Effect of Co-Doping of Charge Compensator Ions on the Photoluminescence Emission of Calcium Titanate Doped with Europium (III) Phosphor

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Abstract: ***Calcium Titanate doped with 1.5 mol% concentration of Europium (III) was prepared using solid - state reaction method. The trial to understand the effect of charge compensator ions in the emission spectrum was done. Li+, Na+ and K+ ions were considered in present case as co - dopants. Therefore, three samples of $CaTiO_3$ doped with Eu^{3+} (1.5 mol%) and co - doped Li+, Na+ and K+ ions respectively were prepared. The sample doped with Eu^{3+} was characterized with an X - ray diffraction pattern. The pattern observed expressed good agreement with the standard XRD pattern card 96 - 101 - 1212 from the crystallographic open database. The said card was reported for $CaTiO_3$ which followed the Cubic crystal system with space group Pm - 3 m (221). Fourier Transform Infrared spectrum of CaTiO3 doped with 1.5 mol% Eu3+ was recorded which supported the presence of Ti - O stretching and Ca - O. The FTIR spectrum Photoluminescence emission spectra were recorded for the prepared samples exhibited peaks centred at 590 nm and 617 nm and may be attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ respectively. It was observed that there wasn't a significant variation in the shape or the characteristics of the emission spectra whereas the intensity of photoluminescence emission increased. The relative increase in the intensity of the emission spectrum of Li+, Na+, K+ co - doped samples were 1.42, 1.62 and 1.78 when compared to Europium (III) doped Calcium Titanate.***

Keywords: Pervoskite, Phosphor, Europium, Charge Compensator ions, Photoluminescence

1. Introduction

Calcium titanium oxide ($CaTiO_3$) is considered to be the initiamember of the family of materials called perovskites. Chadha et al. published first article about the same in 1994 [**1**]. After that many more investigators have been attracted to the study the optical properties of this first compound of pervoskite family. Different properties of $CaTiO_3$ doped with various dopants have already been reported [**2 – 4**]. Europium (Eu^{3+}) doped phosphors are being investigated exceedingly because of their capability of giving transitions in red colour emission $^5D_0$® ^7F_J (J=1, 2, & 3) suitable for LED applications. Titanate (TiO3) $^{2\ -}$ - based ceramics systems have proven to be prominent hosts in terms of their optical, electrical, mechanical and thermal properties [**5**]. These properties can surely be factors of consideration while fabricating promising materials with phosphoresce. Europium (III) ions that are doped into the CaTiO3 host can replace the Ca^{2+} ions, because of the similar ionic radius. Some distortions may also be created due to valence mismatch in the structure of the crystal [**6, 7**]**.** The phosphor must avoid blue colour reabsorption by green and red components for the fabrication of LED. As the trivalent europium gives deep orange - red emission hence shows a wide application in television sets and fluorescent lamps, which also increase the general efficiency of the fluorescent lamp [**8**].

In the present work, the photoluminescence emission of CaTiO3 doped with 1.5 mol% Eu3+ ions and the effect of various charge compensator ions on the said luminescence emission was discussed.

2. Material and Methods

Calcium Titanate doped with 1.5 mol% concentrations of Europium (III) was prepared using the solid - state reaction technique. All the ingredients such as $CaCO_3$, TiO_2 and Eu_2O_3 were thoroughly ground for almost an hour using pastel and mortar then the ground sample was pre - sintered at 900°C and last fired at 1200°C for about two hours, with Boric Acid (1.6 mol %) used as the flux [**9 - 17**]. Similarly, Calcium Titanate doped with 1.5 mol%, co - doped with 1.5 mol% of Li+/Na+/K+ were also prepared using the solid - state reaction technique using carbonates of co - doping ions. The Spectrofluorophotometer (SHIMADZU, RF - 5301 PC) was used for the measurement of Photoluminescence (PL) excitation & emission spectra where the Xenon light source was used to excite the material. Panalytical Xpert PRO MPD equipped with copper kα as an anode was utilized to obtain the X - ray diffraction (XRD) pattern of the sample.

3. Result and Discussion

3.1. X - Ray Diffraction Analysis

Figure 01 exhibits the comparison of observed and calculated XRD pattern of $CaTiO_3$ having 2.0 mol% of Europium (III). The pattern observed was imported in software Match! Version 3.13 Build 220 to retrieve the best possible match from the dataset of standard reported cards. It was found that the imported pattern exhibited a high resemblance with the crystallographic open database card (COD – 96 - 101 - 1212). It isa standard card which has already been reported for $CaTiO_3$ specifically. This match enabled us to conclude that, the sample prepared has a cubic structure with space group Pm - 3 m (221). Refinement of the observed XRD pattern was carried out using Celref v.3

taking the various parameters of the COD – 96 – 101 – 1212) as a reference for the same.

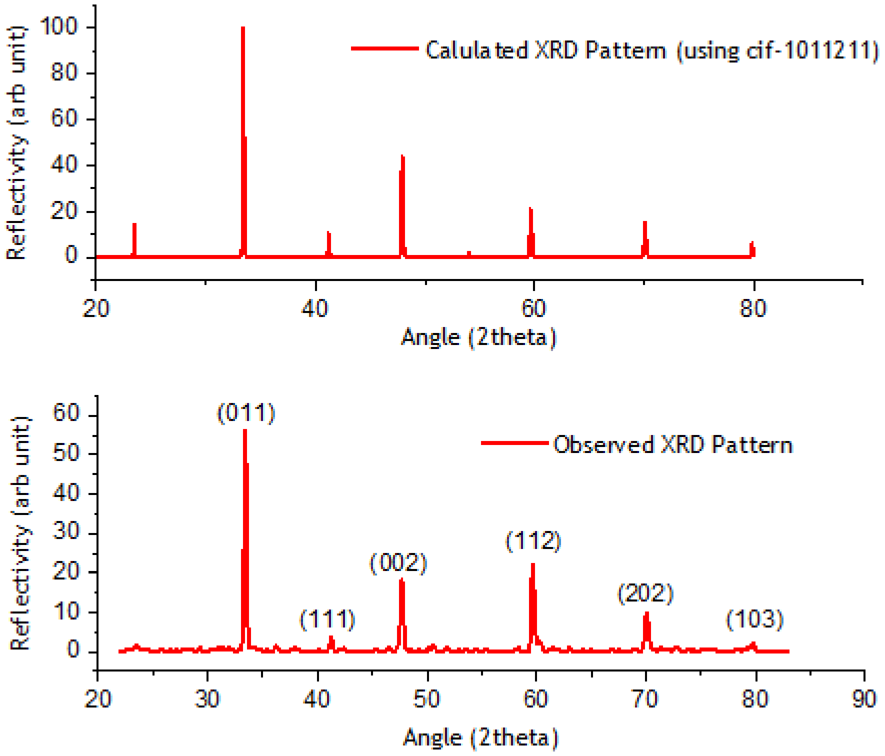

Figure 1: Comparison between Calculated & Observed XRD

The crystallographic information file (1011211. cif) referring to the Crystallographic Open Database COD – 96 – 101 – 1212 was downloaded from the website http: //www.crystallography. net/. The information contained in the crystallographic information file was utilized as a reference in the process of lattice parameter refinement. Initial and refined lattice parameters are shown in **Table 01**.

Table 1: Initial and refined lattice parameter of $CaTiO_3$ doped with Eu^{3+}

Initial values: (Refinement keys on 2nd line)								
Zero	Lambda	a	B	C	alpha	beta	gamma	Vol.
0	1.5418	3.795	3.795	3.795	90	90	90	54.7
Final values: (Standard errors on 2nd line)								
Zero	Lambda	a	B	C	alpha	beta	gamma	Vol.
0	1.5418	3.7977	3.7977	3.7977	90	90	90	54.8
H	K	l	2T (Obs)	2T - Zero	2Th (Cal)	Dif		
0	1	1	33.39	33.39	33.3652	0.0248		
1	1	1	41.236	41.236	41.1689	0.0671		
0	0	2	47.695	47.695	47.9048	- 0.2098		
1	1	2	59.663	59.663	59.6324	0.0306		
2	0	2	70.075	70.075	70.0788	- 0.0038		
1	0	3	79.795	79.795	79.8684	- 0.0734		

3.2. Fourier Transform Infrared (FTIR) Spectrum

Figure 02 exhibits the FTIR spectrum of $CaTiO_3$ doped with 1.5 mol% of Eu3+ ions. This is a graph between the Transmittance and the wave number. There are three prominent peaks at 509, 575 and 700 cm^{-1} respectively and each of them were attributed to Ti - O Stretching whereas the peaks less than 500 cm^{-1} may be attributed to Ti - O - Ti bending. A sharp and prominent peak centred at 1597 cm^{-1} is indicative of the existence of Ca - O and may also be present due to the distortion created in the host lattice. Peaks towards the higher wave number i. e.3534, 3700 and 3780 cm - 1 are present due to the O - H group. The presence of these peaks points towards the existence of moisture in the prepared sample. **Table 02** provides the cumulative information about the assignment of FTIR peaks.

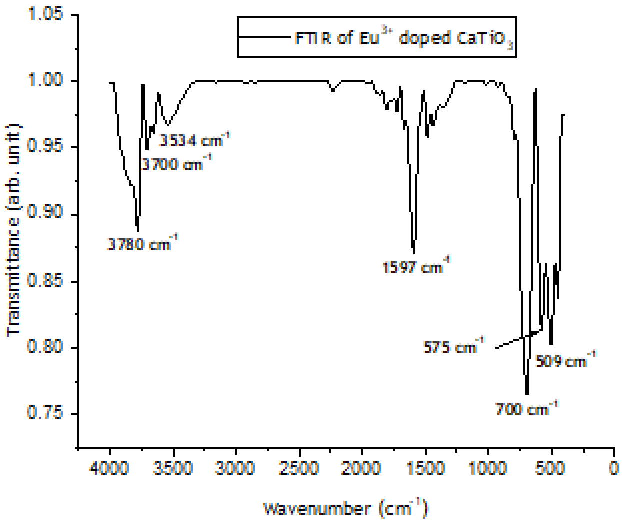

Figure 2: FTIR spectrum of $CaTiO_3$ doped with Eu^{3+} (1.5 mol %)

Table 2: FTIR assignment of peaks

Peak (cm - 1)	Assigned to	Type
509	Ti - O	Stretch
700	Ti - O	Stretch
575	Ti - O	Stretch
1597	Ca - O	Stretch
3534	O - H	Stretch
3700	O - H	Stretch
3780	O - H	Stretch

3.3. Photoluminescence Studies

To study the emission from Eu^{3+} doped $CaTiO_3$ phosphor under ultraviolet excitation, PL emission spectra of the sample with 1.5 mol% concentration of dopant under an excitation of 390 nm was recorded. The emission spectra exhibited two prominent peaks centred at 590 and 617 nm respectively attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ respectively. In efforts to increase the PL emission intensity, sample doped 1.5 mol% Eu^{3+} were co - doped with various charge compensator ions like K+, Na+ and Li+. The comparative PL emission recorded for each of the cases is shown in **Figure 03**. It was observed that there was not a significant difference in the shape of the emission spectra whereas photoluminescence emission intensity increased. The relative increase in the intensity of the emission spectrum of Li+, Na+, K+ co - doped samples were 1.42, 1.62 and 1.78 when compared to Europium (III) doped Calcium Titanate.

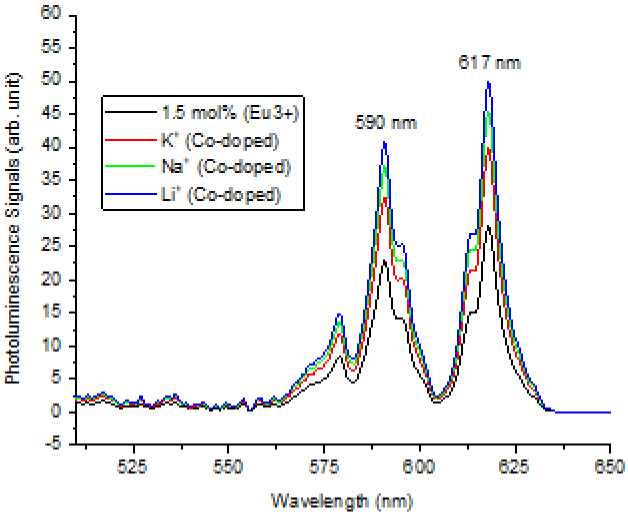

Figure 3: PL emission spectra for CaTiO3 doped 1.5 mol% Eu^{3+} and co - doped with various charge compensators ions like K+, Na+ and Li+

It may be concluded that the introduction of these charge compensator ions increases the efficiency of the charge transfer from Oxygen (II) to Europium (III). Therefore co - doping of these ions start behaving like a bridge for excitation energy transfer from host lattice to the dopant (Europium (III) in the present case) **[18]**. This results in enhancing the PL intensity. This improvement of PL intensity with Li+, Na+, K+ may be attributed to the improved crystallinity which leads to higher oscillator strength for the optical transitions [**19**], as well as enlarged grain sizes inducing lower scattering loss. Further, the substitution of these charges compensating ions into Ca^{2+} sites would consequently produce an adequate number of vacancies of oxygen on the surface of the material. These vacancies might behave as a sensitizer for the transfer of energy from the host to Europium (III) ion due to the strong mixing of charge - transfer states, therefore, enhancing the degree of luminescence **[19 - 21]**.

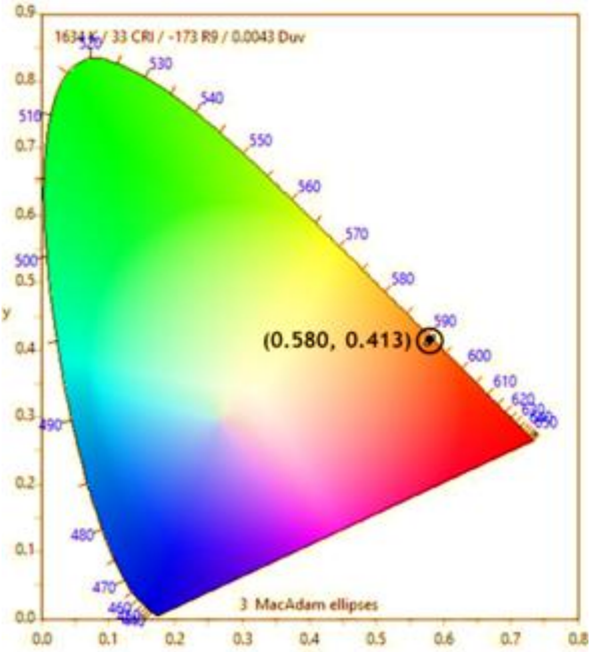

Figure 4: Colour Chromaticity Diagram (CIE 1931) of $CaTiO_3$ doped with Eu^{3+} (2.0 mol %)

Figure 4 Colour Chromaticity Diagram (CIE 1931) of $CaTiO_3$ doped with Eu^{3+} (2.0 mol %). The coordinate found was (0.580, 0.413) which lies in the intense red region of the diagram.

4. Conclusion

Calcium Titanate doped with 1.5 mol% concentration of Europium (III) was prepared using solid - state reaction technique. The effort was made to study the effect of charge compensator ions in the emission spectrum. In the present case, the charge compensator ions considered were Li+, Na+ and K+ ions. Therefore, three samples of $CaTiO_3$ doped with Eu^{3+} (1.5 mol%) and co - doped Li+, Na+ and K+ ions respectively were prepared again using solid - state reaction technique. The sample doped with Eu^{3+} was characterized with an X - ray diffraction pattern. The pattern observed expressed good agreement with the standard XRD pattern card 96 - 101 - 1212 from the crystallographic open database. The said card was reported for $CaTiO_3$ which followed the Cubic crystal system with space group Pm - 3 m (221). Photoluminescence emission spectra were recorded for the prepared samples exhibiting peaks centred at 590 nm and 617 nm and may be attributed to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ respectively. It was observed that there wasn't a significant difference in the characteristics of the shape of the emission spectra whereas PL intensity increased. The relative increase in the intensity of the emission spectrum of Li+, Na+, K+ co - doped samples were 1.42, 1.62 and 1.78 when compared to Europium (III) doped Calcium Titanate.

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