# ROLE OF Gd<sup>3+</sup>: Ag CO-DOPING ON STRUCTURAL AND OPTICAL PROPERTIES OF LEAD TELLURITE GLASS CERAMICS

# M. BOSCA<sup>1\*</sup>, E. CULEA, L. BOLUNDUT, P. PASCUTA, V. POP, N. TOTHAZAN, I. VIDA-SIMITI

**ABSTRACT.** Fourier transform infrared (FTIR) and diffuse reflectance ultravioletvisible (DR-UV-VIS) spectroscopies were used to investigated the lead tellurite glass ceramics doped with different contents of  $Gd^{3+}$  ions and co-doped with fixed amounts of Ag<sub>2</sub>O or metallic Ag nanoparticles (AgNPs). FTIR spectral studies have been made to put in evidence the presence of basic structural units in the studied glass ceramics samples. The obtained FTIR spectra reveal vibrational IR bands which are attributed to the presence of TeO<sub>3</sub>, TeO<sub>4</sub>, PbO<sub>3</sub> and PbO<sub>4</sub> structural units in the glass ceramics network. DR-UV–VIS spectra were used to calculate the optical band gap energy (E<sub>g</sub>). The obtained E<sub>g</sub> values depend on the Gd<sup>3+</sup> ions content and the nature of the codopant (Ag<sub>2</sub>O or AgNPs) present in the studied glass ceramics samples.

**Keywords:** Lead tellurite glass ceramics;  $Gd^{3+}$  ions; Silver oxide; Silver nanoparticles; FTIR; DR-UV-VIS.

# INTRODUCTION

Glasses and glass ceramics containing rare-earth (RE) ions attracted much attention in the last years due to their important properties promising for technological applications [1-8]. Thus, studies of these materials draw important potential applications in areas such as solid state lasers, optical fiber amplifiers, optical data storage, sensors, infrared to visible convertors, solar concentrators, phosphors, electro-luminescent devices, display monitor etc. [4, 9-13]. In this view, a considerable interest was accorded to glasses and glass ceramics doped with gadolinium ions [14-18]. The optical and magnetic properties of glasses and glass ceramics containing gadolinium ions are determined by the content and distribution of Gd<sup>3+</sup> ions in the host matrix as well as by the local environment of gadolinium ions.

<sup>&</sup>lt;sup>1</sup> Technical University of Cluj-Napoca, 103-105 Muncii Avenue, 400641 Cluj-Napoca, Romania.

<sup>\*</sup> Corresponding author e-mail: Maria.Cleja@phys.utcluj.ro

On the other hand, the properties of glasses and glass ceramics doped with RE ions and co-doped with silver ions or AgNPs are intensively studied because of their interesting optical and luminescent properties that make them suitable for important technological applications in electronics and telecommunication [2, 6, 12, 19-22].

In order to extend the available information concerning lead tellurite glasses and glass ceramics doped with  $Gd^{3+}$  ions and co-doped with silver ions or AgNPs, in this paper we present the experimental data obtained by studying such materials by using FTIR and DR-UV-VIS spectroscopies. The aim of this study was to observe the influence of the  $Gd_2O_3$  doping level and of the co-dopant nature (Ag<sub>2</sub>O or AgNPs) on the structural and optical properties of the studied samples.

#### **EXPERIMENTAL**

Reagents, grade pure  $Gd_2O_3$ , TeO<sub>2</sub>, PbO, Ag<sub>2</sub>O and metallic Ag nanoparticles (AgNPs) (particles size of 20-40 nm) were used to obtain samples with the chemical compositions listed in table 1. Required quantities of reagents were mixed together, in stoichiometric amounts, by grinding in an agate mortar to obtain homogeneous mixtures. The obtained mixtures were melted in porcelain crucibles using an electric furnace at 850  $^{\circ}$ C for 15 minutes. The melts were quickly cooled to room temperature by pressing between two stainless steel plates. X-ray diffraction data shows that the samples from both studied series were glass ceramics.

The FTIR absorption spectra were recorded at room temperature with a JASCO FTIR 6200 spectrophotometer. All the samples were measured using the KBr pellet technique where 2 mg powder of each sample is mixed with 300 mg of KBr in an agate mortar for obtaining a homogeneous mixture.

DR-UV-VIS spectra were registered at room temperature using a PerkinElmer Lambda 45 UV-VIS spectrometer equipped with an integrating sphere. The obtained samples were measured in MgO pellets.

Sample no.	(mol%)				
	80TeO₂·20PbO	Ag <sub>2</sub> O	AgNPs	$Gd_2O_3$	
SO	100	-	-	-	
S1	99.50	0.50	-	-	
S1'	99.70	-	0.30	-	
S2	98.50	0.50	-	1	
S2'	98.70	-	0.30	1	
S3	96.50	0.50	-	3	
S3′	96.70	-	0.30	3	

Table 1. Chemical composition for the studied glass ceramics

S4	94.50	0.50	-	5
S4'	94.70	-	0.30	5
S5	89.50	0.50	-	10
S5'	89.70	-	0.30	10

ROLE OF Gd<sup>3+</sup>: Ag CO-DOPING ON STRUCTURAL AND OPTICAL PROPERTIES ...

#### **RESULTS AND DISCUSSION**

## FTIR data

FTIR spectroscopy is an experimental technique that was used to investigate the local structure of lead tellurite glass ceramics doped with gadolinium ions and co-doped with fixed amounts of silver (Ag<sub>2</sub>O or AgNPs). FTIR absorption spectra of studied samples are shown in figure 1. A deconvolution of the experimental FTIR bands was necessary since the majority of these bands are very broad consisting of a superposition of several individual absorption bands where the individual bands are due to vibrations characteristic of the basic structural unis from the studied samples. As a representative example, figure 2 illustrates the deconvolution in Gaussian bands for the FTIR spectra of the samples S2 (figure 2a) and S5' (figure 2b). The obtained individual bands were assigned based on data available in the literature [23-28] and are given in table 2.



Fig. 1. FTIR spectra of the studied glass ceramics samples

The FTIR data show the presence of PbO<sub>3</sub>, PbO<sub>4</sub>, TeO<sub>3</sub> and TeO<sub>4</sub> structural units in the studied lead tellurite glass ceramics network. In order to analyze the effect, of increasing the gadolinium ions content and the influence of co-dopants' nature (Ag<sub>2</sub>O or AgNPs) on the local structure of studied glass ceramics samples, we have calculated the relative integrated intensity  $A_r = A_3/A_4$ , where  $A_3$  and  $A_4$  approximate the relative number of TeO<sub>3</sub> and TeO<sub>4</sub> units.



Fig. 2. Deconvoluted FTIR spectra of the samples S2 (a) and S5' (b)

The compositional evolution of  $A_r$  for the both series of studied glass ceramics samples (co-doped with  $Ag_2O$  or AgNPs) are presented in figure 3. For both series of studied samples,  $A_r$  decreases with increasing the gadolinium ions content over the whole compositional range. This evolution can be explained by the progressive conversion of  $TeO_3$  into  $TeO_4$  structural units with increasing the  $Gd_2O_3$  content. This assumption is well supported by the fact that increasing the  $Gd_2O_3$  content of samples generates the increase of their degree of crystallinity and that in crystalline compounds tellurium ions are present mainly in their 4+ valence state. For glass ceramics co-doped with AgNPs the values of  $A_r$  are slightly higher than for the samples co-doped with  $Ag_2O$ . This suggests that not only the doping level with gadolinium ions but also the nature of the co-dopant ( $Ag_2O$  or AgNPs) plays an important role determining the local structure of these samples.

Wavenumber [cm <sup>-1</sup> ]	Assignment		
362-488	Te-O-Te or O-Te-O bending vibration [23-26]		
	Pb-O stretching vibrations in PbO <sub>4</sub> units [23-26]		
537-561	Pb-O symmetrical bending vibration [23, 25]		
	Ag-O bonds vibration [23]		
583-617	Te-O stretching vibration in TeO <sub>4</sub> units [24, 26, 27]		
644-698	Te-O bonds vibration in TeO <sub>4</sub> units [23, 24, 28]		
	Pb-O vibration in PbO <sub>n</sub> pyramidal units (n = 3 and/or 4) [23, 24, 28]		
742-759	Te-O bonds vibration in TeO <sub>3</sub> units [26]		
773-786	Te-O <sup><math>- bonds vibration in TeO3 units [26]</math></sup>		

Table 2. Assignment of the IR bands for the studied glass ceramics



Fig. 3. The A<sub>r</sub> ratio as a function of the Gd<sub>2</sub>O<sub>3</sub> content for the studied glass ceramics samples

#### **Optical gap energy**

Optical band gap energy is an important property of glasses and glass ceramics which can reveal the structural modifications that can occur due to the compositional variation of the studied glass ceramics. In order to determine the optical band gap energy for the studied glass ceramics samples UV-VIS diffuse reflectance measurements were carried out. Generally the Kubelka–Munk remission function, F(R), is used to convert the diffuse reflectance into the equivalent absorption coefficient because this function can be considered proportional to the radiation absorption [29]. The optical band gap energy is determined using the plot of  $[F(R) \cdot hu]^2$  as a function of hu. The  $E_g$  values were estimated by extrapolation of the linear region of the mentioned plots (see figure 4).



**Fig. 4.** Variation of  $(F(R) \cdot h \upsilon)^2$  vs. hu for some samples containing Ag<sub>2</sub>O (a) and AgNPs (b)

Figure 5 shows the variation of optical band gap energy with the content of  $Gd_2O_3$  for both series of studied glass ceramics. For the host glass ceramic matrix (80TeO<sub>2</sub>·20PbO) the value of  $E_g$  is 3.578 eV. The addition of Ag<sub>2</sub>O (S1) or AgNPs (S1') to the host glass ceramic lead to a slow decrease of  $E_g$ . For samples doped with  $Gd_2O_3$  and co-doped with Ag<sub>2</sub>O, the optical band gap energy first increases up to 3 mol%  $Gd_2O_3$  and after that decreases for a further increase of the gadolinium ions content. A similar behavior was observed for the samples codoped with AgNPs, but in this case the values of  $E_g$  increase up to 1 mol%  $Gd_2O_3$ and decrease for higher  $Gd_2O_3$  contents.



Fig. 5. The evolution of  $E_g$  versus  $Gd_2O_3$  content for the studied samples

The decrease of the  $E_g$  values with increasing the  $Gd_2O_3$  content for both series of the studied samples can be due to the structural changes that are taking place in these samples. These structural changes are accompanied by a decrease of the average bond energy due probably to the forming of non-bridging oxygen's.

#### CONCLUSIONS

FTIR data of studied glass ceramics suggest that the local structure of the studied lead-tellurite samples is modified with the addition and increase of  $Gd_2O_3$  content. Thus, FTIR data show a conversion of  $TeO_3$  into  $TeO_4$  structural units with increasing the  $Gd^{3+}$  ions content for both series of studied samples. In this process, the nature of co-dopant is also important, the amount of  $TeO_3$  structural units being higher for samples co-doped with AgNPs in comparison with those co-doped with Ag2O.

ROLE OF Gd3+: Ag CO-DOPING ON STRUCTURAL AND OPTICAL PROPERTIES ...

The optical band gap energy,  $E_g$ , is affected not only by the increasing gadolinium ions content in the studied glass ceramics but also by the nature of codopant (Ag<sub>2</sub>O or AgNPs). A decrease of  $E_g$  is observed for both kinds of samples. This process is related to a decrease of the average bond energy due to the formation of non-bridging oxygen's in the samples.

## ACKNOWLEDGMENT

This paper was supported by the Post-Doctoral Programme POSDRU/159/1.5/S/137516, project co-funded from European Social Fund through the Human Resources Sectorial Operational Program 2007-2013.

## REFERENCE

- 1. M. Venkateswarlu, M.V.V.K.S. Prasad, K. Swapna, Sk. Mahamuda, A. Srinivasa Rao, A. Mohan Babu, D. Haranath, *Ceram. Int.*, 40, 6261 (2014).
- 2. E. Culea, I. Vida-Simiti, G. Borodi, E. N. Culea, R. Stefan, P. Pascuta, J. Mater. Sci., 49, 4620 (2014).
- 3. A. Lu, X. Hu, Y. Lei, Z. Luo, X. Li, Ceram. Int., 40, 11 (2014).
- 4. M. Reza Dousti, Raja J. Amjad, J. Non-Cryst. Solids, 420, 21 (2015).
- 5. G. Anjaiah, SK. Nayab Rasool, P. Kistaiah, J. Lumin., 159, 110 (2015).
- 6. L. Bolundut, E. Culea, G. Borodi, R. Stefan, C. Munteanu, P. Pascuta, *Ceram. Int.*, 41, 2931 (2015).
- 7. A. Dwivedi, C. Joshi, S.B. Rai, Opt. Mater., 45, 202 (2015).
- 8. S. Arunkumar, K. Marimuthu, J. Alloy Compd., 627, 54 (2015).
- 9. W.S. Souza, R.O. Domingues, L.A. Bueno, E.B. da Costa, A.S. Gouveia-Neto, *J. Lumin.*, 144, 87 (2013).
- 10. R.L. Leonard, S.K. Gray, S.D. Albritton, L.N. Brothers, R.M. Cross, A.N. Eastes, H.Y. Hah, H.S. James, J.E. King, S.R. Mishra, J.A. Johnson, *J. Non-Cryst. Solids*, 366, 1 (2013).
- 11. J. Suresh Kumar, K. Pavani, M.P.F. Graça, M.J. Soares, J. Alloy Compd., 617, 108 (2014).
- 12. E. N. Culea, P. Pascuta, M. Pustan, D. R. Tamas-Gavrea, L. Pop, I. Vida-Simiti, J. Non-Cryst. Solids, 408, 18 (2015).
- 13. Hyun-A Park, Yl Kwon Lee, Won Bin Im, Jong Heo, Woon Jin Chung, *Opt. Mater.*, 41, 67 (2015).
- 14. S. Rada, M. Culea, M. Rada, P. Pascuta, V. Maties, E. Culea, *J. Mol. Struct.*, 937, 70 (2009).
- 15. Y. B. Saddeek, I.S. Yahia, K.A. Aly, W. Dobrowolski, Solid State Sci., 12, 1426 (2010).
- 16. P. Pascuta, J. Mater. Sci.: Mater. Electron., 21, 338 (2010).
- 17. N. Elkhoshkhany, Rafik Abbas, R. El-Mallawany, A.J. Fraih, Ceram Int., 40, 14477 (2014).

M. BOSCA, E. CULEA, L. BOLUNDUT, P. PASCUTA, V. POP, N. TOTHAZAN, I. VIDA-SIMITI

- 18. H. Luo, X. Hu, W. Liu, Y. Zhang, A. Lu, X. Hao, J. Non-Cryst. Solids, 389, 86 (2014).
- 19. Z. Ashur S. Mahraz, M.R. Sahar, S.K. Ghoshal, M.R. Dousti, R.J. Amjad, *Mater. Lett.*, 112, 136 (2013).
- 20. E. Culea, I. Vida-Simiti, G. Borodi, E. N. Culea, R. Stefan, P. Pascuta, *Ceram. Int.*, 40, 11001 (2014).
- 21. R. J. Amjad, M.R. Dousti, M.R. Sahar, S.F. Shaukat, S.K. Ghoshal, E.S. Sazali, Fakhra Nawaz, J. Lumin., 154, 316 (2014).
- 22. M. Reza Dousti, R.J. Amjad, R. Hosseinian S., M. Salehi, M.R. Sahar, J. Lumin., 159, 100 (2015).
- 23. M. Bosca, L. Pop, G. Borodi, P. Pascuta, E. Culea, J. Alloy Compd., 479, 579 (2009).
- 24. S. Rada, A. Dehelean, E. Culea, J. Non. Cryst. Solids, 357, 3070 (2011).
- 25. E. Culea, J. Non-Cryst. Solids, 357, 50 (2011).
- 26. E. Monsour, J. Mol. Struct., 1014, 1 (2012).
- 27. E. A. Mohamed, F. Ahmad, K. A. Aly, J. Alloy Compd., 538, 230 (2012).
- 28. M. Çelikbilek, A.E. Ersundu, S. Aydin, J. Non-Cryst. Solids, 378, 247 (2013).
- 29. G. Theophil Anand, L. John Kennedy, J. Judith Vijaya, J. Alloy Compd., 581, 558 (2013).