophotometer (SolidSpec-3700, Shimadzu). Photoluminescence (PL) excitation and emission maps as well as the PL quantum yield (*QY*) were obtained using an absolute PL quantum yield spectrometer (Quantaurus-QY C11347, Hamamatsu Photonics). PL decay curves were obtained using a fluorescence lifetime spectrometer (Quantaurus-Tau C11367, Hamamatsu Photonics). The TSL spectrum as a function of temperature was measured using a customized setup.[44,45] To obtain the TSL dose response function, the TSL signal was obtained using a commercial TSL reader (TL-2000, Nanogray) after various irradiation doses.[46] As the radiation source, we used an X-ray generator (XRB80P &N200×4550, Spellman) equipped with a

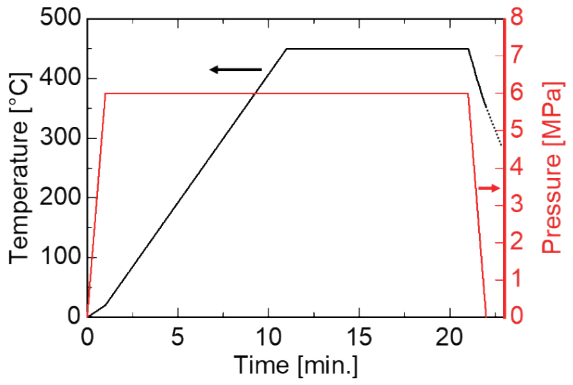

Fig. 1. (Color online) SPS processing conditions.

conventional X-ray tube having a W anode target. The X-ray tube was operated with a tube voltage of 40 kV, and the irradiated dose was calibrated using an air-filled ionization chamber (TN30013, PTW). OSL emission and stimulation maps of CsBr:Cu transparent ceramics after X-ray irradiation (10 Gy) were obtained using a spectrometer. The OSL dose response function was obtained using a spectrofluorometer (FP-8600, JASCO) after X-ray irradiation with various doses during stimulation at 630 nm.[47]

3. Results and Discussion

Figure 2 shows photographs of the CsBr:Cu transparent ceramics under room light and 302 nm excitation. When the sample thickness was fixed at 10 mm, all the samples were transparent. Under 302 nm excitation, all the samples produced a verdigris-colored emission. In-line transmittance spectra of the CsBr:Cu transparent ceramics are shown in Fig. 3. The transmittance increased with increasing Cu concentration.

For all the samples, absorption bands were observed around 275 and 315 nm. Since the absorption bands were similar to those reported for CsBr:$CuBr_2$ and CsBr:CuO crystals, their origin was concluded to be $3d^9 4s$–$3d^{10}$ transitions of Cu^+ and Cu^{2+} ions, respectively.[42,43]

Figure 4 shows PL excitation and emission maps of the CsBr:Cu transparent ceramics. Two excitation bands were observed around 275 and 315 nm, consistent with the absorption bands. The CsBr:Cu samples showed a broad emission band around 460 nm under 275 nm excitation, while all the samples exhibited a broad emission band around 490 nm under 315 nm excitation. The spectral shapes were similar to those in previous reports on CsBr:CuO and CsBr:$CuBr_2$ crystals, and the emissions around 460 and 490 nm were considered to be related to Cu^+ and Cu^{2+} ions, respectively.[42,43] OH^- ions and oxygen impurities may have existed in the matrix because $CuCl_2 \cdot 2H_2O$ was used as a starting powder. The *QY* values of CsBr:Cu (0.01, 0.1, and 1%) were 17.3, 14.4, and 12.2%, respectively, which were higher than those of CsBr:Eu transparent ceramics (0.8–3.4%).[48]

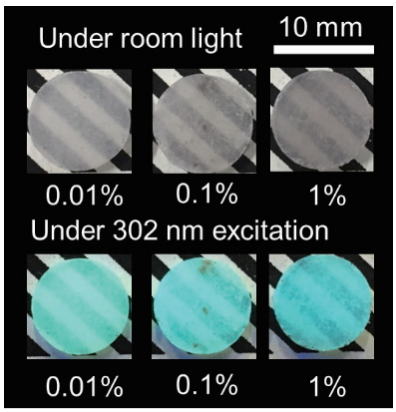

Fig. 2. (Color online) Photographs of CsBr:Cu transparent ceramics under room light and 302 nm excitation.

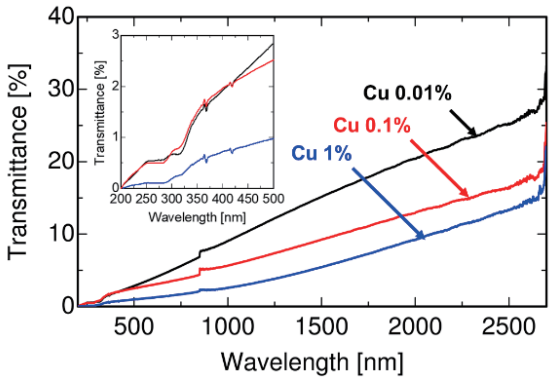

Fig. 3. (Color online) In-line transmittance spectra of CsBr:Cu transparent ceramics. The inset is an enlargement of the 200–500 nm region.

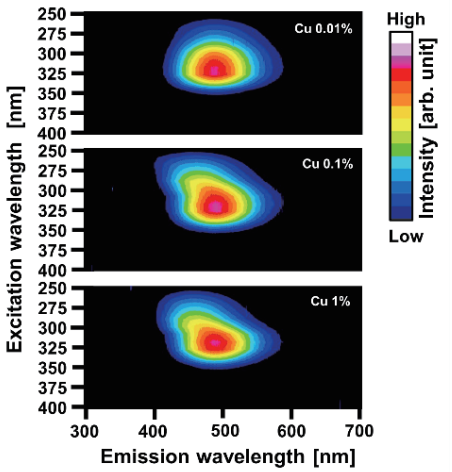

Fig. 4. (Color online) PL excitation and emission maps of CsBr:Cu transparent ceramics.

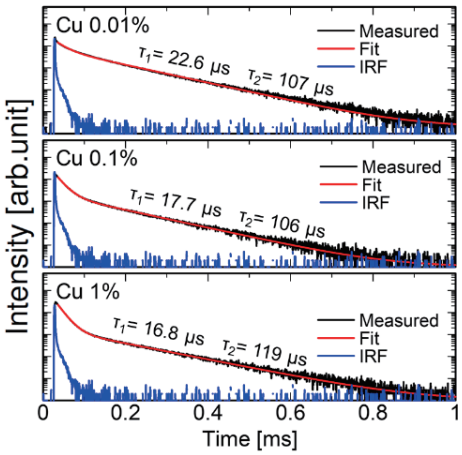

Fig. 5. (Color online) PL decay curves of CsBr:Cu transparent ceramics.

PL decay curves of the CsBr:Cu transparent ceramics are presented in Fig. 5. The monitoring and excitation wavelengths were 490 and 265 nm, respectively. The decay time constants were obtained by fitting the tail part of the decay curves with the sum of two exponential decay functions to avoid the influence of the instrumental response function (IRF). The obtained faster and slower components were 16.8–22.6 and 106–119 μs, respectively, consistent with the values in previous reports on CsBr:CuO crystal and Cu-doped materials.[42,49,50]

Figure 6 shows the TSL spectrum as a function of the temperature of the CsBr:Cu transparent ceramics after X-ray irradiation (10 Gy). TSL glow peaks appeared at around 85 and 150 °C, and the intensity of the peak at around 150 °C increased with increasing Cu concentration. Similar glow peaks have been observed for Eu-doped CsBr. Thus, the peak was considered to originate from the CsBr host.[51] All the samples showed a broad emission band around 400–500 nm in the TSL spectra, consistent with a previous study.[52] Judging from the spectral shapes, the emission originated from $3d^{10}$–$3d^{9}4s$ transitions of the Cu^{+} ion.[42,49,50] TSL dose response functions of CsBr:Cu transparent ceramics are shown in Fig. 7. All the samples showed good proportionality in the dose range of 0.01 to 100 mGy. The detection limit was comparable to that of commercial personal dosimeters.[53]

Figure 8 presents OSL emission and stimulation maps of the CsBr:Cu transparent ceramics. An OSL emission band around 400–500 nm was observed under stimulation with a wavelength of 620 nm. Since the spectral features were similar to those of the TSL, the origin of the emission was considered to be the same. However, the intensity of the peak around 500 nm due to Cu^{2+} ions was lower than that for the CsBr:Cu crystal in previous reports.[42] This may have been because the amount of Cu^{2+} ions was smaller than that in previous studies since SPS was performed in a highly reductive atmosphere in the previous studies. OSL dose response functions of the CsBr:Cu transparent ceramics are shown in Fig. 9. All the samples exhibited dose response functions with a good proportional relationship in the range of 1–1000 mGy, and the detection limit was less than that of CsBr:Eu transparent ceramics.[48] Since the detection

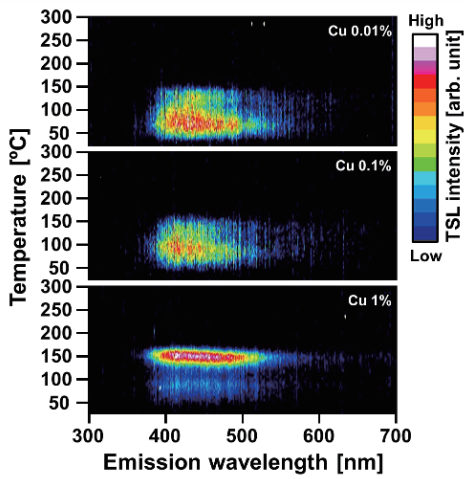

Fig. 6. (Color online) TSL spectrum as a function of temperature of CsBr:Cu transparent ceramics after X-ray irradiation (10 Gy).

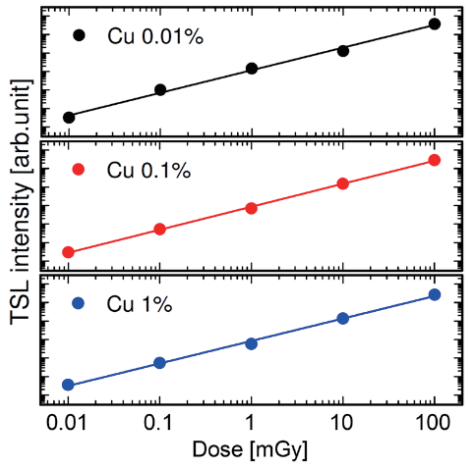

Fig. 7. (Color online) TSL dose response functions of CsBr:Cu transparent ceramics.

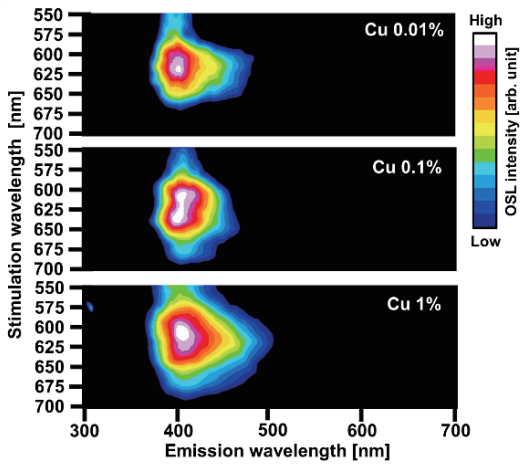

Fig. 8. (Color online) OSL emission and stimulation maps of CsBr:Cu transparent ceramics.

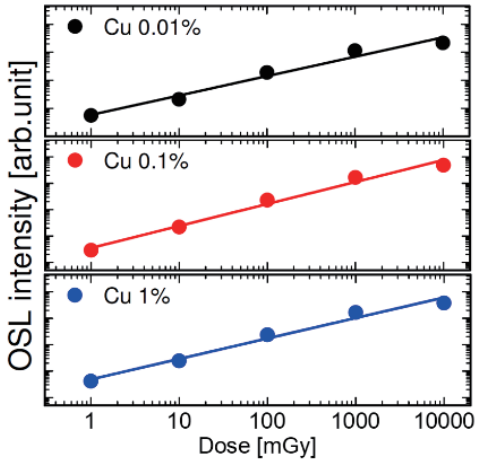

Fig. 9. (Color online) OSL dose response functions of CsBr:Cu transparent ceramics.

limit depends on the measurement setup, it is expected that the detection sensitivity can be improved by optimizing OSL readers.

4. Conclusions

CsBr:Cu transparent ceramics were synthesized by SPS, and their optical, TSL, and OSL properties were investigated. Under excitation at around 300 nm, all the samples showed PL emission bands around 275 and 315 nm, which were related to Cu^{+} and Cu^{2+} ions, respectively. TSL and OSL emission bands were observed around 400–500 nm. Although the spectral shapes

of the samples were consistent with that of the CsBr:Cu crystal, the intensity of the peak around 500 nm due to Cu^{2+} ions was lower than that of the CsBr:Cu crystal. For all the samples, the dose sensitivities using TSL and OSL were confirmed to be as low as 0.01 and 1 mGy, respectively. The detection limit using TSL was comparable to that of commercial products.

Acknowledgments

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References

1 T. Yanagida: Proc. Japan Acad. Ser. B **94** (2018) 75.
2 J. Glodo, Y. Wang, R. Shawgo, C. Brecher, R. H. Hawrami, J. Tower, and K. S. Shah: Phys. Procedia **90** (2017) 285.
3 C. W. E. van Eijk: Phys. Med. Biol. **47** (2002) R85.
4 N. Kawaguchi, G. Okada, K. Fukuda, and T. Yanagida: Nucl. Instrum. Methods Phys. Res., Sect. A **954** (2020) 161518.
5 H. Takahashi, T. Yanagida, D. Kasama, T. Ito, M. Kokubun, K. Makishima, T. Yanagitani, H. Yagi, T. Shigeta, and T. Ito: IEEE Trans. Nucl. Sci. **53** (2006) 2404.
6 T. Itoh, T. Yanagida, M. Kokubun, M. Sato, R. Miyawaki, K. Makishima, T. Takashima, T. Tanaka, K. Nakazawa, T. Takahashi, N. Shimura, and H. Ishibashi: Nucl. Instrum. Methods Phys. Res., Sect. A **579** (2007) 239.
7 T. Yanagida, G. Okada, and N. Kawaguchi: J. Lumin. **207** (2019) 14.
8 S. Yanagisawa, D. Maruyama, R. Oh, Y. Koba, T. Andoh, and K. Shinsho: Sens. Mater. **32** (2020) 1479.
9 S. W. S. McKeever: Radiat. Meas. **46** (2011) 1336.
10 L. E. Colyott, M. S. Akselrod, and S. W. S. McKeever: Radiat. Prot. Dosimetry **72** (1997) 87.
11 P. Covens, D. Berus, N. Buls, P. Clerinx, and F. Vanhavere: Radiat. Prot. Dosimetry **124** (2007) 250.
12 M. S. Akselrod, L. Bøtter-Jensen, and S. W. S. McKeever: Radiat. Meas. **41** (2006) 78.
13 C. C. Gronchi, S. G. P. Cecatti, T. C. N. O. Pinto, and L. V. E. Caldas: Nucl. Instrum. Methods Phys. Res., Sect. B **266** (2008) 2915.
14 H. Nanto: Sens. Mater. **30** (2018) 327.
15 A. Boukhair, C. Heilmann, A. Nourreddine, A. Pape, and G. Portal: Radiat. Meas. **34** (2001) 513.
16 S. V. Moharil: Bull. Mater. Sci. **17** (1994) 25.
17 P. Leblans, D. Vandenbroucke, and P. Willems: Materials **4** (2011) 1034.
18 H. Ohuchi and A. Yamadera: Radiat. Meas. **35** (2002) 135.
19 D. Maruyama, S. Yanagisawa, Y. Koba, T. Andou, and K. Shinsho: Sens. Mater. **32** (2020) 1461.
20 T. Yanagida, Y. Fujimoto, M. Arai, M. Koshimizu, T. Kato, D. Nakauchi, and N. Kawaguchi: Sens. Mater. **32** (2020) 1351.
21 B. Liu: Chin. Sci. Bull. **47** (2002) 1057.
22 D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **32** (2020) 1389.
23 P. Kantuptim, M. Akatsuka, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **32** (2020) 1357.
24 Y. Fujimoto, K. Saeki, D. Nakauchi, T. Yanagida, M. Koshimizu, and K. Asai: Sens. Mater. **31** (2019) 1241.
25 A. M. Bishay: J. Am. Ceram. Soc. **44** (1961) 231.
26 D. Shiratori, D. Nakauchi, T. Kato, N. Kawaguchi, and T. Yanagida: Sens. Mater. **32** (2020) 1365.
27 L.Q. Nguyen, G. Gabella, B. L. Goldblum, T. A. Laplace, J. S. Carlson, E. Brubaker, and P. L. Feng: Nucl. Instrum. Methods Phys. Res., Sect. A **988** (2021) 164898.
28 N. Kawaguchi and T. Yanagida: Sens. Mater. **31** (2019) 1257.
29 H. Kimura, H. Masai, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: J. Mater. Sci. Mater. Electron. **31** (2020) 3017.

30 A.. Lakshmanan, N. Murase, T. Yazawa, J. Qiu, T. Mitsuyu, K. Hirao, A. Tomita, and W. Hoffmann: Radiat. Meas. **33** (2001) 119.
31 S. Yamamoto and H. Tomita: Appl. Radiat. Isot. **168** (2021) 109527.
32 N. M. Winch and A. Edgar: Nucl. Instrum. Methods Phys. Res., Sect. A **654** (2011) 308.
33 D. Jiang, D. M. Hulbert, U. Anselmi-Tamburini, T. Ng, D. Land, and A. K. Mukherjee: J. Am. Ceram. Soc. **91** (2007) 151.
34 T. Yanagida, K. Kamada, Y. Fujimoto, H. Yagi, and T. Yanagitani: Opt. Mater. **35** (2013) 2480.
35 A. Ikesue and Y.L. Aung: Nat. Photonics **2** (2008) 721.
36 H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Sens. Mater. **32** (2020) 1381.
37 T. Kato, G. Okada, and T. Yanagida: Ceram. Int. **42** (2016) 5617.
38 H. Kimura, T. Kato, D. Nakauchi, M. Koshimizu, N. Kawaguchi, and T. Yanagida: Sens. Mater. **31** (2019) 1265.
39 F. Nakamura, T. Kato, G. Okada, N. Kawaguchi, K. Fukuda, and T. Yanagida: J. Eur. Ceram. Soc. **37** (2017) 1707.
40 H. Kimura, T. Kato, D. Nakauchi, G. Okada, N. Kawaguchi, and T. Yanagida: Nucl. Instrum. Methods Phys. Res., Sect. A **954** (2020) 161226.
41 H. Kimura, T. Kato, D. Nakauchi, N. Kawaguchi, and T. Yanagida: Opt. Mater. **100** (2020) 109660.
42 Y. Zorenko, R. Turchak, T. Voznjak, M. Batentschuk, A. Osvet, and A. Winnacker: Phys. Status Solidi Appl. Mater. Sci. **202** (2005) 2537.
43 Y. Zorenko, R. Turchak, T. Voznyak, V. Savchin, M. Batenchuk, and A. Winnacker: Crystallogr. Rep. **51** (2006) 329.
44 G. Okada, N. Kawaguchi, and T. Yanagida: Opt. Mater. **87** (2019) 84.
45 Y. Isokawa, H. Kimura, T. Kato, N. Kawaguchi, and T. Yanagida: Opt. Mater. **90** (2019) 187.
46 T. Yanagida, Y. Fujimoto, N. Kawaguchi, and S. Yanagida: J. Ceram. Soc. Jpn. **121** (2013) 988.
47 H. Kimura, F. Nakamura, T. Kato, D. Nakauchi, N. Kawano, G. Okada, N. Kawaguchi, and T. Yanagida: J. Ceram. Soc. Jpn. **126** (2018) 184.
48 H. Kimura, T. Kato, M. Akatsuka, D. Nakauchi, G. Okada, N. Kawaguchi, and T. Yanagida: Radiat. Meas. **135** (2020) 106367.
49 D. Shiratori, Y. Isokawa, N. Kawaguchi, and T. Yanagida: Sens. Mater. **31** (2019) 1281.
50 H. Masai, H. Ofuchi, G. Okada, N. Kawaguchi, and T. Yanagida: Sens. Mater. **31** (2019) 1297.
51 H. Kimura, F. Nakamura, T. Kato, D. Nakauchi, N. Kawano, G. Okada, N. Kawaguchi, and T. Yanagida: Optik **157** (2018) 421.
52 B. V. R. Chowdari and S. Selvasekarapandian: Cryst. Lattice Defects **9** (1980) 31.
53 D. Y. C. Huang and S.-M. Hsu: Adv. Cancer Ther. InTech (2011).