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ORIGINAL ARTICLE

Near White Light Emission and Concentration Quenching of Calcium Titanate Doped with Dysprosium (III) Phosphors

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Abstract

This paper reports the preparation of $CaTiO_3$ doped with various concentrations of Dysprosium (II) using solid state reaction technique. X-ray diffraction patterns of the sample were taken. Observed XRD pattern was matched using software match2!. The pattern was matched significantly with the crystallographic open database card (COD – 96-101-1212) which is a standard card for $CaTiO_3$. This matching exhibited that, the prepared sample is cubic in structure with space group P m − 3 m (221). Photoluminescence (PL) studies of the samples were also done. PL intensity was found increasing with increasing dopant concentration and maximum intensity was noted at 2.0 mol% concentration of Dy^{3+}, thereafter concentration quenching occurred. Emission Peaks were centered at 483 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and 576 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) respectively. For studying the concentration quenching, the critical distance for energy transfer and electric multipolar character were estimated. The value of multipolar character expressed that, the transition in emission spectra is a dipole – dipole (d-d) transition. Commission Internationale de l'Éclairage (CIE) coordinates was found as (0.36, 0.39), which is near to white light. Colour Correlated Temperature (CCT) was 4489 K which was indicative of cool appearance of the light emitted.

Keywords White LED · Photoluminescence · Concentration quenching

Introduction

Calcium titanium oxide is considered to be the first compound in the family of perovskites. The first article about the optical properties of $CaTiO_3$ was published by Chadha et al. in 1994 [1]. Thereafter many researchers have been attracted towards the luminescence properties of this first compound of perovskites family. Various properties of $CaTiO_3$ doped with various dopants have been reported [2–4]. Dysprosium (Dy^{3+}) doped phosphors are extensively investigated because of its ability to transit in different colour regions such as blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$), yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$), red ($^4F_{9/2} \rightarrow {}^6H_{11/2}$), and brownish red ($^4F_{9/2} \rightarrow {}^6H_{9/2}$). This property of Dy^{3+} makes it enable to produce white light emission which is useful in white LED application. Titanate $(TiO_3)^{2-}$- based ceramics systems have unique optical, thermal, electrical, and mechanical properties [5], which can be exploited to fabricate promising phosphor materials. Dysprosium (III) ions which are doped into $CaTiO_3$ host replace the Ca^{2+} ions, because of the similar ionic radius. Valence mismatch may create some distortions into the crystal structure [6, 7].

In present work, we have doped Dy^{3+} ion in various concentrations into the $CaTiO_3$ host lattice and plotted the CIE coordinates to measure the resultant colour from emission spectra. We have also tried to investigate the reason behind the concentration quenching, which occurred at 2.0 mol% concentration of Dy^{3+} in the present case. For investigating the cause for concentration quenching, the type of transaction was estimated with the help of the concepts provided by Blasse [8] and Van Uitert [9].

Material and Methods

Phosphors $CaTiO_3$ doped with of various concentration of Dysprosium (III) was prepared by solid state reaction. All the materials $CaCO_3$, TiO_2 and Dy_2O_3 were thoroughly ground for approximately 1 h in a mortar, pre-sintered at 900 °C and fired at 1200 °C for approximately 2 h, with H_3BO_3 (1.6 mol%) used as flux [10–12]. Spectrofluorophotometer (SHIMADZU, RF-5301

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PC) using the Xenon lamp as excitation source was used for the measurement of Photoluminescence (PL) excitation & emission spectra. X-ray diffraction (XRD) characterization of the sample is done using Panalytical Xpert PRO MPD with copper k alpha anode of wavelength 1.5405 Angstrom. Scanning Electron Microscopy (SEM) images of the sample were taken using Field Effect Gun – Scanning Electron Microscope (JSM-7600F). Thermoluminescence Reader Type TL1009 designed and offered by NUCLEONIX SYSTEMS is used for TL studies.

Result and Discussion

XRD Analysis

Figure 1 expressed various observed XRD patterns of $CaTiO_3$ doped with a different concentrations of Dy^{3+}. All observed patterns look very similar to each other, which suggests that there is no significant change in the phases of $CaTiO_3$. For the further analysis such as the calculation of lattice parameters and the lattice volume, observed XRD pattern for 2.0 mol% of Dysprosium (III) were used. Figure 2 shows the Comparison between observed, calculated and standard (Matched) XRD pattern of $CaTiO_3$ doped with 2.0 mol% Dy^{3+}. Matching of the pattern is done using Match! Version 2.3.1. Experimental XRD pattern was matched convincingly with crystallographic open database (COD) card No. 96–101-1212 with Figure of Merit (FoM) of 0.801. This is already reported XRD pattern of $CaTiO_3$. It is an indication of the proper formation of the sample.

The datasheet provided by match version 2.3.1 expressed that prepared sample is monoclinic with P m − 3 m (221) space group. Table 1 presents refined lattice parameters of the phosphor $CaTiO_3$ doped with 2.0 mol% of Dy^{3+}. The values of lattice parameters of the phosphor available in COD card No. 96–101-1212. Refinement is done using Celref version 3 (Collaborative Computational Project No. 14 [CCP14] for Single Crystal and Powder Diffraction Birkbeck University of London and Daresbury Laboratory, London, UK). The calculated spectra confirmed the presence of cubic CaTiO3. The calculated lattice parameters are shown in Table 1 and are almost similar to the values obtained in case of standard COD card. This may be due to the presence of Dy^{3+} (dopant) ions (105.2 pm) having similar ionic radii as Ca^{2+}ions (114 pm). There are a few extra peaks in observed XRD pattern, which could be due to a great number of stacking faults induced by the presence of the doping ions and also due to secondary phases and impurities formed during the elaboration process [13].

Photoluminescence Studies of The Samples

Figure 3 is the excitation spectra of $CaTiO_3$ doped with 2 mol% of Dy^{3+}. The excitation spectrum was monitored at a wavelength of 575 nm. The excitation spectrum exhibited three prominent emission peaks at 360 nm, 388 nm and 451 nm originated due to at ($^6H_{15/2}$–$^4P_{5/2}$), ($^6H_{15/2}$–$^4I_{13/2}$) and ($^6H_{15/2}$–$^4I_{15/2}$) respectively [14]. We recorded the emission spectrum of $CaTiO_3$ doped with a different concentration of Dy^{3+} at an excitation wavelength of 360 nm (Fig. 4). The

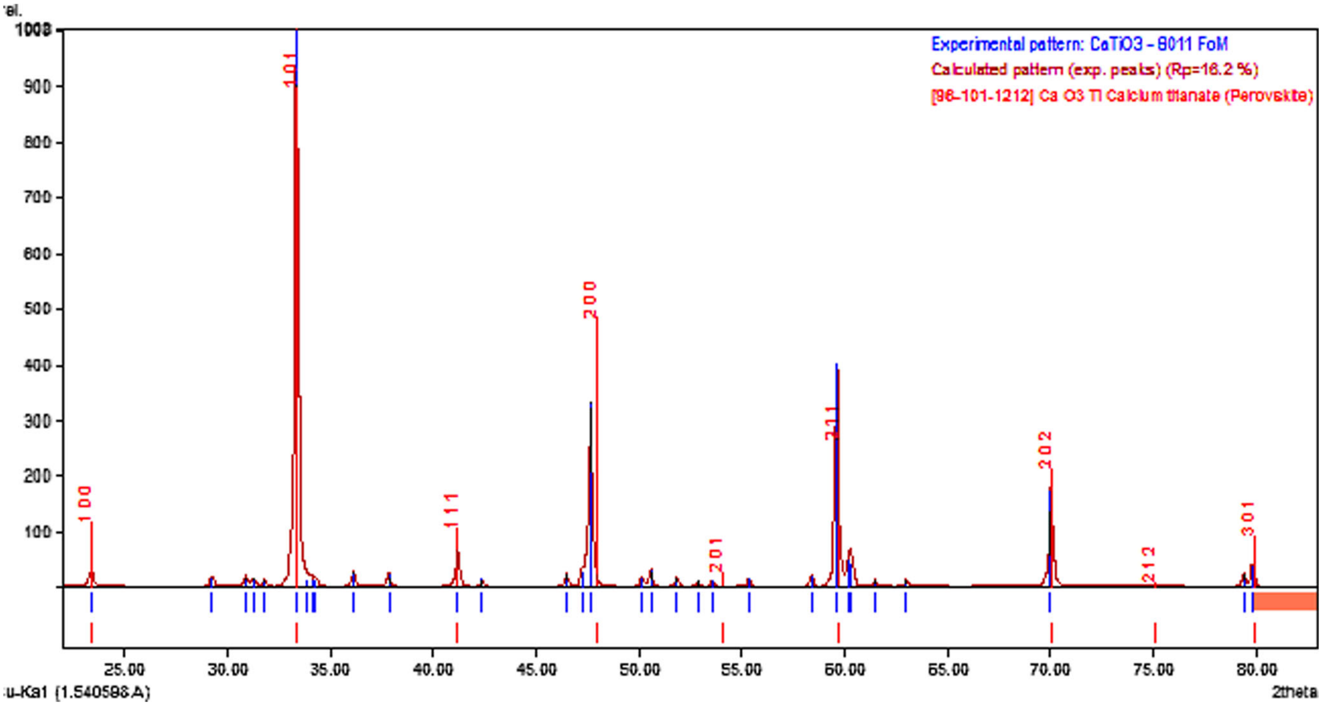

Fig. 1 Observed XRD pattern for $CaTiO_3$ doped with various concentration of Dy^{3+}

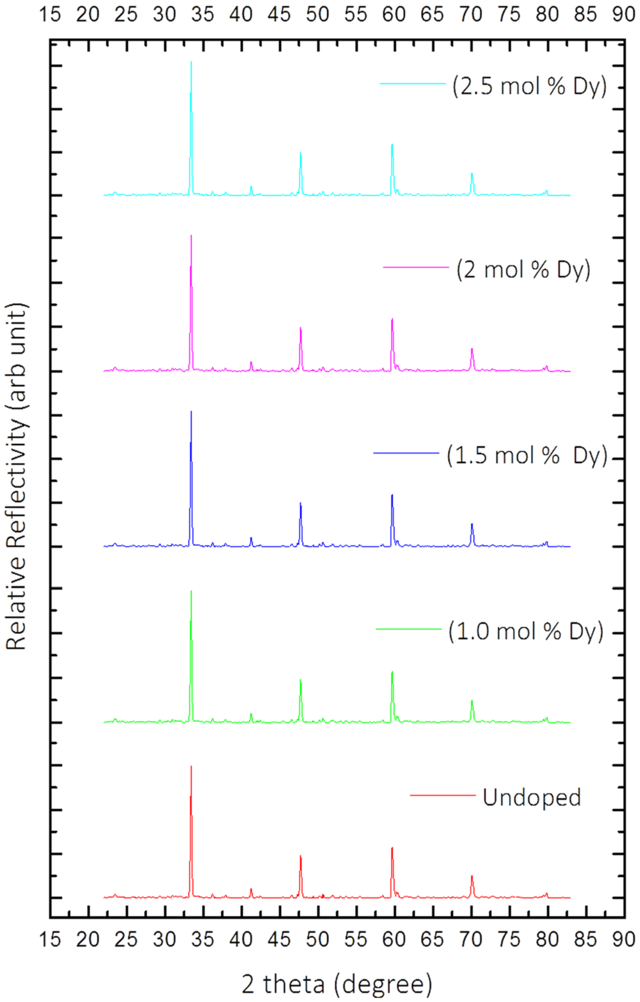

Fig. 2 Observed XRD pattern matched with Standard Card (COD – 96-101-1212)

emission spectrum exhibited two prominent peaks centred at 483 nm and 576 nm respectively. The peak originated at 483 nm is due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and the other peak originated at 576 nm is due $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition of Dy^{3+} doped at different lattice site of different energies.

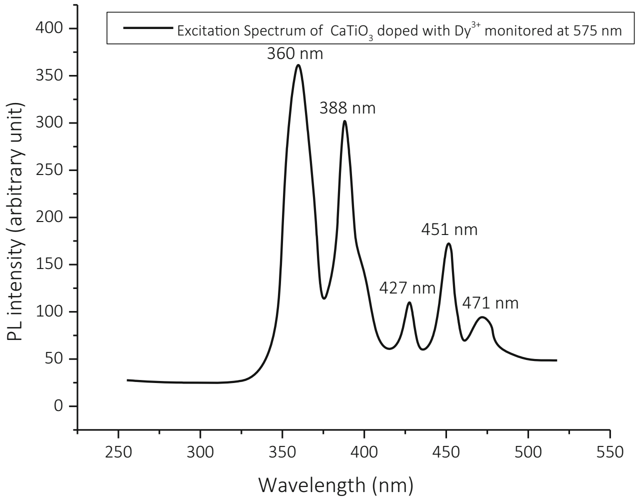

Fig. 3 Excitation spectrum of $CaTiO_3$ doped with 2.0 mol% of Dy^{3+} monitored at 575 nm

Figure 5 expressed the variation in peak emission intensity for various Dy^{3+} doping concentrations. We noticed from Fig. 5 that the emission intensity increases with increasing concentration of Dy^{3+} ion till it reaches 2.0 mol% and then decreases for 2.5 mol% doping of Dy^{3+}. This is due to concentration quenching. When the concentration of Dy^{3+} ions increases, the distance between the Dy^{3+} ions decreases. This results in the non-radiative transitions in Dy^{3+} ions. It points an important fact that the transfer of excitation energy strongly depends on the distance between the Dy^{3+} ions. Blasse [8] gave an important formula to estimate the critical distance for energy transfer (R).

$$R \approx 2\left[\frac{3V}{4\pi X_c N}\right]^{1/3} \tag{1}$$

Where V is the unit cell – volume, N is the number of atoms per unit cell, and X_c is the critical concentration of the dopant. In present case ($CaTiO_3$:Dy^{3+} – 2.0 mol%) the unit cell volume is 54.800 (Å), ^{3} Number of atoms per unit cell is 1 and the critical concentration is 0.020. Using the Blasse's formula, the value of critical distance was found as 8.682 Å. The non-radiative energy

Table 1 Standard and refined lattice parameters of $CaTiO_3$ phosphor

Initial values:								
Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.542	3.795	3.795	3.795	90	90	90	54.700 (Å)^3
Final values:								
Zero	Lambda	a	b	c	alpha	beta	gamma	Vol.
0	1.542	3.798	3.798	3.798	90	90	90	54.800 (Å)^3
h	k	l	2 T(Obs)	2 T-Zero	2Th(Cal)	Dif		
0	0	1	23.450	23.450	23.421	0.029		
0	1	1	33.393	33.393	33.362	0.032		
1	1	1	41.232	41.232	41.164	0.068		
0	0	2	47.689	47.689	47.899	−0.210		
1	1	2	59.652	59.652	59.625	0.027		
2	0	2	70.064	70.064	70.070	−0.006		
1	0	3	79.804	79.804	79.858	−0.054		

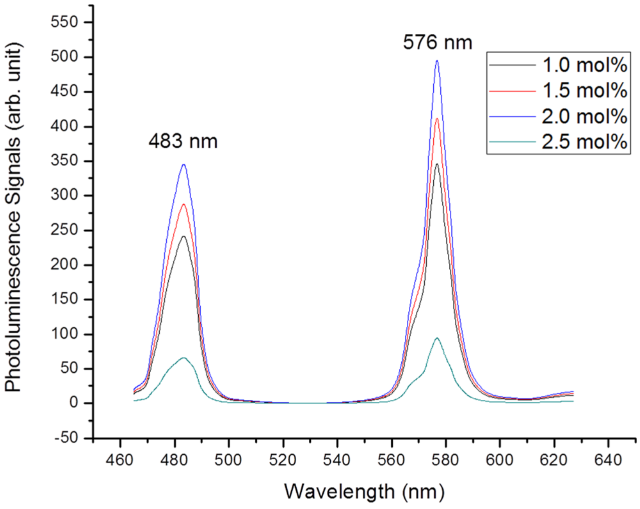

Fig. 4 Emission spectra of $CaTiO_3$ doped with various concentration of Dy^{3+} monitored excited at 360 nm

transfer of the luminescence of oxide phosphors is based the resonance transfer by electric multipole -multipole interaction or exchange interaction [15].

This situation was explained by the Blasse's theorem [16]. It was reported that exceeding critical distance beyond 5 Å, only a multipole-multipole interaction is important where the exchange interaction becomes ineffective. When the critical distance is found less than 5 Å then, the exchange interaction becomes effective [17]. In the present case the critical distance is calculated as 8.682 Å, therefore, the mechanism involved in concentration quenching of $CaTiO_3$ doped with 2.0 mol% of Dy^{3+} is considered to be the multipolar interaction.

For explaining the type of interaction is effective in energy transfer and what produces the non-radiative energy transfer between Dy^{3+} ions due to multipole-multipole interaction, Van Uitert [9] reported, if the energy transfer occurs among the same sort of activators, the strength or the type of the multipole interaction can be determined by the change of emission intensity and per concentration ion level as per the following equation [17]:-

Table 2 Electric multipolar character

S.No.	(θ) value	Type of Integration
1	3	Exchange Interaction
2	6	dipole-dipole (d-d)
3	8	dipole-quadrupole (d-q)
4	10	quadrupole-quadrupole (q-q)

$$ {}^{I}/_{x} = K\left[1+\beta(x)^{\theta/3}\right]^{-1} \qquad (2) $$

Where, (x) is the dopant concentration, which is either equal to or more than the critical concentration. (I/x) is the emission intensity per unit dopant concentration. The (K) and (β) are the constants for the same excitation condition for a given phosphor. The (θ) indicates the electric multipolar character. Table 2 is for estimating the type of interaction based on the value of (θ).

Considering $\beta(x)^{\theta/3} >> 1$ Eq. (2) can be simplified as following [17]:-

$$ \log\left(\left({}^{I}/_{x}\right)\right) = K' - (\theta/3)\log x \quad \left(K' = \log K - \log\beta\right) \qquad (3) $$

The slope of the above eq. (3) gives the value of (−θ/3), by which multipolar character (θ), can be obtained.

The graph between log (x) and log (I/x) was plotted which is shown in Fig. 6 (Table 3). The graph is fitted linearly and the slop was found as – 2.03 and hence the value of (θ) was found as 6.09 which close to 6. The

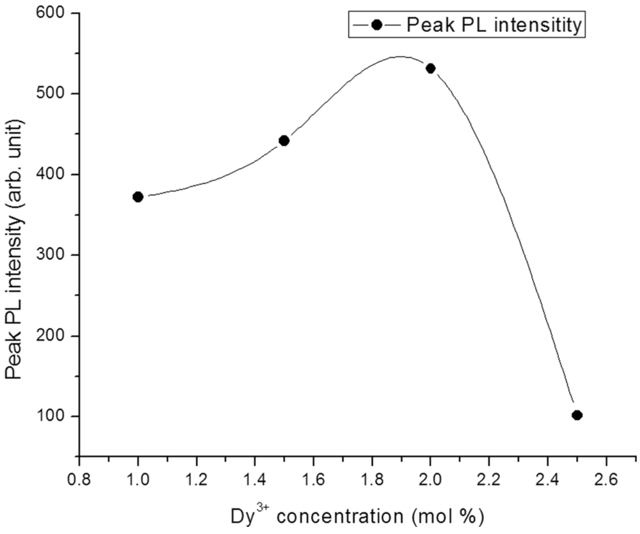

Fig. 5 Peak intensity versus concentration of dopant in mol %

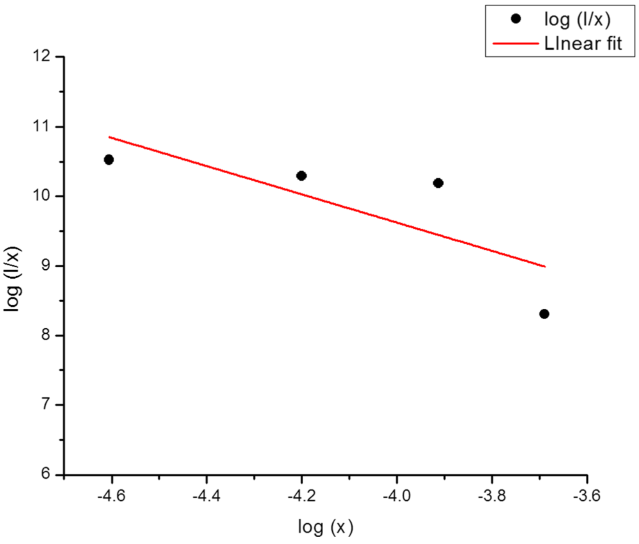

Fig. 6 Graph between log (x) and log (I/x) with linear fit

Table 3 log (x) versus log (I/x)

I (Peak intensity)	x (Concentration of Activator)	I/x	log(x)	log(I/x)
371.464	0.010	37,146.400	−4.606	10.524
442.042	0.015	29,469.477	−4.200	10.292
531.194	0.020	26,559.676	−3.912	10.188
101.410	0.025	4056.387	−3.689	8.309

value (θ) is an indication that the energy transfer mechanism, in this case, is dipole-dipole (d-d) interaction (referring to Table 2).

Emission spectra of the samples exhibited two emission peak originated at 483 nm and 576 nm. These emissions correspond to blue and yellow regions. For extracting the exact colour emitted in the spectra, the CIE coordinates (Fig. 7) were calculated. The coordinates are found as (0.36, 0.39) which are near to coordinates for white light.

To measure the "warmth" or "coolness" of the light, the correlated colour temperature (CCT) is calculated. McCamy has proposed the analytical equation to calculate the CCT which is given [18–19] by.

$CCT = -449\ n^3 + 3525\ n^2 - 6823\ n + 5520.33;$

Where $n = (x-x_e)/(y-y_e)$ is the inverse slope line and ($x_e = 0.332$, $y_e = 0.186$) is the epicenter.

Generally, for the CCT value less than 3200 K, the appearance will be warm and if the value is more than 4000 K, the white light will have a cool appearance. For the present case it is 4889 K which allows us to predict that the appearance of the white light will be cool in appearance.

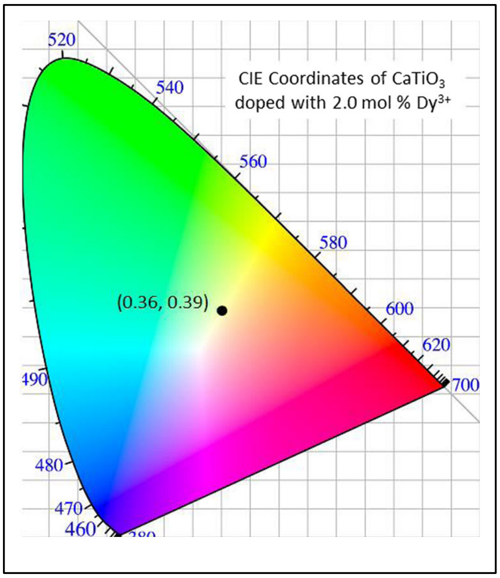

Fig. 7 CIE Coordinate of emission from CaTiO$_3$ doped with 2 mol% Dy^{3+}

Conclusion

Dysprosium doped Calcium Titanate with various dopant concentrations were prepared. Emission spectrum with dopant concentration, 2.0 mol% exhibited the maximum intensity. The XRD spectrum was well matched with crystallographic open database card No. COD – 96-101-1212 with a good figure of merit of 0.8011, which confirmed the proper preparation of the samples. Photoluminescence emission results contained two prominent peaks centered at 483 nm and 576 nm in blue and yellowish green region respectively. The nature of the transition is discussed and the multipolar character was calculated. The value of multipolar character was found near to 6. This result supports the fact that the transitions of Dy^{3+} ions are the dipole-dipole transitions. CIE coordinates for the sample of 2.0 mol% dopant concentration was calculated which exhibited (0.36, 0.39) coordinate which is close to the standard white light emission. Colour Correlated Temperature of the sample expressed the white light is cool in appearance hence the Dy^{3+} doped Calcium Titanate may be considered as a good candidate for white LED application purpose.

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