TL ANALYSES ON FILTER TEST RESULTS OF SYNTHESIZED UN-DOPED AND DOPED Zn_2SiO_4 PHOSPHORS FOR DOSIMETRY PURPOSES

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Abstract

Zinc silicate (Zn_2SiO_4) is defined as a suitable host-matrix having excellent luminescence properties in red, green and blue spectral regions and also having high chemical stability. The aim of this study was to investigate the production and use of new dosimetric materials with the most ideal properties by adding different Rare Earth Element (REE) to Zn_2SiO_4 component using the gel-combustion method. The dosimetric properties of un-doped, Sm^{3+} doped and Ce^{3+} doped Zn_2SiO_4 phosphors were tested by using thermally stimulated luminescence (TL) method. The preliminary part of the study included "filter test" to define optimal measurement parameters. All TL measurements were performed using an automated Lexsyg Smart TL/OSL reader system having different filter combinations (wideband, 365, 410, and 565 nm). The reader also has an internal $^{90}Sr/^{90}Y$ source with a dose rate of 0.11 Gys^{-1}. The glow curve readouts were performed at a linear heating rate (HR) of 5 $^{o}Cs^{-1}$ from room temperature (RT) to 450 ^{o}C with 10 Gy dose.

Results of TL glow curves of each sample showed that TL intensity yielded successful results when using IRSL wideband blue and IRSL 565 nm filters. Thus, pre-heat (PH) tests were performed to analyze dosimetric TL peak(s) for each sample and detection filters used. A single dosimetric peak was obtained for Zn_2SiO_4 (225 ^{o}C with wideband blue and 290 ^{o}C with 565 nm) and Zn_2SiO_4:2.0%Sm (240 ^{o}C with wideband and 282 ^{o}C with 565 nm) phosphors when using both filters. However, visible peak maxima consist of the nested peaks in Zn_2SiO_4:2.0%Ce phosphor when both filters were used. In general, better reusability values of Sm^{3+} and Ce^{3+} doped Zn_2SiO_4 phosphors were obtained when the both filters were used within ± 3%. Fading results represented tunneling effect in some samples related with the fading time using especially IRSL 565 nm filter. The least change was obtained when a 565 nm filter was used. Zn_2SiO_4:2.0%Sm sample showed unexpected results called as "Anomalous Fading" effect when the TL readout was repeated after a week.

Keywords: Zinc Silicate, Thermoluminescence, Dosimetry

1. INTRODUCTION

Zinc silicate, a phosphor material that has been discovered long ago and investigated in many studies related to its dopant type is known as Willemite [1]. According to the literature, this phosphor material has high luminescent efficiency and excellent chemical stability [2-4]. Until recently, traditional solid-state reaction method was generally used to prepare Zn_2SiO_4 phosphors by using the temperature reactions above 1000 ^oC [5]. This procedure has disadvantage by decreasing the structural properties of the material. Recently, many studies on the synthesizing of oxide nanoparticles has been focused on novel combustion process due to its advantages of fast reaction velocity, uniform heating, and efficient energy utilization [6]. In other respects, one of the most important parameters in this process is the kind of fuel. More recently, a mixture of citric acid and glycine has been used [7,8] to recognize common effect of these fuels. Despite the usage of the citric acid contributes to formation of more uniform particles, the intense ignition of the glycine fuel generates better structures [6].

In recent years, there has been a particular focus in the literature on the search for suitable auxiliary activators to establish an appropriate trap level. ZnS phosphors are of great interest due to their broadband range and applications in different fields such as solar cell, photocatalysis, sensors, photonics, photonic devices, X-ray absorbers, cathode-ray tube devices, optoelectronics [9-11]. Hess studied the properties of Ga doped Zinc orthosilicate structure by photoluminescence, phosphorescence, thermoluminescence, and photostimulated luminescence. Zn_2SiO_4:Ga showed UV-blue emission band peaking at 405 nm [12]. Peng et al. prepared a long-lasting cyan light emitting Hf^{4+} doped Zn_2SiO_4 phosphorus sample using the conventional high temperature solid state technique [13]. Mir and Omri, in their studies, synthesized β–Zn_2SiO_4:Mn luminescent phosphor using sol-gel technique and they studied the structures, morphological properties and the photoluminescence (PL) characteristics of these nanophosphors as a function of Mn^{2+} content with various Mn percentages from 5 to 20%. As a result of the study, they observed that these materials present an intensive yellow emission (576–584 nm) generated by $^4T_1(^4G)$ to $^6A_1(^6S)$ inside transition [14]. Dang et al, prepared the barium and manganese-doped zinc silicate rods with hydrothermal method and they investigated the crystallinity and luminescence properties of Mn^{2+} due to the energy transfer from Ba^{2+}. The results of the study show that the prepared rods have single crystalline nature in high crystallinity and luminescence intensity of manganese-doped zinc silicate have been enhanced greatly due to the co-doping of barium [15].

New production techniques in doped dosimeter production, the investigation of the properties of rare earth ions as activators that can be used as thermoluminescence (TL)/optically stimulated luminescence (OSL) detectors are gradually increasing. The sensitivity, chemical resistance, optical and mechanical properties of these materials are studied in detail [16-18]. In this study, it was considered the preliminary dosimetric properties of un-doped, Sm^{3+} doped and Ce^{3+} doped Zn_2SiO_4 phosphors related to the detection filters chosen by using TL method.

2. MATERIAL & METHODS

2.1. Synthesis

Un-doped and REE doped Zn_2SiO_4 materials were prepared by gel-combustion method. High purity zinc nitrate ($Zn(NO_3)_2$) and additive elements nitrates (Ce_2NO_3, and Sm_2NO_3), if

necessary, are weighed in stoichiometric ratio and dissolved in quartz beaker in 10 ml distilled water. 1cc of TEOS (tetraethyl orthosilicate, $Si(OC_2H_5)_4$), citric acid ($C_6H_8O_7$) and 10 ml of ethanol (C_2H_5OH) into the solution in the beaker are added and the mixture is heated on a magnetic stirrer at 80 °C for 2 hours. The solution obtained is taken from the magnetic stirrer and kept in a covered form for 24 hours. After 24 hours, glycine ($C_2H_5NO_2$) is added with stirring the solution at 80 °C on a magnetic stirrer and the procedure is carried out to evaporate the excess water without covering the beaker until the gelation is done. The gel-like solution is placed in the muffle furnace and heated to 800 °C. Immediately after evaporation of the water in the solution, the combustion reaction takes place to form nanocrystalline Zn_2SiO_4 materials in the form of fly ash. The synthesis of the samples remaining in the ash oven for 1 hour is completed without washing or annealing.

Three aliquots having 10 mg powder samples were prepared for the TL measurements.

2.2. Measurement

All TL measurements were performed using an automated lexsyg smart TL/OSL reader system having different filter combinations (IRSL wideband blue, BSL 365 nm, IRSL 410 nm, and IRSL 565 nm). The reader also has an internal $^{90}Sr/^{90}Y$ source with 1.95 GBq emitting beta particles with a maximum energy of 2.2 MeV and a dose rate of 0.10 Gy s^{-1}.

The glow curve readouts were performed at a linear heating rate (HR) of 5 $^{o}Cs^{-1}$ from room temperature (RT) to 450 ^{o}C with 10 Gy dose using all detection filters as BSL 365 nm, IRSL 410 nm, IRSL 565 nm, and IRSL wideband blue (see Table 1). The TL glow curves were recorded over the dose range of 0.1 – 10 Gy (low doses) of beta irradiation and the graphs of the peak area versus the dose were recorded. In addition, reusability and fading features were evaluated to discuss the dosimetric properties of the phosphors.

Table 1. *Detection Filters Present in Lexsyg Smart TL/OSL Device*

Combination Name	**Stimulation**		**To measure:**	**Filter I**	**Filter II**	**Filter III**
BSL/TL – 365 nm	OSL (458 nm)	TL	UV emission of quartz	U340	BP 365/50 EX	-
IRSL/TL – 410 nm	OSL (850 nm)	TL	Blue emission of feldspar & dosimeters	BG39	HC 414/46	-
IRSL/TL – 565 nm	OSL (850 nm)	TL	Green emission of feldspar	BG39	HC 575/25	-
IRSL/TL – wideband blue	OSL (850 nm)	TL	Wideband detection for dosimeters	BG39	BG 25	KG3

3. RESULTS & DISCUSSION

3.1. TL Glow Curve of the Phosphors for each Filter

In this study, three samples which were prepared by weighing 10 mg and irradiated with 10 Gy in the first stage were analyzed by using all filters before without preheat (PH) application and PH application. After the first test, 160 ^{o}C PH was applied to erase shallow traps to avoid from the contaminating signal. As seen in Fig.1, the highest TL intensity has been achieved using wideband blue (wbb) filter as expected.

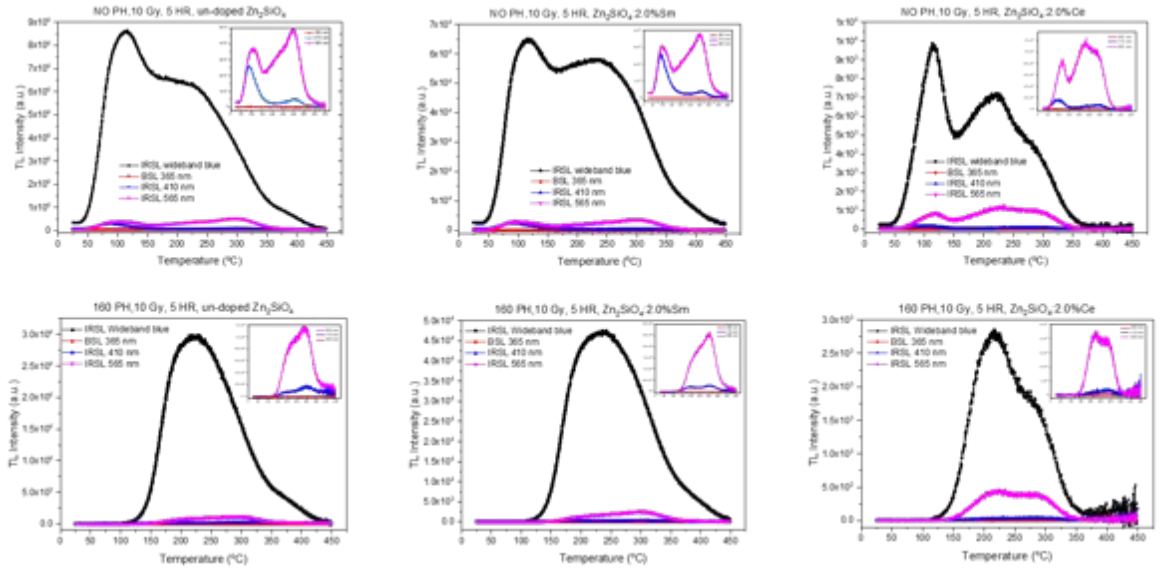


Fig.1. All Filter Test Results in Lexsyg Smart TL/OSL Reader for all Powder Samples (Zn_2SiO_4, Zn_2SiO_4:2.0%Sm and Zn_2SiO_4:2.0%Ce).

In addition, good results were also obtained by using 565 nm filter but it was found that the other filters were inadequate to evaluate the dosimetric characteristics of the phosphors. Therefore, further investigations (dose response, reusability, and fading) were carried out using these two detection filters.

3.2. TL Glow Curves for wbb and 565 nm Filters (with and without PH)

After choosing the most proper detection filters, the study was carried out by defining the each specific PH values for each sample and filters used. As seen in Fig.2, required PH values were defined for all three samples and for two detection filters, respectively.

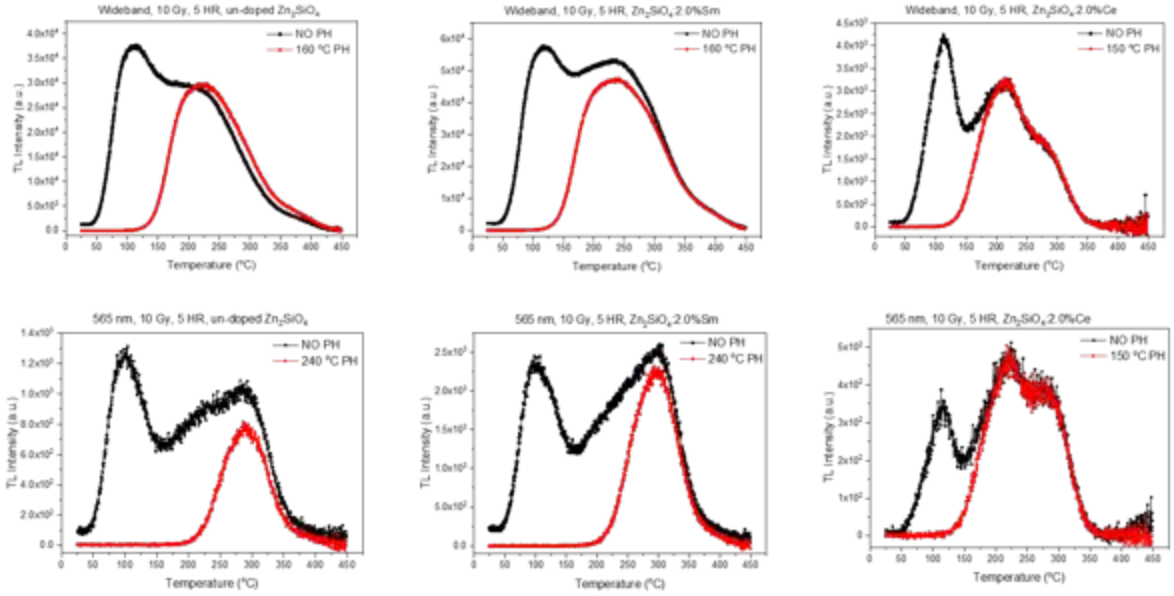


Fig.2. Zn_2SiO_4, Zn_2SiO_4:2.0%Sm and Zn_2SiO_4:2.0%Ce powder samples for wbb and 565 nm filters for 10 Gy, β: 5 $^{o}Cs^{-1}$ at different preheat values.

3.3. Dose Response

The TL glow curves were recorded over the dose range of 0.1 – 10 Gy of beta irradiation and the graphs of the peak area versus the dose were recorded. This study includes low levels of radiation dose to evaluate their responses. Therefore, 0.1, 1, and 10 Gy were applied to evaluate whether the phosphors give a linear response or not. As seen in the Fig.3, linear regressions are quite good and very close to 1.

Although the dose values used are insufficient to make a complete interpretation, it is seen that all materials in the low dose range give linear dose response when both filters are used in general (except Zn_2SiO_4:2.0%Ce phosphor when wbb filter packet is used).

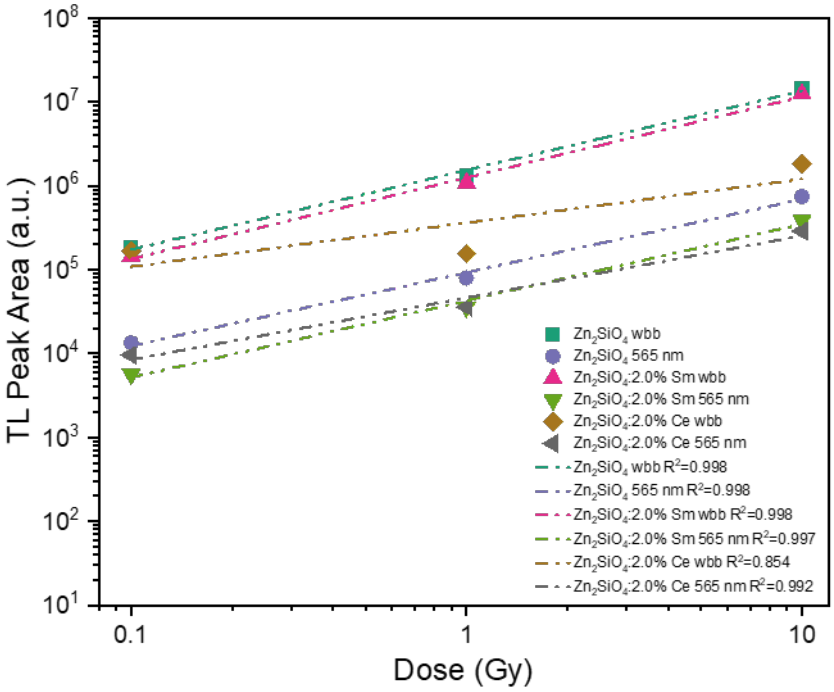


Fig.3. Dose linearity graph curve for the sample as a result of peak area 0.1-10 Gy, β: 2 $^{o}Cs^{-1}$.

3.4. Reusability

The reusability test, which determines whether the luminescence signal observed in the material has undergone any changes, is a method that determines the dosimetric property of the material. Reusability of a good dosimetric material should have less than 5% for repeated measurements under the same dose and reading condition [19]. For this experiment, the glow curve readouts were performed at different PH values determined at a linear heating rate (HR) of 5 $^{o}Cs^{-1}$ from room temperature (RT) to 450 ^{o}C with 10 Gy dose using wbb and 565 nm filters.

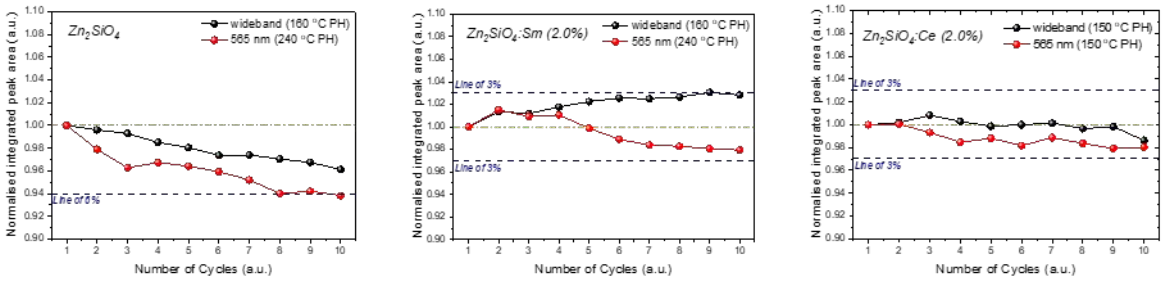


Fig.4. Reusability Result of Zn_2SiO_4, Zn_2SiO_4:2.0%Sm and Zn_2SiO_4:2.0%Ce Samples for wbb and 565 nm Filters for 10 Gy, β: 5 $^oCs^{-1}$ at 240 and 150 ^oC PH Values, Respectively.

As seen Fig.4, better reusability values within ± 3% were obtained when wideband blue detection filter was used except an un-doped sample with ± 4%. In addition, good agreement between the readouts were obtained for REE doped Zn_2SiO_4 phosphor when IRSL 565 nm detection filter is used. However, un-doped Zn_2SiO_4 phosphor gave higher fluctuation (with ± 6%) when 565 nm detection filter was used. A good dosimetric material should have similar results within ± 5% when analyzed under the same repeated conditions, but only un-doped Zn_2SiO_4 was found to be out of this range, especially after the seventh reading.

3.5. Fading

For the storage time experiment, the sample was exposed to a dose of 10 Gy each time, then allowed to fading. During the TL readout procedure, they were preheated at 240 ^oC for Zn_2SiO_4, Zn_2SiO_4:2.0%Sm and 150 °C for Zn_2SiO_4:2.0%Ce and TL glow curves were recorded. The storage time experiments were performed for different time periods from 1 hour to 1 weeks for dark fading. Both filter options were given in Fig.5. According to the results, total TL intensities of Zn_2SiO_4:2.0%Ce sample represented the lowest change by time compared to the other samples when both filters were used. Tunneling effect is seen when IRSL 565 nm detection filter is used for each sample. The increase in the TL intensity of the dosimetric peak after an hour and a day may be explained due to the tunneling effect.

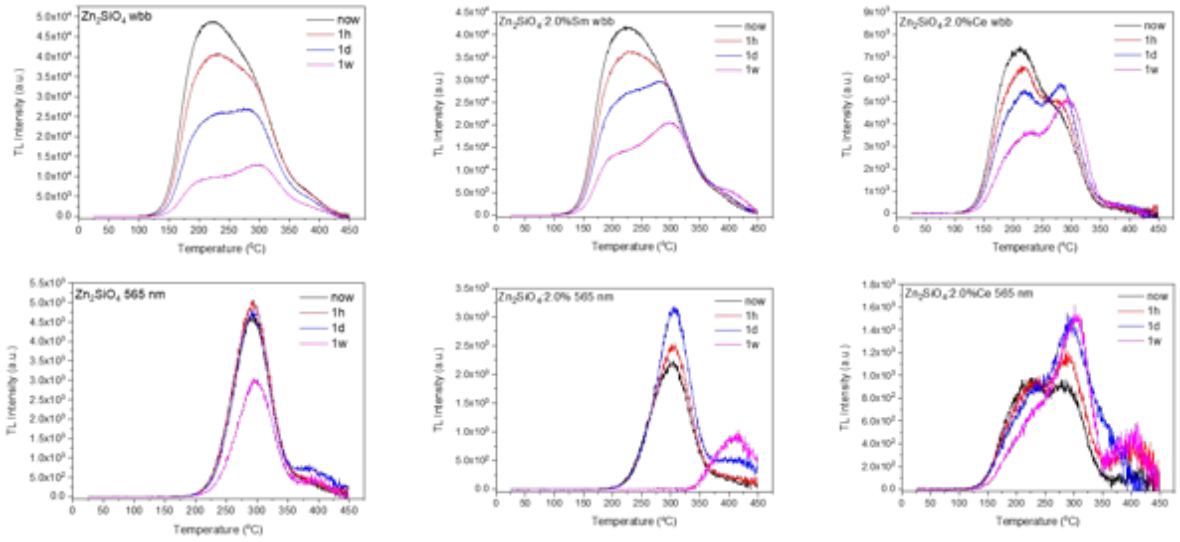


Fig.5. TL Glow Curves for Three Sample Measured after Different Storage Times at RT in Each Filters.

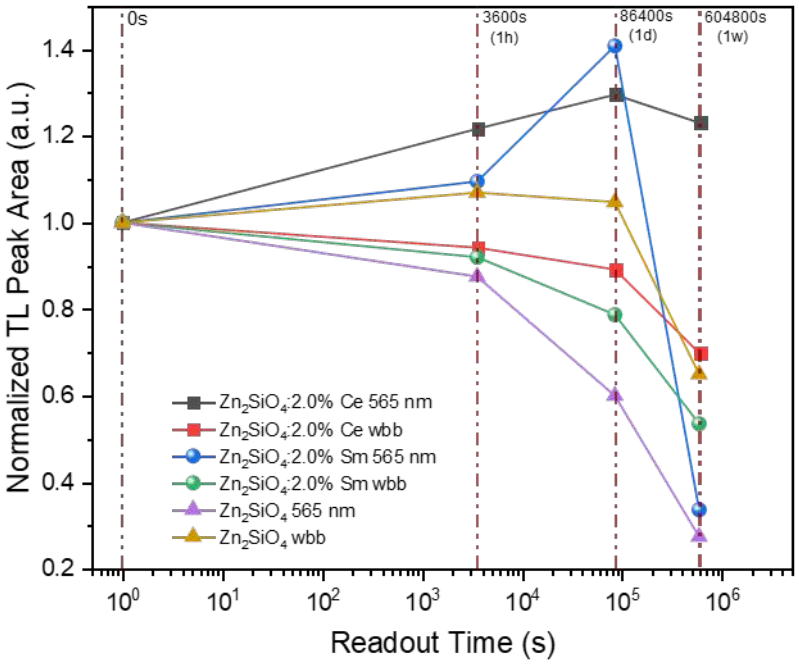


Fig.6. Normalized TL Intensities Fading Results of the Zn_2SiO_4, Zn_2SiO_4:2.0%Sm and Zn_2SiO_4:2.0%Ce in Each Filters.

An unexpected result was observed for Zn_2SiO_4:2.0%Sm sample when IRSL 565 nm detection filter is used. Dosimetric peak at around 300 ^oC disappears and only high temperature peak appears which means deep traps become dominant due to the possibility of phosphorescence activating the deep traps. This unexpected situation is thought to be caused by the charge transfer in deeper traps. The mentioned anomalous effect can also be seen at the graph of normalized peak area versus readout time in Fig.6.

4. CONCLUSION

Results of TL glow curves of each sample showed that TL intensity yielded successful results when using wideband and 565 nm filters. Thus, pre-heat (PH) tests were performed to analyze dosimetric TL peak(s) and it was found that 160 ^oC PH is proper for Zn_2SiO_4 and Zn_2SiO_4:2.0%Sm phosphors when it was 150 ^oC for Zn_2SiO_4:2.0%Ce sample with the usage of the wideband filter. However, 240 ^oC PH was found suitable for Zn_2SiO_4 and Zn_2SiO_4:2%Sm phosphors when 565 nm filter was used to obtain dosimetric TL peak(s). The same PH was used for Zn_2SiO_4:2.0%Ce sample even for the 565 nm filter.

A single dosimetric peak was obtained for Zn_2SiO_4 (225 ^oC with wideband and 290 ^oC with 565 nm) and Zn_2SiO_4:2.0%Sm (240 ^oC with wideband and 300 ^oC with 565 nm) phosphors when using both filters. However, visible peak maxima consist of the nested peaks in Zn_2SiO_4:2.0%Ce phosphor when both filters were used.

In general, better reusability values within ± 3% were obtained when both filters were used for the REE doped Zn_2SiO_4 phosphors. It was seen that only un-doped Zn_2SiO_4 phosphor gave higher fluctuation (with ± 6%) when 565 nm detection filter was used.

Fading results represented tunneling effect in all samples related with the fading time using especially IRSL 565 nm filter. The least change was obtained when a 565 nm filter was used. However, Zn_2SiO_4:2.0%Sm sample showed unexpected results when the TL readout was

repeated after a week which is called as Anomalous Fading effect. This effect is thought to be caused by the charge transfer in deeper traps.

In future work, dose response should be considered for high dose region as well. For better reusability and fading results, each dosimetric maxima will be deconvoluted and the first attention will be given to Zn_2SiO_4:2.0%Sm sample.

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