Wet chemical synthesis of Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce optoelectronics materials

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Abstract. A new Na$_{21}$(SO$_4$)$_7$F$_6$Cl optoelectronics nano phosphor in the Cl–F system doped with Ce$^{3+}$ and synthesized by wet chemical method having particle size up to 100 nm has been reported here and their luminescence properties were investigated by changing the concentration of activators in the host matrix. Polycrystalline Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce$^{3+}$ nanophosphors have been studied for their X-ray diffraction, SEM, TEM, FT-IR and photoluminescence (PL) characteristics. The halo sulphate phosphor Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce$^{3+}$ show an efficient broad band emission at 389 nm in near UV region assigned to $4f_0^5d_1^1 \rightarrow 4f_1^1$ transition when excited at 355 nm. The investigated halo sulphate phosphors may be suitable for a near UV excited solid state lighting devices.

Keywords: Optoelectronic, Sulphohalite, Schairerite, Photoluminescence.

1. Introduction
Sulphate based inorganic phosphors doped with various rare earth ions form an important family of optoelectronic material for solid state lighting devices. These devices offer many benefits and are tipped to be the next generation lighting devices, in the replacement of conventional incandescent and fluorescent lamps which are Hg pollutants, frangible and high energy consumption devices. In the recent years, research on the sulphate based phosphors has become a hot topic and gained importance. A large number of papers have been published in the related journals about the successful synthesis and luminescence of rare earth doped phosphors with the orientation of exploring novel phosphors suitable solid state lighting applications. Up till now, the group of sulphohalites has not been studied in detail in the field of luminescence. The Cl–F substitution in the system has been investigated by Dhoble et al [1–8]. Klement synthesized halo sulfate based phosphor such as, Na$_6$Ca$_3$(SO$_4$)$_6$(F,Cl)$_{1-x}$[9], Na$_6$Ca$(SO_4)_6$F$_2$[10], Na$_6$Pb$_4$(SO$_4$)$_6$Cl$_2$[11,12], and Na$_6$Cd$_4$(SO$_4$)$_6$Cl$_2$[13]. Some investigations are still going on novel halo sulfate based materials for its applications in various purposes. Nanoscale phosphors have a number of potential advantages over traditional micron-sized phosphors providing higher packing densities. In addition, quantum confinement in nanocrystalline materials may result in an enhancement of their luminescence. Therefore, the morphology and size, the stoichiometry and composition, and the surface characteristics must be controlled in order to achieve the desirable objectives of powder phosphors. To our knowledge, no investigations have been reported on studying the photoluminescence properties of rare earth in the hosts of Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce$^{3+}$. Here, we have reported the XRD, SEM, TEM and FT-IR of the undoped and the photoluminescence properties of Ce$^{3+}$ activated alkaline earth Na$_{21}$(SO$_4$)$_7$F$_6$Cl materials by using the conventional wet chemical method successfully for the possible application in near UV excited solid state lighting devices.
2. Experimental

The pure and Ce$^{3+}$ doped samples nanocrystalline Na$_{21}$(SO$_4$)$_7$F$_6$Cl phosphors were prepared by a wet chemical method. While preparing Na$_{21}$(SO$_4$)$_7$F$_6$Cl, raw materials Na$_2$SO$_4$, NaCl and NaF of annular grade were taken in a stoichiometric ratio and dissolved separately in double distilled de-ionised water, resulting in a solution of Na$_{21}$(SO$_4$)$_7$F$_6$Cl stirred for several hours to complete the reaction. The Chemical reaction is as shown below.

$$7 Na_2SO_4 + NaCl + 6 NaF = Na_{21}(SO_4)F_6Cl$$

To obtain Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce$^{3+}$, water soluble Ammonium Hexanitratocerate (NH$_4$)$_2$Ce(NO$_3$)$_6$ was used which is added drop wise to a pure solution of Na$_{21}$(SO$_4$)$_7$F$_6$Cl confirming that no undissolved constituents were left behind and all the salts had been completely dissolved in water and thus reacted. Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce$^{3+}$ in powder form were obtained by evaporating the solution at 80$^\circ$C for 5 hours. The dried samples were then slowly cooled down at room temperature. The resultant polycrystalline mass was crushed to fine particle in agate mortar and then subjected to a post treatment for quenching at 400$^\circ$C for 1 hour in a muffle furnace. This powder was then used for further study. The phase purity and structure of the final products of the Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce$^{3+}$ optoelectronics nanophosphors was examined by x-ray powder diffraction using Cu K$\alpha$ radiation on a BRUKER – analytical x-ray diffractometer, at a scanning step size of 0.015, with a continuing step of 5 sec, in the 2 theta range from 0$^\circ$ to 80$^\circ$. Phosphor morphology was studied by a Geol-6380A scanning electron microscope (SEM). All transmission electron microscopy (TEM) images were obtained on 100 keV and an AMT XR41-B 4-megapixel (2048 x 2048) bottom mount CCD camera. For the TEM measurement, the samples were ground and mixed together with ethylene glycol and dispersed under ultrasonic vibration for 30 minutes. A drop of the dispersed particles was kept over the carbon coated copper grid and evaporated to dryness. Images from the camera are saved as high-resolution TIFF files. Infrared spectra of the pure were recorded on using a Bruker Fourier transform infrared spectrometer. For the measurement of spectroscopic properties, the excitation and emission spectra for all samples were recorded on Shimadzu RF-5301PC spectrophotofluorometer. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm at room temperature.

3. Results and Discussion

3.1 X-Ray Diffraction

Figure 1 shows the diffraction data pattern for the pure Na$_{21}$(SO$_4$)$_7$F$_6$Cl phosphor. It shows good agreement with ICDD data file no. #70-1811. The XRD pattern did not indicate presence of the constituents Na$_2$SO$_4$ or NaF or NaCl and other likely phases. An excellent match is seen indicating formation of single phase, homogeneous final product Na$_{21}$(SO$_4$)$_7$F$_6$Cl phosphor.
3.2 Crystalline Structure
As per available data the historical name of Na$_{21}$(SO$_4$)$_7$F$_6$Cl material is Schairerite having hexagonal basis belongs to space group P31m (No. 157) with cell parameter a = 12.19Å and c = 19.359Å [14]. A ball (sphere) model of crystal structure of Na$_{21}$(SO$_4$)$_7$F$_6$Cl (Schairerite) is as shown in figure 2. The crystal structure may be considered as consisting of 7 sheets of Na$^+$ ions perpendicular to the c axis. These sheets are connected to each other, building up a three dimensional framework. The Na$^+$ ions in these sheets are arranged in an array of hexagons and triangles. Sulphur atoms are lying in the sheets at the centers of each hexagon. The halogen atoms lie between the sheets midway between the centers of two triangles.

Figure 2. Crystal structure of Na$_{21}$(SO$_4$)$_7$F$_6$Cl.

3.3 Surface Morphology.
A typical SEM micrographs of as synthesized Na$_{21}$(SO$_4$)$_7$F$_6$Cl powders is shown in Figure 3. It is clearly seen that the grains of the phosphor are not uniform they are irregular in shape and size with average grain size is nearly 4-5 μm. The SEM micrograph showed different morphology of the phosphor with agglomerated crystallites. The agglomeration may be due to the prolong stirring of the reaction mixture. However the actual particle size may be even smaller due to the wet chemical synthesis rout, in order to find the actual particle size of the phosphor the phosphor material characterized by TEM by dispersing the powder phosphor in alcohol by sonication. The typical TEM image of the Na$_{21}$(SO$_4$)$_7$F$_6$Cl phosphor is illustrated in Figure 4. It shows the formation of round shape particles with average size up to 100 nm. Thus TEM study establishes nano crystalline nature of the prepared phosphor material.
Figure 3. Scanning electron microscope (SEM) image of synthesized $\text{Na}_21(\text{SO}_4)_7\text{F}_6\text{Cl}$.

Figure 4. Transmission electron microscope (TEM) image of synthesized $\text{Na}_21(\text{SO}_4)_7\text{F}_6\text{Cl}$.

3.4. FT-IR Analysis

The infrared spectrum of the synthesized $\text{Na}_21(\text{SO}_4)_7\text{F}_6\text{Cl}$ is shown in Figure 5. The peak at 3183 cm$^{-1}$ region, the O-H stretching frequency, is significant because it indicates a presence of either OH anions or H$_2$O molecules. The peak appeared at 1313 cm$^{-1}$ is assigned to $\nu_1$ asymmetric stretching of (SO$_4$)$^{2-}$ group. The peak appeared at 1090 cm$^{-1}$ is due to $\nu_2$ symmetric stretching of (SO$_4$)$^{2-}$ group. The peak at 833 cm$^{-1}$ is $\nu_3$ out-of-plane bending of (SO$_4$)$^{2-}$ group. The peaks below 700 could be $\nu_4$ in-plane bending of (SO$_4$)$^{2-}$ group.

Figure 5. FT-IR Spectrum of the synthesized $\text{Na}_21(\text{SO}_4)_7\text{F}_6\text{Cl}$ phosphors.

3.5. PL Emission of Ce$^{3+}$ in $\text{Na}_21(\text{SO}_4)_7\text{F}_6\text{Cl}$

The excitation and emission spectra of Ce$^{3+}$ doped $\text{Na}_21(\text{SO}_4)_7\text{F}_6\text{Cl}$ optoelectronic phosphor material are shown in Figure 6. The broad excitation peak is observed at 355 nm and broad emission peak in UV range focusing at 389 nm due to the $^4f_0^5d_1 \rightarrow ^4f_1$ transition of Ce$^{3+}$. The spectroscopy of Ce$^{3+}$ [15] is somewhat different from that of other Ln$^{3+}$ compounds. The promotion of an electron from the $^4f$ to the $^5d$ orbitals is due to lowest energy transition of Ce$^{3+}$. All transitions of Ce$^{3+}$ are spin-allowed because the ground state and the excited states of this $^4f$ ion are spin doublets. Therefore, the excitation
peak appears in the UV spectral region at 355 nm. The emission spectrum centring at 389 nm is due to the $^4f_5^1d_1 \rightarrow ^4f_1$ transition of Ce$^{3+}$ ion from $^5d$ excited state to $^2F$ ground state (the lowest level) showing broad emission peak being regarded as the electric dipole allowed one. Generally it is observed that the emission from these f-d state show two bands as the ground state of the Ce$^{3+}$ ion is a doublet ($^2F_{5/2}$ and $^2F_{7/2}$) with a separation of about 2000 cm$^{-1}$. In the present work, however, such a doublet character of the emission band is not observed. This may be due to lack of symmetry in the host lattice. Thus, the activator Ce$^{3+}$ ion may have experienced a random distribution in local fields of host lattice [16, 17]. The peaks of all concentration of phosphor are centred at 389 nm. With increasing concentration of Ce$^{3+}$ ions, peak intensity of the emission increases as shown in inset of figure 6. Maximum intensity is observed for 2 mole % of Ce$^{3+}$ ions indicating that Na$_{21}$(SO$_4$)$_7$F$_6$Cl:Ce phosphor lattice is more suitable for higher concentrations of Ce$^{3+}$ ions. Beyond this, the emission intensity decreases, this could be attributed to the effect of concentration quenching. This may be due to energy transfer between the Ce$^{3+}$ ions and defects of the Na$_{21}$(SO$_4$)$_7$F$_6$Cl host and/or due to cross relaxation between the Ce$^{3+}$ ions[18].

Figure 7 shows schematic representation of energy levels, energy transitions and configurational coordinate diagram of Ce$^{3+}$. The ion Ce$^{3+}$ has $^4f_1$ electronic configuration. The ground state of Ce$^{3+}$ is the doublet $^4f_{5/2}$ and $^4f_{7/2}$. The lower excited states belong to 5d configuration. The Ce$^{3+}$ emission corresponds to transitions from the lowest 5d level to $^2F_{5/2}$ and $^2F_{7/2}$ states of the $^4f_1$ configuration. The excited state derived from the 5d state is sensitive to the crystal field and is coupled to the lattice vibrations which results in broader band emission rather than line emission. In configurational coordinate diagram, the two lowest parabolas represent the ground electronic configuration $^4f_1$ by spin–orbit interaction into $^2F_{5/2}$ (the ground state) and $^2F_{7/2}$ (the first excited state). The lowest states of excited electronic configuration $^5d_1$ are represented by two higher parabolas. Electron–lattice interaction in the excited electronic manifold causes the shift of the respective parabolas in the configurational space. The potential energy of the luminescent centre Ce$^{3+}$ is plotted on the vertical axis and the value of single parameter describing the effective displacement of the ion surrounding the activator, Q is plotted on the horizontal axis. Promotion of the inner 4f electron to the outer 5d states perturbs the surrounding ions, the lattice relaxes, and the potential energy curve changes as shown below in figure 7. The good adaptability of the position of the 4f–5d absorptions and the corresponding emissions make Ce$^{3+}$ an important ingredient in solid state light emitting materials. The respective excitation and emission pathways are indicated in figure 7 by arrows [19-20].
**Figure 6.** Excitation and emission spectra of Na$_{21}$(SO$_4$)$_7$F$_6$Cl: Ce$^{3+}$ phosphors.

**Figure 7.** Schematic representation of energy levels, energy transitions and configurational coordinate diagram of Ce$^{3+}$.

### 4. Conclusions

A novel nanocrystalline optoelectronic Na$_{21}$(SO$_4$)$_7$F$_6$Cl nanophosphors in the Cl–F system doped with Ce$^{3+}$ has been prepared by the wet chemical synthesis method and the synthesis were confirmed by XRD. The TEM result shows the formation of round shaped nanomaterial. From the results presented here it can be concluded that Ce$^{3+}$ ions are occupied site with symmetric environment in Na$_{21}$(SO$_4$)$_7$F$_6$Cl host matrix. Ce$^{3+}$ emission in the host was observed at 389 when excited at 355 nm. Based on the results obtained, we suggest that these optoelectronic luminescent nanophosphors have possible potential applications as a near UV convertible phosphor for light emitting devices and also for energy transfer process in co-activated phosphors to increase the intensity of f-f transitions in near UV region.

### References

[1] Gedam S C, Dhoble S J and Moharil S V 2006 *J. Lumin.* **121** 450

[2] Gedam S C, Dhoble S J and Moharil S V 2007 *J. Lumin.* **124** 120

[3] Gedam S C, Dhoble S J and Moharil S V 2007 *Eur. Phys. J. Appl. Phys.* **37** 73

[4] Gedam S C, Dhoble S J and Moharil S V 2007 *J. Lumin.* **126** 121

[5] Gedam S C, Dhoble S J, Omanwar S K and Moharil S V, 2007 *Eur. Phys. J. Appl. Phys.* **39** 39

[6] Gedam S C, Dhoble S J, Nagpure I M, Godbole S V and Bhide M K 2007 *J. Phys. D: Appl. Phys.* **40** 6039

[7] Gedam S C, Dhoble S J and Moharil S V 2008 *J. Lumin* **128** 1

[8] Gedam S C, Dhoble S J, Nagpure I M, Godbole S V, Bhide M K and Moharil S V 2008 *J. Mater. Sci.* **43** 3189

[9] Piotrowski A, Kahlenberg V and Fischer R X 2002 *J. Solid-State Chem.* **163** 398

[10] Klement R 1939 *Naturwissenschaften* **27** 568
[11] Schneider W, Jahrb N and Miner F 1967 *Monatschefte* 284
[12] Schneider W, Jahrb N and Miner F 1969 *Monatschefte* 58
[13] Kim H J, Jeong D Y, Zalar B, Blinc R S and Choh H 2000 *Phys. Rev. B* 61 9307
[14] Pabst A, Sawyer D L and Switzer G, 1963 *J. Mineralogical Society of America* 48 5
[15] Dorenbos P 2000 *Phys. Rev. B* 62 15640
[16] Dorenbos P 2000 *J. Lumin.* 87 970
[17] Van Eijk C W E, Andriessen J, Dorenbos P and Visser R 1994 *Nucl. Instr. and Meth.* A348 546
[18] Dorenbos P 2001 *Phys. Rev. B* 64 125117
[19] Curie D 1975 *Plenum* 71
[20] Drickamer H G, Frank C W and Slichter C P 1972 *Proc. Nat. Acad. Sci* 69 933