



Luminescence Properties of TeO₂-LiF-Gd₂O₃ Glasses

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ABSTRACT

In this work, the structural properties and spectroscopic behavior 80 mol.%TeO₂-20mol.%LiF glasses which were doped with 0.05, 0.2 mole% Gd₂O₃ have been studied. It was shown that, by increasing the amount of Gd₂O₃ the glass stability was decreased. The PL emissions at 431nm and 627nm wavelengths were distinguished by 320nm excitation. The FT-IR analysis showed deformed TeO₄ groups in these glasses.

1. INTRODUCTION

In the two past decades, tellurate glasses have attracted a great deal of interest [1–5], they are characterized by good chemical durability; low glass transition, high refractive index and high transmittance, especially in near to middle infrared regions [6–9]. Tellurate glasses are also important in electrical properties enhancement [10–16].

Recent works in these glasses include the fabrication of active lanthanide doped tellurite glass fiber devices, viz laser oscillators and amplifiers [17]. It is a renowned fact that the TeO₂ chemical can't form a glass solely, however by adding an intermediate (Gd₂O₃) and a modifier (LiF), it forms a good, high strength and transparency glass. There exists a substantial amount of literature which reported the thermal, optical and physical properties of TeO₂ based glasses and regarding the structure of pure TeO₂ and M₂O-TeO₂ (where M= Li, Na, K, R band s) glasses characterized by using X-ray Diffraction and spectroscopy techniques.

In the ternary system TeO₂-Li₂O-LiCl₃, Yoko et al.[18] prepared glasses containing LiCl in the 10-60 mol.% range; O'Vec'ogaelu [19] in the 40-60 mol.% range; Ravi Kanth Kumar[20] prepared glasses containing 30 mol.% LiF.

Adding fluoride ions into tellurite glasses is relevant, as it lowers the phonon energy maximum, leads to

fluorescence and laser emission enhancement due to participation of additional energy levels and high quantum efficiencies [21,]. On the other hand, the spectroscopic properties of Pr³⁺, Nd³⁺, Er³⁺ and Eu³⁺ ions in 70 mol.%TeO₂-30 mol.% LiF (TLF) glass have been studied. The phonon energy of this glass was found around 690 cm⁻¹, being much smaller than the values reported for borate, phosphate and germinate glasses. This property enhances the fluorescence responses [20]. The branching ratio for the important laser transition, viz ⁴F_{3/2}—⁴I_{3/2} of Nd³⁺, was found higher in this system compared to fluoride glasses which could have potential for laser applications. Moreover, for each composition system, the glass forming area depends on the preparation conditions, particularly on the cooling down rate.

However, no reported literature is available on the formation of optical properties of TeO₂-LiF-Gd₂O₃ glass systems and thus no detailed studies related to the glass stability has been reported.[17] In this work, we used the photoluminescence (PL) and photoluminescence excitation methods to study the properties of Tellurite glasses doped with Gd³⁺ ions.

The wide energy gap (32000 cm⁻¹) between the ground (⁸S_{7/2}) and the first excited (⁶P_{7/2}) states of a Gd³⁺ ion [22-23] allows one to treat this ion as a hypothetical mediator (sensitizer) between the matrix ions.

When the ⁶I_J energy level of Gd₃₊ is excited by 275nm UV light, the initial population relaxes to its lower energy levels until it arrives at the ⁶P_{7/2} level by phonon

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assistance and Gd_{3+} ions 313.5 nm characteristic emission appears [5].

Also, it was reported that, the gadolinium ions has network former and modifier roles in Tellurite glasses [17] and it depends on glass composition as well as the oxide gadolinium content, This work attempt to see the Gd_2O_3 role in glass forming in one side and on the other side to evaluate the spectroscopic properties of the Gd^{3+} ions in TeO_2 -LiF (TLF) glass.

To the best of our knowledge, this is the first study of the spectroscopic properties of Gd_2O_3 doped oxyfluoride glasses in tellurite-based systems.

2. EXPERIMENTAL PROCEDURES

80mol% TeO_2 – 20mol% LiF glass composition with 0.05, 0.2mole% Gd_2O_3 denoted by G5,G2 were prepared. The conventional casting technique was used. High purity powders of TeO_2 (99.99% purity, Alfa Aesar), Gd_2O_3 (99.8% purity, Alfa Aesar) and LiF (99.95% purity, Alfa Aesar) were thoroughly mixed. 7 g powder batches were melted in a platinum crucible with a closed lid at 750–800 °C for 30 mints in an electrical furnace. To achieve homogeneity, the cast was crushed, pulverized and remelted at the same temperature for additional 30 mints and was cast using the same procedure. Wet chemistry analyses carried out on bulk as-quenched TeO_2 -LiF- Gd_2O_3 glass samples revealed that the initial elemental stoichiometry of samples did not change after quenching. The melts were transferred to annealing furnace immediately and casted on heated stainless steel plate, the plate temperature was 350°C, then the sample was cooled at 10°C/mints. This sample, named slow cooled G2S. The sample quenched in air on cooled stainless steel plate, named fast cooled G2F. Each glass was annealed for 2 h at 350°C (the annealing temperature was chosen according to DTA results which is near to T_g) and then cooled to room temperature at 10 °C/mints. The samples were cut into small pieces with thickness of 2 mm and well polished. Bulk pieces of glasses, have a developed planar surface, are appropriate for a qualitative UV visible evaluation, carried out in the usual diffusion mode. To recognize the thermal behavior of the glass samples, differential scanning calorimetric analyses were carried out in a Netzsch DSC 204 F1 (limit of detection: <0.1 W, with an error estimate of ± 1 °C) using a constant sample weight of 25 ± 1 mg in aluminum pans, under air with a heating rate of 10 °C/mints.

Our first goal was to develop highly stable TeO_2 -LiF- Gd_2O_3 (TLG) glass compositions exhibiting low liquids temperatures and high spectral emission in the visible range. Well stabilized glasses show high resistance to crystallization during the glass casting, quenching and annealing processes. The DTA curves provided us by quantitative evidence for glass stability. Glasses were

prepared and analyzed by DTA for their tendency to crystallize.

The glass transition (T_g), first crystallization onset and peak (T_c/T_p) temperatures were determined from the DTA traces. The glass transition temperatures (T_g) were taken as the inflection point of the endothermic change of the calorimetric signal. Crystallization onset temperatures of glasses were specified as the beginning of the reaction where the crystallization first starts and peak temperatures represent the maximum value of the exothermal. The difference between the glass transition (T_g) and the first exothermic peak onset (T_p) temperature, $T = T_p - T_g$, indicates the value of glass stability, which was calculated. The glasses densities, ρ , were determined at room temperature by the Archimedes principle using distilled water as the immersion liquid and a digital balance of sensitivity 10–4 mg. The density values obtained by repeated measurements showed an error of $\pm 0.2\%$. The molar volume, V_M , was calculated as a function of the molar fraction of each of the three components and the oxygen molar volume, V_O , was calculated by using the following expression [24]:

$$V_O = \left(\sum \frac{x_i M_i}{\rho} \right) \left(\frac{1}{\sum x_i n_i} \right) \quad (1)$$

Where x_i is the molar fraction of each component i ; M_i is the molecular weight; ρ is the glass density and n_i is the number of oxygen atoms in each oxide.

The long wavelength transmission limit of a glass is usually determined by the multi-phonon absorption edge. This multi-phonon edge is determined by the highest energy vibration of the glass host and may be increased through the use of compositions that include heavy metal oxides as the glass former. For the common glass forming oxides, the multi-phonon edge and infrared transmission increase in the order $B_2O_3 < P_2O_5 < SiO_2 < GeO_2 = Al_2O_3 < TeO_2 < Bi_2O_3$. Therefore, UV– visible absorption from 300 to 800 nm was measured using a Perkin-ElmerS5. Photoluminescence (PL) was measured at room temperature by Xe excitation at 200-400 nm in Perkin-Elmer equipment. The luminescence was measured.

3. RESULT AND DISCUSSION

3.1. DTA Results DTA traces of G2F, S and G5 are shown in Figure 1. T_g temperatures as weak endothermic peaks, two other exothermic crystallization temperatures (T_p), were established in the DTA curves of samples.

The low T_p and the low value of $T_p - T_g$ parameter in the case of G5 sample can be related to the low thermal stability and hence to the modifier role of Gd_2O_3 in G5. It was reported that, weak and broad exothermic peak in DTA test is an indication of surface crystallization.

In G5, the different peak's sharpness with respect to other samples curves is considerable, this behavior may relate to the different crystallization mechanisms (bulk and surface), in the first and second exothermic peaks of G5 [25].

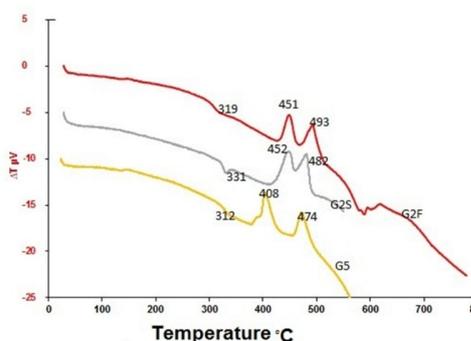


Figure 1. DTA results of G2S,F and G5.

The X-ray diffraction patterns, of samples heat treated at 450°C were presented in Figure 2. The TeO₂, gadolinium telluride, and very trace amount of lithium telluride were detected in these patterns. Obviously, the amounts and intensities of XRD peaks in the case of G5 are higher than two G2 samples. Also it can be said that, the major phase of these samples at 450°C is tellurium oxide which followed by gadolinium telluride crystallization through heat treating at the second DTA peak.

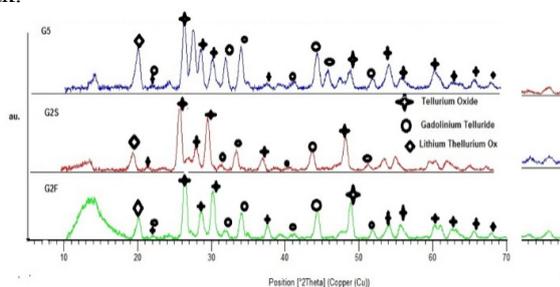


Figure 2. XRD pattern of G5 and G2F, S heat treated at 450°C -1h.

In addition, the molar volume of G5 is higher than G2, it can be said that, expected adding Gd₂O₃ to the tellurite network causes some type of structural rearrangement of the atoms. There is a possibility for the alteration of the geometrical configuration by adding Gd₂O₃ into the tellurite glassy network. The increase in density indicates that the Gd ions enter the tellurite glass network, which is related to variation of the molar volume of the samples (Table 1).

3.2. UV-visible absorption It is clear in Figure 3. that the absorption edge of G2F, G5 glasses occurs in the near-UV region (at 320 nm). This band is caused by forbidden transitions involving the 4f levels, and these 4f orbits are very effectively shielded from interaction with external fields of the hosts by 5s² and 5p⁶ shells.

TABLE 1. The characteristic temperatures and physical properties of glasses.

Sample	T _g (°C)	T _p (°C)	T _{p2} (°C)	T _p -T _g (°C)	V _a (cm ³)	V _m
G2F	319	451	493	132	15.99	25.74
G2S	331	452	482	121	16.33	26.33
G5	312	408	474	96	16.59	26.93

Hence, the states arising from the various ⁴f_n configurations are only slightly affected by the surrounding ions and remain practically invariant for a given ion in various compounds (Ligand field). Reisfeld proposed [26] that the rare-earth ions (like Gd³⁺) in glasses occupy the center of a distorted cube, which is made of a four tetrahedral of phosphate, silicate, borate, and germinate glasses. Each tetrahedron contributes two oxygen atoms to the coordination of the rare-earth ions.

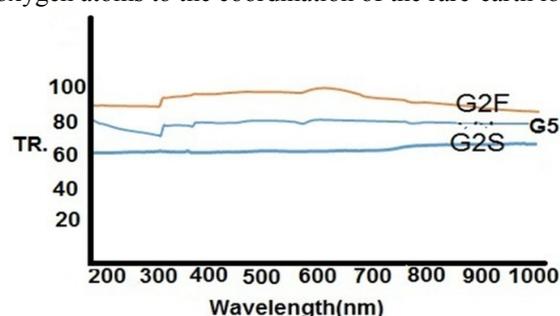


Figure 3. UV-visible absorption of G2F, S and G5 samples.

From the relatively high photon absorption in glasses, multi-phonon relaxation from higher-energy excited levels to lower-energy levels has a high probability. The 320 nm band corresponding to the ⁶P_{7/2} - ⁸S_{7/2} optical transition of the Gd³⁺ ion is observed [27]. In addition, some relatively broad bands are observed in the optical absorption spectra of the G5 and G2 samples. In the following, the 320nm wavelength was used as excitation wavelength to see the PL responses of studied samples.

3.3. Luminescence of the samples According to Figure 4. the main emission bands of G2F are at 431nm and 627nm while excitation wavelength is at 320nm. Emission at 431nm relates to the Te⁻⁴ S² Sp transition [27].

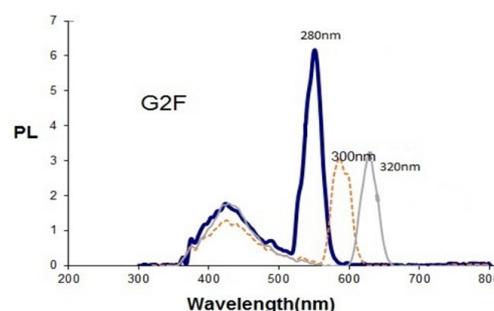


Figure 4. PL response of G2F sample, excited by 280, 300, 320nm.

Emission at 450-600 nm has already been reported in silicate glasses. The basis of this emission was related to optical activated defects. It has been mentioned that a charge transfer transition between a non-bonding orbital of the non-bridging oxygen and one of the three ligand oxygen caused to photoluminescence at 600nm[25]. This clarification may be verified the emission at 627nm wavelength of presented system. In addition, the other reason to emission at 627nm wavelength can be related to the Eu^{3+} impurity being in Gd^{3+} [28]. It is noticeable that, any transition associated with the absorption in the Gd^{3+} ion did not appear in photoluminescence responses of samples. By the varies excitation from 320 to 300 or 280 nm wavelength, the second emissions at 627nm will shift to short wavelength side, while the first wide emission at 431nm will not shifted as expected. If optical activated defects prove the emission at 627nm, it can be concluded that the photoluminescence of each defect's assigned frequencies, altered with the excitation wavelength.

Since the up conversion of Gd doped aluminosilicate glasses have been reported in recent papers, [29] the 600 nm wavelength was used to see the emissions of G2F, S and G5 samples, results are shown in Figure 4. According to Figure 5. excitation ($\lambda = 600\text{nm}$) of the Gd^{3+} doped tellurite glass leads to appearance of up-conversion luminescence with shorter wavelengths of 300, 376, 396 nm (-3.97 eV), i.e., with quantum energy higher than the energy of the exciting radiation. This fact can indicate the occurrence of sequential absorption of two-photon in the Gd^{3+} ion.

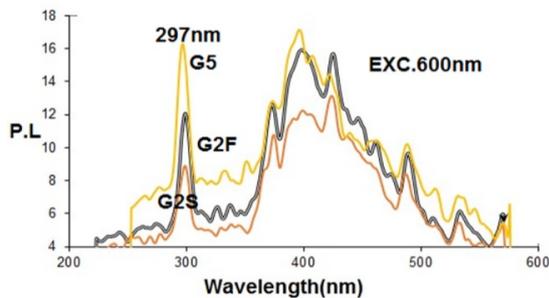


Figure 5. Represent the PL spectra of G5 and G2FS samples with 600nm excitation.

Figure 6. Compares the PL intensities of G2F and G5 samples excited by 320nm wavelength. Accordingly, the emission bands shift to higher wavelength by increasing the Gd_2O_3 content. Apparently, the disorder in the lattice results in varying surroundings of the Te^{4+} ions and, the emission spectra vary from site to site[28].

3.4. FT-IR Results

The infrared (IR) spectra of G5, G2F, S glasses are given in Figure 7. The bands around 542 and 440 cm^{-1} are assigned to the Gd-O vibration of cubic Gd_2O_3 [26]. No characteristic vibrations mode of bonds from Li_2O were directly detected in the FT-IR.

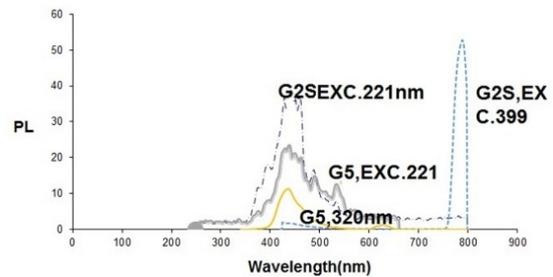


Figure 6. The PL response of G2 and G5 samples to excitation of 320nm.

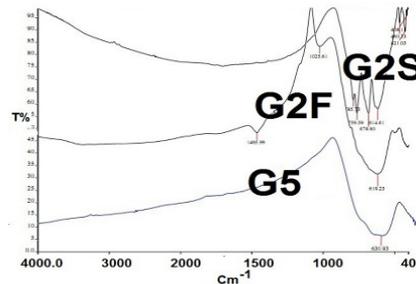


Figure 7. FT-IR results of G2 F,S, and G5 sample.

According to Dimitriva [31], the short-range order of certain tellurite glasses is similar to that of the crystals. This may contain, polyhedra of TeO_4 (C_{2v} symmetry), deformed TeO_4 groups, TeO_3 trigonal Pyramids (C_{3v} point symmetry) or combinations of these polyhedra which are characterized by a Maximum at 670 cm^{-1} and a shoulder at 635 cm^{-1} ; intense bands in the range of about 635–640 cm^{-1} and a shoulder at 670 cm^{-1} and the bands in the 700–670 cm^{-1} respectively. On this basis, the deformed TeO_4 groups in G2F, G5 may explain the FT-IR peak at 630 cm^{-1} . In addition, the small shift of FT-IR shoulder in G2F compared to the G5 was occurred, attributed to the glass structure of G2F, affected by Gd element–oxygen bond vibration in this glass. Most of the sharp absorption bands (in G2S) characteristic of the basic materials TeO_2 , is modified with the formation of broad and strong absorption bands (G2F). Moreover, more broadening and less bending, may be a characteristic of the glassy state in G2F and G5 samples.

4. CONCLUSION

Optical spectroscopic properties and thermal stability of Gd_2O_3 doped in 80mol. % TeO_2 - 20mol. % LiF glasses were studied. FT-IR visible results showed the deformed TeO_4 groups in these glasses. Uv-visible absorption proved some relatively broad bands in the optical absorption spectra of the G5 and G2 samples. Absorption edge in 320nm was recorded. Upon excitation at 320 nm, the emissions at 431nm and 627nm were noted. By modifying the excitation wavelength the PL peaks changes correspond to the disorder arrangement of Te^{4+} ions.

5. ACKNOWLEDGEMENT

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REFERENCES

- Vogel, E.M., Weber, M.J. and Krol. D.M., "Nonlinear optical phenomena in glass", *Physics and Chemistry of Glass*, Vol. 32, No. 6, (1991), 231-235.
- Kim, H.G., Komatsu, T., Shioyaa, K., Matusitab, K., Tanakac, K. and Hiraoc, K., "Transparent tellurite-based glass-ceramics with second harmonic generation", *Journal of Non-Crystalline Solids*, Vol. 208, No. 3, (1996), 303- 307.
- Kim, S.H., "Nonlinear optical properties of TeO₂-based glasses: MO_x-TeO_x", *Journal of American Ceramic Society*, Vol. 78 (1995) 1061-1065.
- Dimitrov, V., Sakka, S., "Electronic oxide polarizability and optical basicity of simple oxides", *Journal of Applied Ceramic*, Vol. 79, No. 3, (1996), 1736-1740.
- Azianty, A., Yahya, A.K. and Halimah, M.K., "Effects of Fe₂O₃ replacement of ZnO on elastic and structural properties of 80TeO₂-(20 - X)ZnO-xFe₂O₃ tellurite glass system", *Journal of Non Crystalline Solids*, Vol. 358, (2012), 1562-1568.
- Bürger, H., Kneipp, K., Hobert, H. and Vogel, W., "Glass formation, properties and structure of glasses in the TeO₂ – ZnO system", *Journal of Non Crystalline Solids*, Vol. 151, (1992), 134-142.
- Duan, X., Yuan, D., Cheng, X., Liu, Z. and Zhang, X., "Preparation and optical properties of Co²⁺-doped Li₂O–Ga₂O₃–SiO₂ glass-ceramics", *Journal of Alloys and Compounds*, Vol. 453, (2008), 379-381.
- Yang, H.X., Lin, H., Lin, L., Zhang, Y.Y., Zhai, B. and PUN, Y.B.E., "Powerful visible upconversion fluorescence of Er³⁺ in novel bismuth gallate glasses compared with in common tellurite glasses", *Journal of Alloys and Compounds*, Vol. 453, (2008) 493-498.
- Gangfeng, Y., Zhang, Q., Shi, D. and Jiang, Z., "Tm³⁺-Doped Gallium–Germanium–Bismuth–Lead Glasses as 1.47 μm Fiber Amplifier Materials", *Journal of the American Ceramic Society*, Vol. 90, No. 1, (2006), 307-310.
- Paul, T. and Ghosh, A., "Ionic conductivity and dielectric relaxation in Y doped La₂Mo₂O₉ oxide-ion Conductors", *Journal of Applied Physics*, Vol. 116, (2014), 1-8.
- Ghosh, A., "Electrical properties of semiconducting amorphous copper-tellurite glasses", *Journal of Physics Condensed Matter*, Vol. 1, No. 42, (1989), 7819-7828.
- Ghosh, A., "Electrical transport properties of molybdenum tellurite glassy semiconductors", *Philosophy Magazine*, Vol. 61, No. 1, (1990), 87-96.
- Ghosh, A. and Pan, A., "Scaling of the Conductivity Spectra in Ionic Glasses: Dependence on the Structure", *Physical Review Letter*, Vol. 84, No. 10, (2000), 2188-2190.
- Wang, J.S., Vogel, E.M. and Snitzer, E., "Tellurite glass: a new candidate for fiber devices", *Optical Material*, Vol. 3, (1994), 187-203.
- Reisfeld, R., "Radiative and non-radiative transitions of rare-earth ions in glasses", *Structure and Bonding*, Vol. 22, (1975), 123-175.
- El-Mallawany, R., "Theoretical analysis of the electrical properties of tellurite glasses", *Materials Chemistry and Physics*, Vol. 37, No. 4, (1994), 376–381.
- Moawad, H.M.M., Jain, H., El-Mallawany, R., Ramadan, T. and El-Sharbiny, M., "Electrical Conductivity of Silver Vanadium Tellurite Glasses", *Journal of the American Ceramic Society*, Vol.85, No. 11, (2000), 2655–2659.
- Yoko, T., Kamiya, K., Yamada, H. and Tanaka, K., "Glass-Forming Region and Structure of Oxyhalide Glasses in the System LiCl-Li₂O-TeO₂", *Journal of American Ceramic Society*, Vol. 71, No.2, (1988), C-70–C-71
- Öveçoğlu, M.L., Özen, G., Demirata, B. and Genç, A., "Microstructural characterization and crystallization kinetics of (1-x)TeO₂-xLiCl (x=0.6-0.4mol) glasses", *Journal of European Ceramic Society*, Vol. 21, (2001), 177-183.
- Kadono, K., "Radiative and non-radiative relaxation of rare-earth ions in Ga₂S₃-GeS₂-La₂S₃ glasses", *Journal Of Non Crystalline Solids*, Vol. 259, (1999), 39-44.
- Lemm, J.M., "Handbook on the Physics and Chemistry of Rare Earths", Vol. 25, (1998).
- Qin, F., Zheng, Y., Yu, Y., Zheng, C., Tayebi, P.S. and Zhang, Z., "Ultraviolet upconversion luminescence of Gd³⁺ from Ho³⁺ and Gd³⁺ codoped oxide ceramic induced by 532-nm CW laser excitation", *Optics Communications*, Vol. 284, (2011), 3114-3117.
- Qin, W., Cao, C., Wang, L., Zhang, J., Zhang, D.M. and Zheng, K., "Ultraviolet upconversion fluorescence from 6D(J) of Gd³⁺ induced by 980 nm excitation", *Optics Letters*, Vol. 33, (2008), 2167-2169.
- Shaaban, E.R., Shapaan, M. and Saddeek, Y.B., "Structural and thermal stability criteria of Bi₂O₃-B₂O₃ glasses", *Journal of Physical Of Condensed Material*, Vol. 20, (2008), 1-9.
- Pe' rez, J.M., Teixeira, S.R., Rincón, J.M. and Romero, M., "Understanding the Crystallization Mechanism of a Wollastonite Base Glass Using Iso conversional, IKP Methods and Master Plots", *Journal of American Ceramic Society*, Vol. 95, (2012), 3441-3447.
- Mazourak, Z., Romanowski, W.R. and Jeżowska-Trzebiatowska, B., "Radiative and non-radiative transitions in ErP5O14 single crystals", *Journal of Luminescence*, Vol. 17, No. 4, (1978), 401-409.
- Raouf A. H. El-Mallawany, "Tellurite Glasses handbook" Physical Properties and Data, (2002) by CRC Press LLC, chapter1, Introduction to tellurite glass.
- Blasse, G., Dirksen, G.J. and Oomen, E.W.J.L., "Luminescence of Tellurite Anti-glass Phases", *Journal Of Solid State Chemistry*, Vol. 63, (1986), 148-153.
- Mal'chukova, E.V., Nepomnyashchikh, A.I., Boizot, B., Shamirzaev, T.S. and Petite, G., "Luminescence of Aluminoborosilicate Glasses Doped with Gd³⁺ Ions", Vol. 52, (2010), 1919-1924.
- Ranfagni, A., Mugnai, D., Bacci, M., Viliani, G. and Fontana, M.P., "The optical properties of thallium-like impurities in alkali-halide crystals", *Advances in Physics*, Vol. 32, (1983) 823-905.
- Dimitriev, Y., Dimitrov, V. and Arnaudov, M. "IR spectra and structure of Tellurite glass" *Journal Of Material Science*, Vol.18, (1983), 1353-1358.