Studies on optical absorption Spectra of certain rare earth ions doped Borotellurite Glasses

P.Suryanagi Reddy [1(*)], Dr P.Saraswathi [2], B.Vani Sree[3], Dr N.Vijaya lakshmi[4]

1. Associate professor of physics S.S.B.N. Degree College, Anantapur. AP. India
2. Asst. professor of physics, S.D.G.S. College, Hindupur. AP. India
3. Asst. professor of chemistry. S.D.G. S. College, Hindupur. AP. India
4. Asst. professor of physics, Govt. Degree College. Kukatpally TS.India.

Author G-mail: bnrp.tdp@gmail.com
drsaraswathiparigi@gmail.com
vanigopal72@gmail.com
vijayanaidu2008@gmail.com

ABSTRACT:

The basic theory which deals with the various physical and the spectroscopic properties of lanthanide activated materials. It has been useful in understanding the lasing efficiencies of the non-crystalline materials towards the progress of the existing awareness in the glass technology. These results describe the formation and property characterization of the Ho^{3+} doped borotellurite glasses. This study gives a detailed analysis on the absorption, have been evaluated for all the glasses are studied. The applicability of Judd – Ofelt theory in understanding the absorption and emission properties of rare earth doped glasses has been verified by combining the absorption spectra computed parametric data with that of measured emission data. **I**n the present study an attempt is made to determine the refractive indices and densities of the glasses and also bring out the formulation of the new series of high quality optical materials and the study carried out the different properties concerning physical, absorption spectra of the rare earth ion Ho^{3+} doped borotellurite glasses.

KEY WORDS: MODEL F-3010 Spectro photometer. H_3BO_3, TeO2, $BaCO_3$, Li_2CO_3, $NaCO_3$, $NaCO_3$, SmF_3, DyF_3 and EuF_3

INTRODUCTION:

According to American Society for Testing Materials (ASTM) "glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing". The glasses found in nature represent molten rock masses, which were extruded and cooled so quickly that they did not have time to become transformed into the usual aggregate of crystalline minerals. The commonest of these natural glasses, obsidian is usually translucent and blackish in color but it is sometimes red, Brown or greenish and some varieties are transparent. It is easily broken into sharp, often elongated pieces, which lend themselves readily to the fashioning of arrow heads, spearheads and knives. Borosilicate glass for laboratory apparatus (Pyrex) is a twentieth century invention. Galileo's work on the motion of the planets with the astronomical telescopes needing glass lenses. Isaac Newton's pioneering work in optics begun in1666. Other basic investigations which required glass apparatus were the classic investigations of the properties of gases (Boyle's law and Charles's law) thermometry, barometry and the development of microscopes. The inorganic non-oxide glasses such as the chalcogenides sharing many general structural similarities with oxides quite unexpected inorganic systems of which the halide, especially fluoride, glasses are the most notable metallic glasses and organic glasses, X- ray diffraction analysis of crystal structures was a particularly exciting field, which had an enormous impact on glass science. Glasses now play an increasingly important role in modern technology. Besides common glass, which is indispensable material in today's economy in architecture, transport, lighting, condition etc., there is a whole set of glasses which enter into more and more sophisticated applications in optics, electronics and opto-electronics, biotechnologies and so on.

EXPERIMENTAL PROCEDURE:

Preparation of Glass: The following are the nine-borotellurite glasses prepared for their spectral analysis.

Table (1)

Glass type	Composition (Mol %)	UV Transmission	IR Transmission
Glass A	$65B_2O_3+2TeO_2+10BaO+22Li_2O+1\ REF_3$	350 nm	4.5 μ m
Glass B	$65B_2O_3+2TeO_2+10BaO+22Na_2O+1\ REF_3$	360nm	4.3 μ m
Glass C	$65B_2O_3+2TeO_2+10BaO+22K_2O+ 1\ REF_3$ (RE = Ho^{3+})	360nm	4.4 μ m

For convenience the glasses have been labeled as Glass A, B, and C respectively. All the chemicals used in the present work were of analytical grade in 99.99% purity. The elements that used were spectrally pure (H_3BO_3, TeO_2, $BaCO_3$,Li_2CO_3,$NaCO_3$,SmF_3,DyF_3 and EuF_3). The rare-earths were purchased from M/S Indian rare-earth Ltd; Udyogmandal, Kerala state and the chemical TeO_2 (99.995 % Purity) was purchased from M/S Aldrich, Toronto, Canada and other chemicals from a local chemical firm. Each of the above batches (8 gm in weight) was collected into an agate mortar to crush them as finer powder for homogeneous mixing. Every time the mortar and the pestle were cleaned properly. The powdered chemicals were collected into silica (or) porcelain crucibles for melting in an electric furnace (900-950^o C). The melts were sand –

witched between two smooth surfaced plates for obtaining the glass samples in circular designs with 1-2 cm in diameter and with thickness of 0.25 cm.

These glasses were prepared by adopting quenching technique [1-5].

Spectral measurements:

Absorption spectra: Absorption spectra for the above mentioned glasses were recorded on Perkin-Elmer 551 in the UV and visible regions. Spectra of solid, liquid and gaseous samples can be recorded by this instrument with an accuracy of 0.5nm. in the range 190-900 nm (5000-12500 cm^{-1}). The block diagram of the instrument is shown in Fig. 1 and the simplified diagram of the optical alignment of the system is shown in Fig.2.

The Wavelength range for these glasses is

Ho^{3+} -------------360----900nm (1)

Judd – Ofelt Theory and Intensity Parameters:

The spectral oscillator – strengths (f) of the absorption bands of rare earth glasses would be in the rage of 10^{-7} -10^{-5}. This has been firstly carried out by Judd and Ofelt in 1966. They have independently brought out an empirical model to calculate the intensities of the forced electric-dipole transitions in the Ln^{3+} spectra. The oscillator strength f_{ed} of the

$(\Psi J \rightarrow \Psi^{|} J^{|})$ transition is given by the equation

$$f_{ed} = \frac{8\pi^2 mcv}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda (\Psi J \| U^\lambda \| \Psi^{|} J^{|})^2 \quad (2)$$

Where n is the refractive index. v is the energy of the transition $(\Psi J \rightarrow \Psi^{|} J^{|})$, Ω_λ are the intensity parameters and $\|U^\lambda\|^2$ are the doubly reduced matrix elements of the unit tensor operator of the rank λ = 2,4,6, calculated from the intermediate coupling approximation. The matrix elements of the unit tensor operator $\|U^\lambda\|^2$ in equation (2) were calculated in the LS-basis using the equation

$$[f^N (\Psi J \| U^\lambda \| \Psi^| J^|] = (-1)^{S-L+J-\lambda} [(2J+1)(2J+1)]^{1\,2} \, X$$

$$\begin{pmatrix} J & J^| & \lambda \\ L^| & L & S \end{pmatrix} [f^N \alpha \, SL \| U^\lambda \| f^N \alpha \, S^| L^|] \qquad (3)$$

The reduced matrix elements on the right hand side are obtained from the works of Nielson and Koster [11]. The matrix elements of the equation (3) were then transformed from the LS-basis to the physical coupling scheme prior to being squared and substituted in the equation (2). The characterization of the spectral intensities of the absorption bands, the material refractive index (n_d) is considered to be playing an important role. Therefore the intensity parameters Ω_λ are obtained by the following expression

$$\Omega_\lambda = \frac{3h\,(2J+1)}{8\,\pi^2\, m\, x\, c} [\, T_\lambda \,] \qquad (4)$$

Where T_λ is Judd-Ofelt intensity parameter; x = [n^2 +2)/9n] = local field correction. The value of Ω_λ could be computed from the factor relating to the glass host T_λ values that are evaluated by performing a least squares fit analysis over the measured absorption band intensities. Now the equation (2) is written as

$$f_{ed} = \Sigma\ \Omega_\lambda\, v\, (\Psi J \| U^\lambda \| \Psi^| J^|)^2$$

$$\lambda = 2,4,6, \qquad (5)$$

The electric dipole and magnetic dipole line strengths (S_{ed} and S_{md}) were calculated from the formulae

$$S_{ed} = e^2 \Sigma\ \Omega_\lambda\, v\, (\Psi J \| U^\lambda \| \Psi^| J^|)^2 \qquad (6)$$

$$\lambda = 2,4,6,$$

$$S^|_{ed} = S_{ed} / e^2$$

And

$$S_{md} = \frac{e^2 h^2}{16\pi^2\, m^2 c^2} (\Psi J \| L + 2S \| \Psi^| J^|)\, 2 \qquad (7)$$

$S^{|}_{md} = S_{md} / e^2$.

The oscillator strength 'f' of a band width energy v (cm^{-1}) is given by

$$f = - \frac{8\pi^2 m \nu [(n^2+2)^2]}{3he(2J+1)\,9n} \; S_{ed} + n^3 S_{md} \qquad \text{------------- (8)}$$

Judd-Ofelt intensity parameters (Ω_λ) for Ho^{3+} glasses are evaluated with procedure along with the required tensor operators are tabulated in (Table.2). On examining the Table.1.we note that the Judd-Ofelt intensity parameters are in the following trend. $\Omega_2 >> \Omega_6 > \Omega_4$

On comparing the results of $\Omega_{2,}$ $\Omega_{4\ \&}$ Ω_6 among the three glasses, it can be observed that glass 'A' is showing better spectral intensities.

Table. 2

Absorption level energies (γ cm $^{-1}$) and squared reduced matrix elements $\| U^\lambda \|^2$ (λ = 2, 4, 6)

For different bands of Sm^{3+} [16] (aquo)

Absorption Levels from the Ground State $^6H_{5/2}$	Energy (γ cm $^{-1}$)	$\| U^2 \|^2$	$\| U^4 \|^2$	$\| U^6 \|^2$
$^4G_{5/2}$	17924	0.0002	0.0007	0
$^4F_{3/2}$	18332	0.0003	0	0
$^4I_{13/2}$	21650	0	0.0030	0.0228

Table.3.

Emission level energies (γ cm $^{-1}$) and squared reduced matrix elements $\| U^{\lambda} \|^2$ (λ = 2, 4, 6)

For different bands of Sm^{3+} [22]

Transition	Energy (γ cm $^{-1}$)	$\| U^2 \|^2$	$\| U^4 \|^2$	$\| U^6 \|^2$
$^4G_{5/2} \rightarrow {}^6F_{11/2}$	7448	0	0	0
$\rightarrow {}^6F_{9/2}$	8842	0.0016	0.0002	0.0002
$\rightarrow {}^6F_{7/2}$	10022	0	0.0015	0.0015
$\rightarrow {}^6F_{5/2}$	10800	0.0062	0.0014	0
$\rightarrow {}^6F_{3/2}$	11394	0.0010	0	0
$\rightarrow {}^6H_{5/2}$	11511	0	0	0
$\rightarrow {}^6F_{½}$	11644	0	0	0
$\rightarrow {}^6F_{13/2}$	12959	0	0	0.0014
$\rightarrow {}^6H_{11/2}$	14364	0	0.0045	0.0018
$\rightarrow {}^6H_{9/2}$	15690	0.0096	0.0061	0.0019
$\rightarrow {}^6H_{7/2}$	16896	0	0.0078	0.0075
$\rightarrow {}^6H_{5/2}$	17930	0.0002	0.0007	0

EXPERIMENTAL SET UP: The experimental set up for this study is shown in the figures.

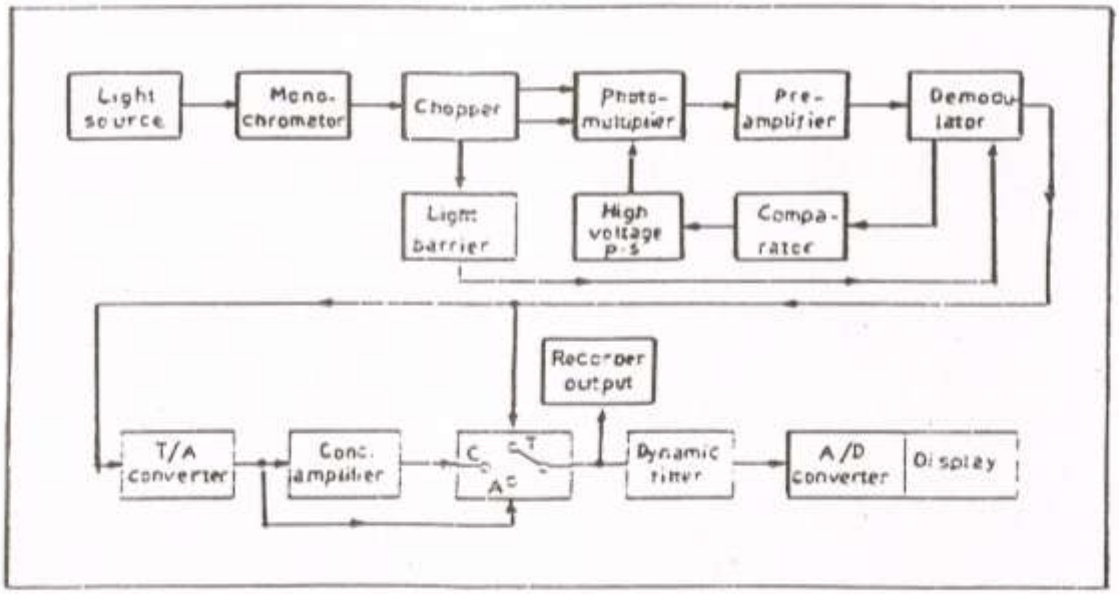

FIG.1: PERKIN-ELMER-551 RECORDING SPECTROPHOTOMETER (Block diagram)

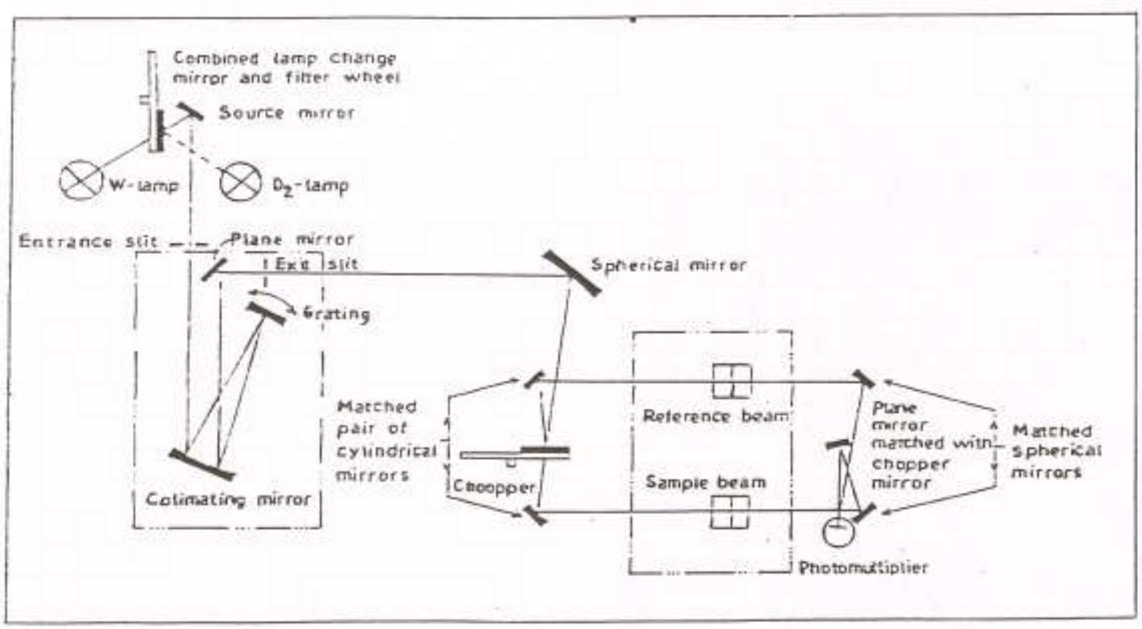

FIG.2: PERKIN-ELMER-551 RECORDING SPECTROPHOTOMETER (Optical alignment)

OUTLINE OF INSTRUMENT

Principle of Measurement

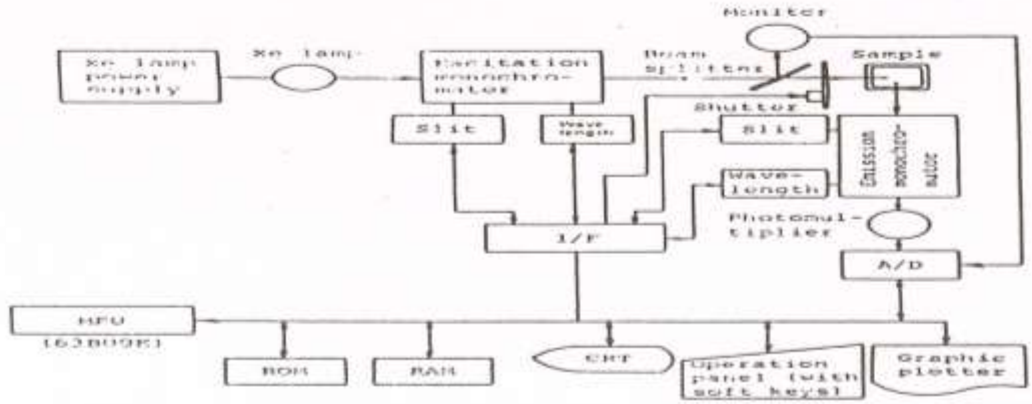

Fig. 3 : Functional block diagram of the Model F-3010

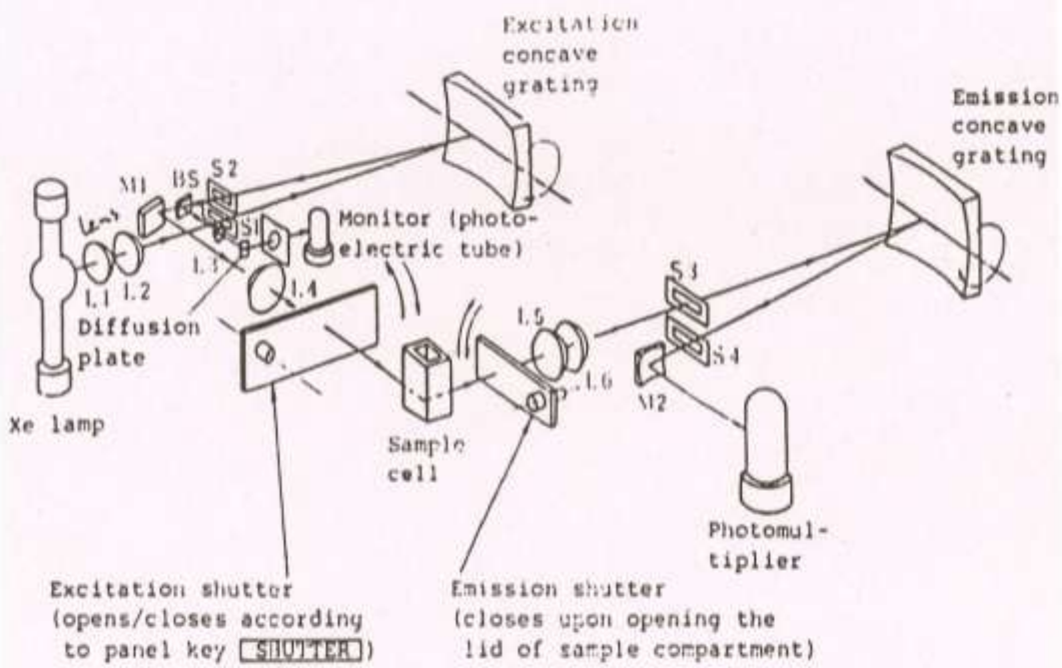

Fig. 4 : Optical system configuration.

RESULTS AND DISCUSSIONS:

Holmium doped glasses as laser glasses: There has been one demonstration [8] of Ho^{3+} doped waveguide laser that employed a silica fiber co-doped with germania. Laser emission due to the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition at 651 nm was excited by an argon laser at 488 nm. The fluorescence peak caused by this transition is relatively narrow at only 3.3 nm, suggesting that only a single pair of stark levels is involved. In fact the fluorescence spectrum of Ho^{3+} in high – silica glass has considerable fine structure [9] suggesting that inhomogeneous broadening of the energy levels is not severe. The detestable level does, however, exhibit a non exponential decay with a life time of 1.7 ms. This long life time, the four-level nature of the system, and large stimulated cross section due to the narrowness of the prospect of an efficient, low- threshold, Q- switched fiber laser [9]. Although the lasing properties of this ion have not been used in a ZBLAN waveguide, the fluorescence spectrum [10] is also finely structured, suggesting that in this host glass Ho^{3+} will exhibit similarly attractive properties. In addition the branching ratio is slightly different, indication that other visible transitions may also be made to laser.The determination of refractive indices (n_d) at 589.3 nm and densities of these glasses were carried out and the results are given below.

TABLE (4)

Glass type	n_d (λ589.3 nm)	D (gm^{-3})
Glass A	1.5656	2.106
Glass B	1.5846	2.199
Glass C	1.5125	2.145

The above table clearly describes the dependence of the refractive index and density values both on the changes made in the alkali content and also on the rare earth ions present in the glass systems examined. Fig (1), fig (2) and fig (3) shows the graphs of Absorption spectra of Glass A, Glass B, and Glass C.

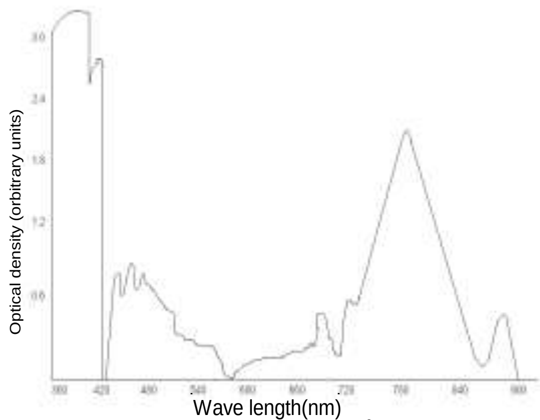

Fig .1.(a):Absorption Spectra of Ho^{3+} doped Glass A

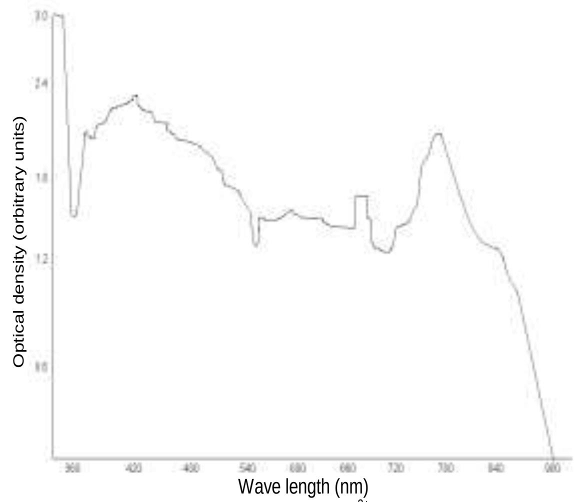

Fig .1.(a):Absorption Spectra of Ho^{3+} doped Glass B

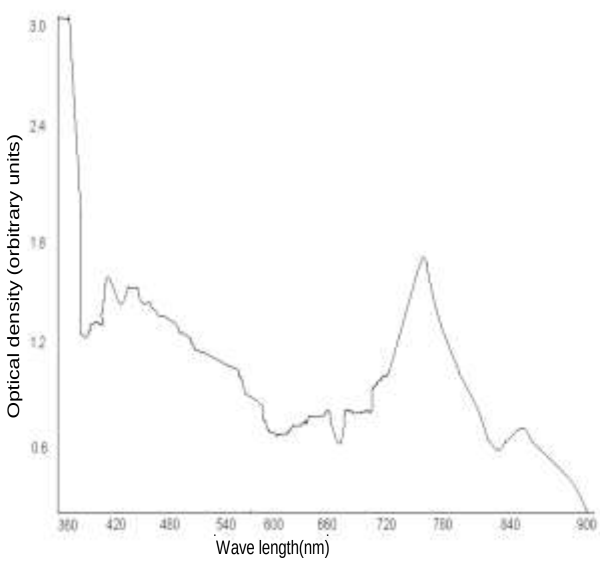

Fig .!.(c): Absorbtion Spectra of Ho^{3+} doped Glass C

Conclusion:

In the present study the refractive indices and densities of the glasses were determined and also brought out the formulation of the new series of high quality optical materials and the study carried out the different properties concerning physical, absorption spectra of the rare earth ion Ho^{3+} doped borotellurite glasses.

Acknowledgements:

It gives me an immense pleasure to express our gratitude to our venerable teacher and research supervisor Dr C.V.Krishna reddy Associate professor of physics P.G.centre Kurnool affiliated to S.K.University Anantapur for his valuable guidance in completing the work , we thank our institution for providing necessary facilities, the support staff, administrative staff, colleagues, family members and friends for their support.

References:

[1]. C.D.Coleman, W.R.Bozman and W.F.Meggers.Tables of Wave numbers

[National Bureau of Standards, Washington D.C., 1960]

[2] A. Pual, Chemistry of glasses, chapman & Hall, London (1983)

[3]. S.V.J.Lakshman and S.Srinivas Wave number Tables (2000-900 A^{o})

1. Maruti Book Depot. Guntur, India (1988)

[4]. S.V.J.Lakshman ,Problems in spectroscopy, COSTED, Madras, India (1988)

[5]. G. Amernath, S.Buddhudu, F.J.Bryant, XiLuo,B.Yu and S.Huang

J.Lumin.47 (19991) 255

[6]. K.Annapurna, and J.V.Sathyanarayna, S.Bhuddhudu and a.Mandelis

J. Alloys & Comp. 216 (1994) 281

[7] K.Annapurna and S.Buddhudu ,J.Phys. D: Appl.Phys.26 (1993) 302

[8]. J.V.Sathyanarayana, K.Annapurna and S.Buddhudu,Mater .Res.Bull. 29 (1994 1263

[9] M.A.Saltzberg and H.H.Yung , J.Amer, Cerarn.Soc.73 (1990) 2897

[10]. Tammann, G , Der Glaszustand Leipzig:L.3 (1933)

[11]. J.Sugar, Phys.Rev.Lett.14 (1965) 731