Optical properties of rare earth (Ce) and transition metal (Ti) doped ZrO₂ phosphors

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Abstract. Thermoluminescence and Photoluminescence of un-doped as well as Titanium (Ti³⁺) & Cerium (Ce³⁺) doped ZrO₂ phosphors, prepared via solid-state reaction method. For the characterization of the sample FTIR, XRD, EDAX and FESEM study were done. FTIR confirms the presence of conventional impurities (such as NO₃, OH⁻) present in the prepared sample. Structural characterization technique (XRD) shows the monoclinic formation and reveals the average grain size in the nano region. EDAX study confirms the chemical composition and through FESEM morphological status is studied. For kinetic parameters study thermoluminescence studies is carried out and try to correlate the XRD results with thermoluminescence behavior of prepared phosphors. Photoluminescence emission spectra show the blue and green emission band for Ti and Ce doped ZrO₂ phosphors respectively.

1. Introduction
Phosphors are most commonly used materials in photonics as well as in optics fields due to its superior hardness, high refractive index, optical transparency, chemical stability, high thermal expansion coefficient, low thermal conductivity and high thermo-mechanical resistance. Zirconium Oxide (ZrO₂) phosphors are most promising host material in the field of electro-optical materials, due to its electrical, mechanical, chemical and optical characteristics. Zirconia has a wide band gap (= 5.4 ev) semiconductor material, has good optical transparency and low phonon energy of 470 cm⁻¹ [1]. This will increase the number and probability of radiative transition and reduce non radiative multiphonon relaxation [2,3]. And hence, it has vast application areas in oxygen sensor, Solid State electrolytes, thermal barrier coatings, and in the field of photonics [4,5,6]. Zirconia is a IV group member, in periodic database table and the main source of zirconia is Baddeleyite (ZrO₂) and zircon (zirconium ortho-silicate ZrSiO₄). Hafnium, Hamatite (Fe₂O₃) Fe and Ti are the major impurities found in a commercial zirconia due to closeness in their crystal radii (Zr⁴⁺ 0.79Å⁰, Hf⁴⁺ 0.78 Å⁰) [7].

ZrO₂ exhibits three polymorphs with increasing temperature at a normal atmospheric pressure: the monoclinic phase (m-ZrO₂) that is stable from room temperature (RT) to 1175°C; the tetragonal phase (t-ZrO₂) stability ranges between 1175°C to 2370°C and cubic phase (c-ZrO₂), exceptional stable at 2370°C to 2750°C (melting point). However, the substitution of dissimilar elements into the ZrO₂ host develops oxygen ion vacancies and as a consequence the phase of the phosphor material stabilized through charge compensation mechanism [8,9]. Phosphors or luminescent materials are mostly inorganic materials consisting of a host lattice intentionally doped with impurities or activators.
Impurities are undesirable elements or substances that lower the things quality or value but depending on its amount and nature of impurity it enhances the mechanical, electrical or optical properties of the host lattice. Oxides, halides, sulfides, nitrides, nitride-carbides or oxy-nitrides are used as host materials for the preparation of optically enhanced luminescent materials. Oxides lattices have proved to be an excellent host material due to its good chemical, thermal and mechanical stability. ZrO$_2$ is a well-known wide band gap material and hence it consider as a semiconductor material. ZrO$_2$ host works as a good sensitizer because it absorbs the incident light and transfers this energy to RE$^{3+}$ ions. Basically RE$^{3+}$ ions are weakly fluorescent due to the parity forbidden f-f transition [10].

Doping of RE ions into the host lattice does not change the structure of the prepared phosphors, however due to the ionic radii of the different RE ions the average crystalline size varies, and hence the luminescence property also varies with their size. For the selection of doping elements we must have clear knowledge about its optical activity and the stability of its valence state within the crystalline host. Doping of RE ions have been considered the most important optical activators for luminescence devices [11].

In present work we report the optical properties of Solid State synthesized undoped as well as Ti and Ce doped ZrO$_2$ phosphors.

### 2. Experimental

Synthesis of desired products is a basic step for the research output, whatever the method we adopt, the product must be reproduce with the same parameters i.e its grain size and morphology of the final product should be same every time. Solid –State reaction synthesis is very useful for the production of undoped as well as RE doped ZrO$_2$ nanophosphors. In nanometer-scale structures it is possible to control the fundamental properties of the material, such as their melting temperature, magnetic properties, charge capacity and even their color without changing the chemical composition [12,13].

For the preparation of undoped as well as doped phosphors through Solid State reaction high purity oxide material (from sigma Aldrich) is used. Zirconium dioxide ZrO$_2$ is used as a host material and, Cerium (IV) oxide CeO$_2$ and Titanium (IV) dioxide TiO$_2$ were used as starting material for doping, all the samples are weighted and mixed thoroughly with agate mortal for 3 to 4 hours and heated at 1200°C for 3 hour in an air atmosphere. The basic mechanism of solid state reaction is diffuse control reaction. The controlled atmosphere is necessary to master the valance of the activators.[14]

After the synthesis characterization is needed, to confirm the morphology and grain size of the phosphor product. In present study FTIR and XRD is carried out for every prepared sample to confirm the reproduction. The FTIR spectra were taken through Shimadzu IR-Affinity between IR region i.e 400 to 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$, before taking FTIR spectra samples are mixed and ground with IR grade KBr powder with a ratio of 1: 100 mg. The crystal structure and phase purity is conformed through X-ray powder diffraction (XPD). The patterns were collected through Bruker D-2 Phaser (Table Top Model) with CuK$_α$ radiation 1.5405 A$^0$. The 20 values are 20$^0$ to 60 $^0$ and the increment is 0.02. For the morphological and elemental composition study FEI Quanta 200 FEG-SEM instrument is used.

Optical studies is carried out by taking thermoluminescence glow curve and photoluminescence spectra of the prepared sample. Nucleonix TL10091 TL analyzer is used to record TL glow curve, before taking TL all the sample is heated at 300°C to clear the previous stored radiation. PL properties of the samples are taken through Shimadzu spectrophotometer RF-5301PC equipped with 150 W xenon light source. The system is operated between wavelength scale 220-900 nm with $\pm$ 1.5 nm accuracy and S/N ratio is 150 which make it highly sensitive over the range. Excitation spectra were recorded within 250-350 nm range whereas the emission spectra were recorded in the 400- 700 nm range. For taking emission spectra four different excitation wavelength is used i.e 220 nm, 250 nm, 295 nm and 320 nm.
3. Results and Discussion

3.1 X-ray Diffraction Studies

XRD is the basic tools to analyze the formation of crystal structure and its grain size. The synthesis of solids possessing desired structure, composition and properties continues to be a challenge to chemist, scientist and engineers. Synthesized phosphors materials exhibit the luminescence properties only if it has crystalline nature, the amorphous nature doesn’t show any kind of luminescence. Doping of RE$^{3+}$ ions because rare earth ions are the most important optical activators for luminescence devices [11]. into the host ZrO$_2$ doesn’t influence the structure of prepared phosphors, however due to the ionic radii of the different RE$^{3+}$ ions the average crystalline size varies, M. Hartmanova et al reported that “The growth of Zirconia crystals stabilized with rare earth oxides of large ionic radii (Pr,Nd and Ce ) leads to a significant decrease of the crystal size” [15]. With the variation in the size of synthesized phosphors we observed drastic variation in their electrical, mechanical as well as in optical properties.

Figure 1(a,b,c) shows the XRD pattern of undoped ZrO$_2$ as well as Ti and Ce doped phosphors prepared by solid state reaction method, the concentration of doping element kept constant (i.e 0.5 mol%). Pattern shows the formation of monoclinic phase in the sample, which is conformed through Crystallography Open database (COD) file no. 9007485 with sub group P1 21/ C1 (14). In figure all the identical peaks are looks similar and having the same position i.e the 2θ values are same. Peak centered at 28.19, 31.49, and 34.23 degree are due to (-1,-1,1), (-1,-1,-1) and (0,0,-2) reflections planes.

Table 1 shows the calculated grain size for undoped as well as doped ZrO$_2$ phosphors. From the observed values we conclude that the average grain size of the prepared phosphor depends on the ionic radii of the doped material also. If the ionic radius of the doped element is lower (Ti$^{3+}$ = 81 pm) than the host radii (Zr$^{4+}$ = 86 pm) then the average grain size of the prepared phosphors (ZrO$_2$:Ti ) is large as compared to the undoped ZrO$_2$ phosphors. If the ionic radius of the doped element is larger ( Ce$^{3+}$ = 115 pm) than the host radii (Zr$^{4+}$ = 86 pm ) then the average grain size of the prepared phosphors (ZrO$_2$: Ce) is lower as compared to the undoped ZrO$_2$ phosphors. M. Hartmanova et al reported that “The growth of zirconia crystals stabilized with rare earth oxides of large ionic radii (Pr,Nd & Ce) leads to a significant decrease of the crystal size”[15].
Figure 1. (a,b,c) XRD pattern of undoped, Ti and Ce doped ZrO$_2$ phosphors.

Table 1. Average crystalline size for undoped, Ti and Ce doped ZrO$_2$ nanophosphors calculated through Diffac.eva software.

| Sample                  | Ionic radii of host material Zr$^{4+}$ (pm) | Ionic radii of doping material (pm) | FWHM  | Calculated grain size (Å) | Size (nm) |
|-------------------------|---------------------------------------------|------------------------------------|-------|----------------------------|-----------|
| ZrO$_2$ undoped         | 86                                          | ---                               | 0.164 | 555.7                      | 55.5      |
| ZrO$_2$:Ti (0.5 mol %)  | 86 Ti$^{3+} = 81$                            | 0.158                             |       | 577.1                      | 57.7      |
| ZrO$_2$:Ce (0.5 mol %)  | 86 Ce$^{3+} = 115.0$                        | 0.256                             |       | 355.1                      | 35.5      |

3.2 Fourier Transform Infrared spectroscopy (FTIR)
 FTIR is one of the most important and emerging tool through which we can analyze and identify different functional groups and conventional impurities (such as NO$_3$, OH-) present in the prepared...
sample. Figure 2 shows the FTIR spectra of undoped as well as Ti and Ce doped ZrO$_2$ phosphors. For taking spectra the sample is mixed with KBr powder because KBr is inert and it does not react with the sample. KBr is optically transparent over the range of wavelengths typically used in an IR analysis, and also it helps for better resolution. Infrared (IR) spectra of samples prepared by Solid State Reaction method show the weak absorption at 3054 cm$^{-1}$ caused by O-H single bond stretching vibration of Zr-OH or absorbed H$_2$O, indicates that the water molecules or moisture contents have low concentration due to high temperature synthesis [16]. A sharp and intense peak at 2355 cm$^{-1}$ corresponds to C-H stretching vibrations of the alkyl groups. Peaks around 1550-1300 cm$^{-1}$ can be respectively assigned to the anti symmetric and symmetric vibrations of carboxylate groups $\nu_{\text{as}}$(COO$^-$) and $\nu_{\text{s}}$ (COO$^-$) and below 1000 cm$^{-1}$ peaks are the characteristic peaks corresponds to Zr-O-Zr vibrations. This confirms the formation of –Zr-O-Zr– networks.[17].

![FTIR spectra](image)

**Figure 2.** shows the FTIR spectra of undoped as well as Ti, Ce doped ZrO$_2$ phosphors prepared by Solid State Reaction method.

### 3.3 Surface Morphology

The morphology of the synthesized undoped ZrO$_2$ and Ti, Ce doped ZrO$_2$ was studied by Field emission electron microscope (FESEM). From the FESEM images shown in the figure 3. We conclude that the particles are in almost irregular in shape and highly agglomerated.

![FESEM image](image)
3.4 EDX Study

Energy–Dispersive Spectrum analysis is performed to investigate the elemental composition of undoped ZrO$_2$ and Ti, Ce doped phosphors. Figure 4 shows the EDX images of undoped and doped phosphors, analysis results confirms the presence of oxygen ions and zirconium ions as well as doping elements in EDX profile.

![Figure 3. FESEM images of (a) Undoped ZrO$_2$, (b) Ti doped ZrO$_2$, (c) Ce doped ZrO$_2$.](image)

![Figure 4. EDX profile of (a) Undoped ZrO$_2$, (b) Ti doped ZrO$_2$, (c) Ce doped ZrO$_2$.](image)
Table 2. Elemental weight percentage concentration of various elements in the synthesized phosphors.

| Sample Name        | O K Wt % | O K At % | Zr L Wt % | Zr L At % | Ti K Wt % | Ti K At % | Ce K Wt % | Ce K At % |
|--------------------|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Undoped ZrO₂       | 36.75    | 73.99    | 63.25     | 26.01     | Nil       | Nil       | Nil       | Nil       |
| ZrO₂:Ti (0.5 mol%) | 36.94    | 76.65    | 61.86     | 22.51     | 01.20     | 00.83     | Nil       | Nil       |
| ZrO₂:Ce (0.5 mol%) | 35.50    | 76.29    | 59.94     | 22.59     | Nil       | Nil       | 04.56     | 01.12     |

3.5 Thermoluminescence Studies

3.5.1 Thermoluminescence glow curve of Undoped ZrO₂ phosphors

Figure 5 shows the glow curve of undoped ZrO₂ phosphors for different UV radiation dose i.e each 5 gm sample is radiated through UV light of 254 nm for 5, 10, 15, 20, 25, and 30 min time and then warmed at uniform heating rate of 10°C/S.

For 5 min irradiation we get single broad peak, when we deconvoluted the peak through Origin 8.1 software we observed that these broad peak is actually constituted with two distinct peak. First peak observed at 107.8 °C/S and second peak at 163.7 °C/S. It indicates that there are at least two types of traps present in the undoped ZrO₂ phosphors.

As we increase the UV irradiation time i.e 10 min, 15 min, 20 min, 25 min, and 30 min we observe separation in broad peak and the position of first peak observed at 94.8, 96.6, 111.2, 95.36, 93.4 °C/S and second peak at 168.5, 170.03, 173.4, 165.2, 173.4 °C/S respectively From the peak position we get clear indication that the TL peak position remains constant only its intensity slightly varies. Hence we say that the chemical nature of defects related to these peaks remains unchanged [18].

Activation energy and frequency factor for both deconculuted peak was calculated through Chen’s method and it was shown in table 3.

Table 3. Kinetic parameters for undoped ZrO₂.

| UV dose | Peak | T₁ 'K | Tₚ 'K | T₂ 'K | τ | δ | ω | μ =δ/ω | Activation Energy E by Chen’s method | Frequenc y factor S |
|---------|------|-------|-------|-------|---|---|----|--------|-------------------------------------|---------------------|
| 05 min  | I¹   | 346.12| 380.85| 415.57| 34.73 | 34.72 | 69.45 | 0.49 | 0.51 | 6.7x10⁷                     |
|         | II¹  | 405.39| 435.42| 465.45| 30.03 | 30.03 | 60.06 | 0.5  | 0.83 | 6.09x10¹⁰                   |
| 10 min  | I¹   | 332.19| 367.85| 402.58| 35.66 | 34.73 | 70.39 | 0.49 | 0.47 | 3.2x10⁷                     |
|         | II¹  | 407.12| 440.91| 472.82| 33.79 | 31.91 | 65.7  | 0.48 | 0.72 | 2.15x10⁹                    |
| 15 min  | I¹   | 333.35| 369.95| 404.67| 36.6  | 34.72 | 71.32 | 0.48 | 0.45 | 1.5x10⁷                     |
|         | II¹  | 411.24| 444.09| 475.99| 32.85 | 31.9  | 64.75 | 0.49 | 0.77 | 7.33x10⁹                    |
| 20 min  | I¹   | 356.52| 384.67| 413.77| 28.15 | 29.1  | 57.25 | 0.5  | 0.67 | 9.3x10⁹                     |
|         | II¹  | 413.77| 445.67| 477.58| 31.9  | 31.91 | 63.81 | 0.5  | 0.81 | 2.02x10¹⁰                   |
| 25 min  | I¹   | 328.29| 365.83| 401.49| 37.54 | 35.66 | 73.2  | 0.48 | 0.42 | 6x10⁶                       |
|         | II¹  | 406.98| 439.83| 471.73| 32.85 | 31.9  | 64.75 | 0.49 | 0.75 | 5.21x10⁹                    |
| 30 min  | I¹   | 330.82| 366.48| 400.27| 35.66 | 33.79 | 69.45 | 0.48 | 0.45 | 1.8x10⁹                     |
|         | II¹  | 411.67| 446.4 | 479.24| 34.73 | 32.84 | 67.57 | 0.48 | 0.71 | 1.26x10⁹                    |
3.5.2 Effect of Ti Concentration on Thermoluminescence property of ZrO$_2$ phosphors

To observe the concentration effect of Ti doping on ZrO$_2$ phosphors, highest intense TL peak at 25 min UV exposure (shown in figure 6 (a)) is taken as raw data and the observed intensity is plotted against the different concentration (ranges from 0.1 – 0.5 mol%) of Ti (shown in figure 6 (b)). For the measurement the heating rate ($\beta = 10^\circ$C/S) and the quantity of the sample (5 mg.) is kept constant.

Single prominent peak at 134.61$^\circ$C, 150.41$^\circ$C, 147.87 $^\circ$C, 144.74 $^\circ$C, 143.48$^\circ$C for 0.1 mol %, 0.2 mol %, 0.3 mol %, 0.4 mol %, and 0.5 mol % respectively. From observed results TL intensity initially increases for increasing the concentration attains a maxima at 0.4 mol % Ti value and then the intensity is decreased this may be due to the concentration quenching effect i.e when the concentration of an impurity ions is higher than an appropriate value, the intensity of the phosphor material decreases. Activation energy and frequency factor for the peak was calculated through Chen’s method and it was shown in Table 4.

| Ti Concentration | $T_1$ °K | $T_m$ °K | $T_2$ °K | $\mu$ | $\Delta$ | $\omega$ | $\mu = \delta/\omega$ | Activation Energy E by Chen’s method | Frequency factor S |
|------------------|---------|---------|---------|-------|---------|---------|----------------|-----------------|------------------|
| 0.1 mol%         | 377.67  | 406.76  | 434.92  | 0.49  | 29.09   | 28.16   | 57.25          | 0.73            | 1.68x10$^{10}$   |
| 0.2 mol%         | 385.9   | 422.5   | 455.35  | 0.47  | 36.6    | 32.85   | 69.45          | 0.59            | 1.23x10$^{10}$   |
| 0.3 mol%         | 384.1   | 419.88  | 454.68  | 0.49  | 35.78   | 34.8    | 70.58          | 0.62            | 3.31x10$^{10}$   |
| 0.4 mol%         | 383.96  | 415.86  | 444.87  | 0.47  | 31.9    | 29.01   | 60.91          | 0.66            | 1.3x10$^{10}$    |
| 0.5 mol%         | 386.04  | 417.01  | 445.17  | 0.47  | 30.97   | 28.16   | 59.13          | 0.69            | 2.96x10$^{10}$   |

Figure 5. TL glow curve for undoped ZrO$_2$ nano phosphors at different UV radiation time.
3.5.3 Effect of Ce Concentration on Thermoluminescence property of ZrO$_2$ phosphors

Figure 7 shows the effect of Ce concentration on ZrO$_2$ phosphors prepared by Solid State reaction method. For the observation of concentration effect different amount of Ce (0.1, 0.2, 0.3, 0.4, 0.5 mol %) is mixed on ZrO$_2$, the amount is calculated according to stoichiometry calculation. From the prepared phosphors taking fixed quantity (= 5 mg) and then irradiated to UV exposure for 25 min and then take the TL glow curve (shown in figure 7(a)). From observed result the intensity is found maximum for 0.2 mol % of Ce doping after that the intensity become saturated and then slightly decreased (shown in figure 7(b)). Activation energy and frequency factor for the peak was calculated through Chen’s method and it was shown in table 5.
Table 5. Kinetic parameters of ZrO$_2$: Ce (0.1-0.5 mol%) for constant 25 min UV exposures.

| Ce Concentration | $T_1$ °K | $T_m$ °K | $T_2$ °K | $\tau$ | $\Delta$ | $\omega$ | $\mu = \delta/\omega$ | Activation Energy $E$ by Chen’s method | Frequency factor $S$ |
|------------------|---------|---------|---------|-------|--------|-------|----------------|-------------------------------|------------------|
| 0.1 mol%         | 388.35  | 418.39  | 448.42  | 30.04 | 30.03  | 60.07 | 0.49          | 0.73                          | 8.88x10$^9$      |
| 0.2 mol%         | 370.64  | 421.89  | 465.39  | 51.25 | 43.5   | 94.75 | 0.45          | 0.38                          | 0.24x10$^6$      |
| 0.3 mol%         | 378.08  | 422.55  | 465.09  | 44.47 | 42.54  | 87.01 | 0.48          | 0.48                          | 0.48x10$^6$      |
| 0.4 mol%         | 377.49  | 415.19  | 451.93  | 37.7  | 36.74  | 74.44 | 0.49          | 0.57                          | 9.3x10$^7$       |
| 0.5 mol%         | 378.45  | 415.19  | 450.96  | 36.74 | 35.77  | 72.51 | 0.49          | 0.58                          | 1.3x10$^8$       |

3.6 Photoluminescence Studies

3.6.1 Photoluminescence glow curve of undoped and doped ZrO$_2$ phosphors

Photoluminescence properties of the sample depend not only the surface quality of the material but also depends on the nature of the optical excitation. Timothy H. Gfroerer reported that when surface structure is poor, the PL spectrum changes with increasing excitation energy whereas the PL spectrum of a high-quality surface is independent of excitation energy. From the PL spectra of undoped ZrO$_2$ (shown in figure 8) and Ti doped ZrO$_2$ (shown in figure 9 a, b, c and d) it is clear that the emission and excitation spectra were essentially little changed and we get shift in both the emission and excitation spectra such that for undoped we get two excitation peaks at 292 nm and 311 nm observed under 470 nm emission. Whereas for Ti doped phosphors we obtain one single broad peak at 275 nm under same emission 470 nm. The emission spectra were taken under 295 nm excitation for both the sample. The results shows that the broad peak at 490 nm (blue emission) for undoped phosphor and for Ti doped phosphor we observed broad peak at 495 nm (blue emission) and also the PL intensity becomes stronger for doped phosphors. Cong et al [19] reported that when TiO$_2$ dissolved into ZrO$_2$ mixed valence states of Ti$^{3+}$ and Ti$^{3+}$ exist and the substitution of two Ti$^{3+}$ ions for a Zr$^{4+}$ ion produces one anion vacancy for charge compensation and hence concentration of anion vacancies in the ZrO$_2$:Ti is higher than that in the undoped ZrO$_2$ to enhance the emission and excitation intensity [20].

![Figure 8. PL spectra of undoped ZrO$_2$: (a) excitation spectrum of ZrO$_2$ ($\lambda_{em} = 470$ nm), (b) emission pectrum of ZrO$_2$ ($\lambda_{exc} = 295$ nm).](image-url)
Figure 9. PL spectra of Ti doped ZrO$_2$: (a) excitation spectrum of Ti doped ZrO$_2$ ($\lambda_{em} = 470$ nm), (b) emission spectrum of Ti doped ZrO$_2$ ($\lambda_{exe} = 295$ nm), (c) emission spectrum of Ti doped ZrO$_2$ under different excitation wavelength i.e ($\lambda_{exe} = 220$ nm, 250 nm, 295 nm and 320 nm), (d) variation of intensity with excitation wavelength.

Figure 10 (a) presents the excitation spectrum for Ce (0.1 mol ) doped ZrO$_2$ sample observed at $\lambda_{emi} = 470$ nm we get broad peak at 275 nm. Figure 10 (b) shows the emission spectra of Ce (0.1 mol) doped ZrO$_2$ phosphors taken at $\lambda_{exe} = 295$nm, we observed a sharp emission peak at lower wavelength region at 359 nm (violet region) and a broad peak at 485nm (green region). For different excitation i.e at $\lambda_{exe} = 220$ nm, 250 nm, 295 nm and 320nm shown in figure 10 (c) .We observed constant sharp emission band at $\lambda_{emi} = 359$ nm for all excitation also we observed second broad peak and 475 nm, 480nm, 485 nm, 489 nm respectively. Hence we conclude that as we increase excitation wavelength i.e from 220 nm to 320 nm the Ce$^{3+}$ emission band is shifted towards the higher wavelength region or lower energy side, and peak becomes broadened [21]. Figure 10 (d) shows the variation of intensity with excitation wavelength. The electron configuration of Ce$^{3+}$ ion is very simple at ground and excited state 4f$^1$ and 5d$^1$ respectively. The 4f$^1$ ground state split up in a doublet $2F_{7/2}$ and $2F_{5/2}$ levels. The PL properties of Ce$^{3+}$ are due to their fully allowed 4f $\rightarrow$5d transitions [22].
4. Conclusion
In present work we have studied the TL and PL properties of undoped and doped (Ti,Ce) Zirconium oxide phosphors. XRD pattern confirms the monoclinic formation and also reveals that the average grain size of the prepared phosphors depends on the ionic radii of the doped. From TL glow curve results we conclude that the doping enhance the intensity of the synthesized phosphors and also the value of kinetic energy and frequency factor for each glow curve is presented in the table. From observed PL spectra it is clear that the emission spectra of undoped ZrO$_2$ and doped with Ti & Ce has similar characteristic of broad band. Hence we conclude, emission is strongly related to the crystal structure of host lattice, which makes it possible to tailor and modify the luminescent properties by selecting different host materials.

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