

Influence of praseodymium on aluminogermanate glasses containing Nd and La inclusions

Cite as: AIP Conference Proceedings **2115**, 030247 (2019); <https://doi.org/10.1063/1.5113086>
Published Online: 12 July 2019

Benedict P. Soares, J. A. Erwin Desa, and P. S. R. Krishna



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Structure of lanthanum-tellurite glass-ceramics: A neutron diffraction study](#)

AIP Conference Proceedings **2115**, 030237 (2019); <https://doi.org/10.1063/1.5113076>

[Physical, structural and optical studies on Er³⁺ ions doped zinc bismuth borate glasses for photonic applications](#)

AIP Conference Proceedings **2115**, 030249 (2019); <https://doi.org/10.1063/1.5113088>

[Structural disordering and refractive index measurements of B⁺ implanted polycarbonate in the mid-infrared region](#)

AIP Conference Proceedings **2115**, 030250 (2019); <https://doi.org/10.1063/1.5113089>

AIP | Conference Proceedings

Get **30% off** all
print proceedings!

Enter Promotion Code **PDF30** at checkout



Influence of Praseodymium on Alumino-Germanate Glasses Containing Nd and La Inclusions

Benedict P. Soares^{1,a)}, J.A. Erwin Desa¹ and P.S.R. Krishna²

¹*Department of Physics Goa University, Goa, Taleigao Plateau, Goa, India*

²*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, India*

^{a)}*Corresponding author: bentopaul1234@gmail.com*

Abstract. Oxides of La, Nd and Pr have been included both singly and as pairs in Alumino-Germanate glasses at molar percentages varying from 5% to 10%. The glass transition temperatures were found by differential thermal analysis in this series of five glasses. Band gap energies were obtained from the absorption coefficient using UV-Visible spectra. The glass transition temperatures and densities of the glasses were found to increase while the band gap energies were found to decrease on addition of rare earth from La to Nd to Pr. The presence of Pr⁴⁺ ions in the network formation could be used to explain the variation of density, glass transition temperature and band gap energy in these samples.

INTRODUCTION

Germanium glasses with rare earth dopants have excellent applications as laser materials since they have better optical non-linearity (1). It is well known that the structure of vitreous GeO₂ consists of a continuous random network formed by corner sharing of tetrahedral GeO₄ units. All oxygen atoms are bridging and are bonded to two Ge atoms (2). The coordination number of oxygen around Ge goes on increasing with increase in the molar % of the modifier oxide. This coordination number becomes maximum for about 20 mole % of the modifier alkali oxide during which there is conversion of tetrahedral coordination (GeO₄ units) to octahedral coordination (GeO₆ units). Further increase of the alkali oxide content in the glass composition encourages the reconversion of GeO₆ units to GeO₄ units by breaking Ge-O bonds and the formation of non-bridging oxygens (3). Henderson et al. did not find any evidence for the formation of six-fold coordinated germanium atoms. The changes in the thermo-physical properties due to the germanate anomaly could result from the formation of three membered rings of GeO₄ tetrahedra. The maximum in the anomaly occurs due to saturation of the three membered rings of GeO₄ tetrahedra in the network. The formation of Q³ tetrahedral units having one non-bridging oxygen leads to the change in the properties due to higher content of modifier oxides (4). Hannon et al. developed a model for cesium germanate glasses to study the dependence of the Ge-O coordination number on the composition. According to that model the formation of GeO₅ units leads to the increase in the coordination number (5). The present study examines the effect of the addition of oxides of La, Nd and Pr both singly and in pairs on alumino-germanate glass.

EXPERIMENTAL

The glass samples were prepared by melting the finely ground powders as per the compositions listed in Table 1, at 1400°C and quenching the melt onto a metal plate in air. The prepared glasses were immediately transferred to an annealing furnace at 450°C and kept for 1hr after which the furnace was put off and the glass was allowed to cool to ambient temperature with the furnace.

Shimadzu DTG-60 differential thermal analyser was used to estimate the glass transition temperature T_g of the glass samples. Each of the glass samples were taken in powder form in a platinum crucible for thermal analysis with an

empty platinum crucible as reference. The temperature was increased from room to 1000°C at a heating rate of 10°C/min

Glass samples were studied using a Rigaku powder X-ray diffractometer (Copper K_{α}), in the 2θ range from 10 to 80 degrees in steps of 0.02 degree.

Fourier Transform Infra-Red spectral data on the glass samples were acquired using the Shimadzu 8900 spectrometer in the range 4000 cm^{-1} to 200 cm^{-1} .

UV-Visible spectra were obtained for the glass samples using Shimadzu UV-2401 PC spectrophotometer in the range 200 nm to 800 nm in reflection mode.

RESULTS AND DISCUSSION

The glass transition temperatures T_g for all the prepared rare-earth alumino-germanate glasses measured from differential thermal analysis are listed in Table 1. It is observed that in these glasses, as the composition of rare-earth oxide included in the host network increases from La to Pr, the measured density of the glass (using the xylene displacement method) was found to increase as shown in Table 1. There is also a concomitant linear increase in the glass transition temperature T_g which may be qualitatively understood as follows: As Nd is added to the host GeO_2 network in G5 and G1, the heavier Nd ion causes the glass to vitrify at higher temperatures. In G3 and G2, the Pr ion is added to the network in the form of Pr_6O_{11} which has the trivalent Pr^{3+} of Pr_2O_3 and the tetravalent Pr^{4+} of PrO_2 co-existing in the glass. The Pr^{4+} ion could participate in network formation and cause the viscosity of the melt to have a higher value as compared to the melt having only Nd^{3+} ions which are known to be network modifiers. The substantial non-linear increase in T_g when Pr^{4+}O_2 is present could be understood from the fact that there are 3 times as many Pr ions as Nd for the same 10 molar percentage of Pr_6O_{11} and Nd_2O_3 .

TABLE 1. Composition, density, glass transition temperature and band gap energy of the glasses.

Rare-Earth oxide included with	Sample ID	Density (gm/cc)	T_g (°C)	E_g (eV)
10 Al_2O_3 :80 GeO_2				
10 La_2O_3	G4	4.1940	816	4.97
5 Nd_2O_3 :5 La_2O_3	G5	4.2581	822	4.89
10 Nd_2O_3	G1	4.3301	830	4.87
5 Nd_2O_3 :5 Pr_6O_{11}	G3	4.7130	858	4.66
10 Pr_6O_{11}	G2	4.8835	867	4.55

The X-ray diffraction pattern of the prepared glasses is shown in Fig. 1(a). The broad halo pattern confirms the amorphous nature of the prepared glasses.

The UV-Visible absorption spectra in Fig. 1(b) shows the transitions from the ground state to the excited states $^2\text{P}_{1/2}$, $^4\text{G}_{11/2}$, $^2\text{G}_{9/2}$, $^4\text{G}_{9/2}$, $^4\text{G}_{7/2}$, $^4\text{G}_{5/2}$, $^2\text{H}_{11/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{7/2}$ in Nd containing glasses G1, G3 and G5. Also shown are the transitions from the ground state to the excited states $^3\text{P}_2$, $^3\text{P}_1$, $^3\text{P}_0$ and $^1\text{D}_2$ in Pr containing glasses G2 and G3.

The relation between absorption coefficient α and the energy of the incident photon energy $h\nu$ as given by David and Mott is $\alpha h\nu = B^2(h\nu - E_g)^r$ where E_g is the optical band gap energy, B is the band tailing parameter and r is index which takes value 2 for indirect allowed, 3 for indirect forbidden, 1/2 for direct allowed and 1/3 for direct forbidden transitions.

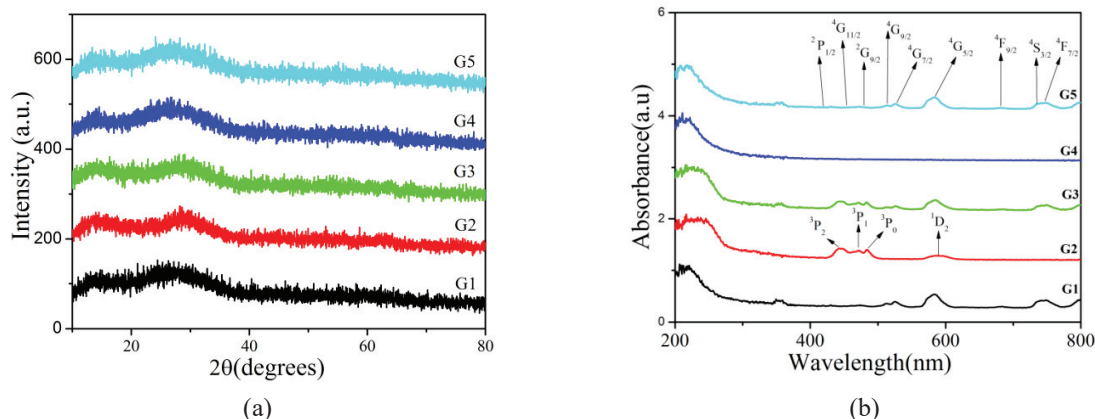


FIGURE 1. (a) XRD pattern of the glasses (b) UV-Visible absorption spectra of the glasses

Tauc's plots $(\alpha hv)^2$ v/s hv for indirect allowed transitions are shown in Fig. 2(a). The linear region of the curve is extrapolated to the hv axis in order to obtain band gap energy E_g . The results of these are listed in Table 1. It may be noted that the smallest value of E_g was found for the glass with the Pr included in the network. The Pr^{4+} ions of PrO_2 could be expected to participate in network formation and have the effect of increasing the total energy of the random network. The presence of the heavier Pr^{4+} ions acting as network formers as compared to the lighter Ge^{4+} ions of the GeO_4 tetrahedral network could be the reason for this higher energy of the random network. Thus, as the percentage of Pr_6O_{11} decreases in G3 and is replaced by the trivalent modifier ions (i.e. Nd^{3+} and La^{3+} of samples G1, G4 and G5), the E_g increases on account of the decrease of valence band or random network energy. Thus the band gap is found to decrease on the addition of Pr in the aluminogermanate glass.

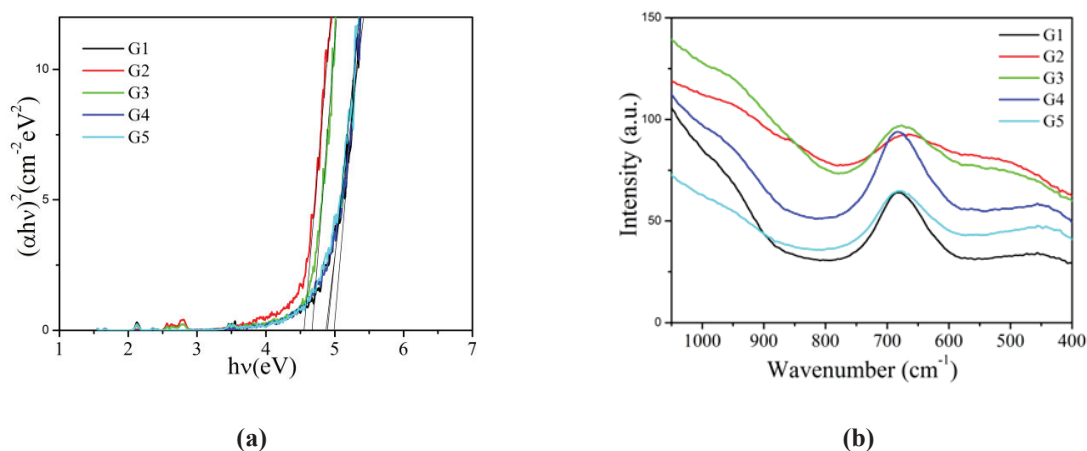


FIGURE 2. (a) Tauc plots at the UV edge for the glasses (b) FTIR spectra of the glass samples

Figure 2(b) shows FTIR spectra in the range 400 cm^{-1} to 1200 cm^{-1} . Broad bands are seen as expected in glasses. The region at about 450 cm^{-1} is due to the rare earth -oxygen vibrations. The absorption band at 650 cm^{-1} to 700 cm^{-1} is due to the Ge-O-Ge stretching mode in which the Ge has six fold coordination. The structure of glass with Nd and La inclusions consists of a network with both Ge having four-fold coordination and Ge having six-fold coordination. The Nd^{3+} and La^{3+} ions play the role of modifiers with O around it. The bridging oxygens in the network are either connecting two tetrahedrally coordinated Ge atoms or connecting one tetrahedrally coordinated Ge atom with one octahedrally coordinated Ge atom(6). On including Pr in the glass, the structure becomes more

compact because in addition to the trivalent modifier Pr^{3+} ions, there are also Pr^{4+} ions. The broad absorption above 450cm^{-1} and the broadening of the band at around 650 cm^{-1} to 700 cm^{-1} in the Pr included alumino-germanate glasses G2 and G3 indicates that the presence of Pr encourages more of four fold coordination around Ge (symmetric stretching mode Ge-O-Ge of GeO_4 units at around 550cm^{-1} - 570cm^{-1}) and that the tetravalent Pr^{4+} ions could participate in the network formation along with Ge.

CONCLUSIONS

Rare earth (La, Nd and Pr) oxides were included in alumino-germanate glass by the melt quenching method. Densities of the prepared glasses were measured using the xylene displacement method and the glass transition temperatures were obtained by differential thermal analysis. Both of these parameters were found to increase with weight of added rare earth with qualitative evidence for Pr^{4+} participating in network formation in the Pr containing glasses. The glasses were also studied using FTIR spectroscopy which found evidence for both Pr^{4+} and Ge^{4+} coordinated vibrations in the Pr containing glasses. UV-Visible spectra have been used to determine the band gap energy E_g in each of these glasses with the participation of Pr^{4+} ions in network formation being used to explain the decrease of E_g when Pr is present.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding of this work through the project CRS-M-209 of UGC-DAE CSR. The XRD measurements were obtained at the National Institute of Oceanography, Dona Paula, Goa.

REFERENCES

1. R. Balda, J. Fernandes, M. Sarz, A. de Pablon, J.M.F. Navarro and J. Mugnier, *Phys. Rev. B*, **61**, 3384-3390 (2000).
2. J.A.E Desa, A.C. Wright and R.N. Sinclair, *J. Non – Cryst. Solids*, **99**, 276(1988).
3. M.K. Murthy and E.M. Kirby, *Phys. Chem. Glasses* **5**,144-146(1964)
4. G. S. Henderson and M.E. Fleet, *J. Non-cryst. Solids*, **134**, 259-269 (1991)
5. A.C. Hannon, D Di Martino, L.F. Santos and R. N. Almeida,*Phy. Chem. B* **111**, 3342-3354 (2007)
6. P. Pernice, A. Aronne, M. Catauro and A. Marotta., *J. Non –Cryst. Solids* **210**, 23-31(1997)