Novel synthesis methods for luminescent materials: spark plasma sintering (SPS) and micro arc oxidation (MAO)

Seong-Hyeon Hong and Eun-Hee Kang

Department of Materials Science and Engineering and Research Institute of Advanced Materials, Seoul National University, San 56-1, Shillim-dong, Kwanak-ku, Seoul 151-744, Korea

Rare-earth doped luminescent materials have been developed for several decades in various industrial applications; lightening, displays, photo-sensors, bio-imaging and so on. Especially, inorganic luminescent materials (phosphors) have been widely used due to its chemical stability, excellent efficiency, and easy fabrication [1,2]. The phosphor materials have been synthesized by conventional methods such as solid state sintering and liquid-phase or gas phase synthesis. In this work, we propose spark plasma sintering (SPS) method as a novel synthesis method for (oxy) nitride phosphors and micro arc oxidation (MAO) method as a new process for rare-earth doped luminescent films.

The SPS method is a sintering technique which combines electric current based heat and mechanical pressure to consolidate metal or ceramic powders. The sintering mechanism is also contributed by momentary high-temperature spark discharges in the gaps between particles, so it is relatively easy to synthesize the difficult-to-sinter materials. In white LED application, green (β-SiAlON:Eu^{2+} and $Ba_3Si_6O_xN_y$:Eu^{2+}), yellow (Ca-α-SiAlON:Eu^{2+}), and red ($M_2Si_5N_8$:Eu^{2+} and $MAlSiN_3$:Eu^{2+} (M=Ca, Sr)) phosphors are the typical oxy nitride phosphors, which show highly efficient emission properties under blue and UV excitation with a superior thermal and chemical stability [3-7]. Despite these excellent advantages, the application of (oxy) nitride phosphors was limited because the synthesis of (oxy) nitride phosphors required relatively high temperature and pressure under highly controlled N_2 (H_2-N_2) atmosphere. At present, gas pressure sintering (GPS) and hot isostatic pressing (HIP) systems are widely used for synthesizing (oxy) nitride phosphors. However they are quite complicated, costly, and time-consuming process [8,9]. Therefore, new synthesis method for (oxy) nitride phosphor is highly required, and the SPS method can be an alternative method due to its many advantages such as low synthesis temperature, high heating rate, and short holding times [10]. However, only a few studies were reported in the field of phosphors. We applied the SPS sintering technology to the synthesis of various (oxy) nitride phosphors shown in Fig. 1, and studied their luminescence property and thermal stability. In this presentation, we will show some of the recent results and discuss the merits and problems of SPSed phosphors.

The MAO process is a surface coating technology and mainly applied to metals and their alloys to modify or coat their surface. It is an environmentally friendly surface treatment technique, which produces a thick, hard, and well adherent ceramic-like coating and enhances the corrosion and wear resistance [11-13]. Recently, we try to extend the applicability of MAO process into the luminescent film formation. During MAO process, high–voltage discharge zone is generated with spark or micro-discharges, and the thick ceramic coating is directly formed on the surface metals. By adding the rare-earth materials in the electrolytic solutions for MAO, the rare earths can be incorporated into the ceramic coatings, and they plays as activators. The photoluminescence spectrum of such an MAO film is shown in Fig.2. In this presentation, new luminescent rare-earth doped metal oxide films, which formed on various metal plates through micro arc oxidation process will be presented.

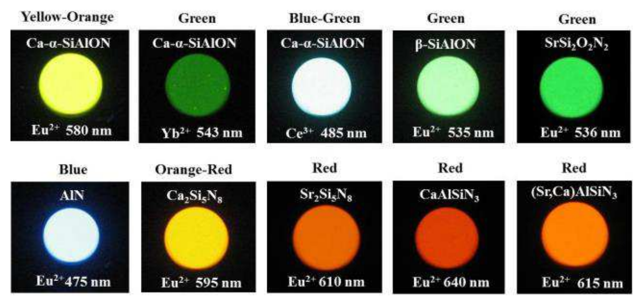

Fig. 1 Luminescence (under UV lamp) of (oxy) nitride phosphors synthesized by spark plasma sintering

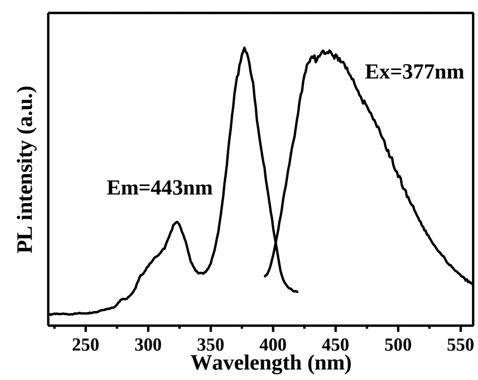

Fig. 2 Photoluminescence property of metal oxide film formed by micro arc oxidation

Reference

[1] W. M. Yen and M. J. Weber, Inorganic phosphors: Compositions, preparation and optical properties, CRC Press, Boca Raton, 2004.
[2] S. Shionoya, W. M. Yen, and H. Yamamoto, Phosphor Handbook (2nd edition), CRC Press, 2006.
[3] N. Hirosaki, R.-J. Xie, K. Kimoto, Y. Yamamoto, T. Suehiro, M. Mitomo, Appl. Phys. Lett., 86, 211905 (2005)
[4] M. Mikami, S. Shimooka, K. Uheda, H. Imura, N. Kijima, Key Engin. Mater., 403, 11 (2009)
[5] R.-J. Xie, N. Hirosaki, K. Sakuma, and N. Kimura, J. Phys. D: Appl. Phys., 41, 144013 (2008).
[6] R.-J. Xie, N. Hirosaki, T. Suehiro, F.-F. Xu, M. Mitomo, Chem. Mater., 18, 5578 (2006)
[7] Y. Q. Li, N. Hirosaki, R.-J. Xie, T. Takada, Y. Yamamoto, M. Mitomo, K. Shioi, J. Appl. Ceram. Technol., 7, 787 (2010)
[8] J. H. Ryu, Y.-G. Park, H. S. Won, S. H. Kim, H. Suzuki, J. M. Lee, C. Yoon, M. Nazarov, D. Y. Noh, B. Tsukerblat, J. Electrochem. Soc., 155, J99 (2008)
[9] H. Peng, Ph. D. Thesis, Diss. Stockholm University, (2004).
[10] Z. A. Munir, U. A. Tamburini, M. Ohyanagi, J. Mater. Sci., 41, 763 (2006)
[11] A. L. Yerokhin, X. Nie, A. Leyland, A. Matthews, and S. J. Dowey, Surf. Coat. Technol., 122, 73 (1999).
[12] C. Blawert, W. Dietzel, E. Ghali, and G. Song, Adv. Eng. Mater., 8, 511 (2006)
[13] H. S. Ryu, S.-J. Mun, T. S. Lim, H.-C. Kin, K.-S. Shin, and S.-H. Hong, J. Electrochem. Soc., 158, C266 (2011).