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Luminescence properties of erbium doped sodium barium borate glass with silver nanoparticles

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Abstract. Alteration in the absorption features of rare earth (RE) doped glasses with silver nanoparticles is ever-challenging in photonics. Erbium (Er^{3+}) doped glasses with composition (60-x-y)B_2O_3-30Na_2CO_3-10BaO-xEr_2O_3-yAgCl where (x=0.5, 1.0 and y=1.0 mol %) are synthesized using melt-quenching method.The density is determined by Archimedes principle and molar volumes are calculated. Glass samples were characterized by XRD and UV-Visible spectroscopy. UV-Visible spectra shows eleven prominent absorption peaks centred around 366,378,408, 442,452, 489, 521,547,652,800 and 977 nm equivalent to the rare earth (Er^{3+}) ion transitions. The sample without rare earth shows no peaks which specifies that rare earth ion plays a spirited role in the glass matrix. The glass samples with silver and without rare earth ion shows plasmon peak on heat treatment.The energy band gap values calculated for direct and indirect transitions are in the range of 3.126-3.440eV and 2.58-3.177eV respectively. The refractive indices and Urbach energies are also determined. Photoluminescence spectra are recorded and studied for excitation of the most intense peaks of wavelengths 378 and 521nm.The luminescence of erbium ion is enhanced by the presence of silver when the concentration of rare earth ion is less than that of silver.

1.Introduction

Glasses can be easily prepared to any shape and personalized to specific applications. Borate glasses are studied more because of their structure made up of random network of BO_3(boroxyl) groups which changes into BO_4 groups on addition of modifier into the glass matrix and forms more open structure due to the increase in number of non-bridging oxygen atoms [1]. Boron Trioxide is an excellent glass former that exists in both three and four coordinated bonding, has high covalent B-O bond strength able to form stable glasses, and shows high potential for new optical devices because of their good rare earth ions solubility [2, 3]. In recent times, RE and silver doped germinate, tellurite, phosphate, bismuth glasses are widely explored for luminescence improvement [4-8].But the increase in florescence is limited by energy transfer between lanthanide ions known as quenching due to concentration of RE ions. In order to overcome the concentration quenching of rare earth ions [9] metallic nanoparticles are receiving considerable attention as nanoparticles contribution for enhancement of the rare earth ions photoluminescence [10-17]. As the intensity of electric field in the vicinity of the lanthanide ion increases, the luminescence of the rare earth ion enhances [18] or there is sufficient energy relocation to the glowing centers [19].Keeping this in intention , more attempt were put to create noble metal and lanthanide doped glasses [20,21]. The noble metals such as copper, gold and silver develop as nanoparticles on the action of heat, this happens due to the conversion of noble

metal ion into neutral atoms which in turn stimulate joint wavering known as surface Plasmon resonance (SPR) in these metal particles in the visible frequency range [22].This collective oscillation in turn leads to the amplification of the luminescence of the lanthanide ions [23]. Here in this piece of work we have created erbium doped sodium barium borate glass with and without silver chloride and physical, structural, optical absorption and luminescence properties are investigated which can be used as high efficient luminescence materials.

2. Experimental

Glass samples with composition $(60\text{-}x\text{-}y)B_2O_3+30Na_2CO_3+10BaO+xEr_2O_3+yAgCl$ (where x=0,0.5,1.0 and Y=0.0, 1.0 mol %) created by the usual melting and quenching route.All the chemicals involved in the glass preparation were weighed carefully using microbalance and powdered using mortar and pestle and then mixed thoroughly. The crucible containing this mixture is placed in the furnace and when a clear melt is formed without any bubbles then melt is quenched at temperature 1050^0C in the brass moulds. Glass samples of size 1cm diameter and thickness 1mm are prepared. These samples were annealed at 300^0C for 2 hours to remove the thermal strain. The glass samples are polished and the glass pieces are powdered for different measurements and characterization. Archimedes principle is employed to determine the densities, of the glasses prepared, which makes use of toluene (density is 0.867g/cm^3) as raptness liquid as it does not react with the samples. Then by knowing the molar mass and density the molar volume (V_m) can be calculated. Powdered x-ray diffraction spectra is taken and analyzed for glassy nature of the samples.

The spectra of absorption were obtained in the standard UV Visible range of 200nm to 1100nm by means of Perkin-Lambda-30 spectrometer**.** The densities (ρ), molar volumes (V_m) refractive indices (n) values optical band gaps for direct and indirect transitions Urbach energy(E_u), polaron radii(R_p),ionic radii(R_i) and Field strength(F) found were arranged in the table 1. and table 2. Photoluminescence emission spectra was recorded for the most intense absorption peaks 378nm and 521nm.The glass sample with only silver chloride and without erbium oxide is studied after heat treatment.

3. Results and Discussion

3.1. *Density and Molar volume*

The values of densities and the molar volumes found are as depicted in the figure 1.The density increases with increase in rare earth concentration as rare earth oxide is heaviest among all chemicals used. The values of densities and molar volumes obtained are exactly reciprocal of the other as expected.

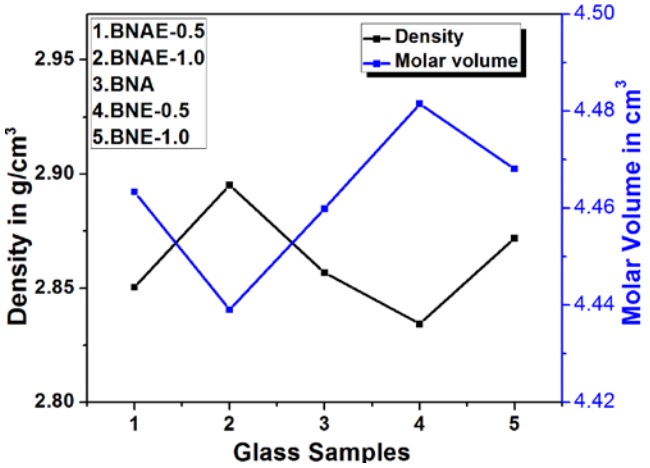

Figure 1. Density and molar Volumes of the erbium doped sodium barium borate glass with and without silver chloride**.**

3.2. *Powdered X-Ray Diffraction*

The D-8 X-ray diffractometer is used for the x-ray spectrum of powdered diffraction pattern using 1.5406 A^0 from Cu K_α radiations in the scanning rate of 2^0/min. The obtained x ray pattern is shown in the figure 2.The spectra shows no sharp absorption peaks instead a broad hump at 28.34^0 and a small hump at 44.65^0 is seen which indicates the amorphous nature of the glass samples.

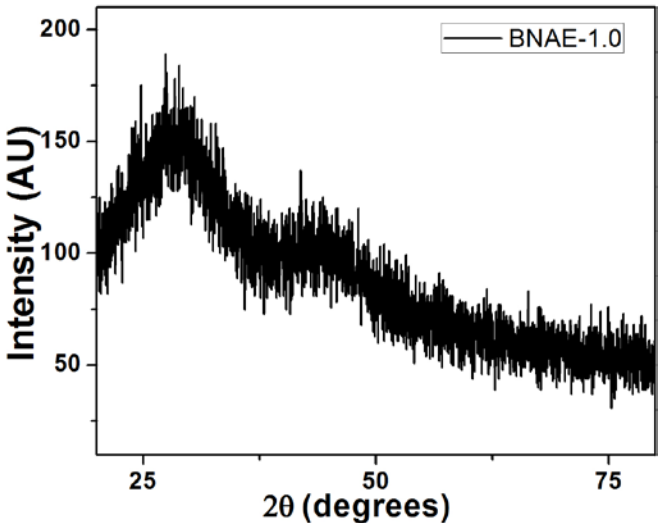

Figure 2. X-ray diffraction Pattern of the erbium doped sodium barium borate glass with silver chloride.

3.3.*UV-Visible Spectra*

The UV-Visible absorption spectra of Erbium doped borate glass is shown in the figure 3. and figure 4. The absorption spectrum consists of eleven absorption peaks at 366,378,408,442,452,489, 521,545,652,800 and 977nm corresponding to transitions to $^4G_{9/2}$, $^4G_{11/2}$, (^2G ^4F $^2H)_{9/2}$, $^4F_{3/2}$,$^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ from ground $^4I_{15/2}$ of Erbium in the 4f - 4f electronic transition [24,25].

The most intense peaks observed are $^4G_{11/2}$, $^2H_{9/2}$ at 378 and 521nm respectively. The optical coefficient of absorption [25]

$$\alpha(\lambda) = 2.303(A/d) \quad (1)$$

where d is the thickness of the sample A is the absorbance.

The optical band gap energy E_{opt} which describes direct(E_d) and indirect (E_i) band energy difference between valance and transmission bands of these glasses were obtained by the equation[25]

$$\alpha h\nu = B(h\nu - E_{opt})^n \quad (2)$$

where α is the coefficient of absorption , incident packet of energy being hν, B is constant of electron transition constant n=2 and n=1/2 for indirect gap and direct gap energies respectively. The E_d and E_i are found by drawing the tangents at $(\alpha h\nu)^2=0$ and $(\alpha h\nu)^{1/2}=0$ to the plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ against energy of the photon incident in turn.

A typical plot of $(\alpha h\nu)^2$ versus hν of Erbium doped Sodium Barium Borate glass with Silver chloride and the variation of direct and indirect transition energies of the samples are as depicted in the figure 5a and figure 5b.

In noncrystalline substances Urbach predicted, that the absorption at the phonon energy lower than the optical gap is the termination absorption that depends exponentially on the energy of the photon. The degree of band tail in the not permitted energy, band gap can be predicted by means of the formula [25]

$$\alpha(\nu) = Be\hat{}(h\nu/E\_tail\ ) \quad (3)$$

where B, a constant and E_{tail} the size of the band tails in the transition states of electrons.

Table 1. Density(ρ), Molar volume($V_)$, Refractive index(n), Band gap Energies(E_d and E_i) and Urbach Energy(E_u) of erbium oxide doped Sodium Barium Borate glass with silver chloride

Glass Sample Code	Density (ρ)g/cm^3	Molar Volume V_m(cm$^{3)}$	Refractive Index n	Band Gap Energy(eV)		Urbach Energy (eV)
				Direct E_d	Indirect E_i	E_u
BNEA-0.5	2.8503	4.463	2.364	3.126	2.580	0.953
BNEA-1.0	2.8952	4.439	2.330	3.260	2.999	0.337
BNA	2.8568	4.460	2.288	3.440	3.102	0.277
BNE-0.5	2.8343	4.482	2.299	3.390	3.177	0.247
BNE-1.0	2.8719	4.468	2.313	3.330	2.870	0.385

where B, a constant and E_{tail} the size of the band tails in the transition states of electrons.

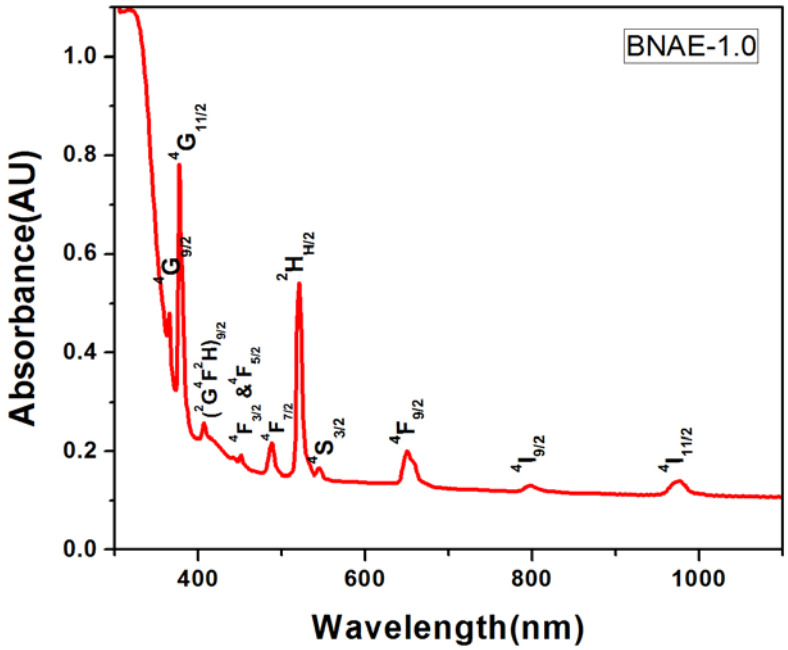

Figure 3.A typical UV-Visible Spectrum of the erbium doped sodium barium borate glass with silver chloride with transitions labeled

The values of Urbach energies are found by (1/ slope) in the straight-line part of the curves of ln(α) against hν in the lesser photon energy areas. The Variation of ln(α) versus hν is shown in the figure 6.The Urbach energy is a measure of the amount of defects in the network of glass.

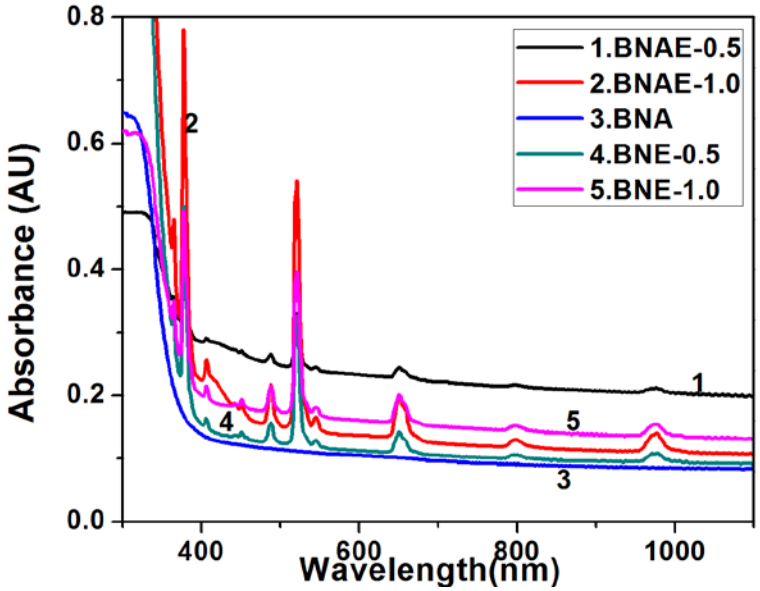

Figure 4. UV-Visible Spectra of the Erbium doped Sodium Barium Borate glass with and without silver chloride.

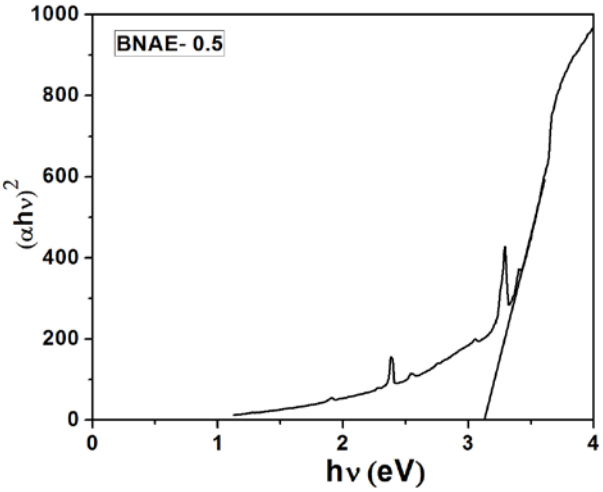

Figure 5a) .A typical $(\alpha h\nu)^2$versus hν of Erbium doped Sodium Barium Borate glass with silver chloride.

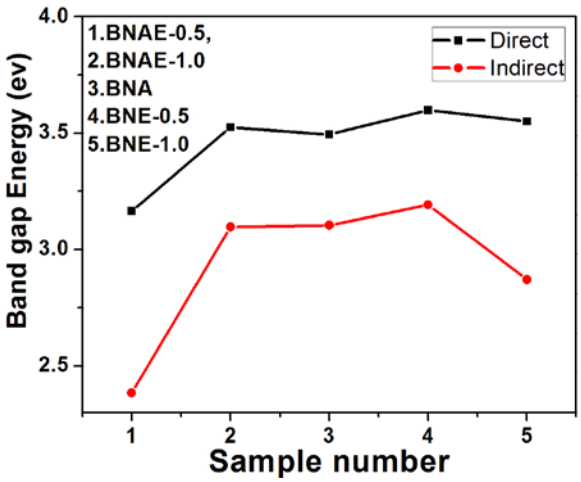

Figure 5b). Variation of Direct (E_d) and Indirect ($E_{i)}$ energy gap of the samples

Table 2. Polaron radii,Ionic radii and Field strength of erbium ion in erbium oxide doped sodium barium borate glass with silver chloride

Glass Code	Rp	Ri	F
BNEA-0.5	$2.132*10^{-8}$	$5.292*10^{-8}$	$6.600*10^{15}$
BNEA-1.0	$1.700*10^{-8}$	$4.193*10^{-8}$	$1.038*10^{15}$
BNE-0.5	$2.135*10^{-8}$	$5.299*10^{-8}$	$6.582*10^{15}$
BNE-1.0	$1.693*10^{-8}$	$4.203*10^{-8}$	$1.047*10^{15}$

3.4. *Surface Plasmon Resonance*

The AgCl doped glass without rare earth oxide shows Surface Plasmon peak shown in the figure 7.at around 437nm and 431 nm on heat treatment of 450^{0}C for 2 and 4 hrs respectively due to the formation of silver nanoparticles. The SPR peak depends on the matrix and the annealing temperature and duration.

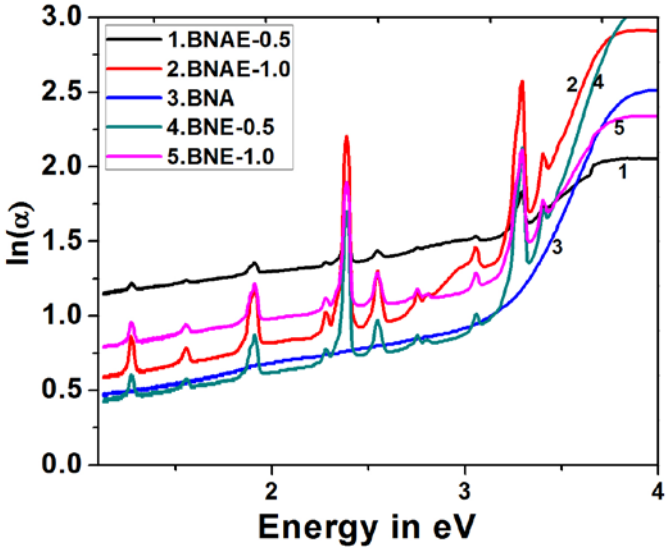

Figure 6. Variation of ln(α) Versus Energy(hν) for the calculation of UrbachEnergy Erbium doped Sodium Barium Borate glass with and without silver chloride.

A collective resonance oscillations of conduction electrons of metal nanoparticles with optical electromagnetic wave is well known as surface plasmon resonance changes the radiative decay rates [26].The position of SPR peak depends on the refractive index of the matrix, the particle size and shape of the silver nanoparticles [27].

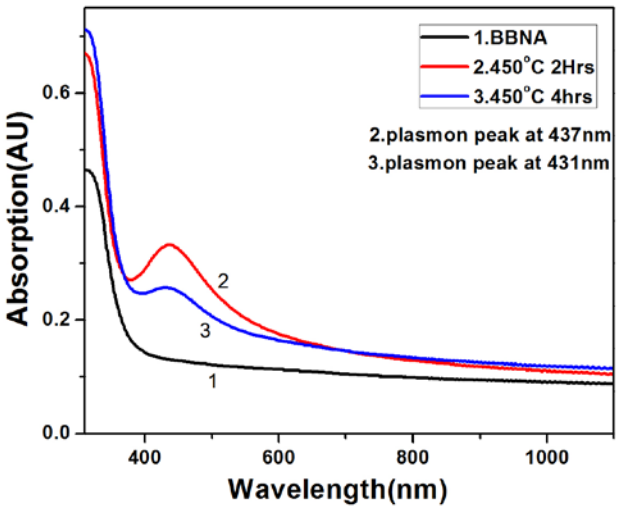

Figure 7. Absorption spectra of Sodium Barium Borate glass with silver chloride with and without nanoparticles after heat treatment

3.5. *Photoluminescence Studies*

Photoluminescence spectra shows peaks at 417,517 and 622nm for 378nm excitation, 417nm being the most prominent one. For 378nm excitation intensity of the 417nm peak intensity enhances by a factor 37.5% for 0.5 mol% of erbium and the same peak decreases its intensity by a factor 28.83% for 1mol% of erbium in presence of silver chloride as shown in the figure 8a and 8b.

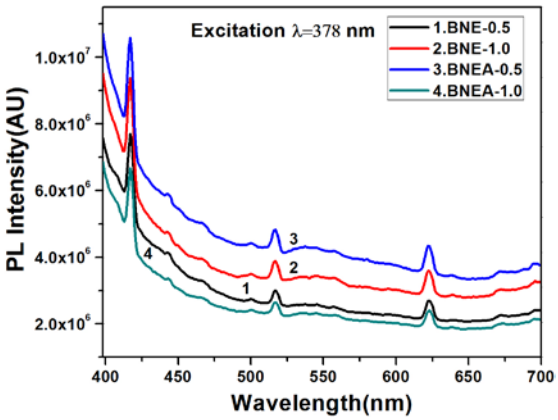

Figure 8a) Photoluminescence spectra of Sodium Barium Borate glass with silver chloride for excitation wavelength 378nm.

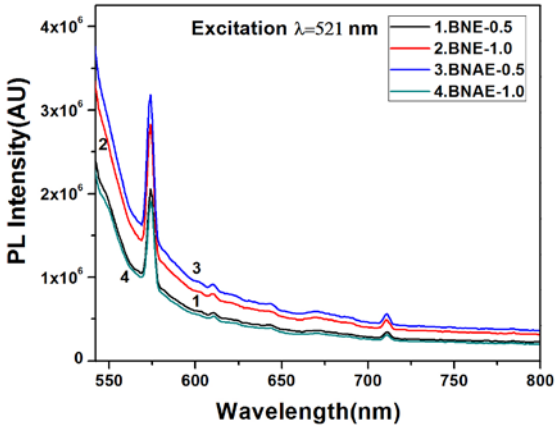

Figure 8b) Photoluminescence spectra of Sodium Barium Borate glass with silver chloride for excitation wavelength 521nm

For 521nm excitation photoluminescence spectra shows peaks at 574, 610 and 711 nm where 574 nm being the most intense emmission peak. With 521nm excitation, intensity of the 574nm peak enhances by a factor 54.89% for 0.5 mol% of erbium and the same peak decreases its intensity by a factor 32.76% for 1mol% of erbium in presence of silver chloride.

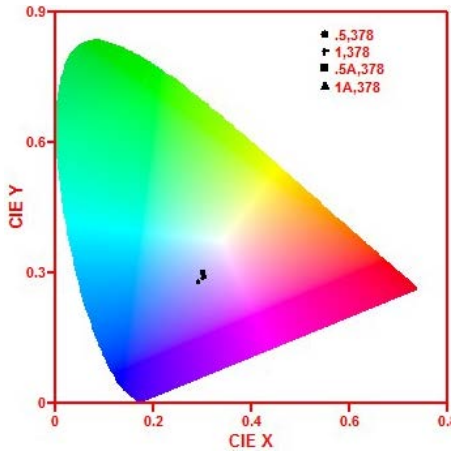

Figure 9a). CIE Chromaticity diagram of Erbium oxide doped Sodium Barium Borate glass with silver chloride for 378nm excitation.

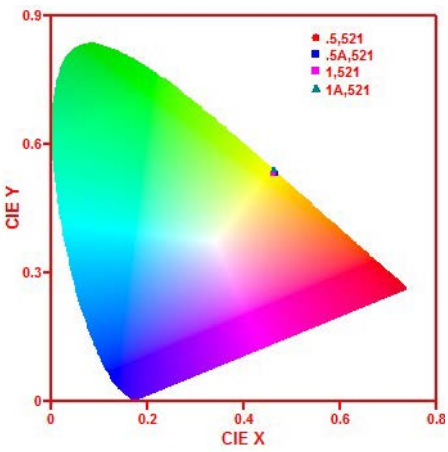

Figure 9b). CIE Chromaticity diagram of Erbium oxide doped Sodium Barium Borate glass with silver chloride for 521nm excitation.

Lower concentration of erbium oxide is favoured by the presence of silver chloride.The upsurge in the luminescence is attributed to the increase in local field around the rare earth ion due to the SPR of silver nanoparticles and also due to the transfer of energy from silver nanoparticles to the rare earth

ions and the quenching of luminiscence credited due to the reverse transfer of energy from rare earth to the silver nanoparticle. From the Commision International de l'Eclairage de France 1931 Standards(CIE) Chromaticity diagram it also confirmed that 378nm excitation emmites in the violet and 521nm excitation emmites in the yelow region as shown in the figure 9a and figure 9b respectively. Hence these materials can be used as luminescent material in the violet and yellow region.

4.Conclusion

Variation of the Absorption characteristics of rare earth (Er^{+3}) doped glasses with silver is an important concept in photonics. Erbium (Er^{3+}) doped glasses with composition (60-x-y) B_2O_3- 30Na_2O_3 -10BaO-x Er2O3-yAgCl where x=0.5, 1.0 and y=1.0 mol% are synthesized using melt-quenching method. The density increases with the rare earth concentration. As there are no sharp peaks in the x-ray spectrum which ratifies non-crystalline arrangement of the sample. The effects of Er_2O_3 concentration on the absorption spectral features of these glasses with and without silver chloride are examined. The UV-Visible spectra reveal eleven absorption peaks corresponding to the transitions of Er^3+ ion among them 378 and 521nm are highly intense. The sample without rare earth shows no peaks which indicate rare earth ion plays an important role in the glass matrix. The energy band gap values are found to be in the range 3.126 to 3.440eV for direct and 2.580 to 3.177eV for indirect transitions. The Urbach energy and refractive indices are calculated and tabulated. These Erbium doped glasses catch place in solid state laser applications. The silver doped glass shows surface plasmon peak due to the formation of silver nanoparticles on heat treatment which in turn may change the luminescence of erbium ion is the scope of further study. The photoluminescence studies and the CIE chromaticity diagrams confirm the emission is in the blue and yellow parts of the visible spectrum for the excitation wavelength of 378nm and 521nm respectively.

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