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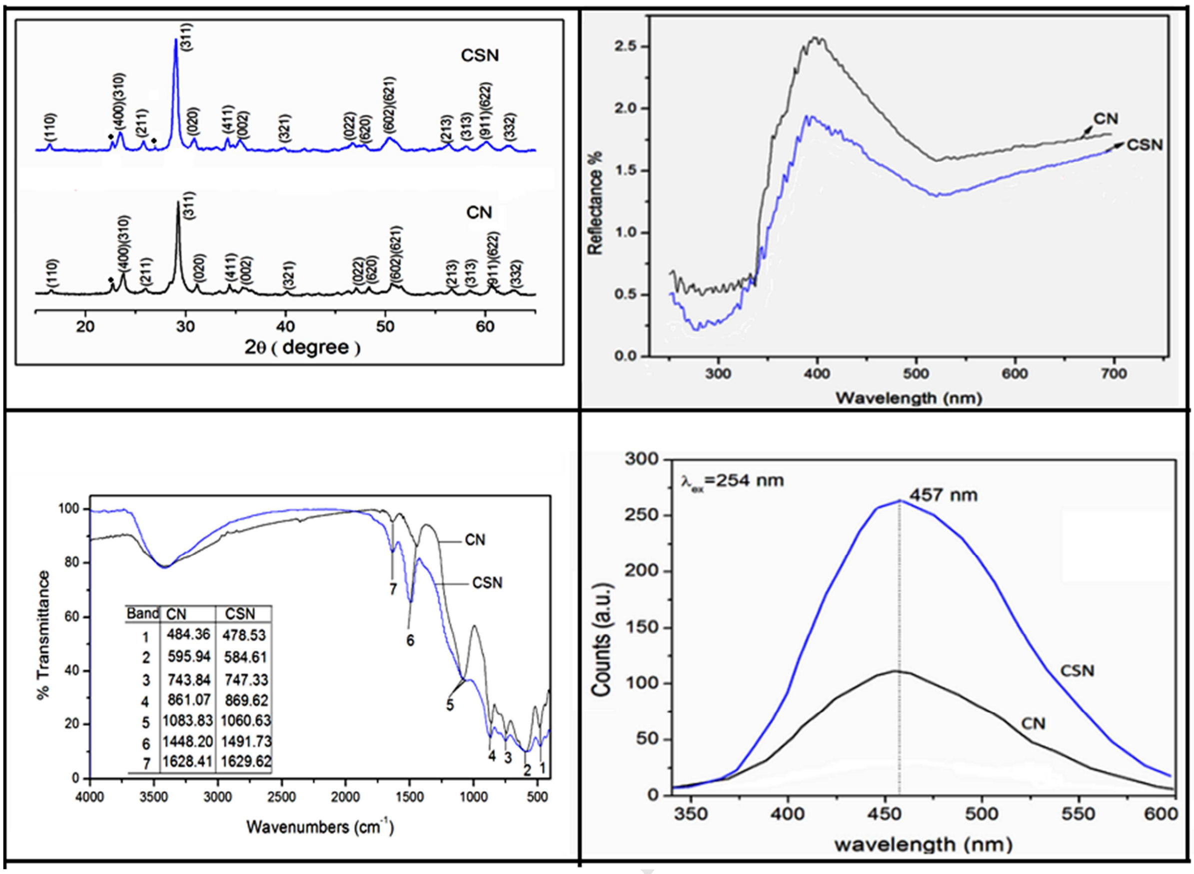

Band	CN	CSN
1	484.36	478.53
2	595.94	584.61
3	743.84	747.33
4	861.07	869.62
5	1083.83	1060.63
6	1448.20	1491.73
7	1628.41	1629.62

Synthesis and characterization of a novel alkaline earth niobate $Ca_{0.5}Sr_{0.5}Nb_2O_6$

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Abstract

$Ca_{0.5}Sr_{0.5}Nb_2O_6$ (CSN), a novel compound with crystal structure similar to the well-known orthorhombic columbite compound $CaNb_2O_6$ (CN) of alkaline earth niobates family was synthesized by a simple co-precipitation technique. The synthesized material was characterized by using X-ray diffraction (XRD) technique, transmission electron microscopy (TEM), UV-Vis diffuse reflectance spectroscopy, FTIR spectroscopy, and photoluminescence emission spectroscopy. It was found that the CSN compound stabilizes in *P b c n* space group with the improved symmetry as compared to the CN. The lattice parameters of CSN were found to be comparable with those of CN, and they are: **a** = 15.013Å, **b** = 5.757Å and **c** = 5.198Å. The morphology of CSN and CN particles synthesized by a similar method was found to be identical. However, in CSN stronger self activated luminescence than that of CN was observed. The self-activated luminescence property of CSN was assigned to the niobate octahedral group $[NbO_6]^{7-}$ similar to the CN.

Keywords:

B. Chemical synthesis; C. Crystal structure; D. Optical spectroscopy; D. Luminescence

1. Introduction:

The space group *P b c n* (space group no. 60) belongs to a large family of orthorhombic centrosymmetric point group *mmm*. Calcium niobate ($CaNb_2O_6$, CN), a well known compound of the alkaline earth niobates belongs to this space group. It is well known that the magnitude of any property of the material is related to the atom types that make the solid, however, the presence or absence of a property is often controlled by the symmetry of the solid [1]. Hence, compounds like $CaNb_2O_6$, $BaNb_2O_6$ and $SrNb_2O_6$ although have similar atomic compositions, their crystal structures and physical properties are different [2,3]. On the other hand, if compositions and symmetries of materials are similar, the probability of getting similarities in their properties at the same or different extent is expected to be more [4,5]. The novel material undertaken in the present study i.e. $Ca_{0.5}Sr_{0.5}Nb_2O_6$ (CSN) shows structural and compositional similarities with the CN. Therefore, the investigation of CSN under the light of known properties and applications of CN will be very exciting.

The initial investigations on CN have been done for its very important applications in holography and laser, as it possesses a strong source of coherent light and very high refractive index (2.07 – 2.20) [6-8]. According to the literature, the CN possesses a strong, self-activated, blue luminescence with the excitation by UV radiations of $253cm^{-1}$, even at the room temperature due to the niobate octahedral group $[NbO_6]^{7-}$ [9]. Later on, many investigations on CN regarding the symmetry, size, shape, and from applications point of view have been reported. These studies show that the CN compound is a low symmetry material. Nanoparticles of the CN have irregular sphere like, rod like and fiber like morphologies and useful for the photo-catalytic

H_2 evolution from pure water under UV irradiation, stimulated Raman scattering laser and low cost lamp phosphor [3,10-17].

As far as CSN compound is concerned, to the best of our knowledge the material is not reported yet and therefore the investigation of properties and applications analogous to CN is a prolong work. In the present study, however, some important properties such as structural, morphological, optical characterizations and self activated luminescence of CSN are undertaken.

Now-a-days the synthesis of compounds by chemical route becomes highly popular because, by this route the reduction in the size of particles can be easily achieved; and also the route shows better composition control, better particle morphology control, and good powder reactivity [18]. Thus in the present study CSN and CN compounds (for the comparison) were synthesized by a chemical co-precipitation synthesis method.

2. Material and methods

The synthesis of $Ca_{0.5}Sr_{0.5}Nb_2O_6$ (CSN) compound, as mentioned, was carried out by a co-precipitation method. The starting materials were Nb_2O_5, $SrCl_2.6H_2O$ and $CaCl_2.2H_2O$. All they were of AR grade. The method is as described below.

A stoichiometric amount of Nb_2O_5 was converted to NbF_5 by reacting with minimum amount of HF. The reaction was carried out in a Teflon beaker which was maintained at 70^{o}C in a water bath for 15h. During the reaction, Nb_2O_5 was completely dissolved in HF and forms a transparent solution of NbF_5. This solution was added to another solution which was prepared by dissolving stoichiometric amount of $CaCl_2.2H_2O$ and $SrCl_2.6H_2O$ in distilled water. The resultant solution was vigorously stirred with a magnetic stirrer for 3-4 h. While stirring, an excess quantity of concentrated HCl was added to the solution to dissolve calcium fluoride and strontium fluoride formed during the reaction of NbF_5 with $CaCl_2.2H_2O$ and $SrCl_2.6H_2O$. A mixture solution of ammonium oxalate and ammonium hydroxide was then added drop wise until the pH of the solution reached to 9.5 to precipitate niobium as hydroxide and calcium and/or strontium as oxalates. pH of the solution around 9.5 ensures completion of the reaction. The precipitate was filtered out and washed several times with distilled water. The washed powder was then dried at 70^{o}C in an oven, for 24h, and finally calcined at 650^{o}C and 800^{o}C for 8 h.

The synthesis of CN compound was also carried out by the similar method as reported elsewhere [19,20].

X-ray diffractions (XRD) data of the synthesized compounds of CSN and CN were collected by using X-ray diffractometer (D8 ADVANCE, BRUKER, GERMANY) employing Cu-Kα radiation (1.54Å) with step size of 0.02^{o} and step time of 46.5s. The morphology of the particles was observed by using transmission electron microscopy (TEM) (TECNAI G2 20 ULTRA-TWIN, FEL, NETHERLANDS). FT-IR, PL emission and UV-Vis spectra of CSN and CN were obtained by using FT-IR spectrometer (THERMO NICOLET, AVATAR 370, USA), spectroflurometer (F-7000, HITACHI, JAPAN) and UV-VIS spectrometer (UV-VIS 1700, SHIMATZU, JAPAN), respectively.

For the measurements of UV-Vis diffuse reflectance spectra, pellets of the compounds were prepared by mixing the powder with a few drops of 1 wt% solution of polyvinyl alcohol and then pressing isostatically under the pressure of 5-6 t for 5 min. The pellets were heat-treated at 800^{o}C for 5 h to remove the binder. The pellets of CSN were also used for the measurement of bulk density.

3. Results and Discussion

3.1. Structural and morphological

Fig. 1 shows the XRD patterns of synthesized precursors of CSN and CN calcined at 650^{o}C for 8h. The high intensity XRD peak at $2\theta \sim 29.3^{o}$ is a characteristic feature of CN compound which is clearly seen in Fig.1 [6,21]. The XRD pattern of CSN follows the same pattern, confirming at the first sight that the structure of CSN is similar to the CN. Similarities are also observed from Fig.2, which represents the TEM and SAED images of CSN and CN nanoparticles. The morphology of nanoparticles of the both is likely to be an irregular sphere, and they are agglomerated. The size of nanoparticles of the both CSN and CN compound as visualized by the TEM images in Fig.2 is almost same and is ranging from 60-80nm. Beside the XRD pattern, the poly-crystalline nature of these compounds is clearly confirmed from their respective selected area electron diffraction (SAED) patterns (Fig. 2) as concentric rings along with bright spots are observed. The spotty rings patterns are due to the reciprocal patterns of reflections from a large numbers of crystallites under the view of SAED signal [1]. However, individual identities of these compounds can be observed from the energy dispersive X-ray (EDX) patterns shown in Fig. 3, as EDX patterns show different constituents of CSN and CN compounds. Note that the signals of C and Cu were generated from the carbon coated copper grid.

For the better clarity of peaks and for the structural analysis, the precursors of CSN and CN were again heat- treated at 800^{o}C for 8h; the XRD patterns of which are shown in Fig.4. The peaks pattern of CN as seen in Fig. 4 clearly matched with the JCPDS data file no. 31-289. CSN being a novel compound its structural analysis was done by using Rietveld refinement software FULLPROF. The lattice parameters of CN calculated by least square fit method and that of CSN calculated by the refined method are given in Table 1. Although, Fig. 4 shows the identical XRD peak patterns of CSN and CN, the careful observation differentiates these peak patterns. This can also be realized from Table 1, in which the slight difference in lattice parameters '**c**' of CSN and CN is observed. The origin of this change may be associated to the slight difference in the sizes of Sr and Ca ions.

Table 2 shows the coordinates and Wyckoff sites of atoms in CSN. From this table it is observed that the Sr^{2+} ions occupy the same site as that occupied by the Ca^{2+} ions. This may be due to comparable ionic radii of $Ca^{+\ 2}$(1.00Ǻ) and $Sr^{+\ 2}$(1.18Ǻ). The presence of $Sr^{+\ 2}$ ions however can affect the Nb sites, which can be realized by comparing the cell structure of CSN (Fig. 5) with the cell structure of CN [3]. Nb atoms in CSN are arranged more mannerly than they are in CN, result in the increase in symmetry of the crystal structure of CSN as compared to the CN.

Solid solution reaction $CaNb_2O_6$- $SrNb_2O_6$ is not reported in the literature unlike to $SrNb_2O_6$ -$BaNb_2O_6$ and $CaNb_2O_6$- $BaNb_2O_6$ reactions. However, we assume that such a reaction is there and CSN is the end product of such reaction. It is to be noted that the general phase of CN is orthorhombic, and that of SN is monoclinic [3]. Therefore, in CN- SN reaction the CN may be a dominant reactant over the SN as the product CSN is orthorhombic. Our prediction is well supported by the finding on non-sensitivity of nanocrystalline $SrNb_2O_6$ powders to the applied electric field intensity [3]. Thus, in CN-SN solid solution reaction, the orthorhombic columbite structure is formed initially and Sr^{2+} ions get completely diffused into the lattice by sharing the sites with Ca^{2+} ions. Zhou and Liu [22] reported a similar observation on diffusion of $BaNb_2O_6$ (BN) into the lattice of $Bi_{0.5}Na_{0.5}TiO_3$ compound without any significant change in the $Bi_{0.5}Na_{0.5}TiO_3$ cell structure.

3.2. Establishing the formula $Ca_{0.5}Sr_{0.5}Nb_2O_6$

The chemical formula $Ca_{0.5}Sr_{0.5}Nb_2O_6$ was established getting corroboration from the following ways:

For the synthesis of the compound the stoichiometric ratio of Nb_2O_5, $SrCl_2.6H_2O$ and $CaCl_2.2H_2O$ was taken as 2:1:1. The synthesis was not carried out at high temperature therefore there is no ablation of Ca^{2+} or Sr^{2+} ions during the calcinations. Since the synthesis method is well- established [19], the final product after removal of bi-products such as water, oxygen, HCl etc by the filtering process and the calcinations is $Ca_{0.5}Sr_{0.5}Nb_2O_6$.

Secondly, using the lattice parameters determined by Rietveld refinement and taking 4 molecules of $Ca_{0.5}Sr_{0.5}Nb_2O_6$ per unit cell (Fig. 5) the density was calculated. The value was found to be 3.028 g cm^{-3}. Experimentally, the bulk density measurement of $Ca_{0.5}Sr_{0.5}Nb_2O_6$ was also carried out and it was found to be 2.82 g cm^{-3}. Within experimental error the assessment of theoretical and experimental density values is acceptable.

Finally, the quantification results obtained by using EDX shows that the values of atomic % of Ca(K) and Sr(K) were 2.77 ± 0.7 and 3.01 ± 0.19 respectively. Considering the reliability and uncertainty of EDX quantification analysis, the compositions of Ca^{2+} and Sr^{2+} ions in $Ca_{0.5}Sr_{0.5}Nb_2O_6$ compound may be treated as equal. (Note that the elements from the carbon coated copper grid C(K) and Cu(K) were also counted in the quantification result and together with they carry atomic% ~ 44%).

3.3. Optical characterization

Fig. 6 shows the FTIR spectra of the synthesized CN and CSN compounds. The intense absorption is observed in the fingerprint range 1000-400 cm^{-1}. FTIR spectrum of CN match with the spectrum reported earlier by Mathai et al [23]. Accordingly, the absorption band 861.07 cm^{-1} is assigned to the ν_1 (B_2u) mode of the vibration, the band 743.84 cm^{-1} is assigned to the ν_2 (B_2u) mode of vibration, the strong broad band 595.94 cm^{-1} is due to the broadening caused by overlapping of the ν_3 mode of vibrations i.e. ν_3 (B_1u), ν_3 (B_2u) and ν_3 (B_3u) symmetries, and finally the band 484.36 cm^{-1} is due to the overlapping vibrations of ν_4 (B_1u) and ν_4 (B_3u) modes. The corresponding absorption bands for CSN were found at 869.62, 747.33, 584.61, and 478.53 cm^{-1}, respectively. These modes of vibrations are due to Sr-O and/or Ca-O stretching, Nb-O stretching and O-Nb-O bending [23]. Some changes in band 5 (Fig. 6) are observed, which can be assigned to the higher symmetry of CSN structure as compared to the CN.

Fig. 7 shows the UV-VIS diffuse reflectance spectra of CN and CSN nanoparticles. UV-VIS spectra show that the % reflectance of CSN is smaller than that of CN. Corresponding to the spectra shown in Fig. 7, the Kubelka-Munk (K-M) transformed spectra are shown in Fig. 8. The K-M transformed spectra is a plot of $[F(R_\infty)h\nu]^{1/n}$ against $h\nu$. According to the K-M theory the relation between these two is given by a straight line equation [24]:

$$[F(R_\infty)h\nu]^{\frac{1}{n}} = C(h\nu - E_g) \qquad \ldots 1$$

where C is a constant, and n= ½ for the estimation of direct band gap energy.

Function $F(R_\infty)$ is called Kubelka-Munk function or remission and given by the equation

$$F(R_\infty) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \qquad \ldots 2$$

where S and K are the Kubelka-Munk scattering and absorption coefficients respectively.

The term R_∞ is called limiting reflectance [25], and it is given by

$$R_\infty = \frac{R_{sample}}{R_{reference}} \qquad \ldots 3$$

From extrapolations of the linear region, the values of optical band-gap energy were determined. The direct (n=1/2) band-gap energies of CN and CSN are found to be 3.56 and 3.76 eV respectively. The corresponding absorption edges are observed at wavelength 348nm and 330 nm respectively for CN and CSN compounds. The obtained values of bandgap energies and their absorption edges show good agreement with the reported values of alkaline earth niobates [2].

3. 4. Luminescence study

It is well known that the alkaline earth niobate $CaNb_2O_6$ exhibits luminescence property when doped with activators like Eu^{3+}, Yb^{3+} and Tm^{3+} [14-16,26]. Beside this, it possesses the self-activated luminescence due to edge-shared $[NbO_6]^{7-}$ octahedra group [13,27]. This luminescent effects depend on the Nb-O-Nb bonding as the conduction band is composed of Nb^{5+} 4d orbitals, and the valence band of O^{2-} 2p orbitals between the corner sharing octahedra [13,28]. The fact is also observed in our synthesized CN and CSN nanoparticles. The room temperature emission (λ_{ex}=254nm) spectra of CN and CSN are shown in Fig. 9. These spectra show broad blue emission peaks at about 457 nm for the both compounds. The blue emission is found stronger for CSN (more than twice the value of CN) than the CN.

In CSN, though the structural symmetry of the cell is improved by sharing the 4c sites between Ca^{2+} and Sr^{2+} ions, the charge distribution between the Ca/Sr ions and the $[NbO_6]^{7-}$ octhedra may be anisotropic if Ca^{2+} ions occupy inner 4c sites and Sr^{2+} ions occupy edge shared 4c sites (Fig. 5) or vice-versa, because Ca atom lose its electron from $4s^2$ whereas Sr atom from

$5s^2$. Due to this charge anisotropy the probability of radiative transitions increases which leads to the increase in emission intensity.

4. Conclusion

$Ca_{0.5}Sr_{0.5}Nb_2O_6$ (CSN) nanoparticles were successfully synthesized by the co-precipitation method and they stabilize in orthorhombic columbite phase with the space group P b c n. In the cell structure, Sr^{+2} ions get completely distributed and share the Wyckoff position 4c with the Ca^{+2} ions because of their comparative ionic radii. The morphologies of nanoparticles of CN and CSN are found to be similar. The structure of the CSN was found more symmetric than the CN. The luminescence of CSN was found to be intense than the CN. The photoluminescence properties of CSN is assigned to the $[NbO_6]^{7-}$ octahedral similar to CN.

Because of similarities of CSN and CN, profound result in symmetry and self activated luminescence, we believe that the CSN is a good alternative for CN in many applications like laser host material, low cost lamp phosphor, photocatalytic activity etc, however further investigation is required for the confirmation.

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Captions of Figures

Fig. 1 X-ray diffraction patterns of precursors of CN and CSN calcined at 650°C, for 8h.

Fig. 2 TEM images of precursors of (a) CN and (b) CSN calcined at 650°C. Inset shows SAED patterns, confirming polycrystalline nature of CN and CSN.

Fig. 3 Energy dispersive X-ray spectrum of (a) CN and (b) CSN showing their compositions (signals of C and Cu were generated from the carbon coated copper grid).

Fig. 4 X-ray diffraction patterns of precursors of CN and CSN further heat treated at 800°C, for 8h (● insignificant unknown phase).

Fig. 5 Cell structure of CSN orthorhombic nanoparticles as visualized by Powder cell (PCW) program.

Fig. 6 FT-IR spectra of 800°C heat treated compounds of CN and CSN.

Fig. 7 UV-VIS diffuse reflectance spectra of 800°C heat treated compounds of CN and CSN nanoparticles.

Fig. 8 K-M transformed absorption spectra of CN and CSN nanoparticles for (n=1/2).

Fig. 9 PL emission (λ_{ex}=254nm) spectra of 800°C heat treated compounds of CN and CSN at room temperature.

Table 1. Lattice parameters of CN and CSN

Compounds	a(Å)	b(Å)	c(Å)
CN	15.014	5.741	5.302
CSN	15.013	5.757	5.198

Table 2. Refined atomic positions of $Ca_{0.5}Sr_{0.5}Nb_2O_6$ compound

Atom	Wyck.	x	y	z	Occ
Ca	4c	0	0.823(1)	0.25	0.5
Sr	4c	0	0.823(1)	0.25	0.5
Nb	8d	0.169(1)	0.287(1)	0.305(1)	1
O1	8d	0.063(3)	0.048(10)	0.471(10)	1
O2	8d	0.064(4)	0.391(6)	-0.343(6)	1
O3	8d	0.248(3)	0.157(6)	0.094(7)	1

Goodness-of-fit (square root of χ^2) = 2.22

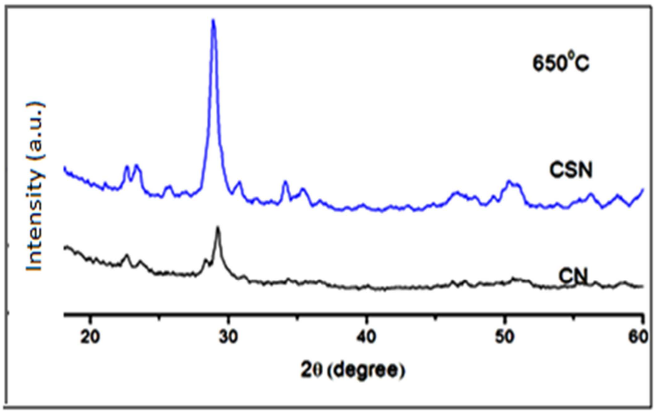


Figure 1

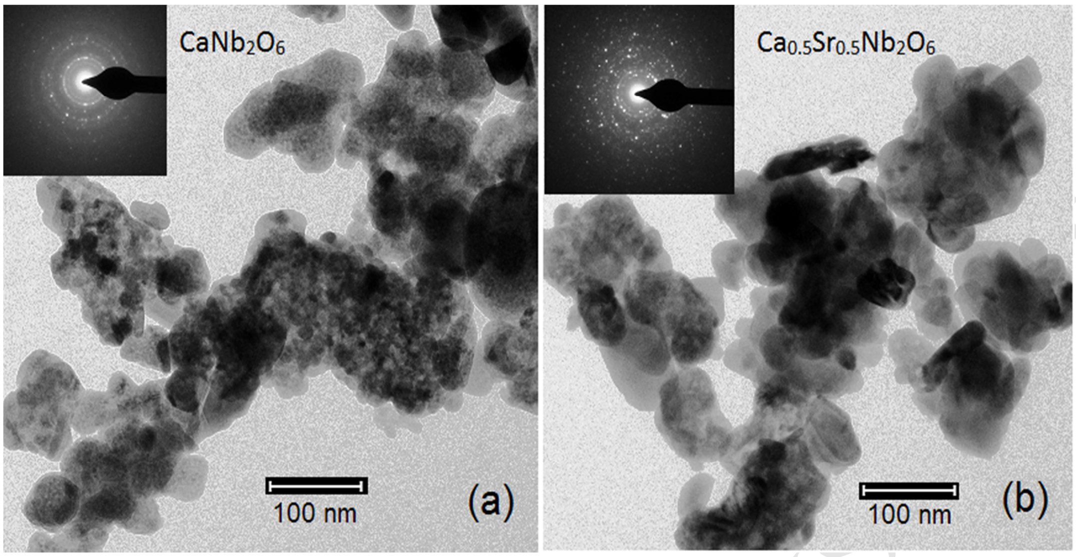


Figure 2

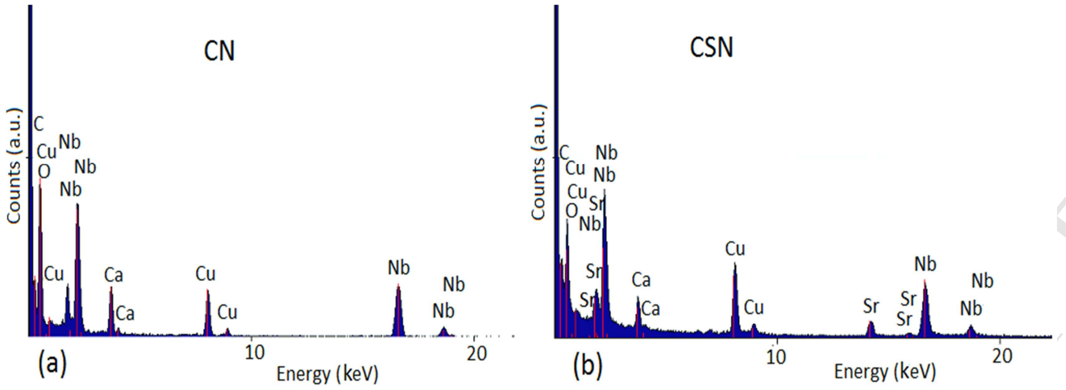

CN
Counts (a.u.)
C
Cu
O
Nb
Nb
Nb
Cu
Ca
Ca
Cu
Cu
Nb
Nb
Nb
10
20
Energy (keV)
(a)
CSN
Counts (a.u.)
C
Cu
Cu
O
Nb
Nb
Nb
Sr
Sr
Sr
Ca
Ca
Cu
Cu
Sr
Sr
Sr
Nb
Nb
Nb
10
20
Energy (keV)
(b)

Figure 3

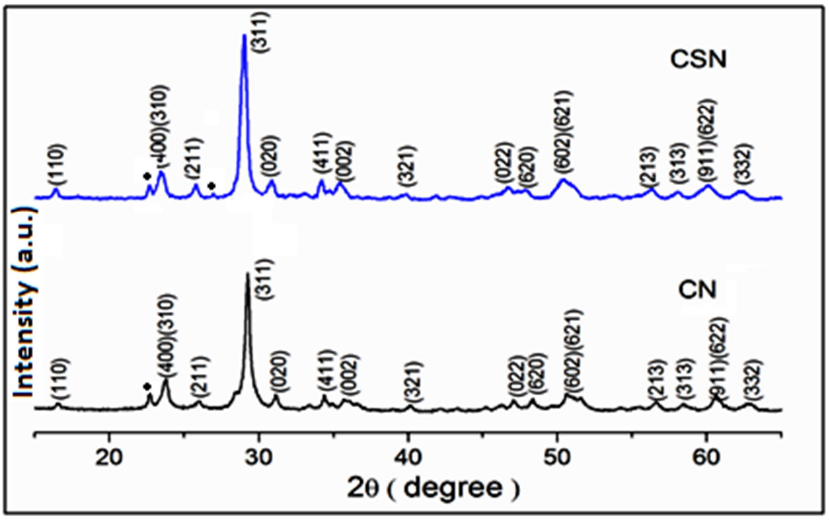

CSN
CN
(110)
(400)(310)
(211)
(311)
(020)
(411)
(002)
(321)
(022)
(620)
(602)(621)
(213)
(313)
(911)(622)
(332)
Intensity (a.u.)
2θ (degree)
20
30
40
50
60

Figure 4

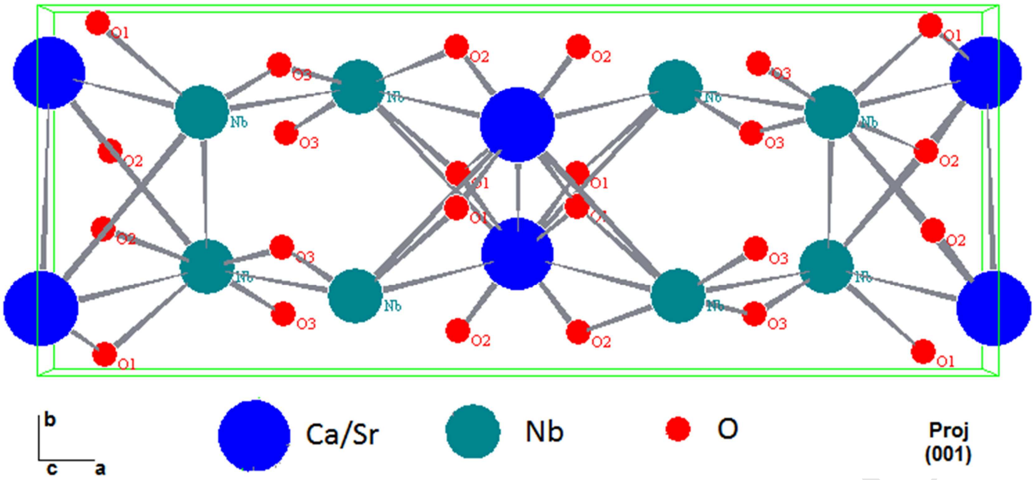
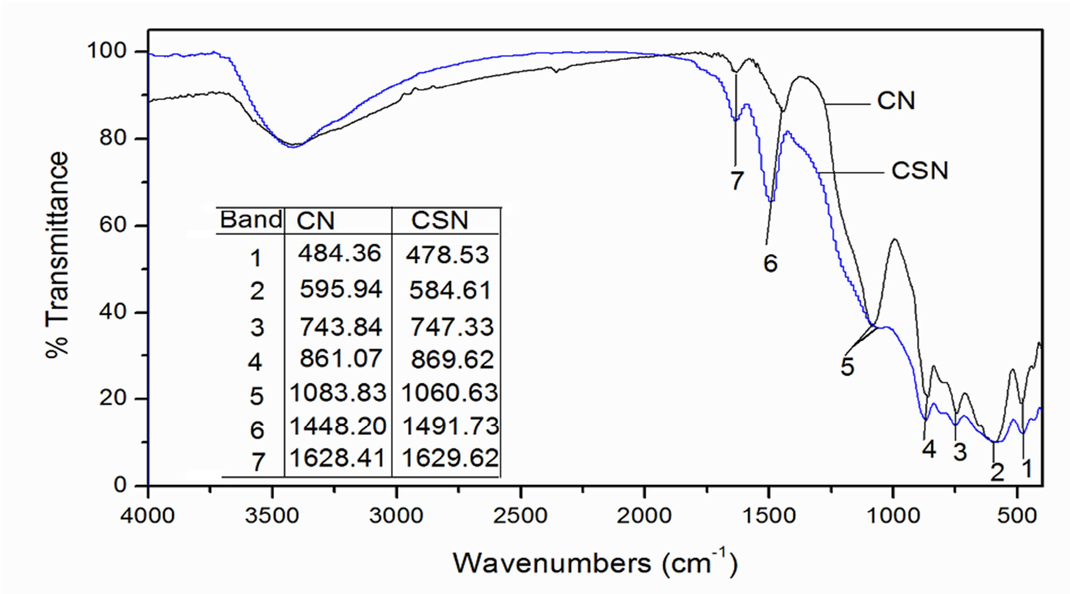


Figure 5



Band	CN	CSN
1	484.36	478.53
2	595.94	584.61
3	743.84	747.33
4	861.07	869.62
5	1083.83	1060.63
6	1448.20	1491.73
7	1628.41	1629.62

Figure 6

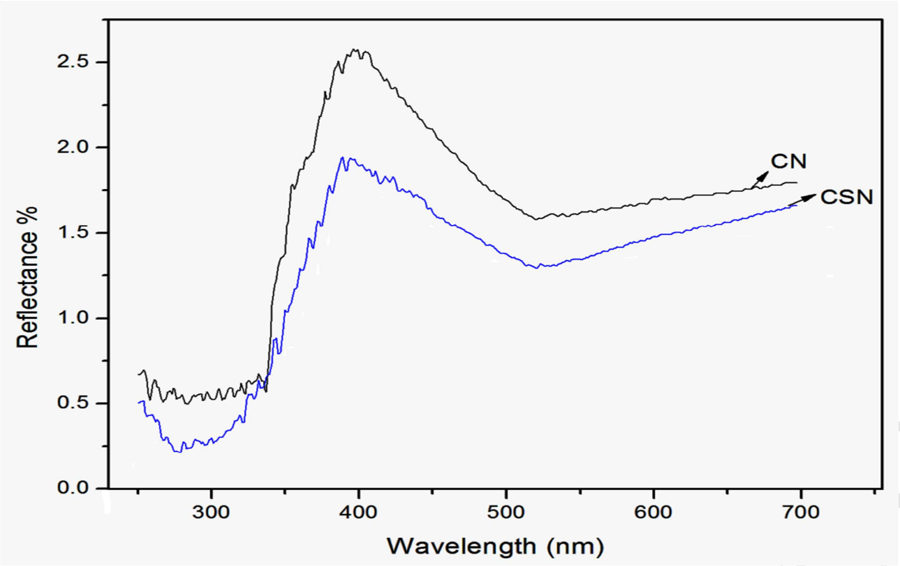

Reflectance %
Wavelength (nm)
2.5
2.0
1.5
1.0
0.5
0.0
300
400
500
600
700
CN
CSN

Figure 7

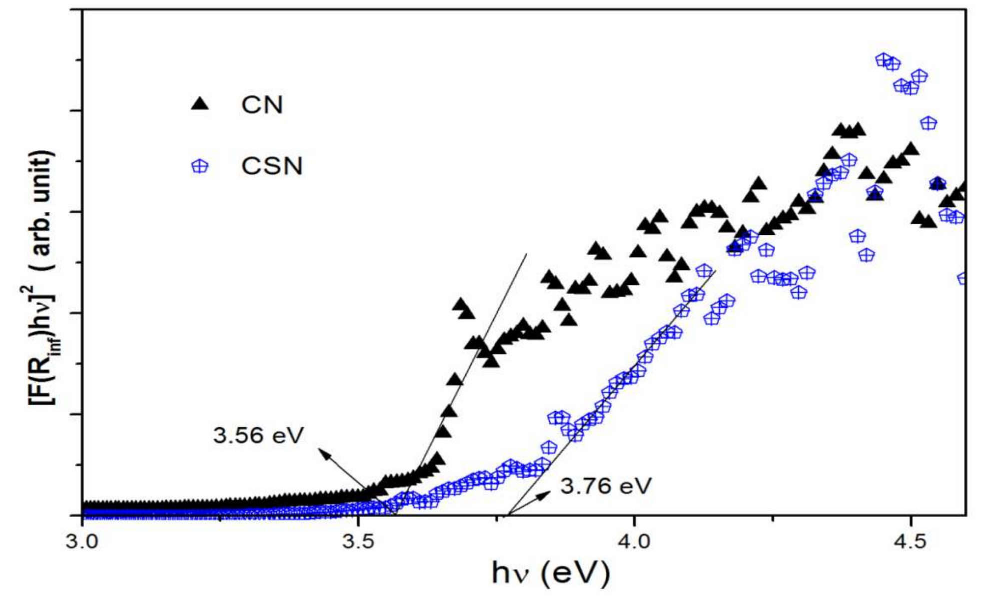


Figure 8

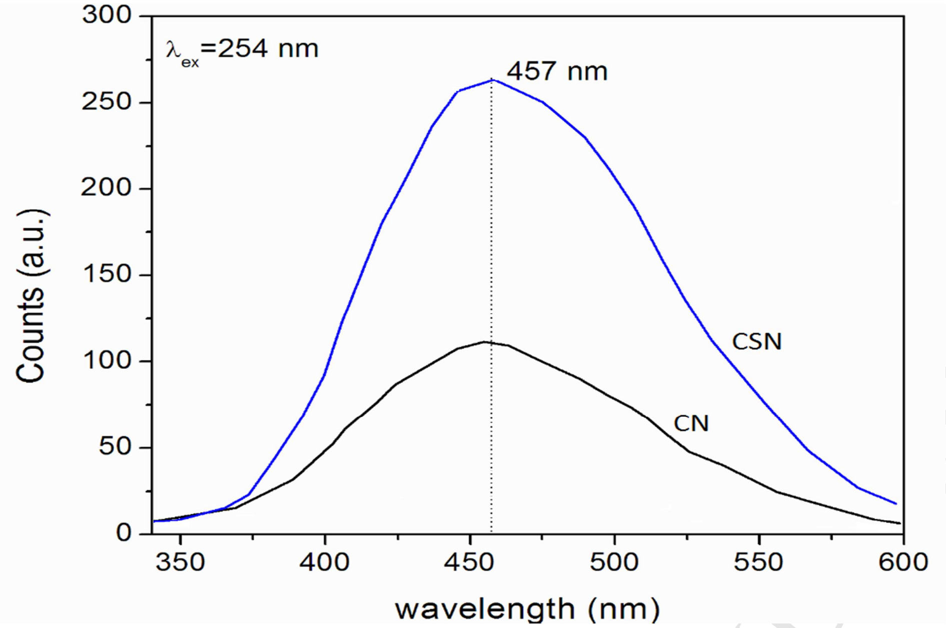

λ_{ex}=254 nm
457 nm
CSN
CN
Counts (a.u.)
0
50
100
150
200
250
300
350
400
450
500
550
600
wavelength (nm)

Figure 9

- Study on a novel compound $Ca_{0.5}Sr_{0.5}Nb_2O_6$ is reported.
- It possesses properties similar to the $CaNb_2O_6$.
- Cell structure is more symmetric than the $CaNb_2O_6$.
- The self luminescent intensity was found more than twice the intensity of $CaNb_2O_6$.