Available online at www.sciencedirect.com

SciVerse ScienceDirect

CERAMICS INTERNATIONAL

Ceramics International 39 (2013) 861–864

www.elsevier.com/locate/ceramint

Short communication

A high efficient $Ba_2TiP_2O_9$ phosphor for X-ray and UV excitation

Yanlin Huang[a], Taiju Tsuboi[b], Hyo Jin Seo[c,*]

[a]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China
[b]Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto 603-8555, Japan
[c]Department of Physics, Pukyong National University, Busan 608-737, Republic of Korea

Received 28 April 2012; received in revised form 2 May 2012; accepted 31 May 2012
Available online 13 June 2012

Abstract

Polycrystalline $Ba_2TiP_2O_9$ phosphor was synthesized and its crystalline state was checked by X-ray diffraction. Its luminescence properties were investigated under UV excitation and X-ray excitation. The phosphor is efficiently excited by UV light and X-ray irradiation and presents a bright blue green luminescence band with a peak centered at about 490 nm. The luminescence quantum efficiency (QE) and the X-ray excited emission spectra of $Ba_2TiP_2O_9$ phosphor were compared with those of a highly efficient scintillation material, $Bi_4Ge_3O_{12}$. $Ba_2TiP_2O_9$ phosphor shows higher QEs under UV excitation and comparable QE under X-ray excitation. It is suggested that the luminescence of $Ba_2TiP_2O_9$ arises from isolated centers of octahedral TiO_6.

Keywords: C. Optical materials and properties; Ceramics; Luminescence

1. Introduction

Polyhedral oxides consisting of transition-metal ions without electron in the 3d state like Ti^{4+}, Nb^{5+}, Ta^{5+}, and W^{6+} ions have attracted attention from scientists and optical engineers who are looking for a good optical material [1–6]. Of various transition-metal ions without 3d-electrons, extensive study has been made for Ti^{4+}-doped polyhedral oxides because of their applications in tunable solid-state laser host [7], nonlinear optical material [8], phosphor [9], and long-lasting phosphorescence material [10]. For example, Ti^{4+}-doped $20Na_2O$–$10CaO$–$70SiO_2$ glass has applications in high-density optical storage and three-dimensional color displays [11], and $Ba_2TiSi_2O_8$ nano-crystallized ceramics are used as nonlinear optical material [8].

Ti^{4+} ions have shown two type luminescence of blue and yellow emissions [12,13]. The blue emission is due to the charge-transfer transition from 2p orbits of oxygen to 3d orbit of Ti^{4+}, i.e., $O^{2-}-Ti^{4+} \rightarrow O^{-}-Ti^{3+}$, while the yellow emission is due to titanium octahedron associated with oxygen defects [13]. Most luminescence studies on Ti^{4+} ion have been made under UV excitation. Few studies have been made under X-ray excitation.

In this paper, we report the self-activated luminescence of polyhedral oxide, $Ba_2TiP_2O_9$ (called BTP). The luminescence is measured under not only X-ray excitation but also UV excitation, and compared with $Bi_4Ge_3O_{12}$ (BGO) which is currently known as a good scintillation material. The photoluminescence quantum efficiency (QE) is investigated for BTP and BGO.

2. Experimental

Polycrystalline $Ba_2TiP_2O_9$ was grown by the crystallization from the glass composition of 50 BaO:25 TiO_2:25 P_2O_5, which is the stoichiometric composition of $Ba_2TiP_2O_9$ crystal. The starting material was a stoichiometric mixture of reagent grade $BaCO_3$, TiO_2, and P_2O_5. Firstly, the mixture was heated up to 500 °C and kept at this temperature for 5 h. After that, the samples were thoroughly mixed and melted in a platinum crucible at 1250 °C for 1 h in an electric furnace. Crystal growth was carried out from the melts by cooling from 1250 °C to 850 °C at 20 °C/h, and then cooling to room temperature by switching off the electricity power source.

---

*Corresponding author. Tel.: +82 51 629 5568; fax: +82 51 629 5549.
E-mail address: hjseo@pknu.ac.kr (H.J. Seo).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.05.107

X-ray diffraction (XRD) data were collected on a Rigaku D/Max diffractometer operating at 40 kV, 30 mA with Bragg–Brentano geometry using Cu Kα radiation (λ = 1.5405 Å). The UV-excited luminescence spectra were recorded on a Perkin-Elmer LS-50 B luminescence spectrometer. The X-ray excited luminescence (XEL) spectra were measured by using an X-ray-excited spectrometer, FluorMain, where an F-30 movable X-ray tube (*W* anticathode target) was used as the X-ray source. The QE was measured by a Hamamatsu-Photonics C9920-02 Absolute Photoluminescence Quantum Yield Measurement System with an integral sphere at room temperature.

3. Results and discussion

Fig. 1 shows the XRD pattern of BTP powder. For comparison, XRD pattern of the PDF2 card number No. 34-1467 ($Ba_2TiP_2O_9$) in the International Centre for Diffraction Data (ICDD) database is shown in the lower part of Fig. 1. The observed XRD pattern is quite similar to the standard pattern, indicating that the powder consists of micro-crystals of pure crystal of $Ba_2TiP_2O_9$

The photoluminescence (PL) spectrum of $Ba_2TiP_2O_9$ excited at 250 nm is shown in Fig. 2. A broad emission band with a peak at 490 nm (2.53 eV) is observed in the blue-green range. This spectrum is in agreement with the previously reported spectra [14,15]. The CIE (Commission International de l'Eclairage 1931) coordinate is calculated to be (x = 0.222, y = 0.313). The blue-green emission has a PL decay time of 90 μs which was estimated under a 355 nm pulsed laser. Therefore we can call $Ba_2TiP_2O_9$ as a phosphor.

Fig. 3 shows the luminescence intensities of $Ba_2TiP_2O_9$ single crystal in a 150–500 K temperature range. The luminescence intensity decreases slightly with increase in temperature from 150 K to 350 K, while decreases sharply above 350 K. Such an abrupt thermal quenching is suggested to arise from nonradiative transition from the excited state to the ground state due to thermal energy at high temperature. From Fig. 3, it is concluded that $Ba_2TiP_2O_9$ has an excellent thermal stability with higher thermal-quenching temperature (TQT) of 350 K than the other titanates and PO_4-compounds such as $LiTiOPO_4$ (with TQT of 125 K), $KTiOPO_4$ (100 K) and α-$NbOPO_4$ (150 K) [16,17]. High thermal-quenching temperature is important for the practical application to lighting, display, and phonon-detectors.

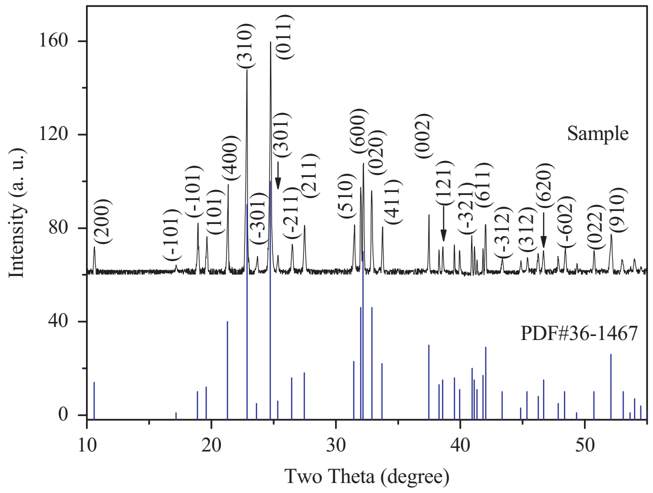

Fig. 1. XRD pattern of $Ba_2TiP_2O_9$ compared with the PDF2 card 36-1467.

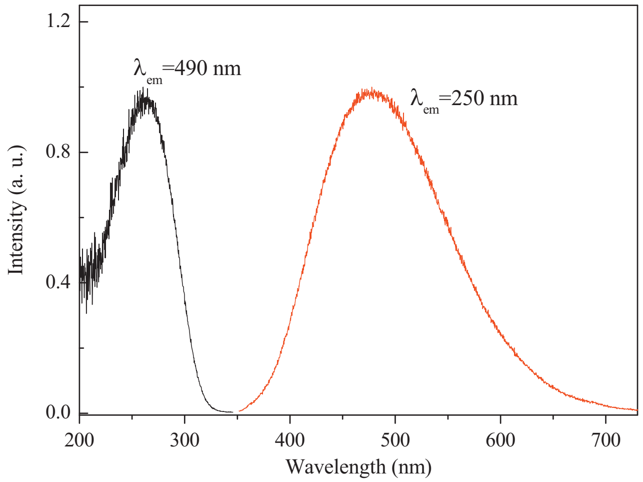

Fig. 2. Photoluminescence (PL) and PL excitation (PLE) spectra of $Ba_2TiP_2O_9$. The PL was obtained at 250 nm excitation, while PLE was obtained for 490 nm emission.

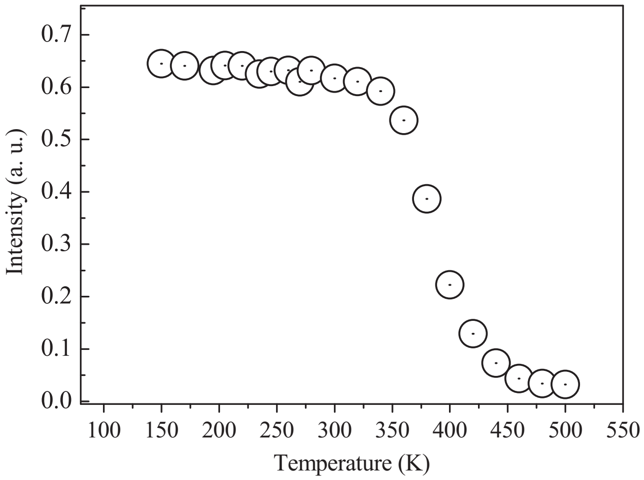

Fig. 3. Temperature-dependent luminescence intensities of $Ba_2TiP_2O_9$ excited by 266 nm Nd:YAG laser.

In Fig. 2 the excitation spectrum is also shown, which was obtained by monitoring the emission at 490 nm. The excitation band has a peak at 250 nm. This peak position is much shorter (higher energy) than the previously reported PLE peak positions of various titanates. The Stokes shift of $Ba_2TiP_2O_9$ was estimated to be $20 \times 10^3\ cm^{-1}$.

Fig. 4 shows the comparison of emission spectrum excited at X-ray (XEL) of BTP with XEL of BGO.

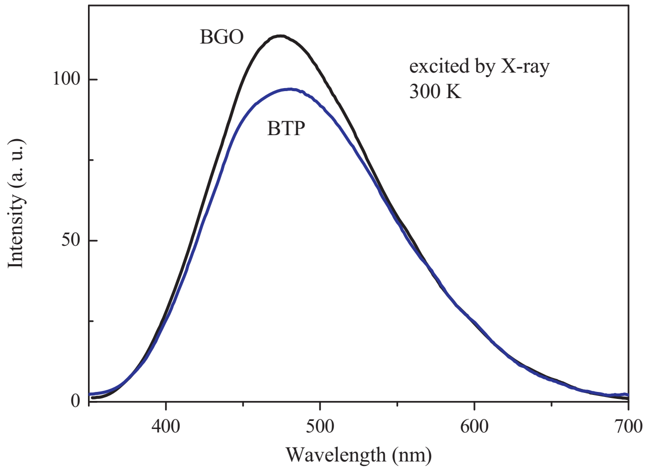

Fig. 4. X-ray excited luminescence of BGO and BTP measured under the same conditions.

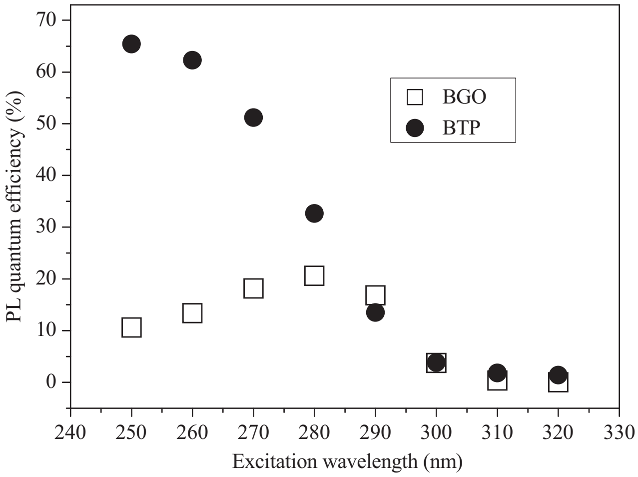

Fig. 5. Photoluminescence quantum efficiencies of BGO and BTP in UV excitation.

The two XELs were obtained under the same experimental conditions. It is noted that BTP has a broad emission band similar to BGO. The integral emission intensity ratio of BTP to BGO is 0.9, indicating the quantum yield of BTP is comparable to that of BGO. It has been reported that the QE ratios of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$, and $Sr_9Ga(PO_4)_7$ powders to BGO powder are about 0.15, 0.50, 0.50, and 0.57, respectively [18,19]. The results indicate that BTP is useful as a material for X-ray medical diagnostic imaging system or scintillator. Scintillation materials for X-ray intensifier screen are useful in micro-crystal powder form, because the powder provides not only qualitative measurement of luminosity but also reliable measurements of time response and scintillation spectrum.

The photoluminescence QE of BTP which was excited at various excitation wavelengths in the UV range is shown in Fig. 5, together with QE of BGO. The maximum QE is 20% for BGO which is obtained at 280 nm excitation, while 65.4% for BTP which is obtained at 250 nm. The efficiency of BTP increases by shortening the excitation wavelength from 320 nm to 250 nm. At excitation of 250 nm, the QE of BTP is much higher than QE of 10.6% for BGO.

The large Stokes shift and broad emission band observed for BTP are similar to the case [20] of materials consisting of transition metal without electron in the 3d state. It is suggested that the blue-green luminescence in BTP is due to the intrinsic luminescence centers, namely isolated TiO_6 octahedra as proposed in Ti-doped oxides [12,13]. Bouma et al. reported the detailed investigation for the luminescence dependence of titanates on their crystal structures [16]. They have suggested that compounds with isolated TiO_6 octahedra and short Ti–O distances give rise to efficient luminescence with large Stokes shift, short-wavelength (ultra-violet) absorption spectrum, and high thermal quenching temperature in the luminescence. When TiO_6 octahedra are closely located with each other, the luminescence quenching temperature decreases, whereas the absorption band shifts to lower energy (long wavelength) due to the broadening of the energy bands. In fact, since three-dimensional TiO_6 coupling occurs in the perovskites $BaTiO_4$ and rutile-type TiO_2, the low absorption band ($BaTiO_4$: 340 nm, TiO_2: 380 nm), small Stokes shifts ($BaTiO_4$: 9×10^3 cm^{-1}, TiO_2: 5.5×10^3 cm^{-1}), and low quenching temperatures ($BaTiO_4$: 45 K, TiO_2: 20 K) are obtained for the two materials [16,21].

The crystal structure of BTP has not been established yet. It is suggested, however, that the host lattices contain the isolated TiO_6 octahedra with the extremely short Ti–O distance. This suggestion is based on the luminescence results of BTP phosphor, e.g., the high excitation energy (250 nm), the large Stokes shift (20×10^3 cm^{-1}), and the high quenching temperature (350 K). Certainly, the lattice defects such as oxygen-vacancies and cation vacancies are conceivable to play an important role in the property of luminescence. Further study to clarify the luminescence mechanism of BTP is needed in the future work.

4. Conclusions

The well crystallized $Ba_2TiP_2O_9$ phosphor was prepared from the crystallization of the glass composition 50 BaO:25 TiO_2:25 P_2O_5 The phosphor shows bright blue-green luminescence (peaked at 490 nm) with CIE coordinates of ($x=0.222$, $y=0.313$) under UV light excitation and also under X-ray excitation. The emission quantum efficiency (QE) is 90% of BGO in case of X-ray excitation, while much higher QE than BGO under UV excitation. $Ba_2TiP_2O_9$ is not only a scintillation material but also a photoluminescence material. Compared with the previously reported titanates, $Ba_2TiP_2O_9$ has a large Stokes shift (20×10^3 cm^{-1}), high excitation energy (250 nm), and high quenching temperature (350 K). From these luminescence characteristics, it is suggested that $Ba_2TiP_2O_9$ lattices contain the isolated TiO_6 octahedral intrinsic luminescence centers with the short Ti–O distance.

Acknowledgements

This work was supported by Mid-career Researcher Program through National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (MEST) (Project no. 2009-0078682), and by a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References

[1] S. Sailaja, B. Sudhakar Reddy, Structural and luminescence properties of RE^{3+} (RE = Eu, Tb):$(MgCa)_2Bi_4Ti_5O_{20}$ ceramics, Ceramics International 37 (2011) 1781–1787.

[2] R. Anlin Golda, A. Marikani, D. Pathinettam Padiyan, Mechanical synthesis and characterization of $Bi_4Ti_3O_{12}$ nanopowders, Ceramics International 37 (2011) 3731–3735.

[3] G.J. Xing, R. Liu, C. Zhao, Y.L. Li, Y. Wang, G.M. Wu, Photoluminescence and photocatalytic properties of uniform $PbMoO_4$ polyhedral crystals synthesized by microemulsion-based solvothermal method, Ceramics International 37 (2011) 2951–2956.

[4] Y. Takahashi, K. Kitamura, N. Iyi, S. Inoue, Phase-stability and photoluminescence of $BaTi(Si, Ge)_3O_9$, Journal of the Ceramic Society of Japan 114 (2006) 313–317.

[5] M. Bharathy, V.A. Rassolov, S. Park, H.C. Loye, Crystal growth of two new photoluminescent oxides: $Sr_3Li_6Nb_2O_{11}$ and $Sr_3Li_6Ta_2O_{11}$, Inorganic Chemistry 47 (2008) 9941–9945.

[6] M. Bharathy, V.A. Rassolov, H.C. Loye, Crystal growth of Sr_3NaNbO_6 and Sr_3NaTaO_6: new photoluminescent oxides, Chemistry of Materials: A Publication of the American Chemical Society 20 (2008) 2268–2273.

[7] P.F. Moulton, Spectroscopic and laser characteristics of Ti: Al_2O_3, Journal of the Optical Society of America B, Optical physics 3 (1986) 125–133.

[8] Y. Takahashi, K. Kitamura, Y. Benino, T. Fujiwara, T. Komatsu, Second-order optical nonlinear and luminescent properties of $Ba_2TiSi_2O_8$ nanocrystallized glass, Applied Physics Letters 86 (2005) 091110–091112.

[9] D. Kan, T. Terashima, R. Kannda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, M. Takano, Blue-light emission at room temperature from Ar^+-irradiated $SrTiO_3$, Nature Materials 4 (11) (2005) 816–819.

[10] C. Moon, M. Nishi, K. Miura, K. Hirao, Blue long-lasting phosphorescence of Ti-doped $BaZrO_3$ perovskites, Journal of Luminescence 129 (2009) 817–819.

[11] X. Meng, K. Tanaka, K. Fujita, S. Murai, Intense greenish emission from d_0 transition metal ion Ti^{4+} in oxide glass, Applied Physics Letters 90 (2007) 051917–051919.

[12] M. Gaft, L. Nagli, G. Waychunas, D. Weiss, The nature of blue luminescence from natural benitoite $BaTiSi_3O_9$, Physics and Chemistry of Minerals 31 (2004) 365–373.

[13] Y. Takahashi, K. Kitamura, N. Iyi, S. Inoue, Visible orange photoluminescence in a barium titanosilicate $BaTiSi_2O_7$, Applied Physics Letters 88 (2006) 151903–151905.

[14] D.E. Harrison, The system $BaO-TiO_2-P_2O_5$: phase relations, fluorescence, and phosphor preparation, Journal of the Electrochemical Society 107 (1960) 217–221.

[15] D.E. Harrison, W.A. Tiller, Study of the growth mechanism and twin habits of $Ba_2TiP_2O_9$, Journal of Applied Physics 33 (1962) 2451–2457.

[16] B. Bouma, G. Blasse, Dependence of luminescence of titanates on their crystal structure, The Journal of Physics and Chemistry of Solids 56 (1995) 261–265.

[17] A.J.H. Macke, Investigations on the luminescence of titanium-activated stannates and zirconates, Journal of Solid State Chemistry 18 (1976) 337–346.

[18] C. Duan, J. Yuan, J. Zhao, Luminescence properties of efficient X-ray phosphors of $YBa_3B_9O_{18}$, $LuBa_3(BO_3)_3$, α-$YBa_3(BO_3)_3$ and $LuBO_3$ 178 (2005) 3698–3702Journal of Solid State Chemistry 178 (2005) 3698–3702.

[19] F.P. Du, Y.L. Huang, S.I. Kim, H.J. Seo, The self-activated luminescence properties of blue-emitting $Sr_9Ga(PO_4)_7$, Chemistry Letters 43 (2012) 15–17.

[20] G. Blasse, B.C. Grabmaier, Luminescent Materials, 4, Springer, Berlin, 1994 (2) 72.

[21] G. Blasse, Luminescence of inorganic solids: From isolated centres to concentrated systems, Progress in Solid State Chemistry 18 (1988) 79–171.