Novel ZnO:Li Phosphors for Electronics and Dosimetry Applications

J. L. Iriqui-Razcón[1], C. Cruz-Vázquez[1], R. Bernal[2], H.A. Borbón-Núñez[3] and VM.Castaño[4,*]

[1] Departamento de Investigación en Polímeros y Materiales de la Universidad de Sonora, Hermosillo, Sonora 83000, México.
[2] Departamento de Investigación en Física de la Universidad de Sonora, Hermosillo, Sonora 83000, México
[3]Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada, B. C., 22800 México.
[4]Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México, Querétaro, Querétaro 76230, México
[*] E-mail: meneses@unam.mx

Abstract

Novel ZnO:Li thermoluminescent phosphors were synthesized by a chemical method. Pellet-shaped samples were exposed to beta radiation to investigate their dosimetric capabilities. Some samples were exposed to beta particle irradiation for doses from 50 up to 1600 Gy, and it was found that the thermoluminescence response is a linear function in all over the dose range studied. The glow curve exhibits two maxima, centered at 385 and 507 K. The maximum located at 507 K shifts to lower temperatures as dose increases, indicating that second order kinetics thermoluminescence processes are involved. The results indicate that these new ZnO:Li phosphors are promising detectors and dosimeters for beta radiation.

Keywords: Zn:Li phosphors, thermoluminescence, beta radiation.

1. Introduction

ZnO is a promising material for a range of optoelectronics applications, due to its direct wide band gap (E_g ~3.3 eV at 300 K) and large exciton binding energy (60 meV). Its applications include UV light emitters, varistors, surface acoustic wave devices,

piezoelectric transducers, and chemical and gas sensing [1]. For energy source applications, ZnO is ideal for use as front electrodes in thin film solar cells, given its high electrical conductivity and high optical transparency [2]. However, pure ZnO films and nanostructures have some technical limitations; therefore, doping with various dopants is usually necessary. Some chemical elements used as dopants to improve optoelectronic properties are Mn, Co, Sn, Ga, In, Bi, and Al [3]. Moreover, some optoelectronic uses of ZnO overlap with that of GaN, another wide-gap semiconductor (E_g~3.4 eV at 300 K) that is widely used for production of green, blue-ultraviolet, and white light-emitting devices [4].

The band gap can be modified by incorporating impurities during the synthesis. For instance, by Cd doping the band gap decreases (to as low as ~3.0 eV), whereas Mg doping increases the band gap (to as high as ~4.0 eV) [2]. Alkali metals can also be incorporated into the ZnO structure [4]. For instance, Li can be incorporated either as substitutional (Li_{Zn}) or as interstitial (Li_i) impurity. The substitutive Li in Zn sites creates one hole per alkali atom in the neighboring oxygen atom, giving rise to acceptor levels. Due to its small ionic radius, Li is very mobile in the ZnO lattice and can easily occupy interstitial positions, where it acts as a donor [5,6].

The traditional description of thermoluminescence (TL) normally proceeds by invoking the absorption of energy from an ionizing source by an insulating or semiconducting material. The absorption causes the excitation of free electrons and free holes and the subsequent trapping of these electronic species at defects (trapping states) within the material. After removal of the excitation, the sample is heated such that thermal energy causes the liberation of charge carriers of one sign (say, electrons) which are then able to recombine with charge carriers of the opposite sign. If the recombination is radiative, luminescence (TL) is emitted [7].

ZnO TL properties were firstly reported in the late '60s and early 70's, concerning on low temperature TL features as a tool to study defects, with no interest in dosimetry applications [8,9]. In 2005, Cruz-Vázquez *et al.* reported on the synthesis of ZnO nanophosphors by thermal annealing of ZnS synthesized using a chemical bath deposition reaction, with TL properties suitable for use in TL dosimetry [10]. Afterwards, a number of authors have reported on the TL properties of both ZnO and doped ZnO, synthesized through different chemical routes in an attempt to improve their dosimetric characteristics [11-14].

Accordingly, in this article we report results on the TL of ZnO: Li, synthesized by a controlled precipitation chemical method. Structural, morphological, and thermoluminescence characteristics were analyzed to evaluate its properties and potential practical application in TL dosimetry.

2. Experimental

A controlled chemical precipitation was carried out to synthetize Li (5 %) doped ZnO powder as follows: 80 mL of a 0.1 M $CS(NH_2)_2$ (thiourea) solution and 50 mL of a LiCl solution were added to 250 mL of a 16 mM $ZnCl_2$ solution with stirring. Then, 40 mL of a 1 M NaOH solution was added. The reaction was allowed to proceed at 20 °C by stirring for 5.5 h. White ZnO:Li powder was collected by filtration and dried in vacuum. Then, 0.06 g of the synthesized ZnO:Li powder was weighted and placed into a 7 mm diameter cylindrical mold to make each pellet-shaped sample by pressing at 0.5 ton during 3 min using a hydraulic press. Afterwards, the pellets just obtained were subjected to a sintering process at 900 °C during 24 h under air atmosphere using a Thermolyne 1300 furnace.

A Risø TL/OSL reader model TL/OSL-DA-20 unit equipped with a ^{90}Sr beta particle source was used to perform beta particle irradiations and TL measurements. All

irradiations were accomplished using a 5 Gy/min dose rate at room temperature. The TL readouts were carried out under N_2 atmosphere using a heating rate of 5 ºC/s. The X-Ray diffraction (XRD) patterns were collected with a Bruker model D8 Advance diffractometer equipped with a graphite monochromator by using Cu-Kα radiation (1.542 Å wavelength). Scanning electron microscopy (SEM) images and the samples composition were obtained using a JEOL JSM-5140LV scanning electron microscope equipped with an Oxford EDS analyzer operating at 15 keV. Photoluminescence spectra were collected using a FluoroLog Horiba Jobin Yvon Spectrofluorometer equipped with a Xe lamp.

3. Results and discussion

Figure 1 shows the scanning electron microscopy image of a powder sample before being sintered (a), and after thermal annealing at 900 °C for 24 h under air atmosphere (b). As Figure 1(a) shows, previous to thermal annealing ZnO:Li tends to form spherical particles with sizes between 3 and 6 μm, which in turn are formed by a kind of small flakes of nanometric sizes. Figure 1(b) shows morphological changes of ZnO:Li after annealing: on the particles surfaces are now visible the namometric flakes-shaped structures that aggregate to form spheres with sizes ranging between 400 nm and 2 μm about. EDS Analysis was carried out on non-sintered powder revealed a proportion of 50:40:10 weight percent for Zn:O:C. The absence of Li signal by EDS is due to their low atomic number.

Figure 2 shows the X-Ray diffraction patterns of ZnO:Li before (a) and after (b) thermal annealing. All diffraction peaks coincide with those of the ZnO zincite (ICDD # 36-1451), which are shown as vertical lines for comparison. No presence of other crystalline structures was observed. No shift of the diffraction peaks is observed by Li

doping, due to the very close values of Li^+ and Zn^{2+} ionic radii. The increase in the intensity of the diffraction peaks after thermal annealing indicates a higher crystallinity of the material.

Figure 3 shows the photoluminescence spectra of ZnO and ZnO:Li samples, both of them after being subjected to thermal annealing. As can be seen, Li doping leads to a shift of the visible – range emission toward longer wavelengths. This red-shift has been reported when doping ZnO, and it is explained by the incorporation of Li^+ into the ZnO structure [15].

Figure 4 shows the glow curves of ZnO:Li samples before (a) and after (b) thermal annealing, as obtained after being exposed to 100 Gy of beta particle irradiation. A remarkable enhancement of the TL sensitivity and a great improvement in the shape of the glow curve for the thermally annealed samples can be noted. After annealing, the glow curve exhibits TL emission above 200 °C, which is of interest for dosimetry applications.

Figure 5 shows the TL glow curves of ZnO:Li pellets sintered during 24 h at 900 °C after exposure to beta particle irradiation in the dose range from 50 to 1600 Gy. In this new phosphor material, two maxima are observed, located at 385 and 507 K, respectively. As irradiation dose increases, the intensity of the whole glow curve grows. No evidence of saturation in the dose range studied is observed. A shift of the maximum located at 507 K toward lower temperatures can be observed, which indicates that TL processes with order kinetics other than first order are involved.

Figure 6 shows the integrated TL of beta particle ZnO:Li samples as a function of the irradiation dose, in the dose range from 50 up to 1600 Gy. No pre-irradition thermal annealing was applied to the samples before each irradiation. The ZnO:Li pellets exhibit a linear behavior for doses below 500 Gy, and a sublinear dependence for larger doses

with no response saturation clues. This sort of the TL dependence on the dose is suitable for radiation dosimetry applications.

4. Conclusions

In this work, we report on a method to obtain new ZnO:Li phosphors, as well as their thermoluminescence properties after being exposed to beta particle irradiation in the dose range from 50 to 1600 Gy. A maximum that shifts to lower temperatures as dose increases is observed around 507 K; it is considered that TL peaks with maximum between 473 and 523 K are ideal for radiation dosimetry applications. The higher temperature TL maximum shift indicates TL processes with kinetics order different to 1. The TL as a function of dose display a linear dependence for doses lower than 500 Gy, and sublinear for greater doses, with no saturation clues in the studied dose range. Based on the experimental evidence here reported, we conclude that the new ZnO:Li phosphor is a promising material to develop detectors and thermoluminescence dosimeters. Furthermore, there is no precedent for the use of this material in the field of radiation dosimetry.

REFERENCES

[1] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, *J. Appl. Phys.* **98**, 041301-2 (2005).

[2] Geun-Hyoung Lee, *Electron. Mater. Lett.* **6**, 155 (2010).

[3] Soaram Kim, Min Su Kim, Giwoong Nam, and Jae-Young Leem, *Electron. Mater. Lett.* **8**, 445 (2012).

[4] D.P. Norton, Y.W. Heo, M.P. Ivill, K. Ip, S.J. Pearton, M.F. Chisholm, T. Steiner, *Materials Today* **7**, 34-35 (2004).

[5] C. Rauch, W. Gehlhoff, M. R. Wagner, E. Malguth, G. Callsen, R. Kirste, B. Salameh, A. Hoffmann, S. Polarz, Y. Aksu, and M. Driess, *J. Appl. Phys.* **107**, 024311-1 (2010).

[6] Santa Chawla, K. Jayanthi and R. K. Kotnala, *Physical Review B* **79**, 125204-1 (2009).

[7] S. W. S. McKeever and R. Chen, *Radiation Measurements* **27**, 626 (1997).

[8] D. De Muer and W. Maenhout-Van Der Vorst, *Physica* **39**, 123-132 (1968).

[9] M. A. Seitz, W. F. Pinter and W. M. Hirthe, *Mat. Res. Bull* **6**, 275-282 (1971).

[10] C. Cruz-Vázquez, R. Bernal, S. E. Burruel-Ibarra, H. Grijalva-Monteverde and M. Barboza-Flores, *Optical Materials* **27**, 1237-1238 (2005).

[11] U. Pal, R. Meléndrez, V. Chernov and M. Barboza-Flores, *Applied Physics Letters* **89**, 183118-2 (2006).

[12] C. Cruz-Vázquez, V.R. Orante-Barrón, H. Grijalva-Monteverde, V.M. Castaño, R. Bernal, *Materials Letters* **61**,1099-1100 (2007).

[13] U. Pal, R. Meléndrez, V. Chernov, M. Barboza, *Journal of Nanoscience and Nanotechnology* **8**, 1-6 (2008).

[14] Dojalisa Sahu, B. S. Acharya, B. P. Bag, Th. Basanta Singh, R. K. Gartia, *Journal of Luminescence* **130**, 1371-1378 (2010).

[15] Mingsong Wang, Eun Woo Shin, Jin Suk Chung, Seung Hyun Hur, Eui Jung Kim, Sung Hong Hahn, Kee-Kahb Koo, *Journal of Materials Science* **45**, 4111-4114 (2010).

FIGURE CAPTIONS

Figure 1. Scanning electron microscopy (SEM) images of ZnO:Li powder before being sintered (a), and after being sintered at 900 °C during 24 h in air (b).

Figure 2. X-ray diffraction patterns of ZnO:Li of a powder before being sintered (a), and after sintered at 900 °C during 24 h (b). Vertical lines corresponding to ZnO *zincite* (ICDD # 36-1451) are included for comparison.

Figure 3. Photoluminescence of ZnO and ZnO:Li samples.

Figure 4. Thermoluminescence (TL) glow curves of a pellet-shaped ZnO:Li sample before being sintered (curve (a)), and after being subjected to thermal annealing at 900 °C during 24 h (curve (b)). A 100 Gy beta radiation dose was delivered previous to each TL readout.

Figure 5. Thermoluminescence of ZnO:Li pellet-shaped samples, obtained after being exposed to beta particle irradiation in the dose range from 50 up to 1600 Gy.

Figure 6. Integrated thermoluminescence (ITL) as a function of dose, of ZnO:Li pellet-shaped samples, in the dose range from 50 to 1600 Gy of beta particle irradiation.