

Luminescence characterization of gamma ray-irradiated ZnAl₂O₄: Dy phosphor by using various fuels.**K.K.Satapathy¹, F.Khan²**¹Department of Applied Chemistry, O.P. Jindal Institute of Technology, Raigarh 496001 India. Email: kabita.satapathy@gmail.com²Department of Applied Chemistry, National Institute of Technology, Raipur 492001 India. Email: fkhan.chy@nitrr.ac.in .**ABSTRACT**

Dy activated ZnAl₂O₄ phosphor was synthesized by combustion technique using hydrazine, carbonylhydrazide and urea as fuels. XRD pattern and photoluminescence spectra of the sample were recorded to confirm the formation of the sample and incorporation of dopant to the host material respectively. It is found that Dy enters in the lattice in trivalent form. Thermoluminescence (TL) and mechanoluminescence (ML) of the gamma-ray irradiated samples have also been studied. ML was excited impulsively by dropping a piston of mass 0.7 kg on to the samples with various impact velocities. Two peaks were observed in the ML intensity versus time curve. The thermo luminescence (TL) glow curve of ZnAl₂O₄: Dy exhibits two thermally stimulated luminescence (TSL) peaks around 165°C and 345°C. Although sample prepared using different fuels show similar luminescence characteristics but the relative luminescence yield is different. In present investigation it is found that urea is a better fuel for preparing ZnAl₂O₄: Dy phosphors.

Keywords: ZnAl₂O₄, Thermo luminescence, mechanoluminescence**INTRODUCTION**

Rare-earth and non-rare-earth-doped inorganic phosphors are widely used in a variety of applications such as lamp industry, radiation dosimetry, X-ray imaging, and colour display etc. [1]. In particular, the luminescent properties of rare-earth doped ZnAl₂O₄ phosphors have

been studied extensively for their applications in these areas. The zinc aluminate (ZnAl_2O_4) offers many advantages, such as high thermal and chemical stability, hydrophobic behaviour, high mechanical resistance, low sintering temperature, and high quantum yields [2]. It is a wide-band gap semiconductor, which occurs naturally as the mineral gahnite and is a member of the spinel family; it can be used as transparent conductor, dielectric material, and optical material [3]. Spinel represents an important class of chemically and thermally stable crystalline materials. ZnAl_2O_4 spinel shows cubic, orthorhombic space group $Fd\bar{3}m$. The Dy^{3+} ion will substitute the Al^{3+} ion in an octahedral site in the ZnAl_2O_4 spinel, without charge compensation [4].

Combustion synthesis or self-propagating high temperature synthesis is an effective method for various industrially useful materials. It has displayed unique advantages of lower synthesis temperature, shorter synthesis time and controlled size of particle. It is well known that quality of luminescent material is largely influenced by the synthesis [5]. In present investigation we prepared ZnAl_2O_4 : Dy by combustion technique using three fuels namely hydrazine, carbonylhydrazide and urea and effect of fuels on its luminescence properties as mechanoluminescence (ML), thermoluminescence (TL), photoluminescence (PL) etc. have been studied.

Mechanoluminescence (ML) is the phenomenon of light emission induced by any mechanical action such as elastic deformation, plastic deformation, fracture and rubbing of solids, and separation of two solids in contact [6]. In recent years the investigation of mechanoluminescent materials exhibiting intense ML during their elastic deformation and fracture has attracted the attention of a large number of workers and some important applications of ML materials have been made. Rare earth doped aluminate phosphors have been found useful in the real-time visualization of stress distribution in solids [7–10] and also in the visualization of stress-distribution near the tip of a crack [11]. TL has also been studied for better understanding of the ML mechanism in this system.

EXPERIMENTAL

The samples were prepared by combustion synthesis. The detailed description of this method can be found in the original work of Patil and co-workers [12]. The ingredients used were $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, fuel (urea, hydrazine or carbonylhydrazide) and dysprosium

nitrate. Zinc nitrate, Aluminium Nitrate, fuel and the desired amount of dopant were taken in a glass beaker and dissolved in distilled water. The solution was then boiled by keeping the glass beaker on hot plate, after which the beaker was kept in a furnace set at 250 °C. Once the water boils off, the metal nitrate and fuel react and ignite. The reaction is self-propagating and is able to sustain this high temperature long enough, from 1 to 5 s typically, to form the desired product. The entire combustion process was over in about 5 min. This technique can produce a homogeneous product in a short amount of time, without the use of an expensive high-temperature furnace. To confirm the formation of the samples XRD pattern of the sample was recorded by X-ray diffractometer (PW-1710). The gamma-ray-irradiation was carried out using ^{60}Co source. ML was excited impulsively by dropping a load on the sample placed on a Lucite plate with different impact velocities. The luminescence was monitored by a 931A photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (SM-340). A PC based thermoluminescence analyser system (TL-1009I) was used for recording TL. All the TL and ML measurements were carried out after gamma irradiation. Photoluminescence (PL) of the rare earth doped samples were recorded using spectrofluorophotometer (Shimadzu RF-5301 PC).

Result and discussion:

Figure 1(a), 1(b), 1(c). XRD pattern of ZnAl_2O_4 : Dy phosphors

Figure 1 shows XRD pattern of the ZnAl_2O_4 : Dy phosphors. XRD pattern obtained is almost similar to the JCPDS card No. 05-0669 and it may be concluded that small amount of impurity doped in the host material does not affect the XRD pattern.

Figure 2. PL emission spectrum of ZnAl_2O_4 : Dy (0.1 mol%) phosphors under 354 nm excitation.

Figure 2 shows PL emission spectra of ZnAl_2O_4 : Dy(0.1 mol%) phosphors. Two distinct peaks one around 470 nm and another around 570 nm were observed. PL emission observed is the characteristic emission of Dy^{3+} [13].

Figure 3. TL glow curves of γ -ray-irradiated (γ -ray dose 1.1kGy) ZnAl_2O_4 : Dy (0.1 mol%) phosphors.

TL glow curves of gamma-ray irradiated ZnAl_2O_4 : Dy (0.1 mol%) phosphors are shown in fig. 3. Two thermally stimulated luminescence (TSL) peaks almost around 165°C and 345°C was observed in the TL glow curve of the samples using different fuels.

Figure 4. Time dependence of ML intensity of ZnAl_2O_4 : Dy (0.1 mol%) phosphors. γ -dose 1.1kGy; mass of the piston dropped on the sample 0.7 kg from different height.

Figure 4 shows the ML intensity versus time curve of gamma ray irradiated ZnAl_2O_4 : Dy (0.1 mol%) phosphors. Double peak was observed when ML was excited by dropping a load of mass 0.7 kg on to it. ML intensity increases linearly with increasing the impact velocity of the piston dropped on to the sample. ML intensity initially increased with time attained an optimum value for a particular time then decreased again increases to a value than decreases and finally disappeared for all the samples using urea, carbohydrazide and hydrazine as a fuel. The ML peak intensity increased with increasing the impact velocity of the piston dropped on to the phosphor; however, t_m , i.e. the time corresponding to ML peak shifted towards shorter time value with impact velocity.

In the TL glow curve each and every peak represent one type of trap present in the lattice. The observed TL glow curve appears to be superposition of at least two distinct centres. In ZnAl_2O_4 , the most probable centres which can be observed are the V centres (a hole trapped at a cation vacancy) and F centres (an electron trapped at an anion vacancy). It is known that the cation disorder and non-stoichiometric of aluminates like ZnAl_2O_4 provide a large number of lattice defects, which may serve as trapping centres. In such a case, oxygen vacancies should lead to F centres by trapping electrons. On the other hand, hole trapping at aluminium and zinc vacancies can lead to formation of V centres. It seems that during the preparation of ZnAl_2O_4 : Dy phosphor, two ions of Dy^{3+} replace three Zn^{2+} ions, creating Zn^{2+} ion vacancies. The Dy^{3+} ion can easily enter the lattice, in place of Zn^{2+} ion, as the ionic radius of Dy^{3+} (0.091 nm) is close to the ionic radius of Zn^{2+} ion (0.083 nm)[14].

Like thermal energy mechanical energy can not be imparted to the trapped charge carriers directly, therefore some intermediate states are responsible for ML emission in this system. When the piston is dropped onto the sample it seems that very intense electric field is produced due to the charging of newly created surface. In case of the crystals such as ZnAl_2O_4 : Dy, because of the deformation induced electrical field some of the detrapped electrons reaching and moving in the conduction band are captured in the excited state of the

activator ions located adjacent to the bottom of the conduction band, whereby excited ions are produced and the de-excitation of excited activator ions gives rise to the light emission characteristic of the ions. Similarly, if there is detrapping of holes, then they may recombine with the reduced state of activators and luminescence may be produced [15–17].

In the PL spectra of the emission of ZnAl₂O₄: Dy, Dy³⁺ originates from the $^4F_{9/2} \rightarrow ^6H_J$ (J=7/2, 9/2, 11/2, 13/2 and 15/2) transitions in the visible and near infrared regions. Within these transitions, the yellow band at ~570 nm corresponding to $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition and the blue band at 470 nm corresponding to $^4F_{9/2} \rightarrow ^6H_{15/2}$ transition are predominant [18].

It is also observed that ML, TL and PL intensity are optimum for fuel urea than hydrazine and carbohydrazide. Urea concentration and combustion temperature in the combustion technology greatly influenced the crystalline structure and optical properties of the products [19].

CONCLUSIONS

ZnAl₂O₄: Dy phosphor was prepared by combustion synthesis with fuels urea, hydrazine and carbohydrazide separately. TL glow curve of ZnAl₂O₄: Dy exhibits two peaks around 165 °C and 345 °C. Two defect centres are identified in gamma irradiated ZnAl₂O₄: Dy phosphor and these centres are tentatively assigned to V centre and F centre, respectively. According to the result obtained in this work, it can be concluded that with change of fuels to prepare the phosphor sample by combustion technique it changes the TL and ML intensity of the phosphors. It is also found that different fuels do not change the crystal structure measurably. We found that urea is the best fuel for the synthesis of ZnAl₂O₄: Dy phosphor.

REFERENCES

- [1] Shionoya, S.; Yen, W.M., in Phosphor Hand Book, CRC Press, Washington DC, **1999**, 391–432.
- [2] M.Zewadzki, Solid State Sciences 8, 14, 2006.
- [3] S.C. Shen, K. Hidajat, L.E. Yu, S. Kawi, Adv. Mater. 16 (2004) 541.
- [4] A. R. Phani, M. Passacantando, S. Santucci, Mater.Chem. Phys. **68**, 66 (2001).
- [5] Jin Y, Qin WP, Zhang JS, Wang Y, Cao CY. J Solid State Chem.2008;181:724–9.

- [6] B.P. Chandra, in: D.R. Vij (Ed.), *Luminescence of Solids*, Plenum Press, New York, , 1998, pp. 361–389.
- [7] C.N Xu, T. Watanabe, M. Akiyama, X.G. Zheng, *Appl. Phys. Lett.* 74 (1999) 2414.
- [8] M. Akiyama., C.N. Xu, M. Taira, K. Nonaka, T. Watanabe, *Philos. Mag. Lett.* 79(1999) 735.
- [9] C.N. Xu, X.G. Zheng, M. Akiyama, K. Nonaka, T. Watanabe, *Appl. Phys. Lett.* 76(2000) 179.
- [10]C. Li, C.N. Xu, H. Yamada, Y. Imai, H. Zhang, L. Zhang, *Key Eng. Mater.* 368–372 (2008) 1407.
- [11] K.S. Sohn, S.Y. Seo, Y.N. Kwon, H.D. Park, *J. Am. Ceram. Soc.* 85 (2002) 712.
- [12] S. Ekambaram, K.C.J. Patil, *J. Alloys Compd.* 248 (1997) 7.
- [13] J.Li, J. Q. Hao, C. Y.Li, C. X. Zhang, Q.Tang, Y. L. Zhang, Q.Su, S.B.Wang, *Rad. Meas.*, 39(2)(2005), 229.
- [14] S. Menon, B. Dhabekar, E. Alagu Raja, S.P. More,T.K. Gundu Rao, R.K. Kher, *J.of Lumine.*, 128 (2008) 1673–1678.
- [15] F. Clabau, X. Rocquelte, T.L. Mercier, P. Deniard, S. Jobic, M. Whangbo, *Chem. Mater.* 17 (2005) 3904.
- [16] F. Clabau, A. Garcia, P. Bonville, D. Gonbeau, I.L. Mercier, P. Deniard, S. Jobic, *J. Solid State Chem.* 181 (2008) 1456.
- [17] K.V.D. Eeclhout, P.F. Smet, D. Poelman, *Materials* 3 (2010) 2536.
- [18] Pradhan A S, Chandra B, Bhatt R C (1984) *Int. J. Appl. Radiat. Isotops*, **35**:226.
- [19] Nguyen Manh Son, Ho Van Tuyen, Pham Nguyen Thuy Trang, *J. of Science, Hue University*, Vol. 69, No. 6, 2011.

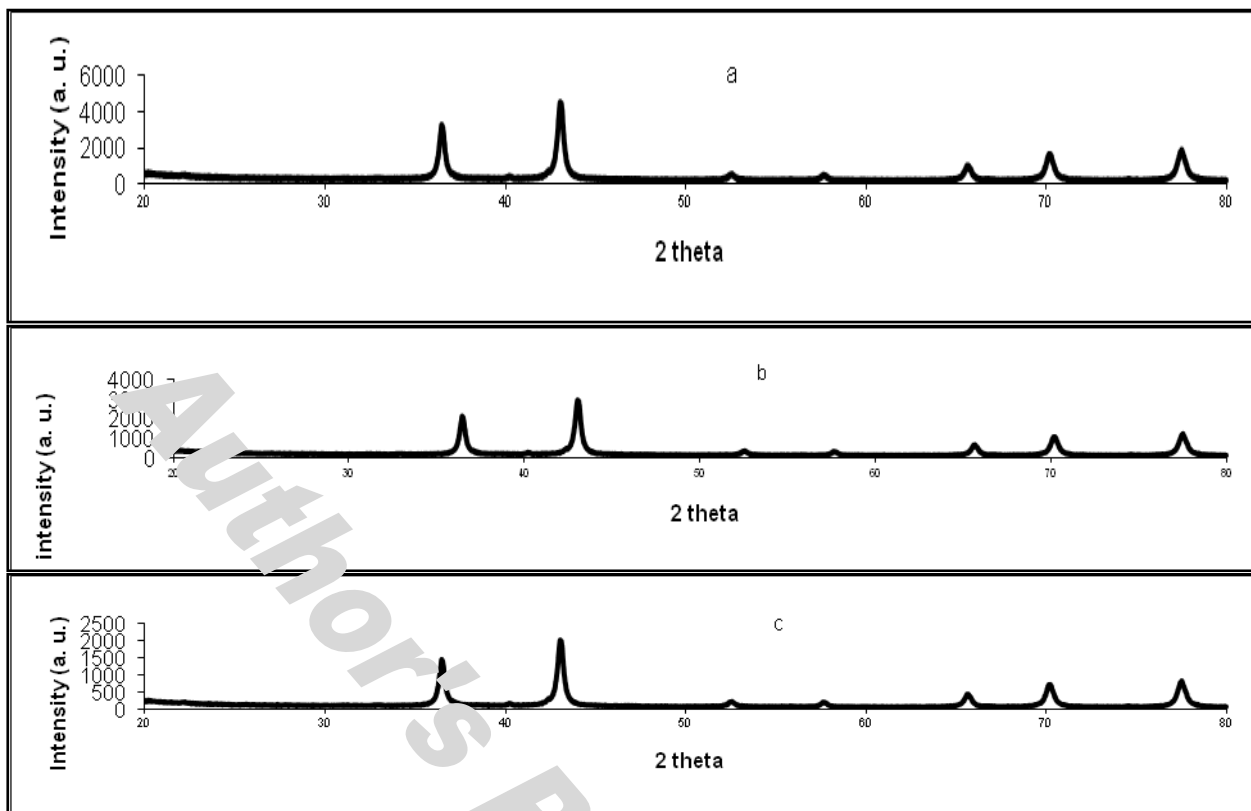


Figure 1(a) Urea, 1(b) Hydrazine, 1(c) Carbonylhydrazide. XRD pattern of ZnAl₂O₄: Dy phosphors

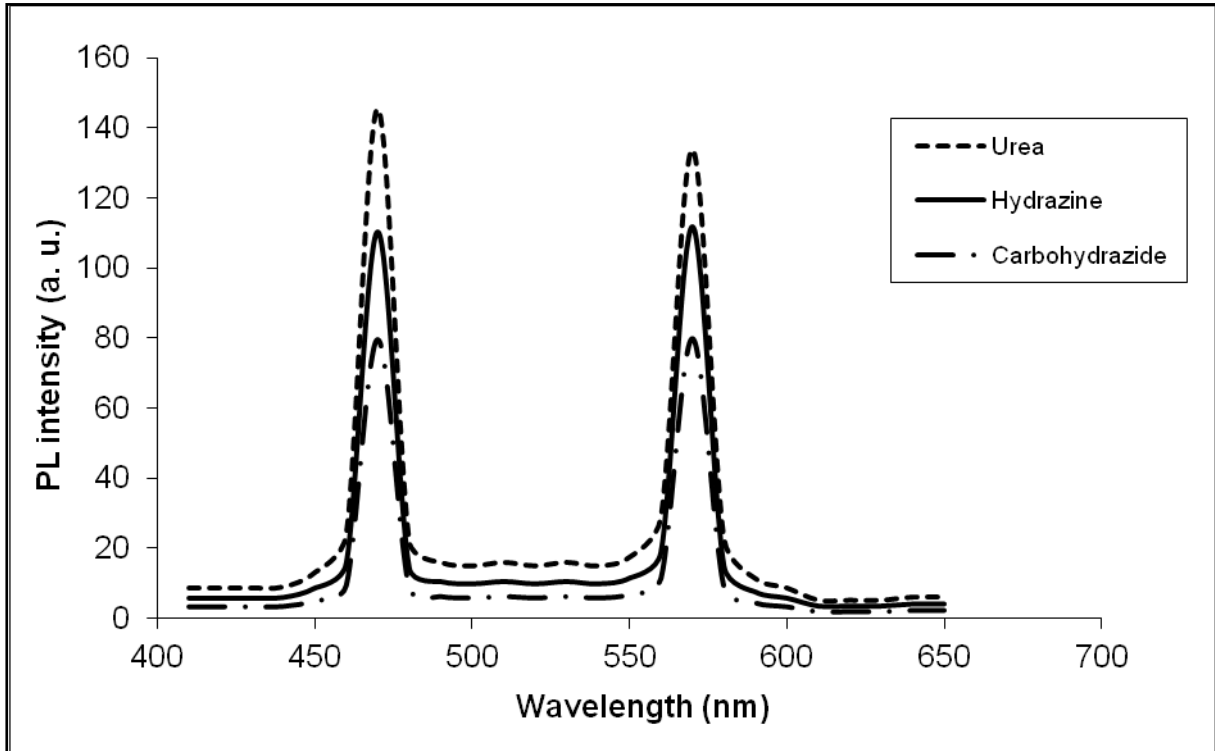


Figure 2. PL emission spectrum of ZnAl_2O_4 : Dy (0.1mol%) phosphors under 354 nm excitation.

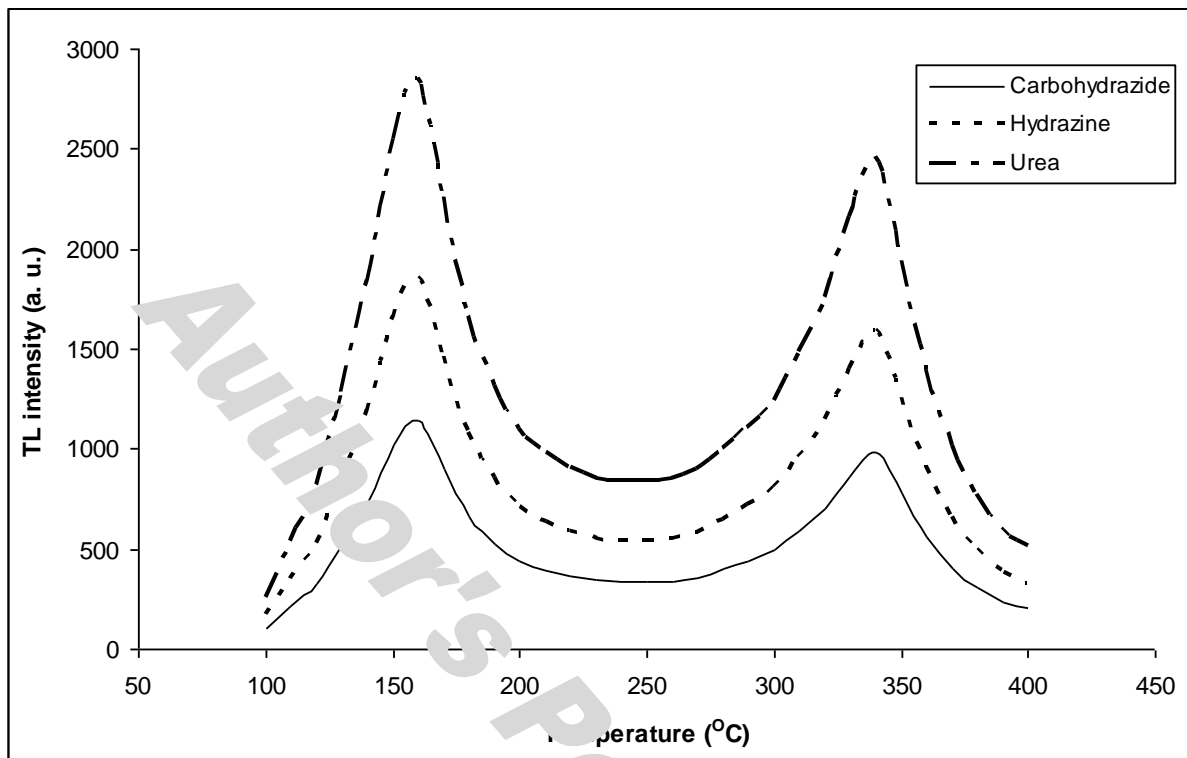


Figure 3. TL glow curves of γ -ray-irradiated (γ -ray dose 1.1kGy) ZnAl_2O_4 : Dy (0.1mol%) phosphors.

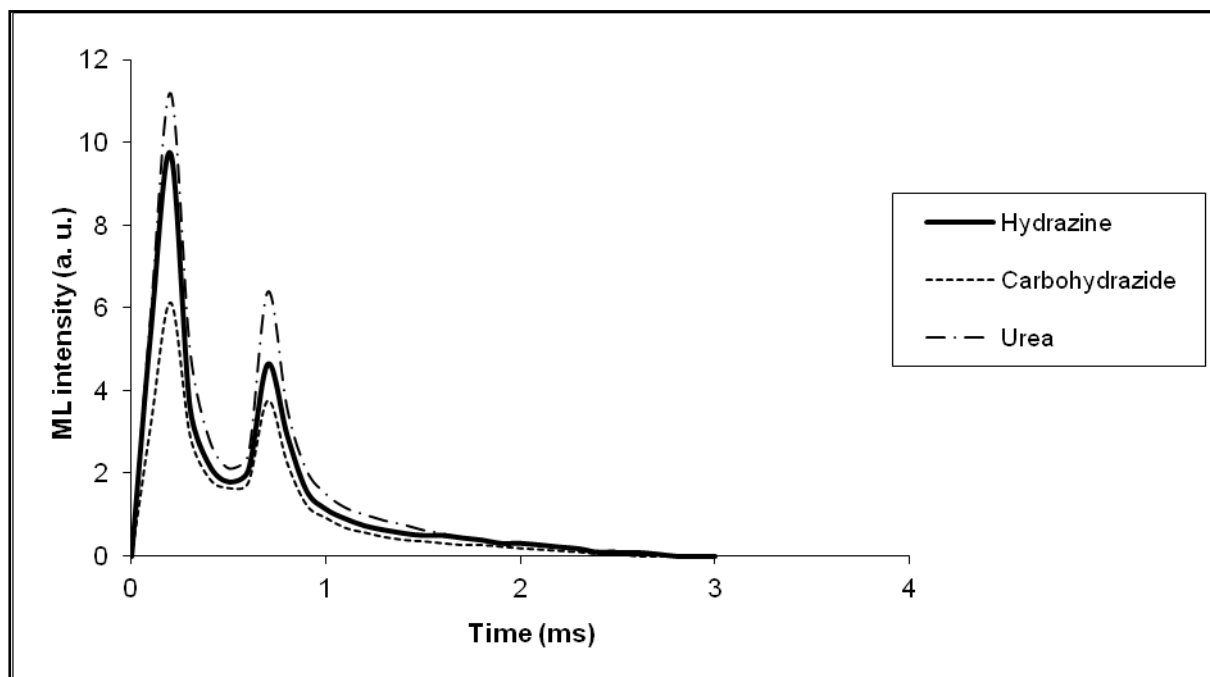


Figure 4. Time dependence of ML intensity of ZnAl_2O_4 : Dy (0.1mol%) phosphors. γ -dose 1.1kGy.