Article

Spectroscopic studies on PbO-As2O3 glasses doped with V2O5

A. Chitti Babua, D.V. Krishna Reddya, T. Sambasiva Raoa , P. Arun Kumara, B. Shiva Rami Reddya, M. Rami Reddy [a*]

[a]Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar 522510, India
[b]Department of Physics, Govt. Degree College, Atmakur, Kurnool, A.P,India.

Abstract

The system of glass samples PbO-As_2O_3 containing different concentrations V_2O_5 (ranging from 0.2 to 1.0 mol %) were prepared by a conventional melt quenching technique. The glasses were characterized by optical absorption, infrared Spectra, photon luminescence spectra and electron spin resonance studies. The Optical absorption and ESR studies indicated vanadium exist mainly in two oxidation states viz,V^{5+}(diamagnetic) and V^{4+}(a paramagnetic $3d^1$ ion) in the present glass matrices. The IR spectra of the present glasses suggests the presence of vanadium ions in $V^{4+}$and V^{5+} states in the glass network. In the PL spectra with increase in the concentration V_2O_5, the intensity of the peak is observed to increase with a red shift.

1. Introduction

As_2O_3 glasses were identified as the low loss materials for long distance optical transmission. Theses glasses have exponentially high Raman scattering coefficients and found to be suitable for acting fiber Raman applications [1]. As_2O_3 is the most important oxide of arsenic and is obtained by burning in air [2, 3] of by the hydrolysis of $ASCl_3$ [4]. The basic structural unit in AS_2O_3 at temperatures below 800^0C is the AS_2O_3 pyramid. In the vapors Phase below 800^0C four AS_2O_3 units share (oxygen) corners to form the As_4O_6 molecule [5, 6]. An alternative way of viewing this molecule is as a tetrahedral As_4 molecule with each As-As bond replaced by an AS-O-AS bridging oxygen atoms, oxygen atoms being arranged at the vertices of the regular octahedrons. Solid As_2O_3 is interesting material in that, it exists in the crystalline state as both a molecular solid and as to polymers having an infinite layer stricture.

The structure of arsenolite is similar to that of diamond with each carbon atom is replaced by an AS_4O_6 molecule, the molecules on the two sub lattices being rotated by $\pi/2$ relative to each other [7]. As_2O_3 is a strong network former with corner sharing AsO_3 pyramids; earlier neutron diffraction studies indicates that normal bond lengths As-O lie between 1.7 2-1.81A^0 and O-As -O and As-O-As bond angles lie in the range 90-103A^0, and 123-135 A^0 respectively [8].

Addition of PbO to these glasses makes them to be relatively moisture resistant and also lowers the rate of crystallization, since PbO, has the ability to form stable glasses due to its dual role-one as modifier, if Pb-O is ionic and the other-as glass former, if Pb-O is covalent [9, 10]. When Pb^{2+} ions are present in the glass as network formers they impart a three-dimensional character to the glass. This fact accounts for the ability of PbO to form glasses up to 90 mol % clearly the peculiar behavior, which distinguishes lead from alkali and alkaline earth metals, depends on the electronic structure of the Pb^{2+} ion. In fact the easily polarizable valence shell of the Pb^{2+} ion strongly interacts with also highly polarizable O^{2-} ion, giving rise to a rather covalent Pb-O bond [11].

Vanadium ions are very interesting ions to probe in the glass network because their outer d-electron orbital functions have rather broad radial distributions and their responses to surrounding actions are very sensitive; as a result these ions influence the physical properties of the glasses to a substantial extent.

In view of these, it is felt worthwhile to have some understanding over the spectroscopic properties of PbO-As_2O_3 glasses containing another transition metal ion i.e. vanadium. V_2O_5 is known to participate in the glass network with VO_5 pyramidal structural units. Several vanadate glasses show semiconducting behavior with the electrical conductivity of 10^{-3} to 10^{-5} $(cm)^{-1}$, which is known to be electron hopping between V^{4+} to V^{5+} ions, existing in the glass network. Further, vanadium glasses are identified as the n- type semiconductors for low value of the V^{4+} / V^{5+} ratio. The vanadium ions may also exist in the glass network in V^{2+} and V^{3+} states [12].

The investigations on spectroscopic (viz., optical absorption, photoluminescence, infrared spectra and electron spin resonance) give the information on the position and oxidation states of the transition metal ions in the glass network and help to assess the suitability of these glasses for practical applications.

2. Experimental

V_2O_5 doped PbO-As_2O_3 glasses were prepared; using melt-quenching technique [13-15].The content of vanadium in the glass composition is varied from 0.2 to 1.0 mol%. The details of glass compositions chosen for the present study are listed in table-1. The starting materials used for the preparation of the present glasses were analytical grade reagents (99.9 % pure) of PbO, As_2O_3, and V_2O_5. The compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a PID temperature controlled furnace. The glasses were melted at about 600 - 650 ^{o}C for an half an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) held at room temperature. The samples were subsequently annealed at 250 ^{o}C in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the electrical and optical properties are 1 cm x 1 cm x 0.2 cm.

Table 1. Glass compositions

Glass Code	As_2O_3 (mol %)	Pbo (mol%)	V_2O_5 (mol %)
V_0	60	40.0	-
V_2	60	39.8	0.2
V_4	60	39.6	0.4
V_6	60	39.4	0.6
V_8	60	39.2	0.8
V_{10}	60	39.0	1.0

The optical absorption spectra of the glasses were recorded using a JASCO Model V-670 Spectrophotometer in the wavelength range 400-1200 nm. The electron spin resonance spectra of PbO-As_2O_3 doped with vanadium transition metal ions were recorded at room temperature using E11Z Varian X-band (ν = 9.5GHz) ESR spectrometer of 100 kHz field modulation that works. Infrared transmission spectra were recorded on a Bruker IFS 66 V – IR spectrophotometer with a resolution of 0.1 cm-1 in the range 400-2000 cm-1 using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680 MPa. The photoluminescence spectra of glasses were recorded on Photon Technology International fluorescence spectrophotometer in UV and NIR regions with a monochrometer and photomultiplier tube for detecting the luminescence response in the appropriate wavelength regions. By using Archimedes's principle, the density (d) of the glasses was determined to an accuracy of ±0.001 by means of o-xylene (99.99% pure) as the buoyant liquid.

3. Results

Physical Properties

By means of conventional formulae and practically measured density, various physical parameters such as v^{5+} ions concentration ,Mean separation ,polaron radius of the glasses have been evaluated and presented in Table 2.

Table 2. Various physical parameters of PbO-As_2O_3 glasses doped with V_2O_5

Glass	Density d (g/cm^3)	Avg. Mol. Weight ($\bar{M}$)	Conc. of V^{5+}ions Ni (10^{20}/cm^3)	Inter ionic distance r_i(A°)	Polaron radius r_p(A°)
V_0	5.0742	207.98	-	-	-
V_2	5.1631	207.90	2.99	2.99	2.79
V_4	5.1930	207.81	6.02	6.02	2.21
V_6	5.5525	207.73	9.66	9.66	1.89
V_8	5.6985	207.65	13.2	13.2	1.70
V_{10}	5.7250	207.57	16.8	16.8	1.57

Optical absorption spectra

Fig. 1 shows the optical absorption spectra of PbO-As_2O_3:V_2O_5 glasses recorded at room temperature in the wavelength region 400-1200 nm.

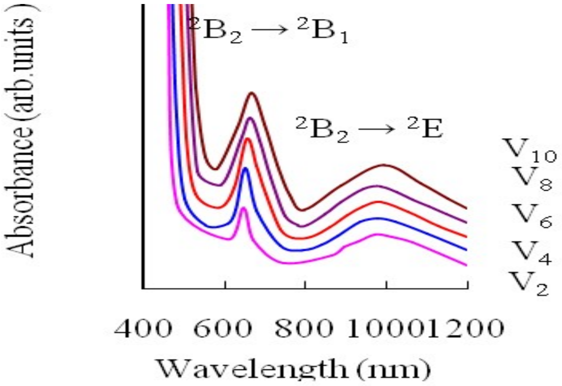

Fig. 1.Optical absorbtion spectra of PbO-As_2O_3: V_2O_5 glasses

The spectrum of vanadium free glass does not exhibit any absorption bands. The spectra of glasses doped with 0.2 mol % of V_2O_5 have exhibited two broad absorption bands at 645 and 971 nm corresponding to $2B_2 \rightarrow 2B_1$ and $2B_2 \rightarrow 2E$ transitions of VO^{2+} ions [16, 17]; with increase in the concentration of V_2O_5 up to 1.0 mol%, the half width and peak height of these bands are observed to increase.

From the observed absorption edges, we have eva luated the optical band gaps (E_o) of these glasses by drawing Urbach plot (fig-2) between $(\alpha\ \eta\,\omega)^{1/2}$ and $\eta\,\omega$ as per the equation:

$$\alpha(\omega)\,\eta\,\omega = C\,(\eta\,\omega - E_o)^2$$

The optical band gap has been found to decrease gradually with increase in the concentration vanadium in the glass matrix. The data related to optical absorption spectra of these glasses like cut of wavelength band positions and band gap(E_0) are presented in Table 3.

Table 3. Summary of the data on optical absorption spectra of PbO-As_2O_3: V_2O_5 glasses

Glass	Cut-off Wavelength (nm)	2B2 →2B 1 (nm)	2B2 → 2E (nm)	Optical band gap E0 (eV)
V2	458	645	971	2.43
V4	469	651	979	2.38
V6	460	656	986	2.29
V8	503	663	988	2.14
V10	515	667	993	2.04

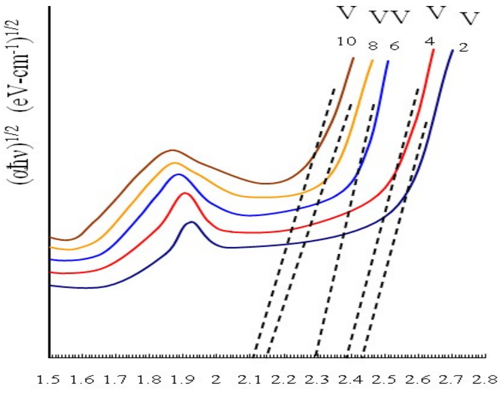

Fig.2.Optical band gap for the PbO-As_2O_3: V_2O_5 glasses

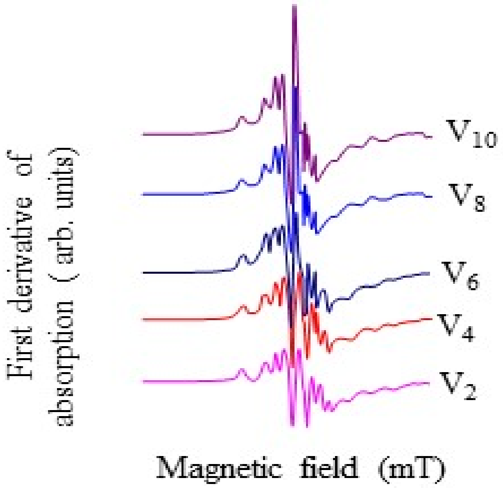

Fig. 3.ESR Spectra of PbO-As_2O_3: V_2O_5 glasses

Electron spin resonance spectra

Fig. 3 shows the ESR spectra, recorded at room temperature for PbO-As_2O_3:V_2O_5 glasses. The spectra are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron with ^{51}V isotope whose spin is 7/2. As the concentration of V_2O_5 is increased, an increasing degree of resolution and the intensity of signal is found to be maximum for the glass doped with 1.0 mol % of V_2O_5. The values of $g_{\parallel}$ and $g_{\perp}$ (obtained from these spectra) along with the other pertinent data are furnished in Table 4.

Table 4. Data on ESR spectra of PbO-As_2O_3: V_2O_5 glasses

Glass	$g_{\parallel}$	$g_{\perp}$	$\Delta g_{\parallel}/\Delta g_{\perp}$
V_2	1.909	1.996	14.80
V_4	1.911	1.995	12.50
V_6	1.914	1.914	9.49
V_8	1.916	1.992	8.37
V_{10}	1.917	1.991	7.54

Infrared transmission spectra

Fig. 4 shows infrared transmission spectra of PbO-As_2O_3:V_2O_5 glasses. IR spectrum of crystalline As_2O_3 is expected to exhibit 4 fundamental absorption bands ν_1 (1050 cm^{-1}), ν_2 (618 cm^{-1}) ν_3 (795 cm^{-1}) and ν_4 (505 cm^{-1}) which can be attributed to symmetric stretching vibrations, symmetric bending vibrations, doubly degenerate stretching vibrations and doubly degenerate bending vibrations respectively [18]. The spectrum of crystalline V_2O_5 is expected to exhibit band at 1020 cm^{-1} due to the vibrations of isolated V=O groups in VO_5 polyhedral, participating in the formation of layered structure, another absorption band with a meta center at 815 cm^{-1} related to V-O-V chains and a weak shoulder at about 600 cm^{-1} corresponding to bending vibrations of V-O-V chains [19].In the infrared spectrum of pure glasses (V_2O_5 free glasses), the band due ν_1, ν_2, ν_3, ν_4 vibrations of As_2O_3 structural groups are observed at 1050 cm^{-1} (ν_1), 614 cm^{-1} (ν_2), 750 cm^{-1} (ν_3) and 471 cm^{-1} (ν_4).

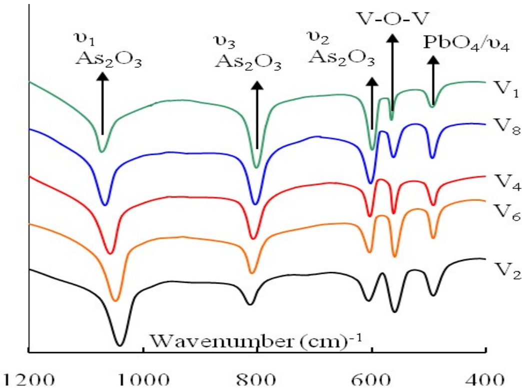

Fig. 4.IR Spectra of PbO-As_2O_3: V_2O_5 glasses

With the introduction of V_2O_5 into the glass network, a new band at 815 cm^{-1} related to V-O-V chains is observed. In the region of ν_1 vibrations of As_2O_3 structural groups band due to isolated V=O groups of VO_5 structural groups is also expected. Hence the band observed at about 1040 cm^{-1} may be considered as the band due to common As-O-V vibrations. With increase in the concentration of V_2O_5 in the glass network, the vibration bands ν_2 and ν_3 are observed to shift gradually towards lower wave number with increasing intensity. The intensity of the band due to As-O-V vibration band shows a gradual decrease in the intensity in the composition range. In the region of ν_4 vibrations of As_2O_3 structural groups it is also quite likely that the vibrations due to PbO_4 structural groups are also present; in fact earlier it was reported that the vibration band due to PbO_4 units lies at around 470 cm^{-1} [20, 21] The summary of the data on various bands observed in the IR spectra of PbO- As_2O_3 glasses is presented in Table 5

Table 5. Summary of the data on FT-IR spectra of PbO-As_2O_3: V_2O_5 glasses

Glass	ν_1/ VO_5 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	V-O-V (cm^{-1})	PbO_4/ν_4 (cm^{-1})
V_2	1040	606	813	560	492
V_4	1049	604	810	561	492
V_6	1058	603	808	562	492
V_8	1067	602	805	563	494
V_{10}	1073	599	803	565	494

Photoluminescence spectra

Fig. 5 shows the photoluminescence spectra of PbO-As_2O_3 glasses recorded at room temperature with excitation wavelength of 645 nm. The spectrum of each glass exhibits a broad emission band in the region 765-775 nm; this band is identified due to $^2E \rightarrow {}^2T_2$ transition of vanadyl ion, the band exhibits a slight asymmetry in the higher wavelength region. With the growing content of V_2O_5 in the glass matrix, the half width of the peak is observed to increase.

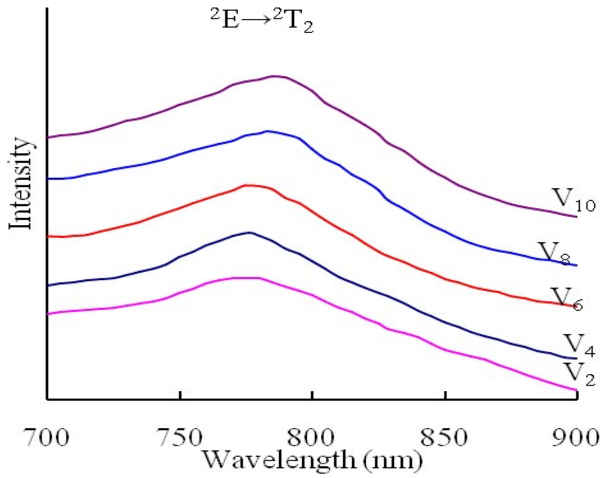

Fig. 5.Emission spectra for some of the PbO-As_2O_3: V_2O_5 glasses

4. Discussion

As_2O_3 is a strong network former with corner sharing AsO3 pyramidal units; normal bond lengths of As-O lie in between 1.72-1.81 Å and O-As-O and As-O-As bond angles lie in the range 90-1030 and 123-1350 respectively [22-23]. PbO in general is a glass modifier and enters the glass network by breaking up the As-O-As bonds (normally the oxygen's of PbO break the local symmetry while Pb^{2+} ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. However, PbO may also participate in the glass network with PbO_4 structural units when lead ion is linked to four oxygen's in a covalence bond configuration. V_2O_5 is an incipient glass network former and as such does not readily participate in the network forming but does so in the presence of modifiers like PbO with VO_5 trigonal bipyramids and VO_4 tetrahedral units [24]. Vanadium ions are expected to exist mainly in V^{5+} states in the present PbO-As_2O_3 glass network. However, during the melting of the glasses at higher temperatures there is every possibility for the following redox equilibrium to take place: Further, Chung and Mackenzie [25] suggested that that a small number of V^{5+} ions may also reduce to V^{3+} state, as per the following equations:

$$As_2O_3 + V_2O_5 \rightarrow AS_2O_5 + V_2O_3$$

The V^{5+} ions take part network forming positions with VO_5 structural units where as the V^{4+} ions may distort the glass structure. As mentioned earlier AS_2O_3 participate in the glass network with the three membered rings of ASO_3 pyramids. Addition of VO_4 tetrahedral into the PbO- AS_2O_3 glass network will twist or distort the interconnected chains of ASO_3 units and increase the randomness of the glass matrix.

The intense band observed in the IR spectra centering at 811 cm^{-1} of crystalline V_2O_5 is a characteristic related to stretching modes of V-O-V bridge bonds of VO_4 tetrahedral units and the band observed at 1040 cm^{-1} is due to the common vibrations of AS-O-V trigonal bipyramids as mentioned earlier. The preservation of these bands in the spectra of the present glasses suggests the presence of vanadium ions in both V^{4+} and V^{5+} states in the glass network. With the gradual increase in the concentration of V_2O_5 caused an increase in the intensity of asymmetrical bands indicating that there is an increasing concentration of VO^{4+} ions that act as modifiers in the glass matrix.

The variation of ESR line width and the resolution with the concentration of V_2O_5 is obviously due to the variation of concentration of V^{4+} ions and also due to structural and micro structural modifications that can produce fluctuations of the degree of distortion or even of the co-ordination geometry of V^{4+} sites. The observed broadening of ESR signal with concentration of V_2O_5 indicates the growing presence of V^{4+} ions [26]. The ESR spectra recorded at room temperature for the glasses containing V_2O_5 show a well-resolved hyperfine structure, typical of isolated vanadium ions in a ligand field of C_{4v} symmetry present as VO^{2+} species. The spectra indicate that VO^{2+} ions exist in the glass network in an octahedral site symmetry with tetragonal compression since $g_{ii} \leq g_{\perp} \leq g_e$ [27]; further, the increase in the value of $\Delta g_{||} / \Delta g_{\perp}$ with increase in the concentration of V_2O_5 in the composition range $0.2 \leq x \leq 1.0$ (Table 1), indicates that the tetragonal distortion around vanadyl ions increases with the concentration of V_2O_5. The broadening of ESR signal with the concentration of V_2O_5 in this composition range is obviously due to the presence of the larger concentration of V^{4+} ions and may also be due to exchange coupling between V^{3+} ions (if any) and V^{4+} ions [28]. The poor resolution of the ESR signal with low intensity for the glasses V_2 may be understood due to the presence of low concentration of V^{4+} ions or larger concentration of diamagnetic V^{5+} ions that take network-forming positions.

The optical absorption spectrum of V_2O_5 glass shows two broad absorption bands at 645 and 971 nm; there is a noticeable shifting of the Meta centers of these bands towards higher wavelength side with a gradual hike in the intensity with increase in the concentration of V_2O_5 up to 1.0 mol%. V^{4+} ion belongs to d^1 configuration with a ground state of 2D. The presence of pure octahedral crystal field the 2D state splits into $2T_{2g}$ and $2E_g$, while an octahedral field with tetragonal distortion further splits the $2T_{2g}$ level into 2Eg and $2B_{2g}$; and $2E_g$ level splits into $2A_{1g}$ and $2B_{1g}$.. Among these, the $2B_{2g}$ will be the ground state. Thus the vanadyl ions we can expect 3 bands (on the basis of energy level scheme for molecular orbital's of VO^{2+} ion in a ligand field of C4v symmetry provided by Bullhausen and Gray [29]) corresponding to the transitions $2B_{2g} \rightarrow 2B_{1g}$ $(\Delta_{\perp})$, $2B_{2g} \rightarrow 2E_g$ $((\Delta_{||})$and$2B_{2g} \rightarrow 2A_{1g}$. However, for the present glasses, only the first two bands are observed. The largest intensity and the half width of these bands for glass V_{10}, indicates the largest concentration of VO^{2+} ions that act as modifiers in these glasses.

It is now obvious from the results of ESR and optical absorption spectra, vanadium exist mainly in two oxidation states viz., V^{5+} (diamagnetic) and V^{4+} (a paramagnetic $3d^1$ ion) in the present glass matrices.Excitation of PbO-As_2O_3:V_2O_5 glass samples with the wavelength corresponding to $2B_2 \rightarrow 2B_1$ transition resulted a broad emission band at about 645 nm. Since the wavelength of this band is close to the maximum of the band $2B_2 \rightarrow 2E$, we attribute this band as the $2E \rightarrow 2T_2$ transition of V^{4+} ions; the emission band is relatively broad and structures less. With increase in the concentration of V_2O_5, the intensity of the peak is observed to increase with a red shift. The shift of this PL peak, the shape and the structured nature of the PL emission band are a signature of shallow levels with an electron–phonon coupling [30].

5. Conclusion

The optical absorption spectra of $PbO\text{-}As_2O_3{:}V_2O_5$ glasses have exhibited two clearly resolved bands due to ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ transitions of vanadyl ions. The intensity and the half width of these bands have been observed to be maximal in the spectrum of glass V_{10}; from this observation it is concluded that VO^{2+} (vanadyl) ions present in larger concentrations in this glass network. The ESR spectra of $PbO\text{-}As_2O_3{:}V_2O_5$ glasses recorded at room temperature are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron of ${}^{51}V$ isotope having spin 7/2. As the concentration of V_2O_5 is increased, an increase in the degree of resolution and the intensity of signal, have been observed. From this analysis it is also concluded that there is an increase in the degree of disorder of the octahedral and in the glass network as a whole with increase in the concentration of V_2O_5. With the gradual increase in the concentration of V_2O_5, the gradual increase in the intensity of asymmetric bands with a shift towards considerably lower frequencies has been observed. Such changes have been understood due to increasing modifying action of vanadyl ions in the glass network with increase in the concentration of V_2O_5. The photoluminescence spectra of these glasses recorded at room temperature with the excitation wavelength of 645 nm exhibited a broad emission band in the region 765-775 nm due to ${}^2E \rightarrow {}^2T_2$ transition of vanadyl ion. With increase in the concentration of V_2O_5, the intensity of the peak is observed to increase with a red shift. The shift of this PL peak, the shape and the structured nature of the PL emission band have been identified as a signature of shallow levels with an electron–phonon coupling.

References

1. .K. Nassau, D.L. Chadwick and A.E. Miller, *J. Non-Cryst. Solids* 93 (1987) 115.
2. G.D.Parkes, Mellor,s *Modern Inrganic Chemistry* (Logemans London. 1967)
3. P. J. Durrant and B. Durrant, *Introduction to Advanced Inorganic Chemistry 2nd ed* (Logemans London. 1970)
4. .D. Smith andA. F. Trotman Dickenson, *Comprehensive Inorgnanic Chemistr*y (Pergamon, Oxford, 1973).
5. L.R.Maxwell, S.B. Hendricks and L.S. Deming, *J.Chem.Phys.* 5(1937) 626.
6. G.C.Hamposon and as J.Stosick, *J.Amer. Chem.Soc.* 60 (1938)1814.
7. F.Perlik, Chech.*J.Phys.B* 28(1978)170
8. A.G.Clare, A.C.Wright, R.N.Sinclair, F.L. Galeener and A.E., Geissberger *J.Alloys and Compounds* 111 (1989) 123.
9. V.Ravikumar, N. Veeraiah, *J.Mater.Sci. Lett.* 16 (1997) 1816.
10. V. Ravikumar and N. Veeraiah *J. Phys. Chem. Solids* 59 (1997) 91.
11. Y.S. Bobovich and T.P. Tulub. *Sov. Phys. Usp.* (Adv. Phys. Sci. Engl.Transl.) 66 (1958) 1.
12. AI. Nicula, E. Culea and I. Lupsa, *J. Non-Cryst. Solids* 79 (1986) 325.
13. C. N. R. Rao, G. V. Subbarao, *Phys. Status Solidi A I* (1970) 597 and C. N.R. Rao, G. V. Subbarao. *Transition Metal Oxides*, NSRDS-NBS Monogr. 49.Washington, DC: Natl.Bur. Stand.
14. J. B. Goodenough, *Progr. Solid State Chern.* 5 (1971) 149.
15. C. N. R. Rao, J. Gopalakrishnan, *New Directions in Solid State Chemistry.*Cambridge: Cambridge Univ. Press in 1986.
16. C. J. Ballhausen, "*Introduction to Ligand Field Theory*", McGraw Hill, New York, (1962).
17. S. F. Fang, H. Bihui, *J. in.Sizho Bopuxue Zazhi* 10 (1993) 9.
18. F.A. Khalifa, A.A. Elhadi, A. A El-Keshen and F.A.Moustaffa, *Indian J. Pure. Appl. Phys.* 34 (1996) 201.

19. R. Iordanova, V. Dimitrov, Y. Dimitriev, *J. Non- cryst. Solids* 180 (1994) 58
20. G. Srinivasarao, N.Veeraiah, *J.Phys.Chem. Solids* 63 (2002) 705.
21. G. Venkateswara Rao and N. Veeraiah, *J. Phys. Chem. Glasses* 43 (2002) 205.
22. J. B. Goodenough, *Progr. Solid State Chern*. 5 (1971) 149.
23. D. Beeman, R.Lynds, M.R.Anderson, *J.Non-Cryst. Solids* 42 (1980) 61.
24. G. Lucovsky, F.L.Galeener, *J.Non-Cryst.Solids* 37 (1980) 53.
25. O. Miroschnichenko and O.Klimaschevski, *Nerog. Mater*. 6 (1970) 1893
26. A.I. Nicula, E. Culea, I. Lupsa, *J. Non-Cryst. Solids* 79 (1986) 325.
27. S. Khasa, V. P. Seth, Ashish Agarwal , R. Murali Krishna, S. K. Gupta and Prem Chand, *Mater.Chem.Phy*.72 (2001) 366.
28. R.Balaji.Rao, N.Veeraiah, *J.Alloys and Compounds* (in press)
29. C. J. Ballhausen, H.B. Gray, *J.Inorg. Chem*. 1 (1962) 111.
30. W. Ryba-Romanowski, S. Golab, G. Dominiak-Dzik, M. Berkowski,*J.Alloys Comp*. 288 (1999) 262.