# Synthesis and Structural Characterization of Niobium Doped Lead-Telluride Glass-Ceramics



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# Synthesis and Structural Characterization of Niobium Doped Lead-Telluride Glass-Ceramics

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**Abstract.** The basic glasses with composition (70-x) $TeO_2$-30PbO-x$Nb_2O_5$ (where x=0.1 mol % and 0.2 mol %) were prepared by melt quenching method and heat treated at $280^0$C for 30 min. The samples becoming glass ceramics was confirmed by SEM. The XRD parameters such as crystallite size of these glass ceramics decreases as increase the impurity and is the order of 184-109$A^0$. However, micro strain (ε) and dislocation density (δ) increases. Glass transition and thermal stability estimated from DSC measurements and it has been found that both increase with increasing of impurity. Infrared Absorption spectra were measured for $TeO_2$ glass and glass ceramic doped with $Nb_2O_5$. The recorded bands attributed to the different modes of vibration and stretching of Te-O band. Optical Absorption spectra of $TeO_2$-PbO-$Nb_2O_5$ system shows that the absorption edge has a tail extending towards the lower energies and shifts towards for higher energies for rare earths-doped glass-ceramics. The degree of the edge shift was found to depend on the structural rearrangement and the relative concentrations of the glass basic units. The general appearance of the absorption spectra of these rare earth doped $TeO_2$ glasses are similar to the spectra observed for other glasses doped with the same kind of rare earth oxides.

## 1. Introduction

Tellurium oxide glass and glass ceramics have been considered as the best materials for use in memories, laser hosts and non linear optical devices like optical amplifiers and optical filters in view of their high refractive index, low phonon energy, high dielectric constant, good infrared transmission and large third order non-linear susceptibility[1-3]. It is important to study the thermal behaviour and the crystallization mechanisms of these glasses because transparent glass ceramic materials, especially once manufactured via controlled crystallization ,are recently perceived as a new type of non linear optical materials because of their extremely fine grain sizes, many different techniques are to be used to find a correlation between physical characteristics, structural characterizations and the atomic arrangement observed in these glasses such as XRD , SEM , DSC and UV-Visible.

## 2. Experimental Procedure

### *2.1 Sample Preparation*

The basic glasses with composition (70-x) $TeO_2$-30PbO-x$Nb_2O_5$ (where x=0.1mol % and 0.2 mol %) were prepared by melt quenching method. The starting materials, $Nb_2O_5$, PbO and $TeO_2$ taken in the appropriate proportion weighed in digital electronic balance and mixed thoroughly in a porcelain crucible, then heated in an electrical furnace by the temperature gradually the mixture was melt at a temperature around $850^0$C. Thus obtained homogeneous melt was quenched between two brass plates. Prepared samples were annealed at $280^0$C for 30 minutes and during which the base glass transfers into glass ceramic composite.

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## 3. Results and discussion

*3.1 X-Ray diffraction*

A Typical XRD patterns of niobium doped lead telluride glass and glass ceramics as shown in figure (1). It observed that prepared glasses at room temperature possess broad peak indicating amorphous structure. The presence of intense peak at $2\theta = 29^0$ in (111) direction for heat treated samples reveals that these glasses are crystalline in nature. The 2θ values observed in the XRD and those of JCPDS (01-0582) data were found in fair agreement between them. Doped glasses were found to exhibit two diffraction peaks associated with (111) and (110), of which the intensity of (111) orientation is predominant.

**Table 1.** XRD parameters of glass ceramics.

| Sample name | d($A^0$) | D($A^0$) | ε $10^{-3}$($lin^{-2}$ $m^{-4}$) | δ $10^{15}$ (lin/ $m^2$) |
|---|---|---|---|---|
| 0.1 mol% | 2.92 | 184 | 1.876 | 2.93 |
| 0.2 mol% | 3.02 | 109 | 3.175 | 8.389 |

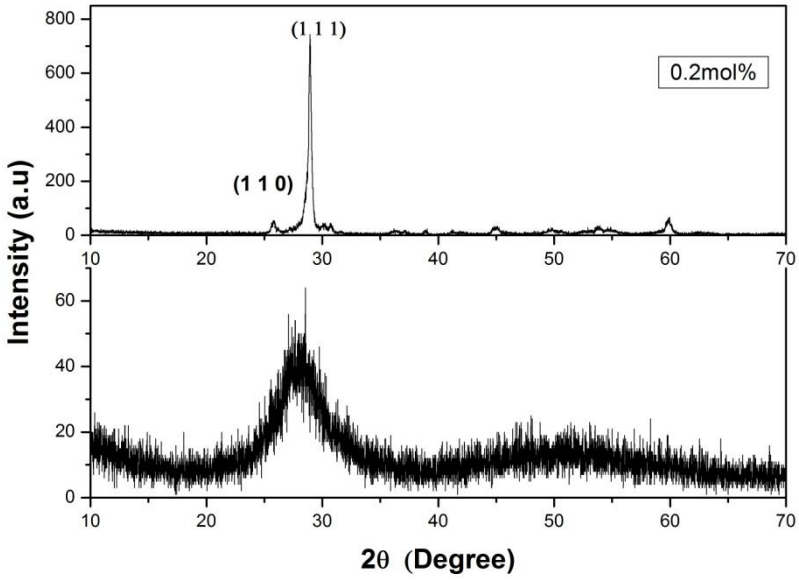


**Figure 1.** A typical XRD spectra for 0.2 mol % doped glass and glass-ceramic

*3.2 Scanning electron microscopy*

SEM investigations were performed on glass and glass ceramics. Figure (2) show Typical SEM photographs of the samples undergo translation from amorphous to partial crystallization. It appears that the process of annealing with impurity decreases the number of grain boundaries. As a result, an improved microstructure and morphology are created. Average grain size was found to be 49.2μm for 0.1mol% and 58.1μm for 0.2mol%. Grain growth in similar materials is well known and reported for solid state re-crystallization method.

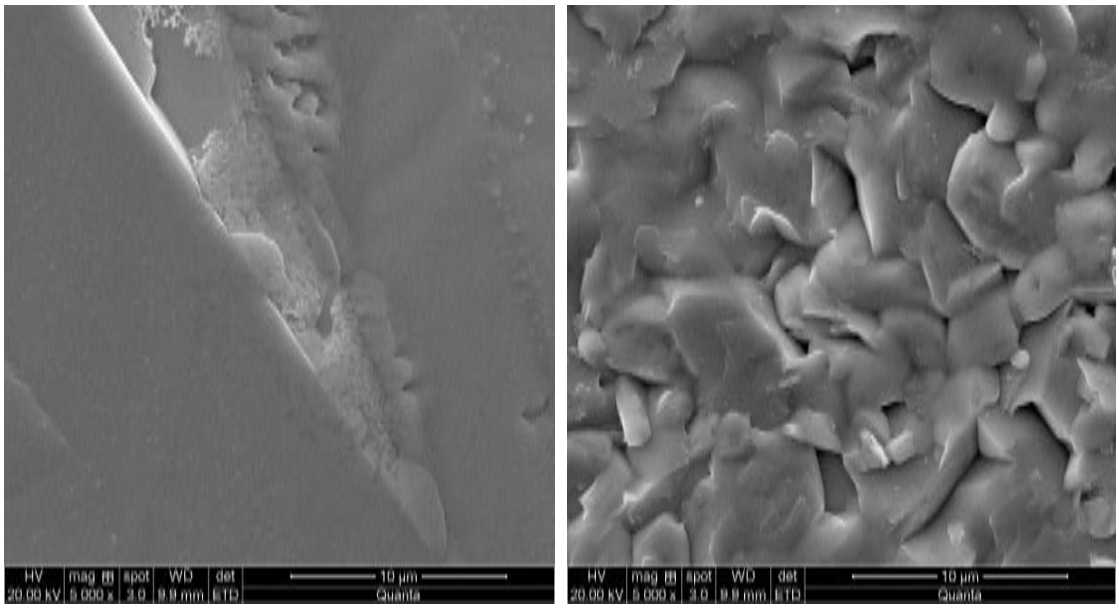

**Figure 2.** A typical SEM photographs of 0.1 mol % and 0.2 mol % doped glass-ceramics.

*3.3 Differential scanning calorimetric Studies*

A typical DSC trace of glass is as shown in figure (3) and its clear that the 0.1mol% and 0.2mol% impurity sample contains only one endothermic hump corresponds to glass transition $T_g$ and two endothermic peaks confined to crystallization temperatures $T_{C1}$ and $T_{C2}$, however , for annealed glass ceramic powders recorded at the same heating rate of $10^0$C/min .Of the two thermal events observed, the first one for 0.1 mol %, appearing as an endothermic hump, is the glass transition and exothermic hump was crystallization peak. Secondly for 0.2 mol % consists of two endothermic peaks consider to melting peaks and annealing makes glass transition temperature to decrease from $300^0$c to $275^0$c. The reason for increase in the $T_g$ is that Nb-O-Te and Nb-O-Nb linkages are increasing as shown in table 2, requiring higher temperature for relaxation [4]. The difference between the onset crystallization temperature and glass transition temperature ($T_X$-$T_g$) has been frequently been quoted as a rough indicator of glass stability ($\Delta T$) as depicted in the table 2. It represents the temperature interval during which nucleation takes place [5].

**Table 2.**Variation of Transition temperature $T_g$ with impurities

| Glass composition (mol%) | | | $T_g$ in $^0$C | $T_c$ in $^0$ C | $\Delta T = T_x - T_g$ in $^0$C |
|---|---|---|---|---|---|
| $TeO_2$ | PbO | $Nb_2O_5$ | | | |
| 69.9 | 30 | 0.1 | 298 | 350 | 50 |
| 69.8 | 30 | 0.2 | 300 | 360 | 62 |

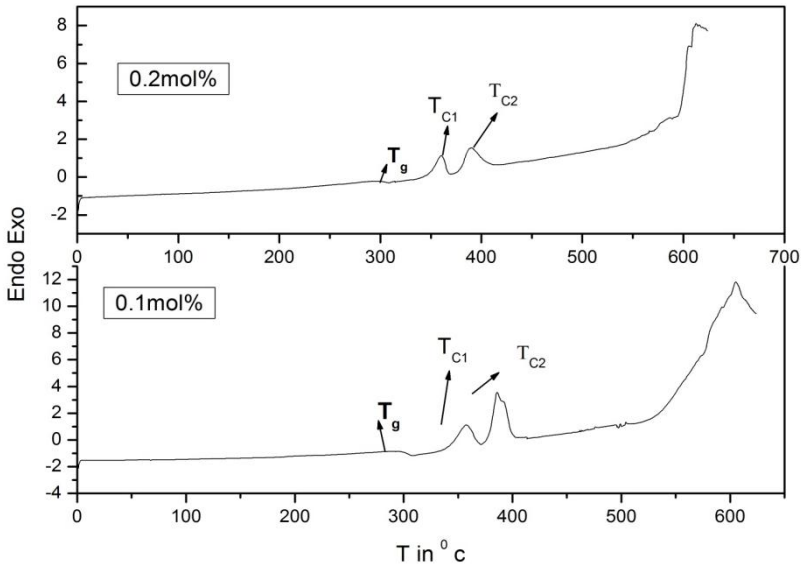


**Figure 3.** A typical DSC spectra for 0.1 mol % and 0.2 mol % doped glass.

*3.4 Optical absorption*

Figure4 (A) shows the typical UV absorption spectra of glass. It has been found that the UV of $TeO_2$ edge shifts to shorter wavelengths with increasing the $Nb_2O_5$ content in the binary telluride glasses. In this study, the position of fundamental absorption edge shifts to higher energy (shorter wavelength) with increasing $Nb_2O_5$ in the system. The shift of the ultraviolet absorption band to shorter wavelengths corresponds to transitions from NBO with bound exited electron less tightly than the bridging oxygen [6]. The general appearance of the absorption spectra of the present samples is similar as found by burger et al and other glasses doped with same kind of rare earth oxides, such as $P_2O_5$-$Pr_6O_{11}$ glass and vanadium-phosphate glasses doped with different rare earth oxides [7-8].

It can be seen that there exists a linear dependence of $(h\nu)^2$ in the photon energy as shown in figure 4(B). This suggests that at higher photon energies the transitions occurring in the present glass and glass ceramics are of indirect type. In the present work the addition of rare earths to $TeO_2$ is to produce replacement of the O-Te-O ,and/or O-Te-O bands in the glass network and to be replaced by RE-Te-O,RE-O-Te and/or O-RE-O bands which is reflected in the absorption spectra by a significant shifting of the absorption edge are most likely to related to structural rearrangement of the glass and the relative concentration of the various fundamental units.

The optical band gap for glass with impurity 0.1mol% and 0.2mol% is the order of 1.70eV and 2eV,wherese as the annealed samples of the order of 1.73eV and 2.04eV respectively. The absorption edge depends on the oxygen bond strength in the glass forming network. However, by doping $Nb_2O_5$ the optical band gap is constituted by the host materials PbO does not alter much the band gap picture of glass but increases slightly in the case of glass ceramics.

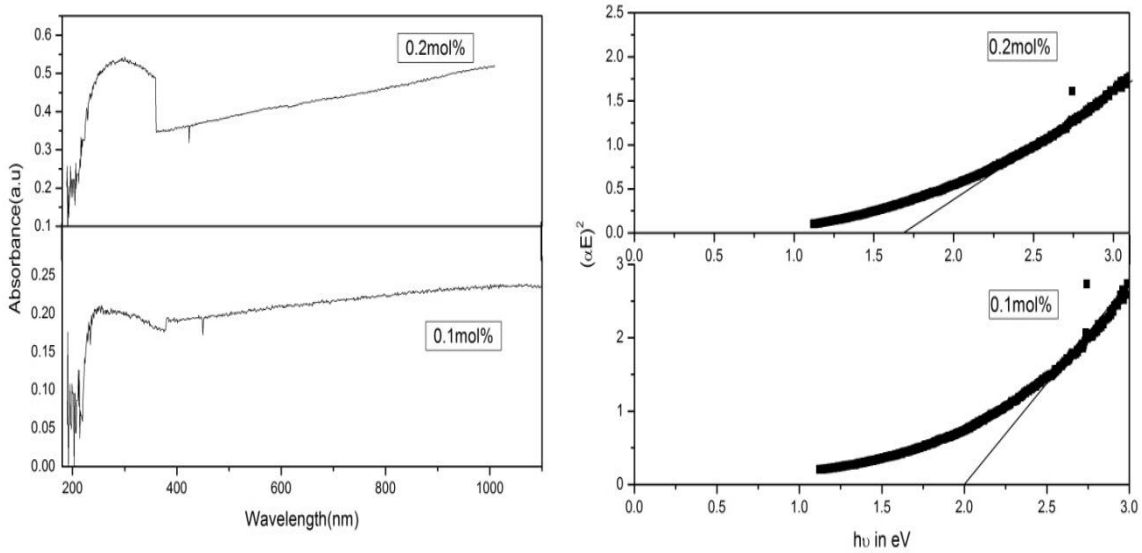


**Figure 4(A).** UV-Visible spectra of doped glass. **(B).** A Typical $(\alpha E)^2$ as a function of energy for the composition (70-x) $TeO_2$-30PbO-x$Nb_2O_5$ glass ceramic samples with 0.0mol% and 0.2mol% impurity.

*3.5 Infrared spectroscopy*

Figure (5) shows the Typical IR spectra of the $TeO_2$ glasses doped with the rare earths oxides of the type $Nb_2O_5$ in the spectral range 400-4000 $cm^{-1}$. For all glass and glass ceramics presented in this work, the spectra showed bands from 640 $cm^{-1}$ to 778 $cm^{-1}$.

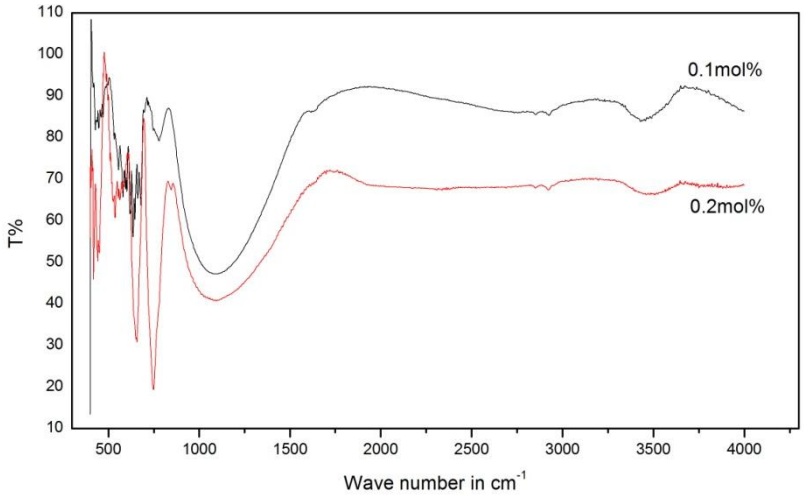


**Figure 5.** A typical IR spectra for 0.1 mol % and 0.2 mol % doped glass.

The main IR band at 640 $cm^{-1}$ attributed to symmetrical vibration oscillations of Te-O bands. Rare earths connected to the chains of $TeO_4$ groups are identified on the basis of simultaneous presence of the bands at 660 $cm^{-1}$-625 $cm^{-1}$. For rare earths-doped samples new bands were detected from 418 $cm^{-1}$ to 594 $cm^{-1}$, respectively. These bands attributed to O-Nb-O stretching vibrations. The spectra of all the studied samples show the typical broadening of the observed bands. In the most cases, they are similar to the spectra of the crystalline phases after heat treatment. This is the direct proof for the similarities of structural units and of the short range order. For this reason, interpretations of spectra of

$TeO_2$ based samples based on the conclusions drawn for their crystalline phases. This is assumed that this is the result of particular structure of trigonal by pyramids of $TeO_4$ groups and presence of a free electron pair in one of the broadening positions [9]. It is clear that beyond the existence of an average deformation of the network and long range disorder in the system [10]. By analogy with the crystalline telluride [9], it may be accepted that with the introduction of other oxides in the telluride samples. As new structural arrangement of the back side of four coordinated tellurium ions favour the stronger polarizability of the free electron pair in certain directions. As a result, parts of the $TeO_4$ groups are transformed into $TeO_3$. 1000 $cm^{-1}$ and 1100 $cm^{-1}$ are attributed to **Pb-O** the asymmetric stretching vibrations **[$PbO_n$]** tetrahedral structural units [11-13]. 816$cm^{-1}$ assigned to vibration of **Nb** and its neighboring non bridging system and to bridging to **Nb-O** group motion [14-15].

## 4. Conclusions

It is observed that the grain size decreases which intern increases the strain and dislocation density. But there are no noticeable peaks in XRD indicating presence of impurity $Nb_2O_5$ into the samples**.** Due to the heat treatment grain growth will takes place which gives the partial crystallinity and good surface morphology. These results good agreement with XRD characteristics.SEM reveals that samples are translated to partial crystalline state. It is clear that glass stability increases as the $Nb_2O_5$ content increases and decrease of glass transition temperature in annealed sample. Quantitative justification of some of the bands for both binary $TeO_2$ rare earth doped system was done. Optical observation characteristic of niobium doped lead telluride glass and glass ceramic were studied. The absorption spectra of rare earth ions in the glass differ from that of rare earth crystals and broadening of the absorption bands is due to the multiplicity of rare earth sites in the system. The results show that optical band gap values increase on addition of impurity to glass. However, upon heat treatment the band gaps were observed to increase.

## References

[1] Vijay Prakash G, Narayana Rao D and Bhatnagar A K 2001 *Solid.State.Commun*. **39** 119
[2] Waber M J, Meyers J D and Blackbum D H 1981 *J.Appl.Phy.* **52** 2944
[3] Vogel E M, Weber M J and Krol D M 1991 *Phys Chem Glasses*. **32** 231
[4] Sene f f, Martinelli J.R and Gomes 2004 *J.Non-Cryst. Solids*. **30** 348
[5] J Chinna Babu and V Chandra Mouli 2009 *Indian J pure & App Phy*. **47** 241
[6] Harini, R R Hogarth C A and Ahamed M M 1984 *J.Mater.Sci.Lett***. 3** 843
[7] Sidek,H A A, S Chow, Z A Talib and S.A.Halim 2004 *Turk.J.Phys*. **28** 65
[8] Khan M N, Harini and Ahamed M M 1985 *J.Mater.Sci*. **20** 2207
[9] Lindqvist O 1968 *Acta .Chem.Scand***. 22** 977
[10] Dimitriv Y and Dimitrow V 1978 *Mater.Res.Bull*. **13** 1071
[11] Mandal S, S Hazara and Ghosh A 1994 *J.Mater.Sci.Lett*. **13** 1054
[12] Hazara S and Ghosh A 1995 *J.Mater.Res*. **10 (9)** 2374
[13] Milanova M, Lardonova R and Kostov K L 2009 *J.Non.Cryst.Solids*. **3536** 379
[14] Senthil Murgan G and Ohishi Y 2005 *Phy.Chem.Glasses*. **46(4)** 359
[15] Takyuki Komatsu, Hiroharu Mhari and Kazumasa Malusita 1991 *J.Non-Cryst Solids*. **135** 105