



Study of crystal structure and PL properties of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$ halophosphor

Anuradha Poddar¹, S. C. Gedam^{2*} and S.J. Dhoble³

¹Department of Physics, Sindhu College, Nagpur, - 440017, India

²Department of Physics, K.Z.S. Science College, Kalmeshwar, Nagpur - 441501, India

³Department of Physics, RTM Nagpur University, Nagpur- 440033, India

Abstract

A new phosphor $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ is very interesting for photoluminescence (PL) properties. In this paper we present results concerning the main PL properties of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ activated by Ce at various concentrations. Polycrystalline $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$ phosphor prepared by wet chemical method have been studied for its PL characteristics showing Ce^{3+} emission at 341 nm at the excitation of 247 nm due to $5d \rightarrow 4f$ transition, This is a good result for the materials which can be used in scintillation applications.

Keywords: Photoluminescence; wet chemical; luminescence spectroscopy.

INTRODUCTION

Luminescence spectroscopy is particularly important in the characterization of materials that contain significant proportions of noncrystalline components, multiple phases, or low concentrations of mineral phases. A number of minerals have distinguishing luminescence properties. These include: diamond, sulphides (chalcocite, sphalerite), oxides (periclase, corundum, cassiterite), halides (fluorite, halite), sulphates (anhydrite, alunite), wolframates (scheelite), phosphates (apatite), carbonates (calcite, dolomite, magnesite, witherite), or silicates (albite, feldspar, quartz, zeolites, kaolinite, forsterite, zircon, garnet, titanite, thorite, willemite). However, the group of sulfate apatites has not been studied in such detail in the field of luminescence. The Cl-F substitution in the system $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_x\text{Cl}_{1-x})_2$ has been investigated by Mackie and Young [1]. Klement [2] synthesized the sulfate apatite $\text{Na}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$ and characterized this compound by X-ray powder diffraction. Also, the compounds $\text{Na}_6\text{Pb}_4(\text{SO}_6)_4\text{Cl}_2$ (Caracolite) [3, 4], $\text{Na}_6\text{Cd}_4(\text{SO}_6)_4\text{Cl}_2$ [5], $\text{Na}_6\text{Ca}_4(\text{SO}_6)_4\text{Cl}_2$ (Cesanite) [6,7] are known as members of the sulfate apatite group, all crystallizing in space group $P6_3/m$. The apatite-like compound $\text{K}_6\text{Ca}_4(\text{SO}_4)_6\text{F}_2$ was described by Vazquez [8] and Fayos *et al.* [9].

Thermoluminescence (TL) technique has wide range of applications such as in radiation dosimetry and to dating techniques in archeology and geology. TL studies are also useful for the study of lattice defects which acts as "traps" to electrons and holes. Analysis of TL glow curves has become more important in view of its applications in dating, dosimetry and defect studies.

In this paper we present the detail studies of a new host $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ such as its crystal structure, PL. The crystal Structure data of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ [10] is given here in Figure 2. As per the literature available, the mineralogical name of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ is d'ansite [11], the name is given in the honour of Professor Jean D'Ans (1881–1969), German mineralogist, student of salt deposit chemistry, Technical University, Berlin, Germany. D'ansite occurs as a component of marine evaporite deposits, n.d. type material. It is semitransparent, colorless, yellow, pale brown having, optical class: Isotropic. $n = 1.488-1.489$. We have reported some inorganic materials as phosphors [12-22]. The $\text{KZnSO}_4\text{Cl}:\text{Ce}$, Mn and $\text{KMgSO}_4\text{Cl}:\text{Ce}$, Mn phosphors were

prepared by wet chemical synthesis method. Other than these materials, $\text{KZnSO}_4\text{Cl}:\text{Ce}$; Ce , Dy and $\text{KMgSO}_4\text{Cl}:\text{Ce}$; Ce , Dy ; $\text{KMgSO}_4\text{Cl}:\text{Eu}$; $\text{Na}_3\text{SO}_4\text{F}:\text{Ce}$; $\text{NaMgSO}_4\text{Cl}:\text{Ce}$; $\text{KCaSO}_4\text{Cl}:\text{Ce}$; Dy have been reported as phosphors by wet chemical, solid state diffusion and melting route and characterized XRD, photoluminescence (PL), thermoluminescence (TL). Here we report $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ as a host for luminescent (PL and TL) material by doping Ce and Dy first time. Excellent photoluminescence (PL) and thermoluminescence (TL) results are observed. The phosphor may be used as a TLD material.

EXPERIMENTAL

$\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ (pure) and $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$ phosphors were prepared by a wet chemical method. MgSO_4 and Na_2SO_4 and NaCl of AR grade were taken in a stoichiometric ratio and dissolved separately in double distilled de-ionized water, resulting in a solution of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$. Then water-soluble sulphate salt of Cerium was added to the solution to obtain $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$. Confirming that no undissolved constituents were left behind, and all the salts had completely dissolved in water and thus reacted.



The compounds $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ (pure) and $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$ in its powder form was obtained by evaporating on 80°C for 8 hours. The dried samples were then slowly cooled at room temperature. The resultant polycrystalline mass was crushed to fine particle in a crucible. The powder was used in further study. Formation of the compounds was confirmed by taking the x-ray diffraction (XRD) pattern that matched with the standard data available. The photoluminescence (PL) emission spectra of the samples were recorded using Fluorescence spectrometer (Hitachi F-4000). The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

RESULTS AND DISCUSSION

Study of XRD and Crystal Structure

Figure 1 shows X-Ray diffraction pattern of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ material that matched with the standard JCPDF data No. 41-1473. The XRD pattern did not indicate the presence of the constituents such as Na_2SO_4 , MgSO_4 or NaCl and other likely phases, which is the direct evidence for the formation of the desired compound. These results indicate that the final product was formed in homogeneous form. According to the data available the D'ansite crystal structure has the following parameters; Crystal Data: Cubic. *Point Group*: 43m. as tetrahedral {211} crystals, modified by {211} and {110}. Polysynthetic twinning observed. Hardness = 2.5–3 D (meas.) = 2.63–2.655 D (calc.) = 2.60 Soluble in H_2O , *Space Group*: $I4_3m$. $a = 15.95$ $Z = 4$, Synthetic. (ICDD 41-1473). 3.396 (100), 2.815 (100), 3.123 (60), 2.584 (40), 4.257 (30), 3.982 (30), 2.518 (25), symmetry class: cubic, space group: $I4_3m$, unit cell parameters: $a = 15.9130$, unit cell volume, Å^3 : $V_c = 4029.55$, number of atomic position per full unit cell, $P/U = 324$, molar volume, $V_m = 606.79 \text{ cm}^3/\text{mol}$, number of reflexes used in structure determination, $\text{NR} = 810$, X-ray density, $\rho = 2.66 \text{ g/cm}^3$, R-factor, $R = 0.0360$, $\text{MU}, 1/\text{cm}, \mu = 108.219$, wavelength for calculated powder diffraction pattern $\text{Cu} = 1.54056$, mass attenuation coefficient (μ/ρ) = $40.662 \text{ cm}^2/\text{g}$, theta-interval for CPDP (T/I) = 1-45.

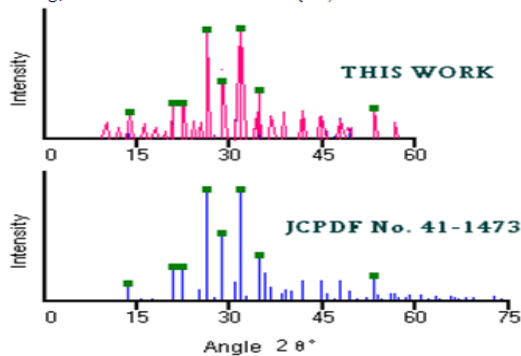


Fig 1. XRD pattern of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$

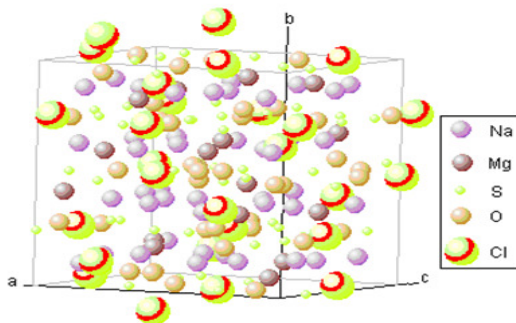


Fig 2. Crystal structure of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ (Ref.10).

Photoluminescence (PL) in $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3: \text{Ce}^{3+}$

Figure 3 shows the PL excitation spectra of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3: \text{Ce}^{3+}$ phosphor ($\lambda_{em} = 341\text{nm}$), broadband is observed at around 247nm. Figure 4 shows the PL emission spectra of Ce^{3+} ions in $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ phosphor with different concentration under excitation of 247nm wavelength of light. Peak is observed at 341nm, which are assigned to the $5d \rightarrow 4f$ transition of Ce^{3+} ions. With increasing concentration of Ce^{3+} ions the peak intensity of 341nm, increases the maximum intensity observed for 5-mole % concentration of Ce^{3+} ions (Figure 5). This indicates that the $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ lattice is more suitable for higher concentrations of

Ce^{3+} ions. Figure 6 indicates the energy level diagram for $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3: \text{Ce}^{3+}$.

The PL emission spectra of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3: \text{Ce}^{3+}$ (5mole%) phosphors show very strong Ce^{3+} emission at 341nm due to $5d \rightarrow 4f$ transition of Ce^{3+} ions. The variation of PL emission intensity observed may be due to cross relaxation between Ce^{3+} ions in case of heavy concentration of Ce^{3+} . The strong Ce^{3+} emission in $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ lattice may be useful for a scintillator. PL emission peak intensity of Ce^{3+} ion in $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$ lattice is not having the same intensity for different concentration of Ce^{3+} ions. The PL emission peak intensity dependent on the concentration of Ce^{3+} ion. The intensity of Ce^{3+} ion in above phosphor shows the maximum Ce^{3+} emission observed in Ce (5 mole%) phosphor. Ce^{3+} phosphors are useful where rapid decay times are required (e.g. in time of flight camera and in scintillator), however quantum efficiency and other related measurements should be done. It can be used as a sensitizer for other rare earths.

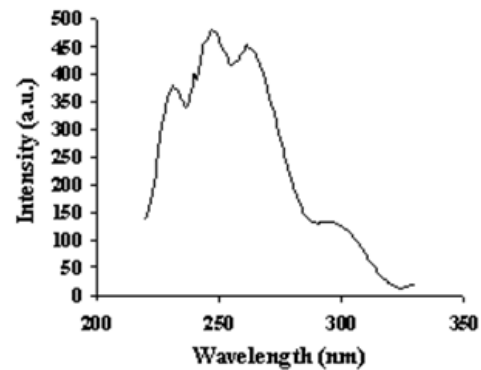


Fig 3. Excitation spectra of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3: \text{Ce}$ ($\lambda_{ex} = 247\text{nm}$) for the $\lambda_{em} = 341\text{nm}$

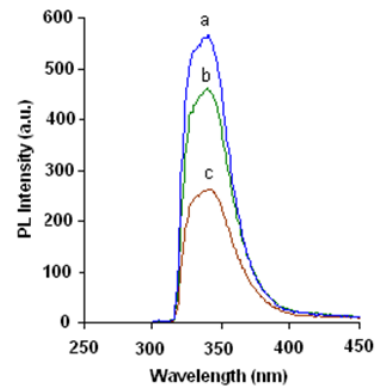


Fig 4. PL emission spectra $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3: \text{Ce}$ 5mole% b) 2 mole% c) 1 mole% (exci at 247nm)

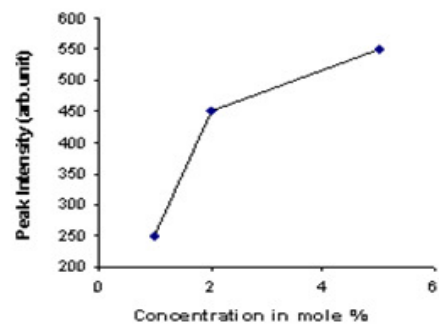
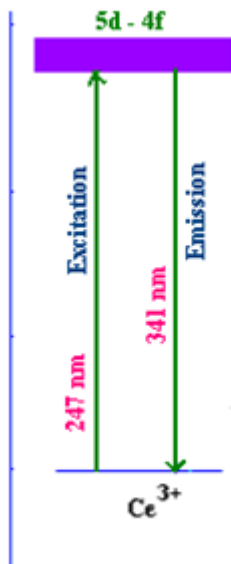


Fig 5. Effect on intensity with variation in concentrations in $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$ Fig 6. Schematic energy level diagram of Ce^{3+} in $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$

CONCLUSION

$\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Dy}^{3+}$, Ce^{3+} and Dy^{3+} has been prepared by wet chemical method and characterized on the basis of its PL and TL characteristics. The results show a Strong PL emission of Ce^{3+} at 341 nm due to $5d \rightarrow 4f$ transition of Ce^{3+} ion and Dy^{3+} ions is observed at 483 and 577 nm due to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition respectively. The main property of $\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3:\text{Ce}$ or Dy is its good PL and TL sensitivity.

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