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Measurements of Defect Structures by Positron Annihilation Lifetime Spectroscopy of the Tellurite Glass $70TeO_2$-$5XO$-$10P_2O_5$-$10ZnO$-$5PbF_2$ (X = Mg, Bi_2, Ti) Doped with Ions of the Rare Earth Element Er^{3+}

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Abstract

The objective of the study was the structural analysis of the $70TeO_2$-$5XO$-$10P_2O_5$-$10ZnO$-$5PbF_2$ (X = Mg, Bi_2, Ti) tellurite glasses doped with ions of the rare-earth elements Er^{3+}, based on the PALS (positron annihilation lifetime spectroscopy) method of measuring positron lifetimes. Values of positron lifetimes and the corresponding intensities may be connected with the sizes and number of structural defects, the sizes of which range from a few angstroms to a few dozen nanometers. Experimental positron lifetime spectrum revealed existence of two positron lifetime components τ_1 and τ_2. Their interpretation was based on two-state positron trapping model where the physical parameters are the positron annihilation rate and positron trapping rate.

Background

Tellurite glasses belong to a group of materials which, due to their properties, can be applied in optoelectronics and photonics, as fast ion conductors, photonic materials and in lasers [1, 2]. Tellurite glasses are treated as special glasses on account of the separately molten TeO_2, which does not display glass-making properties. If TeO_2 is connected with a stabilizing oxide, the glass-making properties of the tellurite oxide are determined. Due to the fact that the tellurite glasses are characterised by high linear as well as nonlinear index, they have become the major research topic of nonlinear optics [3, 4]. High density of tellurite glasses, their low glassy state transition temperature and wide range of IR permeability (melting point lower than 1000 °C) [1] should also be noted.

Tellurite glasses are characterized by photon energy which is 750 cm^{-1}, thus determining the probability of radiative transitions as well as longer lifetime levels of energetic ions of the rare earth elements [5]. Low energy of the photons of the tellurite glasses allows to use them as materials for building optical amplifiers and laser devices. An important characteristic of tellurite glasses is their ease of dissolving rare earth elements, such as Pr^{3+}, Er^{3+}, Nd^{3+}, etc. An inseparable element of this phenomenon is the increase of the luminescence effects required in laser glasses [6, 7]. Due to their physic-chemical properties, there is a need for further research on the glasses. Changing the chemical constitution of the glasses as well as different methods of synthesis make possible a wide range of their formation in terms of optical and technological properties [8–11].

It is certainly true that one of the most important properties of tellurite glasses is their ability to attach ions of the rare earth elements, which results in an increased effectiveness of the luminescence, which is required in laser glasses. Unique properties of the tellurite glasses cause that there is a very wide potential for their application. Application of tellurite glasses are results from the atomic structure of the material, as well as from the structure of the voids (gaps, free volumes). The structure of telluric glasses have areas with different degrees of order in the form of a coordination polyhedrons forming the roof construction: glass and

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having their crystalline counterparts, and empty spaces in which ions may be glass modifiers [12, 13]. To describe the actual structure of glass and nanocrystalline glass-ceramics is necessary to develop alongside conventional methods such as X-ray diffraction, electron or neutron diffraction of high energy synchrotron radiation Raman spectroscopy, infrared spectroscopy, the new experimental methods sensitive to the voids in the structure of glasses. This idea can be realized thanks to the free annihilation of particle with an anti-particle, with a simultaneous emission of two gamma quanta (2γ). In such cases, two positron lifetime components τ_1 and τ_2 are obtained during measurements of positron lifetime spectroscopy PALS [14–17]. The τ_1 component is responsible for positron and electron free annihilation, as well as for the annihilation with electrons localized in point defects of the vacancy type, whereas the τ_2 component is connected with the electrons of volume anionic defects created in monovacancies as well as in defects formed on grain boundaries or dislocations [18–20]. Mathematical formalism of the known two-state positron trapping model with only one kind of traps [21] was utilized to parameterize mean τ_{av} and defect-free bulk τ_b lifetimes, as well as trapping grate in defects κ_d. In addition:

1. average positron lifetime τ_{av} reflecting defectivity of the medium dominating in the examined glasses:

$$\tau_{av=}\frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2} \tag{1}$$

2. bulk positron lifetime τ_b in the defect-free part of the material:

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}} \tag{2}$$

3. positron capture rate by the traps (defects) κ_d:

$$K_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right) \tag{3}$$

4. a quantity connected with the average size of defects in which annihilation takes place:

$$\tau_2 - \tau_b \tag{4}$$

5. the parameter change reflects the change in the geometry of defects in volume, nature of capture and positron trapping centres [22]:

$$\tau_2/\tau_b \tag{5}$$

6. trapped positron fraction η:

$$\eta = \tau_1 \kappa_d \tag{6}$$

Experiment and methods

Tellurite glasses were melted in an electric furnace at the temperature of 850 °C in the air atmosphere in platinum-gold melting pots with lids. Next, the melted material was poured into a brass form at the temperature of 380 °C. In order to eliminate the stresses created in the material, the glasses were subjected to relief annealing at the temperature of 380 °C for 2 h. Before the measurements were started, the tellurite glasses were subjected to grinding and polishing. The tellurite glasses, the composition of which was presented in Table 1, were examined. Positron annihilation lifetime spectroscopy PALS and spectrum analyses carried out with the use of the LT9 software were applied to examine parameters of tellurite glasses structural defects [23]. Measurements of positron lifetimes were made at room temperature with the use of ORTEC spectrometer [24, 25] based on the start-stop principle. Peak resolution FWHM of the apparatus was determined with the use of a ^{60}Co radioactive source and was equal to 260 ps. The source of positrons was the ^{22}Na sodium isotope of 4×10^{-5} Bq activity closed in kapton film. Together with the samples, it formed a "sandwich" type system. The measurements were carried out at room temperature. The examples of experimental PALS spectra of tellurite glasses and tellurite glasses doped Er^{3+} samples are shown in Fig. 1.

Results

The best fitting in tellurite glass samples was found to occur at the resolution of the annihilation spectrum into two components of τ_1 and τ_2 lifetimes and respective I_1 and I_2 intensities (Table 2). No τ_3 component, responsible for formation of the positronium (hydrogen-like atom) has been found in the examined samples. When analysing values of τ_1 and τ_2, the double-state model of positron annihilation was investigated, according to which a positron annihilates from a free state and from one of the states localized in a defect at the absence of the de-trapping process. Having calculated the main annihilation parameters with the use of the LT programme, positron lifetimes τ_1 and τ_2 and their intensity, as well as positron capture parameters

Table 1 Chemical composition of tellurite glasses

Sample	Composition [%mol]
Te 1	$70TeO_2$-$5MgO$-$10P_2O_5$-$10ZnO$-$5PbF_2$
Te 2	$70TeO_2$-$5MgO$-$10P_2O_5$-$10ZnO$-$5PbF_2$ + 600[ppm]Er_2O_3
Te 3	$70TeO_2$-$5Bi_2O$-$10P_2O_5$-$10ZnO$-$5PbF_2$
Te 4	$70TeO_2$-$5Bi_2O$-$10P_2O_5$-$10ZnO$-$5PbF_2$ + 600[ppm]Er_2O_3
Te 5	$70TeO_2$-$5TiO$-$10P_2O_5$-$10ZnO$-$5PbF_2$
Te 6	$70TeO_2$-$5TiO$-$10P_2O_5$-$10ZnO$-$5PbF_2$ + 600[ppm]Er_2O_3

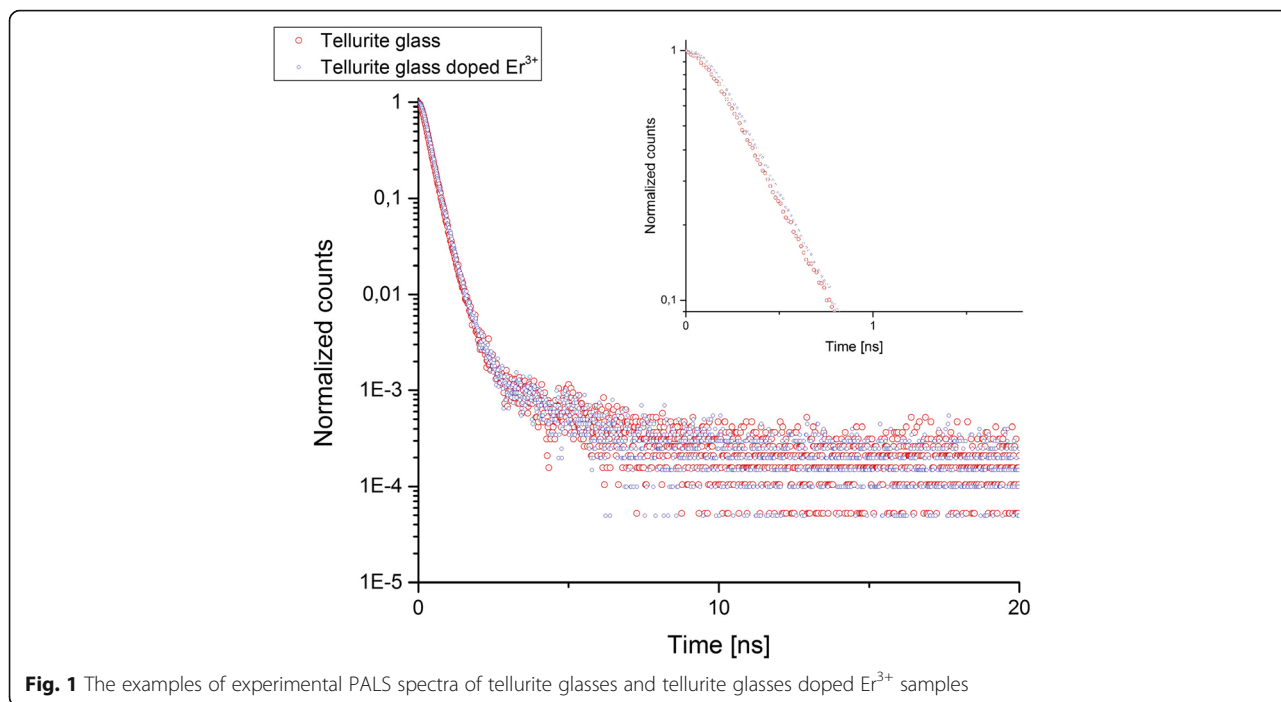Pach *et al. Nanoscale Research Letters* (2017) 12:304

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Fig. 1 The examples of experimental PALS spectra of tellurite glasses and tellurite glasses doped Er^{3+} samples

τ_{av}, τ_b, κ_d, τ_2-τ_b, τ_2/τ_b, η (Table 3) were calculated. The main parameters of annihilation converted as mean ± measurement error were calculated using the program LT. Size was calculated from the average measurements of positron lifetime and intensity [23].

Discussion

On the basis of the taken measurements of positron lifetimes, τ_1 and τ_2 are slightly different, within the margin of errors, for the basic samples and for the doped samples. Distinct changes occur in case of values of the I_1 and I_2 intensities. After doping the basic glass with Er_2O_3 admixture, a significant increase of the I_2 intensity can be observed. In the examined glasses, the number of volume defects increases together with addition of ions of the rare earth elements.

Basing on the taken measurements, it is possible to state that doping the basic sample with the Er_2O_3 ions causes distinct changes in the values of parameters responsible

for positron capture. It can be concluded that the capture of positrons are responsible anionic gaps in the form of voids or defects in the structure.

Taking into account calculations of positron capture parameters (Table 2), it is possible to state that:

➤Rates of the κ_d positron capture, when compared to the basic samples, distinctly increase during doping in all the investigated tellurite glasses. This reflects a much higher concentration of volume defects and positron capture centres in the samples doped with Er_2O_3 ions.

➤The value of the τ_2-τ_b parameter for the Te2 sample remains at the same level, whereas it distinctly falls for the other samples of the investigated tellurite glasses. It means that in the other samples average sizes of

Table 2 Fitting parameters of tellurite glasses mathematically treated with two-component fitting procedure by LT computer program

Sample	τ_1[ns]	I_1 [%]	τ_2 [ns]	I_2 [%]
Te 1	0.181 ± 0.002	75.31 ± 0.51	0.374 ± 0.005	24.69 ± 0.74
Te 2	0.181 ± 0.002	71.63 ± 0.84	0.379 ± 0.006	28.37 ± 0.63
Te 3	0.176 ± 0.003	72.32 ± 0.92	0.353 ± 0.007	27.68 ± 0.82
Te 4	0.171 ± 0.003	67.27 ± 0.83	0.332 ± 0.004	32.73 ± 0.84
Te 5	0.179 ± 0.003	70.64 ± 0.83	0.360 ± 0.006	29.36 ± 0.83
Te 6	0.171 ± 0.003	66.03 ± 0.92	0.342 ± 0.006	33.97 ± 0.85

Table 3 Positron capture parameters

Sample	τ_{av}[ns]	τ_b[ns]	κ_d[ns^{-1}]	τ_2-τ_b[ns]	τ_2/τ_b	η[au]
Te 1	0.229 ±0.005	0.207 ±0.004	0.704 ±0.013	0.167 ±0.003	1.803 ±0.041	0.127 ±0.002
Te 2	0.237 ±0.005	0.212 ±0.004	0.819 ±0.022	0.167 ±0.003	1.784 ±0.042	0.148 ±0.003
Te 3	0.225 ±0.005	0.204 ±0.004	0.789 ±0.022	0.149 ±0.003	1.727 ±0.031	0.138 ±0.003
Te 4	0.224 ±0.004	0.203 ±0.004	0.928 ±0.021	0.129 ±0.002	1.633 ±0.033	0.158 ±0.003
Te 5	0.232 ±0.005	0.210 ±0.004	0.825 ±0.021	0.150 ±0.003	1.714 ±0.032	0.147 ±0.003
Te 6	0.229 ±0.005	0.206 ±0.004	0.993 ±0.021	0.136 ±0.003	1.662 ±0.032	0.169 ±0.003

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defects, in which positron captures occur, decrease during doping.

➢The τ_2/τ_b ratio diminishes during doping of the basic sample, which indicates different nature of volume defects. Places in which positrons are captured are of different nature, depending on embedding erbium oxide in the structure of a glass in the examined materials.

➢The η fraction of the trapped positrons distinctly increases in the investigated samples when the basic sample is doped with the erbium ions, where the value increases by c. 15%, which is evidence of increasing free volume fraction.

Conclusions

To sum up, analysis of the examined tellurite glasses according to the double-state model, for the τ_{av}, τ_b, κ_d, τ_2-τ_b, τ_2/τ_b, and η parameters confirms division of the examined samples into two groups: clean and doped with the Er_2O_3 ions. Three parameters τ_{av}, τ_b,τ_2/τ_b for the samples Te1, Te2 do not demonstrate any distinct division (changes occur within the margin of error), parameters are not changed or are maintained at the same level under the influence of doping. As for the other samples of the examined tellurite glasses both, the nature of volume defects and average size of defects undergo reduction. The changes may result from the properties of an agent that can be found in each of the examined samples. In the samples Te1, Te2 the agent is the oxide which shows paramagnetic properties, whereas in the other samples, it is the oxide which displays diamagnetic properties. The rate of positron capture by the traps increases in all the examined samples and so does the fraction of the trapped positrons.

Abbreviations
FWHM: Full width at half maximum; LT9: Lifetime programme; PALS: Positron annihilation lifetime spectroscopy

Authors' contributions
KP, JF, and EG developed the idea of the research. ESY and VB prepared samples for experiments. KP and JF performed PALS measurements. KP and EG analysis of obtained data using LT9 program. All authors read and approved the final manuscript.

Competing interests
The authors declare that they have no competing interests.

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