International Journal of Academic Research
ISSN: 2348-7666 Vol.1 Issue-4 (1) (Special), October-December 2014

Absorption and photoluminescence spectra of Rare-Earths Doped Chlorophosphate Glasses

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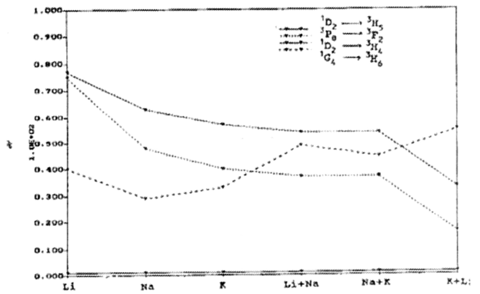
This paper reports on the systematic characterization of absorption and emission spectra of RE-ion such as **Tm^{3+}**-doped **$(NaPO_3)_6$-$BaCl_2$-$ZnCl_2$** with **LiCl / NaCl / KCl** as the glass network modifiers (NWM). These rare-earth doped chlorophosphate glasses play a vital role in the advanced glass technology in the development of glass windows, lenses and other optical components, laser glass hosts and also in energy transfer systems. A good correlation has been made between the emission results with the absorption data successfully. Energy level schemes have been shown to understand the emission mechanisms involved in all the optical materials.

Results: On examining the spectral features concerning the absorption and photoluminescence of six **Tm^{3+}** -doped glasses (A-F), it is clearly evident that glass-**A**, with 20 mol% LiCl as NWM, has shown peak intensities brighter compared with other glasses studied. Also the Judd- Ofelt intensity parameter (**Ω_2**) has got maximum value in glass-A. Based on the emission peak relative intensities , the glasses under study are arranged as following, in describing their fluorescence efficiency.

Glass-A > Glass- C > Glass- B > Glass-F > Glass -E > Glass- D.

The variations in Branching Ratio's (?R%) concerning the emission transitions with cation change in the alkali content (RCl) of the Tm3+-doped glasses is shown in the Fig. below:



1. Introduction:

In recent years a great deal of work in the development and the analysis of a few heavy-metal fluoride (HMF) glasses doped with certain tripositive lanthanides for understanding their optical behavior [1-9]. These glasses were identified as possible optical materials because of their refractive indices (near1.5), hardness, transparency, resistance towards moisture and increased transmission in the IR. Hence, they are being explicitly useful as laser materials (5,6). Recently, we undertook synthesizing and characterizing a new family of glasses based on the chlorophosphates containing the rare earths Pr^{3+} , Nd^{3+} , Ho^{3+} and Er^{3+} [10- 13]. This paper brings out the different physical, absorption and photoluminescence properties of the chlorophosphate glasses doped with Tm^{3+} ions.

2. Experimental:

The chemicals (spectral pure) used in synthesizing the Tm^{3+} glasses are as follows: $(NaPO_3)_6$, $ZnCl_2$, $BaCl_2$, LiCl , NaCl , KCl and

$TmCl_3$ .The chosen chemical compositions (M%) of the chlorophosphate glasses are given in **Table1.**

Table 1. The chemical compositions (in molar %) of Tm^{3+} -doped chlorophosphate glasses

Glass	$TmCl_3$	$(NaPO_3)_6$	$BaCl_2$	$ZnCl_2$	LiCl	NaCl	KCl	Number of Thulium ions (10^{22} cm^{-3})
A	2	48	20	10	20	--	--	1.053
B	2	48	20	10	---	20	–	1.128
C	2	48	20	10	---	--	20	1.077
D	2	48	20	10	10	10	--	0.967
E	2	48	20	10	---	10	10	0.953
F	2	48	20	10	10	--	10	1.127

The chemical mixtures for each of the six batches studied, were powdered on an agate mortar for homogeneous mixing and that were melted in silica crucibles at temperatures of 900 -950^0 C for about 10 - 15 min. in a silicon carbide electric furnace. The melts were transformed into glasses (3- 4 cm in diameter) with a thickness of 0.2 cm, by employing quenching technique [14]. The above glasses exhibited good transmission up to 4 µm.

The refractive indices (n_d) of the glasses were measured on an Abbe refractometer at λ =5893 A^0. The measured indices are in the range of n_d = 1.486 + 0.0004 for all six glasses studied. The glass densities have been determined by the Archimedes principle with xylene as the immersion liquid. The measured and other related physical properties of the Tm^{3+} -doped glasses are listed in **Table 2.**

Table.2. Physical Properties of Tm^{3+} -doped chlorophosphate glasses.

Glass	**Density D (g/cm^3)**	**Av. Molecular weight M (g)**	**Atomic volume V(g/cm^3 at)**	**Molar refraction R_M(cm^{-3})**	**Polaron radius r_p (A^0)**	**Interionic distance r_i (A^0)**	**Electronic polarizability α_e (10^{23} cm^3)**
A	3.256	372.40	7.247	32.87	1.839	4.562	1.30
B	3.517	375.60	6.767	30.68	1.798	4.459	1.22
C	3.386	378.80	7.089	32.14	1.825	4.528	1.27
D	2.986	374.00	7.936	35.97	1.895	4.702	1.42
E	2.984	377.60	8.009	36.29	1.901	4.717	1.43
F	3.516	375.60	6.769	30.68	1.797	4.460	1.22

The recorded absorption spectra of Tm glasses appear similar in peak positions of the levels measured from one to another glass, however, the absorption intensities of these bands were found to vary significantly with changes in the environment surrounding the Tm3+ ions in the glass matrices. Therefore, a single absorption spectrum for Glass A , is shown in Fig.1 ,as the representative specimen profile for the six recoded profiles. The emission spectra of these glasses were recorded on a 650-10 S Hitachi fluorescence spectrophotometer with a xenon arc lamp (150 W) as the source of excitation. A single excitation and emission spectra for Glass A are shown in Figs.2 and 3, respectively.

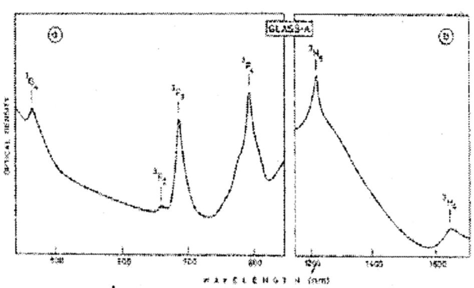


Fig.1. Visible and NIR Absorption Spectra of Tm3+-doped Glass-A.

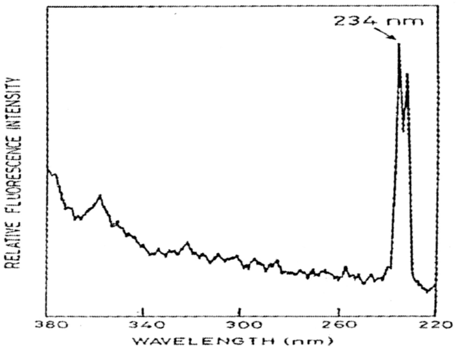


Fig.2. Excitation spectrum of Tm3+ -doped glass.

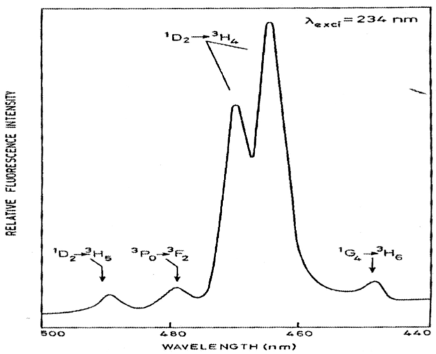


Fig.3. Photoluminescence spectrum of Tm3+ - doped glass-A

3. Results and discussion:

3.1. Physical properties

From the measured densities and refractive indices, other physical properties such as atomic volume, molar refractivity, polaron radius, interionic distance and electronic polarizability for the glasses were computed by using the previously published expressions (1,2).These physical properties are summarized in Table.2. The Tm^{3+} -ion concentration of each glass was evaluated using their molecular weight and density and these results are given in Table.1. Based on the values of the physical properties, glass E appears to be somewhat different compared to the other five glasses. The glasses were found to be unaffected by atmospheric moisture in the laboratory.

3.2. Absorption spectra

The absorption spectra of the Tm^{3+} glasses have shown the following energy states, $^3H_6 \rightarrow {}^3F_4$, $^3H^5$, $^3H^4$, $^3F_3$, $^3F_2$ and $^1G_4$ (fig.1). Among these six, three well defined levels are selected to determine the spectral oscillator strengths of the absorption levels [15]. By performing a least-squares fit analysis [16, 22], the Judd-Ofelt parameters for the absorption spectrum of each glass was computed and are presented in Table.3. On examining the data given in Table.3, it is noticed that the Judd-Ofelt parameter $\mathbf{\Omega_2}$ is found to dominate over $\mathbf{\Omega_4}$ and $\mathbf{\Omega_6}$ in all the six glasses.

Table.3. The Judd- Ofelt parameters of Tm^{3+} -doped chlorophosphate glasses.

Parameter	Glass A	Glass B	Glass C	Glass D	Glass E	Glass F
?$_2$ (10^{20} cm^2)	11.894	5.877	5.086	6.873	6.337	2.122
?$_4$ (10^{20} cm^2)	0.143	0.716	1.489	3.772	3.262	4.135
?$_6$ (10^{20} cm^2)	3.404	4.172	3.678	2.326	2.658	1.289

The relative changes observed in properties such as the Judd-Ofelt and Hypersensitive transitions (for Tm^{3+} ion: $\mathbf{^3H_6 \rightarrow {}^3F_4}$) of these glasses as a function of alkali species are shown in **Fig.4 (a,b).**

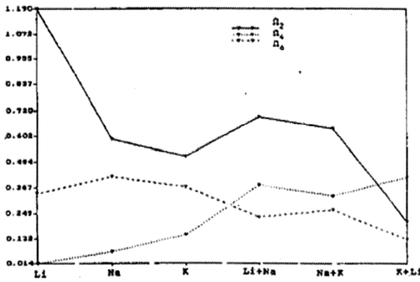


Fig. 4a Variations in Judd-Ofelt Intensity (Ω_λ 10^{20}cm^2) parameters with the cation change in the alkali content (RCl) of the Tm3+: Glasses.

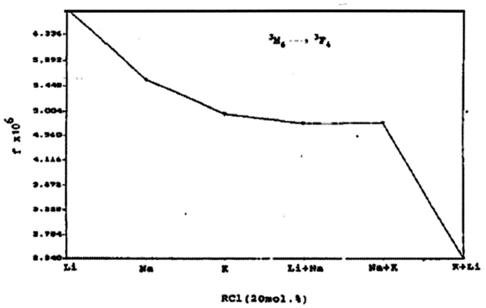


Fig. 4b Variations in Spectral Intensity of the Hypersensitive Transition ($^3H_6 \rightarrow {}^3F_4$) with the cation change in the alkali content of the Tm3+ : Glasses

From the earlier reports, it was understood that Ω_2 could depend mainly on the covalency of the ligand field and Ω_4, Ω_6 possibly be the indicators of the viscosity in vitreous materials. Hence, Ω_2 could depend on the "short range effects" and other two Ω_4, Ω_6 depend mainly on the "long range effects". The hypersensitive transition intensities have been significantly influenced by Ω_2 factor mainly with a little supplement effect from Ω_4 as well.

From the diagrams shown in **Fig.4(a,b),** the trends in intensities of the hypersensitive transitions could be arranged (in descending order) as follows, depending on the variations in the alkali content of the chlorophosphate glasses:

Tm3+ ion ($^3H_6 \rightarrow {}^3F_4$) : Li > Na > K > (Na + K) > (Li + Na) > (K + Li) .

3.3. Emission properties

The recorded photoluminescence spectra of Tm^{3+} -doped glasses show the emission levels given in Table.4.

Emission transition	Wavelength (λ nm)
$^1D_2 \rightarrow {}^3H_5$	490
$^3P_0 \rightarrow {}^3F_2$	480
$^1D_2 \rightarrow {}^3H_4$ (I)	470
$^1D_2 \rightarrow {}^3H_4$ (II)	465
$^1G_4 \rightarrow {}^3H_6$	450

The Judd-Ofelt factors were used [23-26], along with the measured photoluminescence spectral features, to estimate the radiative properties such as the radiative transition probability (A), total transition probability **(A_T)**, branching ratio **(β_R %)** and the stimulated emission cross-section (σ_P^E). Table 5. and 6. Show the branching ratio **(β_R %)** and the stimulated emission cross-sections (σ_P^E) for the measured emission levels of the **Tm^{3+}**-glasses, respectively.

Table.5. The branching ratios (**β_R %**) of the lasing transitions of **Tm^{3+}** -doped chlorophosphate glasses.

Glass	$^1D_2 \rightarrow {}^3H_5$	$^3P_0 \rightarrow {}^3F_2$	$^1D_2 \rightarrow {}^3H_4$ (I)	$^1D_2 \rightarrow {}^3H_4$ (II)	$^1G_4 \rightarrow {}^3H_6$
A	1	75	77	77	40
B	1	48	63	63	29
C	1	40	57	57	33
D	1	37	54	54	49
E	1	37	54	54	45
F	1	16	33	33	55

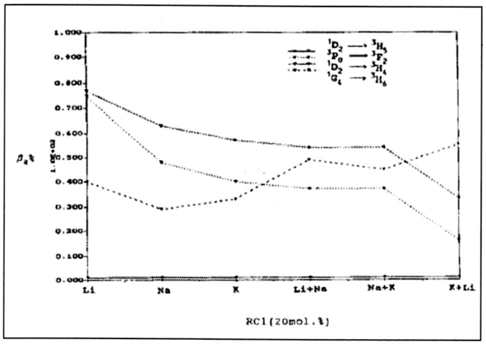
Table.6. Emission wavelength (λnm), effective band-width (Δλ nm), and stimulated emission cross-section (σpEx1020) for the measured emission transitions of Tm^{3+}-doped Glasses.

Tran-sition	Para-meters	Glass-A	Glass-B	Glass-C	Glass-D	Glass-E	Glass-F
$^1D_4 \rightarrow {}^3H_5$	λ	489	491	489	490	491	491.5
	Δλ	2.5	3	3.5	3.5	3	4
	σ_P	0.30	0.30	0.23	0.16	0.21	0.09
$^3P_0 \rightarrow {}^3F_2$	λ	479	481	479	480	481	479.5
	Δλ	5	3.5	4	5.5	4	4.5
	σ_P	57.40	41.20	30.66	48.30	38.84	11.42
$^1D_2 \rightarrow {}^3H_4$ (I)	λ	470	471	468.5	468	470	469
	Δλ	505	4.5	6	6	6	6.5
	σ_P	18.90	11.90	7078	10.68	10.00	3.70
$^1D_2 \rightarrow {}^3H_4$ (II)	λ	465	466	464	464.5	465	464.5
	Δλ	5	8	8.5	7	8.5	8
	σ_P	19.90	6.44	5.29	8.88	6.76	2.89
$^1G_4 \rightarrow {}^3H_6$	λ	448.5	450	451	448.5	450	449.5
	Δλ	3.5	3.5	4	3.5	4	3.5
	σ_P	0.10	0.65	0.59	1.05	0.84	0.70

The variations in the branching ratios (**β_R%**) of the fluorescent transitions of the RE doped glasses are shown in **Fig.5.**, to observe the trends due to change in the network modifier ions in the glass composition. The prominent emission transition with a large **β%** usually known as the lasing transition of that ion and the trends are shown here;

Tm^{3+} ion ($^1D_2$ $^3H_4$) : Li > Na > K > (Li +Na) > (K + Na) > (K + Li)

The branching ratios (**β_R%**) are influenced by the magnitudes of the unit tensor operators and Judd-Ofelt parameters as well.



From the results, it is also noticed that the total transition probability (**A_T**) for the transitions (**$^1D_2 \rightarrow {}^3H_5$, $^3H_4$**) are found maximum in the same host. The fluorescent level (**$^1D_2 \rightarrow {}^3H_4$**) has been found split into two components in **Glass-A.**

Based on the emission peak relative intensities, the glasses are arranged as follows in describing their fluorescence efficiency:

Glass-A > Glass-C > Glass- B > Glass- F > Glass-E > Glass-D

Thus, it is noticed that the Glass-**D** has its fluorescence intensities quite low. Another important fluorescent characteristic property namely, the stimulated emission cross-section (σ_p^E) values relating to the lasing transitions **$^1D^2 \rightarrow {}^3H_4$** (2 components) and **$^3P_0 \rightarrow {}^3F_2$** are in their maximum for **Glass-A**.

In summary, it could be concluded that amongst the six **Tm^{3+}**-glasses studied, particularly the **Glass-A,** with 20 mol% of **LiCl,** becomes a suitable chemical composition as a laser glass. Thus the application of the Judd-Ofelt theory to the absorption and fluorescence spectra of the Tm3+-ions in chlorophposphate glasses has allowed to suggest the Glass-A to be a good optical glass among the six glass systems investigated here.

Acknowledgments: The author is pleased to express his profound gratitude to the University Grants Commission, S.E.R.O , Hyderabad, for giving financial support through Minor Research Project.

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