Influence of the fuels on the Mechanoluminescence properties of Dy doped $ZnAl_2O_4$ phosphors

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Abstract:
Most of commercial phosphors consist of suitably doped polycrystalline compounds. The activation means has been usually discussed, less attention has been paid to the influence of fuels on host preparation in the final performance of the products. In this paper different fuels have been followed to synthesize phosphors based on Dy doped $ZnAl_2O_4$. The mechanoluminescence (ML) properties of the materials have been given special consideration. Finally, various ML curves have been recorded in order to assess which of the fuel yields the most efficient Dy doped $ZnAl_2O_4$ compound. Dy doped $ZnAl_2O_4$ compound has been prepared by solution combustion technique with fuels such as urea, hydrazine and carbohydrazide separately. It is observed that urea enhances the ML intensity of the sample used. XRD result confirms formation of the phosphor. It is suggested that recombination of the trapped charge carriers are responsible for ML in this system.

Keywords: Mechanoluminescence, defects, dislocations.

1.Introduction:

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 [1]. When the phosphor sample deposited on a glass substrate is elastically deformed by applying a load, then initially the ML intensity increases with time, attains a peak value I_m at a particular time t_m, and later on it decreases with time. The rise and decay characteristics of the ML produced during release of the load are also similar to those produced during the application of load [2]. The ML of certain solids is so intense that it can be seen in day light with naked eye. In recent years the investigation of mechanoluminescent materials exhibiting intense ML during their deformation has attracted the attention of a large number of workers. Rare earth doped strontium aluminate phosphors have been found useful in the real-time visualization of stress distribution in solids [3–6] and also in the visualization of stress-distribution near the tip of a crack [7, 8]. The ML materials show promising application to advanced stress sensing techniques. The intense mechanoluminescent materials have been reported to be suitable for the real-time sensing of the strength and location of damages caused by the dynamic events in an object [9–14]. The ML materials have also been found useful in the fuse system for army warhead [15]. Good luminescent materials should have high purity, better chemical homogeneity and high surface area in a rapid, inexpensive single step operation. 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 [16]. 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 [17].

However, since defect structure depends on bulk properties, the preparation route used for host fabrication strongly affects luminescence final performance. For many applications, crystalline environments provide better conditions for controlling the properties of activators than hosts.

Many routes, such as hydrothermal reaction, sol-gel synthesis, micro-emulsion synthesis and mechanochemical synthesis were done to synthesize hydroxyapatite (HA) powder. Currently, solution combustion process is being considered to be a promising method to obtain phosphors because of its several advantages. The method involves a high level of molecular mixing of the components in solution leading to improved chemical homogeneity of the synthesized powder. Further, the process yields powder with high purity, better homogeneity and high surface area in a rapid, inexpensive single step operation [18]. Combustion synthesis technique involves the exothermic chemical reaction between metal nitrates and an organic fuel, typically urea, carbohydrazide or glycine. The maximum reaction temperature generated in this process depends on fuel to oxidizer ratio, initial furnace temperature, nature of the fuel and quantity of the initial precursor [19]. Several researchers [20-22] have tried to control the combustion flame temperature and scale up the synthesis process by adjusting the nature and content of the fuel, solution loading, volume of gases formed and the furnace temperature/environment. Although maximum reaction temperature of a solution combustion process depends strongly on nature and amount of fuel [23, 24]. The objective of this work is to study the effect of fuel on ML properties of $ZnAl_2O_4$ phosphor through solution combustion process.

2.Experiment:

The samples were prepared by solution combustion synthesis technique. The ingredients used were Zn $(NO_3)_2.6H_2O$, Al $(NO_3)_3.9H_2O$, fuel (urea, hydrazine and carbohydrazide) 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 beaker was kept in a furnace set at 250 ºC. 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. 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. Formations of the samples were confirmed by XRD pattern recorded by X-ray defractometer (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 (Fig.1). The luminescence was monitored by a 931A photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (SM-340). All ML measurements were carried out after gamma ray irradiation.

The various chemical reactions with the above fuels are as follows:

by Hydrazine

1. $Zn(NO_3)_2 + 2Al(NO_3)_3 + 10N_2H_4 \rightarrow ZnAl_2O_4 + 20H_2O\uparrow + 14N_2\uparrow$

by Urea

2. $3Zn(NO_3)_2 + 6Al(NO_3)_3 + 20CH_4N_2O \rightarrow 3ZnAl_2O_4 + 40H_2O\uparrow + 32N_2\uparrow + 20CO_2\uparrow$

by Carbohydrazide

3. $Zn(NO_3)_2 + 2Al(NO_3)_3 + 5CH_6N_4O \rightarrow ZnAl_2O_4 + 15H_2O\uparrow + 14N_2\uparrow + 5CO_2\uparrow$

3. Result and discussion:

3.1 Figure 2(a), 2(b), 2(c). XRD pattern of $ZnAl_2O_4$: Dy phosphors

Figure shows XRD pattern of the $ZnAl_2O_4$: Dy phosphors by using urea, carbohydrazide and hydrazine as fuels. 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. It is observed that ratio of peak intensities of all prepared sample were not the same. Comparing the XRD spectra with the fuels used for preparation, it is observed that more intense peak is observed for the fuel urea.

3.2 Figure 3. 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 shows the ML intensity versus time curve of gamma ray irradiated $ZnAl_2O_4$: Dy (0.1 mol %) phosphors. Two distinct peaks were 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 then decreases and finally disappeared for all the samples using urea, carbohydrazide and hydrazine as fuels. 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.

3.3 Figure 4. ML emission spectrum of $ZnAl_2O_4$: Dy (0.1 mol %) phosphors under 354 nm excitation.

Figure shows ML emission spectra of $ZnAl_2O_4$: Dy (0.1 mol %) phosphors. In order to find the luminescence centres responsible for ML emission, we have recorded ML spectrum. Two distinct peaks one around 482 nm and another around 585 nm were observed. ML emission observed is the characteristic emission of Dy^{3+}.

3.4 Figure 5: Dependence of Relative total ML intensity of $ZnAl_2O_4$: Dy (0.1 mol%) phosphors on mass of the phosphors (γ-ray dose 1.1 kGy, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1}).

Figure shows that ML intensity increased almost linearly with increasing the mass of the sample deformed for recording ML, in the rage (0.5 to 2.5 mg) investigated. When we increase the mass of the sample, the number of crystallites in the sample increases and thereby the ML intensity (I_m) and the total ML intensity (I_T) increase.

3.5 Figure 6: Total ML intensity of $ZnAl_2O_4$: Dy as function of γ-ray doses given to the samples (mass of the sample 1mg, mass of the piston 0.7 kg, impact velocity 2.83 ms^{-1})

Figure shows the dependence of ML intensity on γ-ray dose of $ZnAl_2O_4$: Dy (0.1 mol %) phosphors. ML intensity increased almost linearly with γ-ray doses given to the samples. On increasing the γ-dose, the density of defect centres increases and when a sample of a given mass is deformed at a given impact velocity, I_m and I_T should increase with the density of defect centres.

We know that mechanical energy can not be imparted to the trapped charge carriers directly; therefore some intermediate states are responsible for ML emission in this system. The origin of light emission are not due to the separation of the charges on the fracturing surfaces and piezoelectricity as the particle size is very small observed in XRD and $ZnAl_2O_4$ has a centrosymmetric structure (Fd3m). Therefore it is suggested that ML of $ZnAl_2O_4$: Dy is strongly related to the movement of dislocations and the recombination of activated electrons and holes. The movement of dislocations excite carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centres (Dy^{3+}) [25]. 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. 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) [26]. Since ML glow curve shows the characteristic emission of Dy^{3+}. This energy may be transferred non-radiatively to Dy^{3+} ions causing their excitation and subsequent de-excitation of excited Dy^{3+} ions.

It is observed that ML intensity of $ZnAl_2O_4$: Dy phosphor is more for fuel urea than carbohydrazide and hydrazine. Urea concentration and combustion temperature in the combustion technology greatly influenced the crystalline structure and optical properties of the products [27]. The combustion process by using urea has several advantages over the other fuels in terms of simplicity, cost effectiveness, energy saving, purity and homogeneity and also small weight loss after combustion. It is known that transformation of the Al atoms from the octahedral co-ordination to the tetrahedral can occur at higher temperature [28, 29]. The flame temperature during combustion is high with urea (477°C) than hydrazine (433°C) and carbohydrazide (388°C).

4. Conclusions:

$ZnAl_2O_4$: Dy was synthesized via solution combustion process from metal nitrates and organic fuels such as urea, carbohydrazide and hydrazine. Well crystallized powders were obtained at 388°C - 477°C within 5 min. The flame temperature and the amount of gaseous product released during combustion were key factors in determining the ML properties of synthesized phosphors. On varying the fuel the ML properties could be suitably modified and it is found that Urea is the best fuel for solution combustion of $ZnAl_2O_4$: Dy phosphor.

Acknowledgement:

The authors are grateful for the support provided by the O.P.Jindal Institute of Technology, Raigarh (C.G.). They would also like to thank the Department of Chemistry, National Institute of Technology, Raipur (C.G.).

References:

[1] Chandra B.P., Vij D.R.(Ed.) (1998), Luminescence of Solids, Plenum Press, New York, 361–389.
[2] Chandra B.P., Xu C.N., Yamada H. , Zheng X.G. (2010), J. Lumine, 130, 442–450.
[3] Xu C.N, Watanabe T., Akiyama M., Zheng X.G. (1999), Appl. Phys. Lett., 74, 2414.
[4] Akiyama M., Xu C.N., Taira M., Nonaka K., Watanabe T. (1999), Philos. Mag. Lett., 79, 735.
[5] Xu C.N., Zheng X.G., Akiyama M., Nonaka K., Watanabe T. (2000), Appl. Phys. Lett., 76, 179.
[6] Li C., Xu C.N., Yamada H., Imai Y., Zhang H., Zhang L. (2008), Key Eng. Mater. , 1407, 368–372.
[7] Sohn K.S., Seo S.Y., Kwon Y.N., Park H.D. (2002), J. Am. Ceram. Soc., 85, 712.
[8] Kim J.S., Kwon Y.N., Sohn K.S. (2005), Mater. Sci. Forum, 1121,475–479.
[9] Jia Y., Yei M. (2006), Jia W., Opt.Mater., 28, 974.
[10] Sage I., Huberstone L., Geddes N., Kemp M., Bishop S., Bourhill G. (2001), Smart Mater. Struct.,10,332.
[11] Sage I., Badcock R., Humerstone L., Gedders N., Kemp M., Bourhill G. (1999), Smart Mater. Srtuct., 8,504.
[12] Bourhill G, Gedders N., Sage I., Oswall I., Humberstone L., Badcock R., Llyod P., Willamson N., Kemp M. (2000), J. Def. Sci., 5,433.
[13] Sage I., Humerstone L., Oswala I., Lloyed, Bourhill G. (2001), Smart Mater. Struct., 10, 332.
[14] Sage I.., Bourhill G. (2001), J. Mater. Chem., 11,221.
[15] Dante J. G., Reports by the Secretary of Army, USA, Patent no. 43722111983.
[16] Zewadzki M. (2006), Solid State Sciences, 8, 14.
[17] Shen S.C., Hidajat K., Yu L.E., Kawi S. (2004), Adv. Mater., 16, 541.
[18] Ghosh S. K., Nandi S. K., Kundu B., Datta S., De D. K., Roy S. K. and Basu D. (2008), J. Biomed. Mater. Res.: Part B – Appl. Biomater., B86, 217.
[19] Jain S. R., Adiga K. C. and Pai Vernekar V. R. (1981), Combustion and Flame, 40,71.

[20] Fumo D. A., Morelli M. R. and Segadaes A. M. (1996), Mater. Res. Bull., 31,1243.
[21] Purohit R. D., Saha S. and Tyagi A. K. (2001a), J. Nucl. Mater., 288,7.
[22] Purohit R. D., Sharma B. P., Pillai K. T. and Tyagi A. K. (2001b), Mater. Res. Bull. ,36,2711.
[23] Aruna S. T. and Rajam K. S. (2004), Mater. Res. Bull., 39,157.
[24] Sasikumar S. and Vijayaraghavan R. (2007), Ceram. Int., 34,1373.
[25] Choubey A. K., Bramhe N. and Bisen D.P. (2012), Phys. Procedia 29, 104.
[26] Menon S., Dhabekar B., Alagu Raja E., More S.P., Gundu Rao T.K., Kher R.K. (2008), J.of Lumine., 128, 1673–1678.
[27] Son N. M., Tuyen H.V., Trang P. N. T. (2011), J. SCI., Hue University, 69,6.
[28] Assih T., Ayral A., Abenoza M., Phalippou J. (1988), J. Mater. Sci.,23, 3326.
[29] Mimani T. (2001), J.Alloys Compd, 315, 123–128.

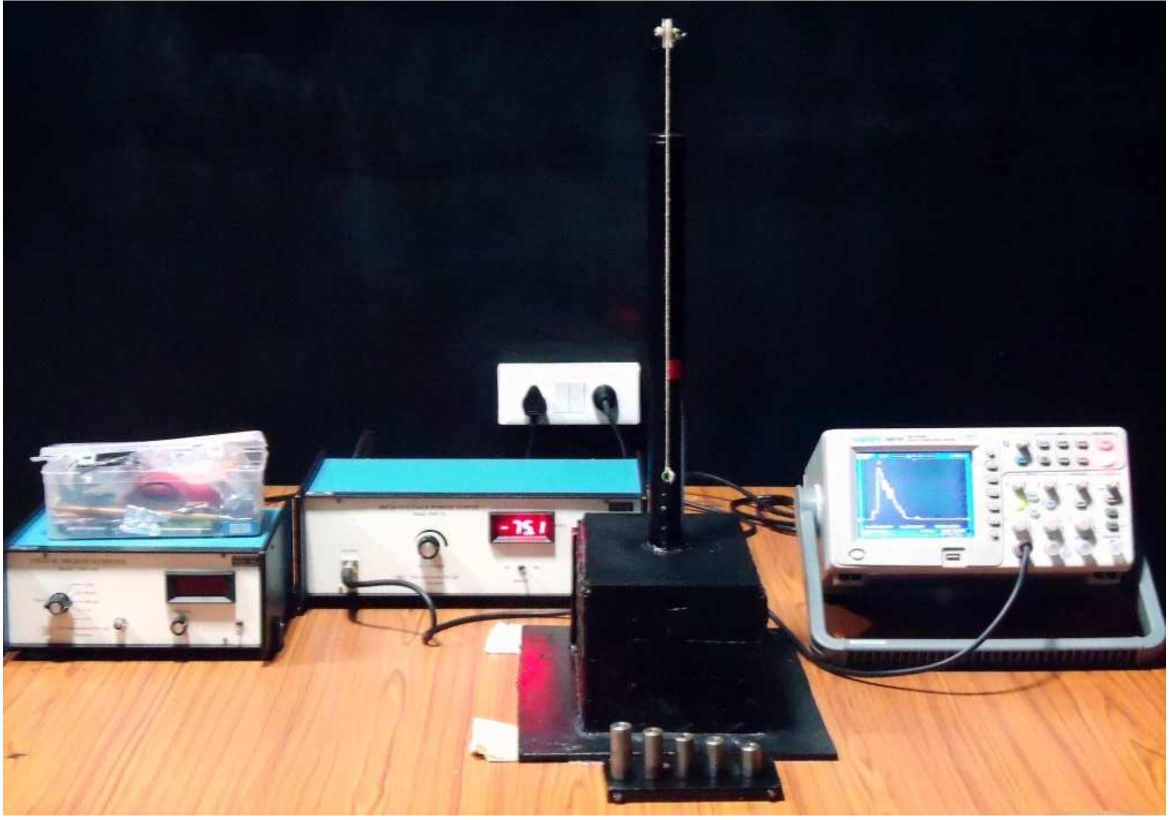


Fig.1 Mechanoluminescence Experiment setup

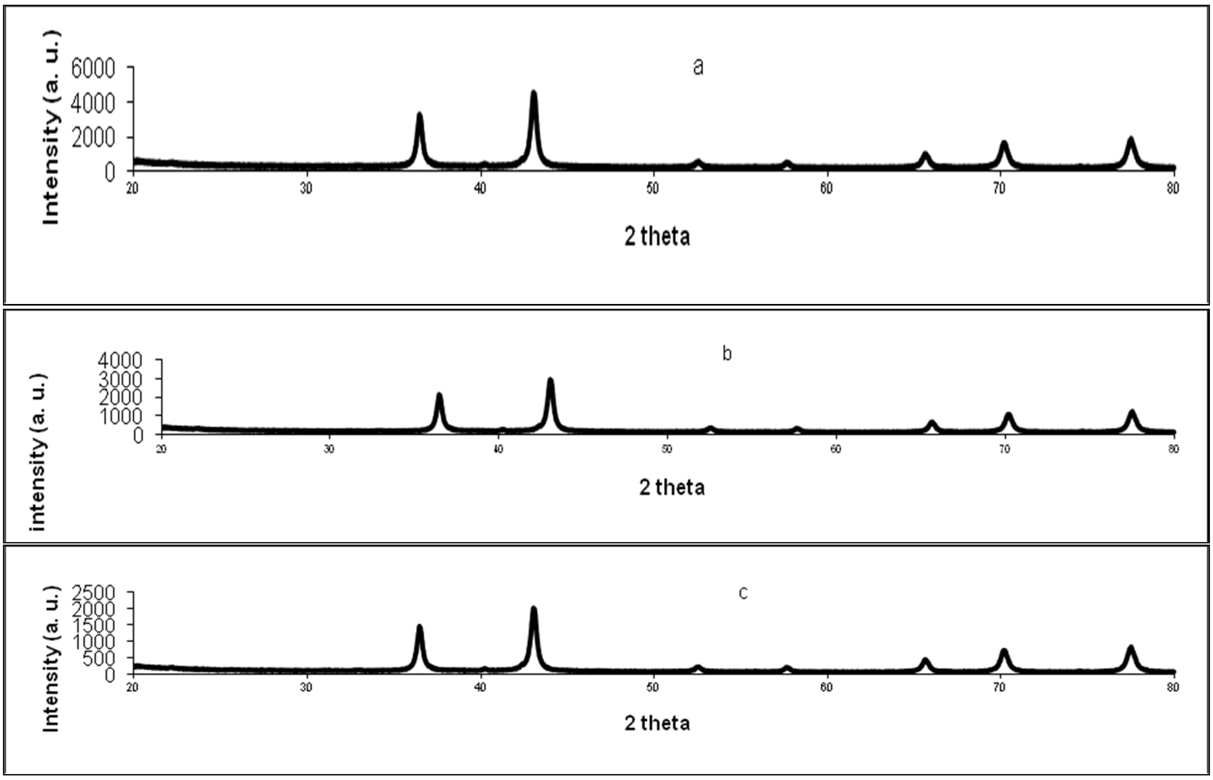
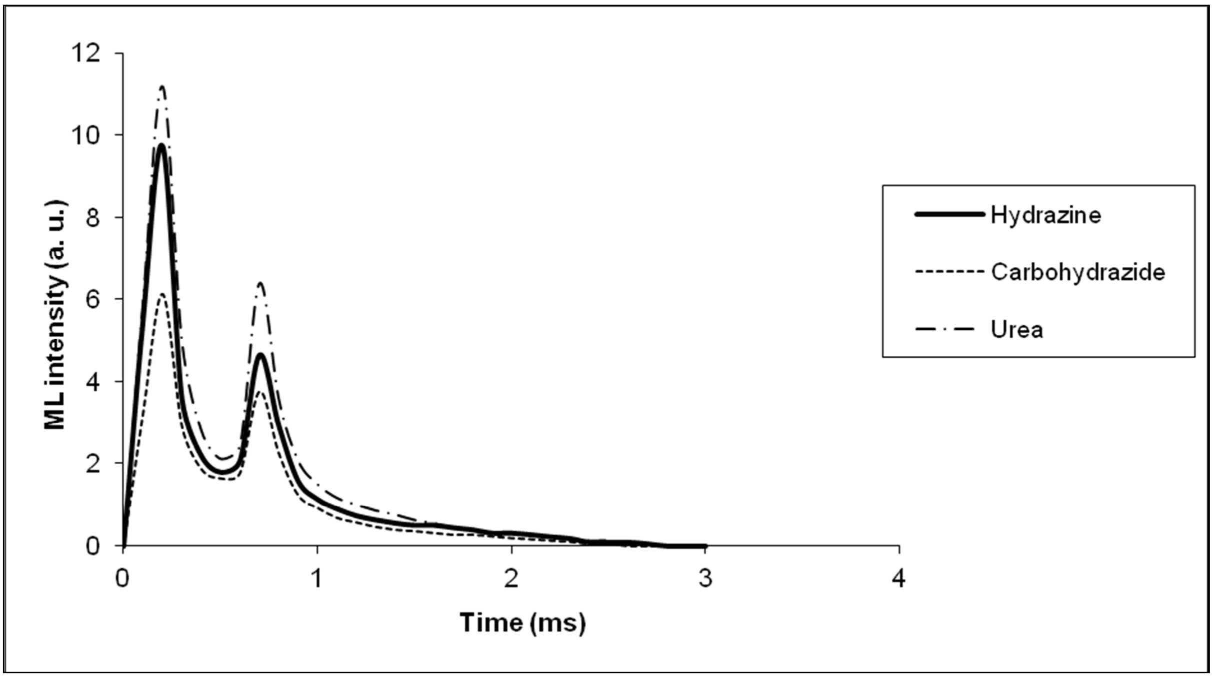


Figure 2(a) Urea, 2(b) Hydrazine, 2(c) Carbohydrazide. XRD pattern of $ZnAl_2O_4$: Dy phosphors.



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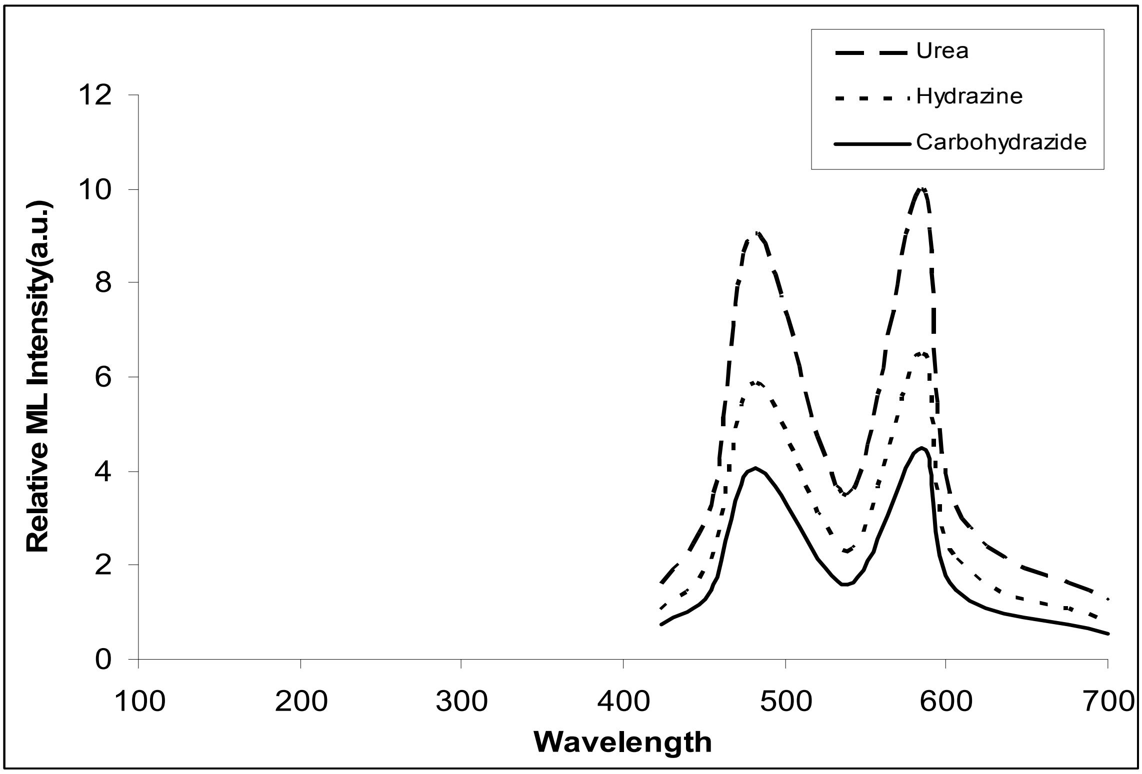

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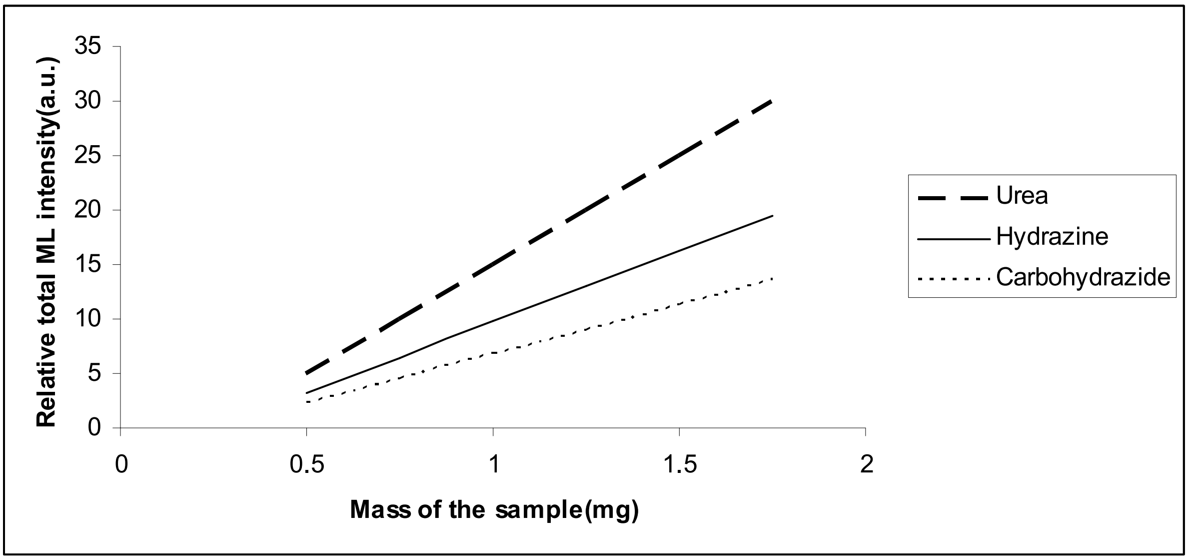

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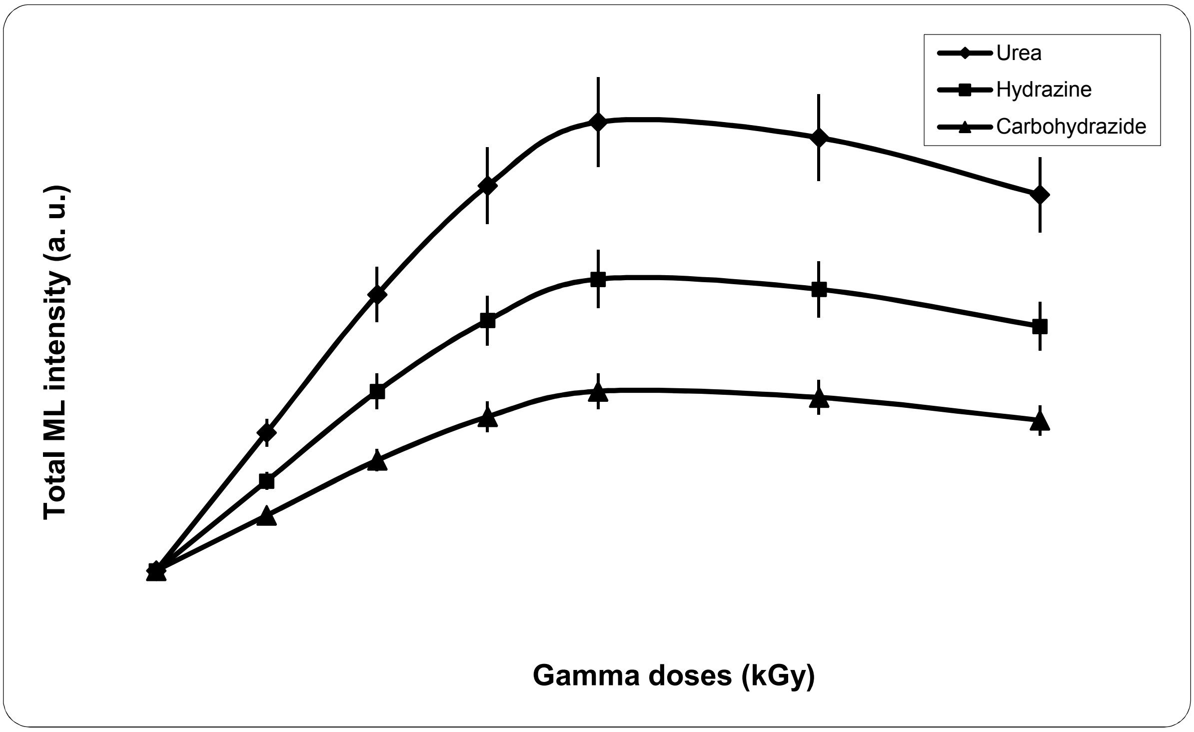

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