

Thermoluminescence Properties of Aluminium Oxide doped Strontium, Lithium and Germanium prepared by Combustion Synthesis method

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Abstract. In this work, Al₂O₃ doped with Sr, Li and Ge was prepared by combustion synthesis techniques for thermoluminescent (TL) ionizing radiation dosimetry applications. Dopants sample concentration were varied from 0.1 mol% to 5 mol% in order to study the effect of the concentration on the TL response. The optimum concentration was found to be 0.3 mol% for Sr and Li and 3.0 mol% for Ge. Based from the comparison of this doped material, the highest sensitivity was found for Ge doped and linear response for doses studied range of 10-80 Gy. X-Ray diffraction (XRD) patterns of the samples were recorded to confirm the formation of the sample. The sharp peaks present in the XRD confirms the sample is crystalline. The TL response of these samples for Co -60 gamma radiation were evaluated. It was observed a TL glow peak around 175°C for doped sample which is suitable for radiation dosimetry.

Keywords: Combustion synthesis, Aluminium oxide, Thermoluminescent dosimeter,

1 Introduction

One of the materials that can be considered for thermoluminescence TLD is aluminium oxide Al₂O₃, as it offers an excellent mechanical property and good mechanical stability [1]. Since the 50's, Al₂O₃ has been used as a radiation detection and dosimetric material using thermoluminescence technique. Another advantage properties of Al₂O₃, as linearity in wide dose range, easy handling and more reasonable price [2]. Other than that, Al₂O₃ attracted scientific interest because of its high optical, chemical and thermal stability under irradiation. The challenges were to make it sensitive to radiation [3]. Akselrod *et al.*, (2003) reported that Al₂O₃ single crystals (sapphire, or α - Al₂O₃) as a material for volumetric optical data storage has several fundamental advantages. Since aluminium oxide shows an effective number close to that of human tissue ($Z_{\text{eff}} = 11.28$), it becomes a better choice to be used in medical and environmental dosimetry [4].

The conventional fabrication process of these dosimeters utilizes Czochralsky or Vernuil crystal growth technique, which involves the use of high temperatures (> 2000°C) and highly reducing atmosphere [5,6,7]. With the development of newer technologies, there are several other techniques to synthesize the material with low cost and easy to handle [7] such as sol-gel technique [8] on beam implantation [9], solvent evaporation [10] and combustion synthesis (CS) [5,11,12]. Among wet chemical methods, CS is an effective, and low-cost method to produce various industrially useful materials [13,14]. The solution preparation for combustion synthesis is quick and easy [15]. Furthermore, it would produce a highly pure and homogeneous powder. There are few studies done on this method, such as [16] where un-doped and Al (2-10 mol%) doped ZrO₂ nano powder were synthesized using solution combustion method having glycine as a fuel in a pre-heated sample of around 500°C. However, the study only concerned on the optical properties of the samples and is not focused on the thermoluminescence properties. Recently, to have a better performance in the dosimetric purposes, Al₂O₃ is always doped with impurities that induce many different types of trapping centers at which charged particles would produce ionizing radiation [15]. Since then, there are a lot of efforts have been directed towards the improvements on its sensitivity via various dopants such as Si, Ti, [17], Mg and Y [18] Cr and Ni [19]. Even though studies of dopant in Al₂O₃ has been done, search for new detector material for radiation monitoring as personal dosimeter is one of the important task in TLD research.

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From previous study Lithium tetraborate, $\text{Li}_2\text{B}_4\text{O}_7$ (LTB) is a good tissue-equivalent material for thermoluminescent dosimetry having effective atomic number $Z_{\text{eff}} = 7.25$ which closely matches with that of human tissue [20], It has also been reported that the doped LTB materials are promising quantum electronics materials [21]. LTB is a versatile insulating material with large band gap [22]. In brachytherapy, the thermoluminescence dosimetry (TLD) using LiF crystals, is an experimental method that has been extensively applied with relative source.

The strontium aluminates have attracted intense research around the world, as they offer excellent properties such as high quantum efficiency, long persistence of phosphorescence and good stability. The long-lasting phosphors (LLP) oxide materials have been developed to replace the conventional sulfide after glow materials because of their improved luminescent properties such as high initial brightness, long lasting time, suitable emission colour and satisfactory chemical stability [23]. However, thermoluminescence properties of Ge doped Al_2O_3 prepared by CS method have not been reported so far. Recently, interest of Ge as dopants for dosimetric purpose has increased. Based on previous study, Ge doped optical fibre as a thermoluminescence dosimeter in radiotherapy is a promising material because it gives good response an fullfill the criteria of thermoluminescence properties [24]. Due to limitation study of CS technique especially for Al_2O_3 doped with Li, Sr and Ge dopants, for this present investigation, we report preliminary studies on the possibility of growing Al_2O_3 with different dopants and characterizing them for thermoluminescnet studies. We tried to explore different type of dopants such as Li, Sr and Ge doped for aluminium oxide to choose the best one for future study in thermoluminescence properties prepared by CS method.

2 Materials and Methods

2.1 Sample Preparation

For preparing powder samples, stoichiometric amount of aluminium nitrate, ($\text{Al}(\text{NO}_3)_3$) urea, ($\text{CO}(\text{NH}_2)_2$) (Sigma Aldrich reagent grade, 99.9% pure) and dopant Sr, Li and Ge were weighed using Shimadzu ATX 224 single Pan Analytical balance. The starting materials were a mixture of 15 g of aluminium nitrate, ($\text{Al}(\text{NO}_3)_3$), 6 g of urea, ($\text{CO}(\text{NH}_2)_2$) and different weight of dopant concentration from 0.1% to 5%. Then, 20 mL distilled water was added to the sample and magnetic stirrer was used to prepare a homogeneous solution stirred for 15 minutes, for completely dissolved before transferring to alumina crucible. An alumina crucible is used as a container within which chemical reaction take place. After the solution is transferred into the crucible, it is placed into a muffle-furnace at 500°C . Within 10 minutes, the reaction starts giving yellowish flames. The reaction was continuing for next few seconds and as it over, crucible was taken out from the furnace and kept in an open to allow cooling. Upon cooling, white foamy product formed which was then crushed using agate pestle mortar to get material in the powder form.

2.2 Measuring instruments

The XRD is used to confirm the crystalline nature of the as synthesized Al_2O_3 and to identify the presence of any impurity phases of different compositions from dopant material using Siemens Diffractometer D5000. The XRD machine is equipped with diffraction software with $\text{CuK}\alpha$ radiation operating at 40 kV, 30 mA with a scanning step length of 0.05° for 2 second counting per step and scanning angle from 10° to 90° with Bragg-Brentano geometry at room temperature. Annealing process was done to removes all residual of TL signals to re-establish TL sensitivity and eliminates unstable low-temperatures glow peak before sample is exposed. Al_2O_3 powders were annealed at 400°C for 1hour followed by cooling process at 80°C for 16 hours [25]. To evaluate the TL response, samples with different dopant at different concentration were irradiated at 50 Gy to Cobalt-60 gamma Cell Model 220 Excel at Universiti Kebangsaan Malaysia, Bangi, Malaysia. The TL response glow curve was measured using a TLD reader Harshaw Model 3500. The TL measurement was carried out at 300°C with heating rate of 3°C s^{-1} . All reading was taken under N_2 gas flow, to ensure good thermal contact between the sample and the heater-plate, as is customary.

3 Results and Discussion

3.1 X-Ray diffraction (XRD) analysis

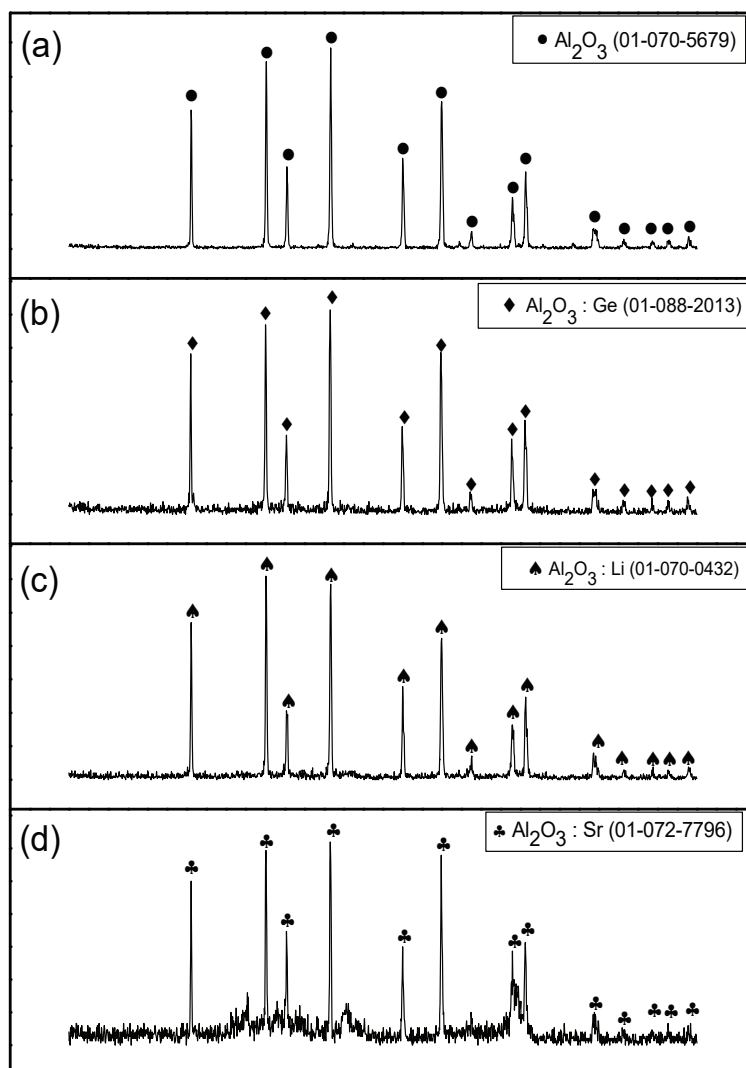


Fig 1. XRD pattern of (a) un-doped Al_2O_3 , (b) Al_2O_3 doped with 3 mol% of Ge samples, (c) Al_2O_3 doped with 0.3 mol% of Li samples, (d) Al_2O_3 doped with 0.3 mol% of Sr samples

The XRD results prove that the prepared samples were crystalline and the respective peaks with their ICDD reference number is shown in Figure. 1 in this work. Changes of dopants do not contribute to any phase change of Al_2O_3 . This finding is also supported by the previous work in [26]. They prepared Al_2O_3 by solution combustion method but using glycine as fuel.

3.2 Determination for the optimum strontium dopant concentration

Figure 2(a) represents the TL intensity and corresponding to standard deviation of Al_2O_3 at different Sr concentration. Figure 2(b) represents the glow curve of the samples at 50 Gy dose. From the results, the TL intensity of the sample was found to vary with decrease Sr concentration from 0.2 mol%. The intensity increases back from 0.3 mol% 531516.04 (a.u) and it is found to be optimum at this concentration. Based from the TL glow curve as in Figure 2 (b), the general nature of TL curves is similar in different cases: each curve peaks at temperature around 175°C. It is observed that varying

concentration of Sr does not affect the peak position much. However, the emission intensity is found to increase with increasing Sr concentration and for $x=0.3$ mol%, the intensity is quenched and decrease for further concentration. The reason for such quenching may be the increase in probability of non-radiative transitions of the luminescent molecules from the excited state to the ground state in comparison to the probability of radiative transition. No such work for Al_2O_3 : Sr has been reported to the best of our knowledge. From previous study this material has been considered to be effective luminescent hosts due to their low temperature synthesis, excellent chemical, physical stability and environmental stability [27]. As a conclusion, it is found that the optimum concentration value of Sr dopants is at 0.3 mol% (535116.04) with very low standard error.

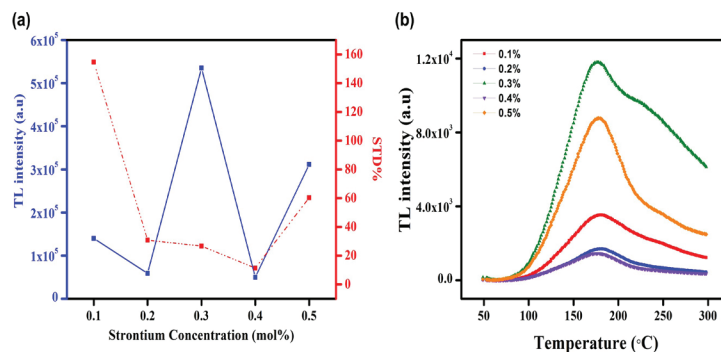


Fig 2. (a) TL intensity and correspond standard deviation as a function of different Sr concentration mole (0.1 to 0.5% mol concentration) (b) Glow curve recorded at different concentration mole (0.1 to 0.5%) of Sr dopant at a constant exposed to dose 50Gy

3.3 Determination for the optimum lithium dopant concentration

Figure 3(a) represents the TL intensity and corresponding to standard deviation of Al_2O_3 at different Li concentration. Figure 3(b) represents the glow curve of the samples at 50 Gy dose. It can be seen from the Figure 3 (a) the TL intensity increase up to 0.3 mol% for Li concentration 126515.14 (a.u). Then the intensity decreases with further increase of Li concentration. This may be due beyond 0.3 mol% concentration, quenching is bound to occur hence the optimum concentration for Li only suite for this concentration. As conclusion, the highest TL intensity were observed for 0.3 mol% of lithium concentration with (low standard error) value. The TL glow curve for Al_2O_3 : Li (0.1 to 0.5% mol concentration) was also studied. From the results, different concentration of Li playing a main role in production of TL glow curve. The prominent glow peak observed at high temperature around 175°C. This high glow curve temperature due to high-energy traps and it is very useful for TLD phosphor characteristics [28]. No such work for Al_2O_3 : Li has been reported so far, but historically, the first basic TL material was LiF:Ti, Mg (TLD 100), whose properties are still being studied extensively. Interest of this material is due to its human tissue equivalence ($Z_{eff} = 8.04$) which is an important factor for personal dosimetry, simple glow curve, high sensitivity and limited fading over a certain research.

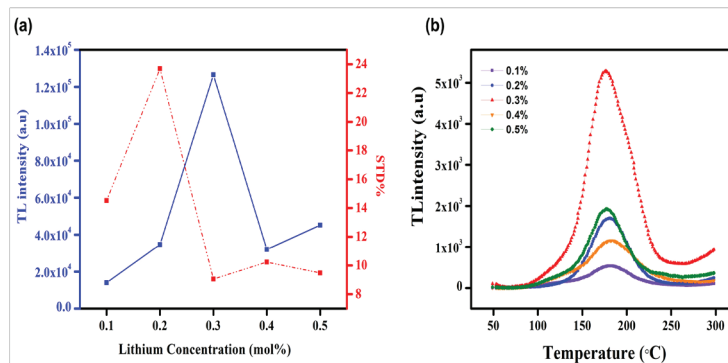


Fig 3. (a) TL intensity and correspond standard deviation as a function of different Li concentration mole (0.1 to 0.5%) (b) Glow curve recorded at different concentration mole (0.1 to 0.5%) of Li dopant at a constant exposed to dose 50Gy

3.4 Determination for the optimum germanium dopant concentration

Figure 4(a) represents the TL intensity and corresponding standard deviation of Al_2O_3 at different Ge concentration. The TL intensity of the sample was found to vary with increasing Ge concentration. The TL intensity increase from 1 mol% Ge to maximum intensity at 3 mol% Ge concentration 349747.04 (a.u). Then the intensity decreases with further increase of Ge concentration. This may be due beyond 3 mol% concentration, quenching is bound to occur hence the optimum concentration for Ge only suite for this concentration. Highest TL intensity at 3 mol% Ge is attributed to the recombination of the excited electrons from the valences band with defects produced via irradiation [29]. As a conclusion, it is found that the optimum concentration value of Ge dopants is at 3 mol% with very low standard error. At the same Figure 4(b) shows the glow curves Al_2O_3 : Ge samples for different concentration mole. Two peaks are observed, one prominent peak at around 175°C and another hump around 230°C. It is apparent that the TL intensity of the TL peak arrive the maximum value at 0.3% mol. For further study, it is found that the optimum concentration value of Ge dopants is at 0.3 mol% with very low standard error.

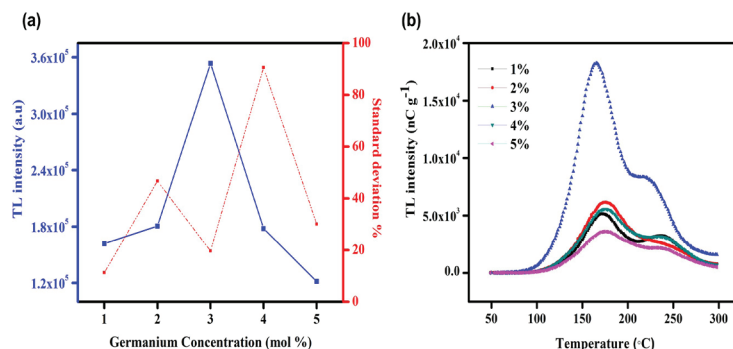


Fig 4. (a) TL intensity and correspond standard deviation as a function of different Ge concentration mole (1 to 5%) (b) Glow curve recorded at different concentration mole (1 to 5%) of Ge dopant at a constant exposed to dose 50Gy

3.5 Comparison of TL glow curve for each sample

Figure 5 represents the glow curve of material from each optimize concentration as mention in section 3.2 to 3.5. A very strong peak appears at 175°C for all samples but a small hump also appears for Ge sample at approximately 230°C. Based from the comparison of these three dopant materials, it can be observed that Al_2O_3 doped 0.3% Germanium gives the highest TL intensity compared to other dopants which is 93 times higher. The highest TL intensity that is reflected from either the total integrated area under glow peaks or that recorded in the reading system is detected at 3.0mol% Ge. Simple glow curve is another important property of a dosimeter. A good TLD material should display a simple glow curve and if possible has a single peak at around 200°C [30]. Furthermore, it should also have high resistance to environmental factor, as well as negligible dependence of its emission on radiation energy. As a conclusion for further study Al_2O_3 : Ge at 3.0mol% was selected to study the glow curve of germanium dopant properties.

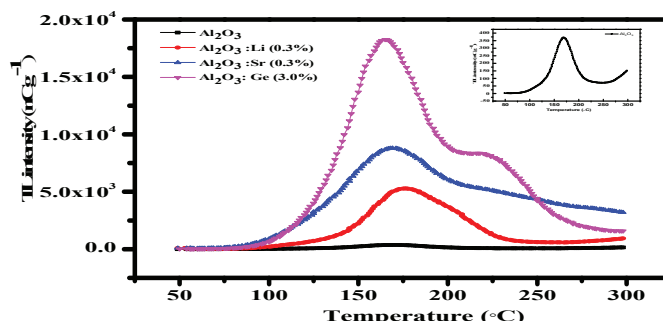


Fig 5. Glow curve recorded at different dopant material from optimum each concentration at a constant exposed to dose 50Gy

3.6 Glow curve analysis

Figure 6 shows the TL glow curve of aluminium oxide doped with 3.0 mol% germanium after being irradiated to Cobalt-60 gamma rays at dose ranging from 10Gy to 80 Gy. The glow curves recorded for all doses delivered the glow peak falls at around 175 °C and 230°C. The figure also indicates the TL intensity increase as the delivered dose increase. This results also agrees when α - Al₂O₃ doped either with Tb³⁺ or Tm³⁺ was prepared by combustion synthesis techniques studied by [11]. In this method the reactants (aluminium nitrate, urea and terbium or thulium nitrate) are ignited in a muffle furnace at temperatures as low as 500°C. The samples were annealed at temperatures ranging from 1000 to 1400°C for 4h in order to obtain the pure α -phase structure and were then irradiated with a Co-gamma radiation source. Tb³⁺ gives clearly TL peaks at around 190°C after sintering the sample at 1400°C. The dose response for 0.1 mol% for Tm³⁺ gives TL peaks around (~190°C) but the TL intensity increased 4 times better using Tm³⁺. Another work also by [31], tried to improve tld material nanoparticles for Al₂O₃ by different element like Eu, Tb, Dy, Cu and Ag were synthesized by chemical combustion (propellant) method. The samples were exposed to 100Gy of gamma-rays from a ¹³⁷PCs source. All the doped samples show poor TL sensitivity with two humps at around 150°C and 260°C except for Tb dopant. The glow curve for Tb has three major peaks; the highest is located at around 370°C, second 230°C and third almost two components located at around 125°C and 90°C.

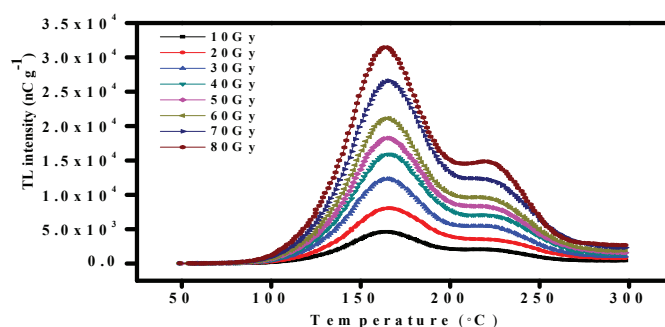


Fig.6. TL glow curve of 3.0 mol% germanium doped aluminium oxide at different doses of Cobalt-60 gamma rays

3.3.2 Linearity

Linearity of dose response is one of the most crucial properties of a TL phosphor. Figure 7 indicates TL intensity versus temperature for Al₂O₃: Ge 3% mol exposed to Cobalt-60 Gamma Rays at various doses ranging from 10-80 Gy. The linear response indicates that the TLD is directly proportional to the dose of radiation it was irradiated with. It clearly reveals a good linear dose response with the delivered dose up to 80Gy. Regression coefficient (R²) for Al₂O₃: Ge 3% is 0.9903. From the figure, the sensitivity of Al₂O₃: Ge 3% is 10019 nCg⁻¹ Gy⁻¹.

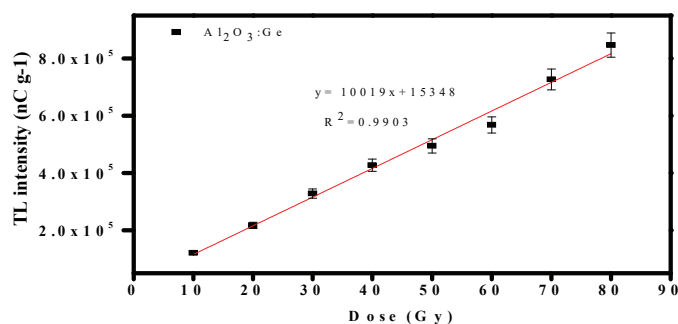


Fig7. TL intensity of Al₂O₃: Ge 3% mol irradiated to Cobalt-60 gamma ray for doses ranging from 10Gy to 80 Gy

Conclusion

From the results, it is possible to conclude that the CS method is very suitable for the preparation of Al_2O_3 doped materials for dosimetric applications. This technique is quick and easy process, with as main advantages the saving time and energy. From the comparison of three doped materials, Ge, Sr and Li, the concentration analysis show that the Ge concentration that optimizes the TL response 3mol% and in order to obtain well TL response peak for dosimetric applications. The crystallinity of the samples is proven by the XRD sharp peaks. The results will provide TL intensity, which depends on the delivered dose. The sensitivity found for $\text{Al}_2\text{O}_3 : \text{Ge}$ 3% is $10019 \text{ nCg}^{-1} \text{ Gy}^{-1}$.

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