Investigation of Luminescence Mechanism in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ Scintillator

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Abstract: $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ is a new and promising scintillator which is based on the host material without doping. Here the time gated X-ray excited optical luminescence is measured by using the excitation energy below, above and at the La L_3 -edge. A relatively slow and broad emission with peak at 415 nm has been observed as the dominant emission. Also, a weak emission at 360 nm is observed at the fast window, associated with the recombination of trapped excitons in Y_2O_3 host. The observations show that the broad emission at 415 nm is most likely due to the recombination of trapped excitons associated with the La^{3+} doping into Y_2O_3 sites.

Keywords: $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$, Nanostructure, Luminescence, Scintillator, X-ray absorption near edge structures (XANES), X-ray excited optical luminescence (XEOL), and time resolved X-ray excited optical luminescence (TRXEOL), Mechanism

Introduction

Recently, polycrystalline transparent ceramics have emerged as an interesting alternative to inorganic single crystal scintillators.¹⁻⁸ This is mainly due to the easiness of fabrication and cost effectiveness alternative to single crystals.^{9, 10} Scintillators are required to be highly transparent for practical applications and this is one of the challenging issues for some ceramics because of their opacity. However, the development of nanotechnology and the vacuum sintering has led to the achievement of highly transparent ceramics.¹¹⁻¹³ Y_2O_3 , for example, is an interesting host material for high power solid state laser due to its high thermal conductivity, broad transparency range, good chemical stability and relatively low phonon energy¹⁴⁻¹⁷. However, the high melting point of Y_2O_3 (2430 °C) and the polymorphic phase from C to a high temperature hexagonal phase H at about 2350 °C make it difficult to fabricate a high quality single crystal.^{18, 19} Nonetheless, with the development of the vacuum sintering technique, transparent ceramic of Y_2O_3 can be fabricated at temperature far below its melting point.²⁰ It has been reported that the addition of La_2O_3 can further lower the sintering temperature of Y_2O_3 ceramic as a result of which transparent $\text{La}_x\text{Y}_{2-x}\text{O}_3$ ceramic can be fabricated at relatively low sintering temperature.^{19, 21} $\text{La}_x\text{Y}_{2-x}\text{O}_3$ has been used as a host for laser active ions²²⁻²⁵ but not as a luminescence material themselves. Recently, we have reported the photoluminescence and scintillation property of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ polycrystalline ceramic.²⁶ $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ is a new scintillator which is based on the host material without doping. This new scintillator has energy resolution comparable to that of NaI(Tl) single crystal but is more stable and less expensive. However, the light output of $\text{La}_x\text{Y}_{2-x}\text{O}_3$ is not as high as expected. The $\text{La}_x\text{Y}_{2-x}\text{O}_3$ sample used for this study showed the light yield of about 15,500 photons/MeV which is about 3 times lower than that of NaI(Tl) single crystal (50,000 photons/MeV). In order to improve the light output and energy resolution, it is important to reveal the luminescence process or mechanism. For that, we study the X-ray absorption near edge structures (XANES), X-ray excited optical luminescence (XEOL), and time resolved X-ray excited optical luminescence (TRXEOL) of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ scintillator and explore the luminescence mechanism.

XANES probes the local structure and bonding of the absorbing atom by monitoring the absorption coefficient using tunable X-ray from a synchrotron light source, and can provide information on oxidation state, coordination, and the local symmetry of the absorbing atom of the system of interest. XEOL is a de-excitation spectroscopy which measures the optical response of the system upon excitation using photon with selected energy, often across an absorption edge of an element of interest, providing elemental and in some cases, site specificity. XEOL can be performed in the energy (wavelength scan, normal XEOL) and time (TRXEOL) domain. In the time domain, using the synchrotron pulse and the dark gap between the pulses, one can track the dynamics of the optical decay (decay lifetime) following X-ray excitation. Time-gated XEOL can be measured by recording the optical luminescence within a selected time window of the decay curve (fast or slow window). When the sample has multiple luminescence at different wavelengths, the decay curve of a selected wavelength

can also be measured to yield the lifetime of the specific emission band.²⁷ XEOL combined with XANES has been shown to be a powerful tool for investigating the local chemical environment of a site that gives rise to a particular luminescent band.²⁷⁻²⁹ XEOL and TRXEOL have been used as a powerful tool for the study of luminescent nanostructured materials.³⁰⁻³⁴ Here we apply the element selective XEOL to determine the origin of luminescence from $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$, and to examine the time un-gated and time gated XEOL from $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ with excitation energy below, above and at the La L_3 -edge and study the TRXEOL of the different emissions from $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ scintillator in order to uncover its scintillation processes.

Experimental Details

Synthesis of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic samples were described in detail elsewhere.²⁶ Briefly, $\text{La}_{0.2}\text{Y}_{1.8}\text{O}$ nanoparticles were prepared using the combustion method. First nitrate solution were prepared from stoichiometric ratio of Y_2O_3 and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in nitric acid and water. Citric acid solution was prepared separately and mixed with nitrate solution and stirred at room temperature for 30 min. Finally, 2 wt % polyethylene glycol (PEG) was added and stirred for further 30 min. Then, the solvent was evaporated by heating at 90 °C in the furnace to get purple red gel. Self-combustion occurred once the gel was heated at 800 °C. Then the powders were calcined at 1150 °C to obtain $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ nanoparticles. The nanoparticles were suppressed into green compact of 16×2 mm², and then sintered in the VFS vacuum furnace with 1×10^{-3} Pa and 1600 °C for 6 hours. At last, the $\text{La}_{0.2}\text{Y}_{1.8}\text{O}$ transparent ceramic was obtained.

Transmission electron microscope (TEM) image of nanoparticles was obtained by JEOL 1200EX STEM. $\text{La}_{0.2}\text{Y}_{1.8}\text{O}$ transparent ceramic was examined by X-ray diffraction (XRD) with Cu K_α radiation to reveal the phase structure. XANES, XEOL and TRXEOL measurements were performed at the Pacific Northwest Consortium-X-ray Operation Research (PNC-XOR) Bending Magnet (BM) beamline at the Advanced Photon Source (APS). As shown in Figure S1, $\text{La}_{0.2}\text{Y}_{1.8}\text{O}$ transparent ceramic was mounted on the sample plate that was oriented at a 45-degree angle to the incident beam. The fluorescence detector that monitors the fluorescence X-ray emitted from the sample was placed at 90-degree angle to the incident beam. XANES was recorded at La L_3 -edge using fluorescence mode. XANES spectrum was normalized to the incident beam current (I_0). For XEOL measurement, a lens was placed in a direction perpendicular to the sample surface. Lens was connected to a spectrometer via optic fiber, which counts the optical photons emitted from the sample after excitation at certain energies (e. g.: below, on and above the La L_3 -edge). TRXEOL (XEOL in the time domain) experiments were conducted in the same way as XEOL in the energy domain except that the photo-multiplier-tube (PMT) signal is time-gated with a selected time window (e. g.: fast and slow windows). TRXEOL were measured with APS operating in a hybrid top-up mode which provides a single bunch (16 mA) with ~ 50 ps bandwidth and a

1.59 microsecond time window for decay studies. The setup for the timing experiments has been described in detail elsewhere.^{35, 36}

The scintillation response to gamma 662 keV (Cs-137) was measured using a super bi-alkali Hamamatsu PMT R6231-100 biased at 900V. PMT output was further amplified with Hamamatsu preamplifier C6438 and shaped with a spectroscopy Ortec amplifier Model 671. Multi-channel analyzer was a Canberra MP11.

Scintillation timing was measured using same gamma excitation (Cs-137) and PMT at 900V and output of the preamplifier applied to a digital oscilloscope (Picotech). Decay time was obtained by exponential fitting of the experimental data. Area under the pulse timing graph compared with the corresponding pulse obtained with a NaI(Tl) scintillator under identical conditions is used for light yield (LY) estimation.

Spectral emissions of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ (LYO) and NaI (Tl) are corrected with the spectral sensitivity of the super bi-alkyl photo-cathode and used to correct the integrals of scintillation timing.

$$\text{LY}_{\text{LYO}} = \text{LY}_{\text{NaI(Tl)}} \times \frac{\sum_{\lambda} [\lambda I_{\lambda} \text{QE}_{\lambda}]_{\text{LYO}} \times I_{\text{LYO}}}{[\sum_{\lambda} [\lambda I_{\lambda} \text{QE}_{\lambda}]_{\text{NaI(Tl)}} \times I_{\text{NaI(Tl)}}]}$$

Where:

$\text{LY}_{\text{NaI(Tl)}}$ is the catalog value for light yield of Saint-Gobain 1 inch X 1 inch NaI(Tl) scintillator, 38,000 ph./MeV.

$\sum_{\lambda} [\lambda I_{\lambda} \text{QE}_{\lambda}]_{\text{LYO}}$, $\sum_{\lambda} [\lambda I_{\lambda} \text{QE}_{\lambda}]_{\text{NaI(Tl)}}$ are the normalized integral emission spectra of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ and NaI(Tl) respectively corrected with PMT spectral sensitivity QE_{λ} ;

I_{LYO} and $I_{\text{NaI(Tl)}}$ are the timing integrals of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ and NaI(Tl) scintillators raised in identical settings.

Results and Discussion

The $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent scintillator was fabricated by sintering $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ nanoparticles powder s at high temperature in vacuum. The size of the $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic used for this study was $\varnothing 11 \times 2 \text{ mm}^2$. Fig. 1 shows the XRD pattern of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic and commercial Y_2O_3 particles. All the peaks are assigned to the cubic phase of Y_2O_3 which means La^{3+} ions is completely dissolved in Y_2O_3 , when sintered at temperature higher than 1100°C. A left-shift in the diffraction peak can be observed in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$. This is due to the larger ionic radius of La^{3+} (117.2 pm) compared to that of Y^{3+} (104 pm). Fig. 2(A) shows the TEM image of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ nanoparticles before the fabrication of transparent ceramic and the average size of the particles is about 28 nm. Scanning electron microscope (SEM) microstructure of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic is shown in Fig. 2(B) with an average grain size of about 200 μm . We measured the scintillation properties of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic using Cs-137 (662 keV) as a gamma excitation source. Fig. 3 shows the scintillation response of

$\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic and 662 keV photo peak associated with Cs-137 can be clearly seen in the gamma spectrum. The energy resolution (FWHM) was obtained from Gaussian fit of the full energy peak area of 662 keV peak. The energy resolution is about 8.2 % FWHM which is close to that of NaI(Tl) scintillator (7.6 %) of dimension 1 inch X 1 inch, as measured in our detection system.

Luminescence and scintillation properties of Y_2O_3 has been reported by several authors but to the best of our knowledge no one has reported the effect of La^{3+} doping on the luminescence and scintillation properties of Y_2O_3 . Recently, our group has reported the luminescence and scintillation properties of La^{3+} doped Y_2O_3 transparent ceramic.²⁶ To further understand the effect of La^{3+} doping on the luminescence and scintillation properties of Y_2O_3 , we have performed XANES, time ungated and time gated XEOL as well as TRXEOL of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic. We have used elemental selective XANES to excite the $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic with excitation energy below, above and at the La L_3 -edge. La L_3 -edge XANES spectrum of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic is shown in Fig. 4(A). The main characteristic of the La L_3 -edge XANES spectrum is a white line at around 5490 eV assigned to electric transition from $2p_{3/2}$ to 5d. The first derivative of La L_3 -edge XANES shown in Fig. 4(B) reflects the splitting of 5d orbital, which is due to the local distortion of the crystal field. Fig. 5(A) shows the time ungated and time gated (fast and slow time windows) XEOL spectra when excited above the La L_3 absorption edge (5800 eV). Relative lifetime of multiple peaks can be determined by applying different time gates.³² Time gates of 0-19 ns and 280-1050 ns were chosen for fast and slow time windows respectively and 0-1590 ns for ungated window. XEOL spectra obtained from the ungated window (black curve) and slow time window (green curve) are both characterized by a broad emission band with peak center at around 415 nm. In the fast time window, weak emission at around 415 nm can be still seen due to very long decay time. Interestingly, a weak emission also appears at 360 nm in the fast window, which was not observed in the slow window as shown in Fig. S2. The fitted XEOL curve from the fast window is shown in Fig. 5(B). The spectrum from the fast window is well fitted using two peaks at 360 and 410 nm via multiple Gaussian fitting. To make it further clear we have measured the TRXEOL of different emission curve. Decay curve of 360 nm and 415 nm emission (excited at 5800 eV) is shown in Fig. 6(A). It shows that the 360 nm emission decays relatively faster than the broad emission at 415 nm. Decay times are approximated by using two exponential fitting of the decay curve. The decay time for 360 nm peak shows a faster component of 25 ns and a slower component of 255 ns whereas the dominant decay time of 364 ns is observed for 415 nm peak along with a fast component of about 55 ns.

The emission at about 360 nm has been observed in Y_2O_3 and reported by several authors.³⁷⁻⁴¹ Based on the ODMR study which showed the existence of a triplet state of trapped excitons, Hayes et al. reported that the 360 nm emission in Y_2O_3 is due the recombination of self-trapped excitons (STE).³⁷ Lushchik et al. reported that the self-trapped excitons emission in Y_2O_3 is similar to that observed in Al_2O_3 but different from STE

emission in alkali halides. In Y_2O_3 electrons and holes do not separately undergo transformation into a stable self-trapped state while self-shrunk excitons are formed and the intrinsic emission is due to the radiative decay of self-shrunk excitons.^{39, 42} Also the scintillation decay time under 662 keV gamma excitation reported by Fukabori et al. showed a fast component of about 34 ns (15%) and a dominant slower component of about 107 ns (85%) for Y_2O_3 transparent ceramic.³⁸ Lushchik et al. also reported that a slow component of about 130 ns dominants in the emission band of Y_2O_3 .³⁹ To make it further clear we have measured the scintillation decay time where the sample is excited with 662 keV gamma source. Our results shows the decay consisting of a relatively fast component of 133 ns and a slower one of about 930 ns. The main decay component is the slower one with 94 % of the emission decaying through this channel and 6 % of emission through fast component as shown in Fig. 6(B). This is further supported by the time gated (fast and slow) XEOL measured below the La L_3 -edge and at the white line as shown in Fig. 7(A) and 7(B) respectively. When the sample is excited both below the La L_3 -edge and at the white line, a strong emission is observed at ungated and slow gated windows whereas a weak emission at the fast window. At the La whiteline, La absorbs preferentially compared to absorption below the edge; since La is a minor component and the dominant energy transfer is to the slow optical channel, the TRXEOL should be similar as observed; that is that the ungated and the slow window gated XEOL are similar and dominant. This suggest that the weak emission at 360 nm at the fast window in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ under 5800 eV excitation is associated with the Y_2O_3 host matrix. The dominant slower emission at 415 nm has not been reported in Y_2O_3 and therefore is associated with the La^{3+} doping in Y_2O_3 . As, no luminescence can be observed from La^{3+} or Y^{3+} ions because La^{3+} , Y^{3+} , Lu^{3+} and Sc^{3+} ions have no 4f electrons, therefore no electronic energy levels that can induce excitation and the luminescence processes. The first derivative of XANES spectrum in Fig. 4(B) shows the local distortion of crystal field in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic. Also the XRD pattern in Fig.1 shows the left shift of diffraction peaks due to the lattice distortion upon larger La^{3+} doping into smaller Y^{3+} sites and the emission at 415 nm is likely due to the defects induced as a result of lattice distortion during La^{3+} doping into Y^{3+} sites. Luminescence studies showed that the recombination of self-trapped excitons is the most common cause of luminescence in wide band gap oxides.^{37, 39, 43, 44} In $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$, we believe the lattice defects are created due to La^{3+} doping in Y_2O_3 ; resulting in trapping of excitons and the emission at 415 nm might be due to the recombination of the trapped excitons in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$.

Conclusion

In summary, $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic scintillator has been fabricated using the nanoparticles synthesized by combustion method. We have measured the time gated XEOL by using the excitation energy below, above and at the La L_3 -edge. A relatively slow and broad emission with peak at 415 nm has been observed as the dominant emission. Also, weak emission at 360 nm is observed at the fast window, associated with the trapping of excitons in Y_2O_3 host. The elemental selective XANES along with XEOL, TRXEOL and scintillation studies

showed that the broad emission at 415 nm is associated with La^{3+} doping in Y_2O_3 . The relatively slow emission in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ is also likely due to the recombination of trapped excitons in $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$. The trapping of excitons might be due to the defects created during La^{3+} doping into Y^{3+} sites.

Acknowledgment: We would like to acknowledge the support from the U.S. Army Medical Research Acquisition Activity (USAMRAA) under Contracts of W81XWH-10-1-0279 and W81XWH-10-1-0234 and the NSF and DHS joint ARI program (2008-DN-077-ARI016-05, CBET-1039068). The PNC/XSD facilities at the APS are supported by the US Department of Energy (DOE) Basic Energy Sciences, the Major Resource Support program of the NSERC, the University of Washington, Simon Fraser University, and the APS. Technical support from the APS scientists Dr. Robert Gordon and Dr. Zou Finfrock are greatly appreciated. Research at UWO is supported by NSERC, CFI, CRC and the Ontario Innovation Trust (OIT).

Fig.1. XRD pattern of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic (blue), commercial Y_2O_3 (red) and Y_2O_3 reference (black).

Fig.2 (A) TEM image of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ nanoparticles and (B) SEM microstructure of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ transparent ceramic.

Fig.3. La_{0.2}Y_{1.8}O₃ ceramic gamma spectrum of Cs-137. The inset shows the photograph of the transparent La_{0.2}Y_{1.8}O₃ ceramic of dimension Ø 11 X 2 mm².

Fig.4. (A) La L_3 -edge XANES spectrum and (B) the first derivative of L_3 edge whiteline of the $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic.

Fig.5. (A) Time ungated and time gated XEOL of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic, excited with 5800 eV X-ray energy and (B) Fitted curve for fast window.

Fig.6. (A) Decay curves of the 360 and 415 nm emissions. The solid red line is the result of bi-exponential curve fitting and (B) Scintillation timing of $\text{La}_{0.2}\text{Y}_{1.8}\text{O}_3$ ceramic excited with gamma 662 keV.

Fig.7. Time ungated and time-gated (fast and slow window) XEOL intensity (A) below the La L_3 -edge (5400 eV) and (B) at the white line (5489 eV).

References

1. N. J. Cherepy, S. A. Payne, B. W. Sturm, S. P. O'Neal, Z. M. Seeley, O. B. Drury, L. K. Haselhorst, B. L. Rupert, R. D. Sanner, P. A. Thelin, S. E. Fisher, R. Hawrami, K. S. Shah, A. Burger, J. O. Ramey and L. A. Boatner, *Hard X-Ray, Gamma-Ray, and Neutron Detector Physics Xiii* **8142**, 81420W (2011).
2. Y. Wang, G. Baldoni, W. H. Rhodes, C. Brecher, A. Shah, U. Shirwadkar, J. Glodo, N. Cherepy and S. Payne, *Hard X-Ray, Gamma-Ray, and Neutron Detector Physics Xiv* **8507**, 850717 (2012).
3. N. J. Cherepy, Z. M. Seeley, S. A. Payne, P. R. Beck, E. L. Swanberg, S. Hunter, L. Ahle, S. E. Fisher, C. Melcher, H. Wei, T. Stefanik, Y. S. Chung and J. Kindem, *Hard X-Ray, Gamma-Ray, and Neutron Detector Physics Xvi* **9213**, 921302 (2014).
4. C. Greskovich and S. Duclos, *Annu. Rev. Mater. Sci.* **27**, 69-88 (1997).
5. J. Xie, Y. Shi, L. Fan and Z. Xu, *Optical Materials* **35** (4), 744-747 (2013).
6. Y. Takayuki, F. Yutaka, K. Shunsuke, W. Kenichi, Y. Hideki, Y. Takagimi, J. Vitezslav, F. Yoshisuke, Y. Yuui, Y. Akira, U. Akira, I. Tetsuo and N. Martin, *Applied Physics Express* **4** (12), 126402 (2011).
7. N. J. Cherepy, J. D. Kuntz, Z. M. Seeley, S. E. Fisher, O. B. Drury, B. W. Sturm, T. A. Hurst, R. D. Sanner, J. J. Roberts and S. A. Payne, *Hard X-Ray, Gamma-Ray, and Neutron Detector Physics Xii* **7805**, 78050I (2010).
8. S. Chen, H. Wei, C. L. Melcher and Y. Wu, *Optical Materials Express* **3** (12), 2022-2027 (2013).
9. D. J. Wisniewski, L. A. Boatner, J. S. Neal, G. E. Jellison, J. O. Ramey, A. North, M. Wisniewska, A. E. Payzant, J. Y. Howe, A. Lempicki, C. Brecher and J. Glodo, *IEEE Transactions on Nuclear Science* **55** (3), 1501-1508 (2008).
10. S. R. Podowitz, R. Gaume and R. S. Feigelson, *Journal of the American Ceramic Society* **93** (1), 82-88 (2010).
11. H. Yagi, T. Yanagitani, K. Takaichi, K.-i. Ueda and A. A. Kaminskii, *Optical Materials* **29** (10), 1258-1262 (2007).
12. A. A. Kaminskii, *Laser & Photonics Reviews* **1** (2), 93-177 (2007).
13. S. F. Wang, J. Zhang, D. W. Luo, F. Gu, D. Y. Tang, Z. L. Dong, G. E. B. Tan, W. X. Que, T. S. Zhang, S. Li and L. B. Kong, *Progress in Solid State Chemistry* **41** (1-2), 20-54 (2013).
14. Q. Hao, W. Li, H. Zeng, Q. Yang, C. Dou, H. Zhou and W. Lu, *Applied Physics Letters* **92** (21), 211106 (2008).
15. R. H. Hoskins and B. H. Soffer, *Applied Physics Letters* **4** (1), 22-23 (1964).
16. J. Sanghera, S. Bayya, G. Villalobos, W. Kim, J. Frantz, B. Shaw, B. Sadowski, R. Miklos, C. Baker, M. Hunt, I. Aggarwal, F. Kung, D. Reicher, S. Peplinski, A. Ogloza, P. Langston, C. Lamar, P. Varmette, M. Dubinskiy and L. DeSandre, *Optical Materials* **33** (3), 511-518 (2011).
17. H. x. Ma, Q. h. Lou, Y. f. Qi, J. x. Dong and Y. r. Wei, *Optics Communications* **246** (4-6), 465-469 (2005).
18. Y. H. Li, Q. H. Yang and S. Z. Lu, in *Materials and Manufacturing, Pts 1 and 2*, edited by J. H. Wang and J. G. Qi (2011), Vol. 299-300, pp. 588-591.
19. Q. H. Yang, J. Ding, H. W. Zhang and J. Xu, *Optics Communications* **273** (1), 238-241 (2007).
20. K. Takaichi, H. Yagi, J. Lu, J.-F. Bisson, A. Shirakawa, K.-i. Ueda, T. Yanagitani and A. A. Kaminskii, *Applied Physics Letters* **84** (3), 317-319 (2004).
21. J. Ding, Q. Yang, Z. Tang, J. Xu and L. Su, *J. Opt. Soc. Am. B* **24** (3), 681-684 (2007).
22. M. Ivanov, Y. Kopylov, V. Kravchenko and S. Zayats, *physica status solidi (c)* **10** (6), 940-944 (2013).
23. C. G. Dou, Q. H. Yang, X. M. Hu and J. Xu, *Optics Communications* **281** (4), 692-695 (2008).
24. Q. Yang, S. Lu, B. Zhang, H. Zhang, J. Zhou, Z. Yuan, Y. Qi and Q. Lou, *Optical Materials* **33** (5), 692-694 (2011).
25. Q. Yang, C. G. Dou, J. Ding, X. M. Hu and J. Xu, *Applied Physics Letters* **91** (11), 111918 (2007).
26. W. Chen, H. Tu, S. Sahi, D. Mao, R. Kenarangui, J. Luo, P. Jin, S. Liu, L. Ma, A. Brandt and A. Weiss, *Opt. Lett.* **39** (19), 5705-5708 (2014).
27. T.-K. Sham and R. A. Rosenberg, *ChemPhysChem* **8** (18), 2557-2567 (2007).
28. J. G. A. Rogalev, *Chemical Appliocations of Synchrotron Radiation, Part II: X-ray Applications*. (world Scientific, Singapore, 2002, 2002).
29. Z. Q. Wang, W. Wang, T. K. Sham and S. G. Yang, *Nanoscale* **6** (16), 9783-9790 (2014).

30. T. K. Sham, D. T. Jiang, I. Coulthard, J. W. Lorimer, X. H. Feng, K. H. Tan, S. P. Frigo, R. A. Rosenberg, D. C. Houghton and B. Bryskiewicz, *Nature* **363** (6427), 331-334 (1993).
31. R. A. Rosenberg, G. K. Shenoy, P. S. G. Kim and T. K. Sham, *The Journal of Physical Chemistry C* **112** (36), 13943-13946 (2008).
32. R. A. Rosenberg, G. K. Shenoy, L.-C. Tien, D. Norton, S. Pearton, X. H. Sun and T. K. Sham, *Applied Physics Letters* **89** (9), 093118 (2006).
33. L. Armelao, F. Heigl, A. Jürgensen, R. I. R. Blyth, T. Regier, X. T. Zhou and T. K. Sham, *The Journal of Physical Chemistry C* **111** (28), 10194-10200 (2007).
34. R. A. Rosenberg, G. K. Shenoy, F. Heigl, S.-T. Lee, P.-S. G. Kim, X.-T. Zhou and T. K. Sham, *Applied Physics Letters* **87** (25), 253105 (2005).
35. M. W. Murphy, X. T. Zhou, J. Y. P. Ko, J. G. Zhou, F. Heigl and T. K. Sham, *The Journal of Chemical Physics* **130** (8), 084707 (2009).
36. F. Heigl, A. Jürgensen, X. T. Zhou, S. Lam, M. Murphy, J. Y. P. Ko, T. K. Sham, R. A. Rosenberg, R. Gordon, D. Brewe, T. Regier and L. Armelao, *AIP Conference Proceedings* **879** (1), 1202-1205 (2007).
37. W. Hayes, M. J. Kane, O. Salminen and A. I. Kuznetsov, *Journal of Physics C-Solid State Physics* **17** (14), L383-L387 (1984).
38. A. Fukabori, T. Yanagida, J. Pejchal, S. Maeo, Y. Yokota, A. Yoshikawa, T. Ikegami, F. Moretti and K. Kamada, *Journal of Applied Physics* **107** (7), 073501 (2010).
39. A. Lushchik, M. Kirm, C. Lushchik, I. Martinson and G. Zimmerer, *Journal of Luminescence* **87-89** (0), 232-234 (2000).
40. V. Babin, A. Fukabori, V. Jary, A. Beitlerova, V. I. Chani, A. Yoshikawa and M. Nikl, *Eur. Phys. J. B* **86** (3), 93 (2013).
41. A. Fukabori, V. Chani, K. Kamada, T. Yanagida, Y. Yokota, F. Moretti, N. Kawaguchi and A. Yoshikawa, *Journal of Crystal Growth* **318** (1), 823-827 (2011).
42. M. Kirm, G. Zimmerer, E. Feldbach, A. Lushchik, C. Lushchik and F. Savikhin, *Physical Review B* **60** (1), 502-510 (1999).
43. R. L. Wood and W. Hayes, *Journal of Physics C: Solid State Physics* **15** (35), 7209 (1982).
44. V. Babin, V. Gorbenko, I. Kondakova, T. Kärner, V. V. Laguta, M. Nikl, S. Zazubovich and Z. Yu, *Journal of Physics D: Applied Physics* **44** (31), 315402 (2011).