

Investigation of Sol-Gel Glasses Doped with Lanthanide Ions by Spectroscopic, Acoustic, and Positron Annihilation Methods

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The results of optical spectroscopic (UV-Vis, absorption, and emission), acoustic (sound velocity of precursor solutions, the solvation numbers of ions in these solutions), and positron annihilation of glasses are presented and discussed for silica glasses obtained by the alcoholic sol-gel technique, doped with selected lanthanides and with some addition of ethylene glycol. The aim of these investigations was the determination of the local structure of glass close to lanthanide ions and its influence on the optical properties of the material. The results show that the existence of alcohol-glycol solvates in glasses decrease the number of empty voids in its structure as well as the size of the remaining ones. One can suppose that this is caused by cooperative interactions of glycol molecules with the network of hydrogen bonds of the glass.

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1. Introduction

Silica glasses obtained by means of alcoholic sol-gel technique are very useful materials because of low temperature of glass formation, very different from the typical glass production. This allows one to introduce many compounds to the final glass, like metal clusters [1], organic molecules [2], including even peptides [3] and porphyrins [4]. Another class of possible additives are lanthanide ions.

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Silica glasses obtained with an addition of diols to initial alcohol solution and doped with lanthanide salts are promising optical materials, which can easily find applications as luminescent diodes, scintillators, lasers, etc. For the latter purpose, glasses doped with Nd^{3+} ions were investigated intensively [5], as well as those containing Er^{3+} [6]. The optical properties of lanthanide doped silica glasses depend strongly on the local structure of glass in the vicinity of lanthanide ions. However, the number of experimental techniques, which are able to give insight into the microscopic structure of amorphous substances like glasses, is very limited.

In this work we are trying to correlate the experimental results obtained from optical spectroscopy with those from positron annihilation. Moreover, the acoustic (sound velocity and adiabatic compressibility) method was also applied for the initial, liquid mixture of ethanol with ethylene glycol and lanthanide salts. The reason of applying the latter technique was to determine the solvation number of lanthanide ions in solution. While silica interacts with these ions rather weakly, it was rational to assume that it does not compete with alcohols in the solvation sphere and, consequently, the structure of solvates existing in the initial (precursor) mixture remains undisturbed after the formation of glass in the sol-gel process. It will be proved that this assumption is valid in the systems under investigation.

2. Experimental

2.1. Chemicals and solutions

Lanthanide hydrated chlorides, $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (where $\text{Ln} = \text{Pr}, \text{Eu}, \text{Yb}$) were prepared by treating respective oxide (99.9%, Fluka AG, Switzerland) by concentrated hydrochloric acid and crystallization. Anhydrous ethyl alcohol (99.8%, Chempur, Piekary Śląskie, Poland) was used without further processing and tested for purity using UV-Vis and IR spectroscopies. Ethane-1,2-diol (ethylene glycol, > 99.0%, Chempur, Piekary Śląskie, Poland) was vacuum distilled and stored over molecular sieves. Initial solutions of the electrolyte, i.e. the most concentrated ones, were obtained by weighing, and the others were prepared by their dilution by volume using the mixed solvent prepared by weighing, the same for all the series.

2.2. Density and ultrasonic velocity measurements

All measurements were performed at 298.15 K, controlled with an accuracy of at least +0.02 K. Density was measured with an accuracy of $\pm 0.1 \text{ kg m}^{-3}$ using a MG-2 vibrating tube microprocessor device (Ecolab, Poland). Sound velocity was determined using a computer-steered OPKUD 01/100 / OPGUD (Optel, Poland) apparatus, with the absolute accuracy better than $\pm 0.2 \text{ m/s}$ and the precision of the same order. From these data, we calculated the adiabatic compressibility coefficients κ_S of solutions, using the Laplace formula $\kappa_S = (c^2 \rho)^{-1}$, where c — sound velocity, ρ — density.

2.3. Preparation of sol-gel glasses

The glasses were prepared by mixing appropriate amounts of tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TESO), with initial solution, i.e. ethanol with (or without) addition of lanthanide salt and/or ethylene glycol, and a catalyser (typically hydrochloric acid). The mixture was stored in small plastic vessels of square base, with only a little hole in its Parafilm closing to avoid too fast drying. Depending on the rate of drying, the transition into glass takes a few weeks or even a few months. Too fast drying yields powder glasses, not useful for our experiments.

Only glasses of a good optical quality (tested by polarized light microscopy) were used in UV-Vis spectroscopy and positron annihilation experiments.

2.4. Spectroscopic measurements

Electronic emission spectra were recorded using a spectrofluorometer SPF-500 (SLM Aminco). The apparatus is equipped with two monochromators and detector-photomultiplier Hamamatsu R955HA, which allows one to work in the spectral range of 200–900 nm. The activation source was a xenon lamp (250–300 W). The resolution was 0.1 nm.

2.5. Positron annihilation measurements

The annihilation experiments were carried out at the room temperature (approx. 20°C) with a standard measuring device based on the “fast–slow” coincidence technique described elsewhere [7].

3. Results and discussion

Glasses are — from the physical point of view — supercooled liquids, so it seemed to us quite rational to suppose that a structure of a solvate existing in the liquid phase remains undisturbed after the formation of glass from the liquid. The problem is to prove this assumption while the experimental methods of investigating the structure of liquids are not the same as for solids.

Determination of the exact structure of solvates of lanthanides is not an easy task, even in aqueous solutions: see for example the paper of Diaz-Moreno et al. [8], where the combination of advanced experimental methods (in particular the X-ray absorption spectroscopy (XAS)) could finally determine the hydration structure of ytterbium bromide (it was eight-fold). In the same work it was found that the structure of these hydrates remains unchanged in glassy state — the observation well proving our assumption stated above.

Our idea was to apply and to compare the results of spectroscopic measurements of absorption and emission (in the UV-Vis region) for both phases with acoustic ones for liquids and the positron annihilation ones for solids.

We started with the initial, liquid solvents containing, respectively, 0, 2, 4, 6, 8, and 10% mol of ethylene glycol in ethanol. In these mixed solvent we measured the sound velocity and density with an addition of PrCl_3 . This lanthanide was chosen arbitrarily and we supposed that replacing praseodymium with any other

lanthanide should cause no significant differences. The reason of this particular choice of components of the solvent (ethanol and ethane-1,2-diol) was that they have molecules similar in size, interactions, and geometry, suggesting that the replacement of one molecule by another one should be easy in the solvation shell.

The sound velocity and density, via calculation of the adiabatic compressibility coefficient κ_S , allowed one to calculate the mean solvation numbers applying the formula of Pasynski [9, 10] — developed initially for electrolytes but undoubtedly valid also for non-electrolytic solutes [11]:

$$n_h = \frac{n_{\text{H}_2\text{O}}}{n_{\text{solute}}} \left(1 - \frac{\kappa_{\text{solution}}}{\kappa_{\text{H}_2\text{O}}} \right), \quad (1)$$

where n_h — the hydration number, $n_{\text{H}_2\text{O}}$ — the number of moles of water in a sample, n_{solute} — the number of moles of the solute in this sample, $\kappa_{\text{H}_2\text{O}}$ and κ_{solution} — compressibilities of water and of the solution, respectively.

The solvation numbers obtained by this procedure were independent of the content of ethylene glycol in ethanol in the whole range of compositions, as it is illustrated in Fig. 1.

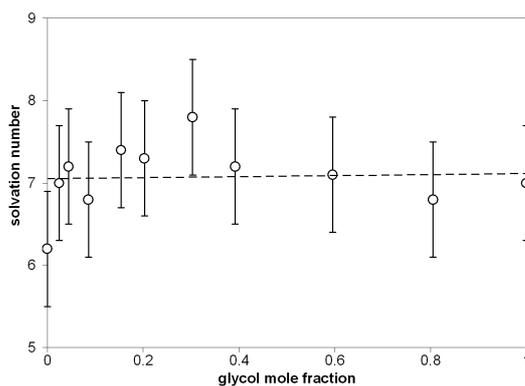


Fig. 1. The solvation numbers of PrCl_3 in ethanol + ethylene glycol mixtures versus the solvent composition.

The value of solvation number n_S , equal approximately to 7 in the whole range of solvent compositions, is quite rational if one remembers that the acoustic method of its determination yields only an average quantity, which combines the solvation numbers of cations and anions. Because of the charge and size of Pr(III) ion, the contribution of chloride anions should be, however, almost to be neglected. Thus, the real n_S of Pr^{3+} cation is most probably equal to *ca.* 6.

The independence of n_S on glycol content is easy to understand if one assumes that glycol molecules can freely replace those of ethanol in the solvation shells of praseodymium ions. The confirmation was possible, quite surprisingly, because in some samples, instead of optically anisotropic glasses, crystals of a green compound were obtained. After X-ray analysis it was found that these crystals

are formed of dimeric ethylene glycol solvates of the formula $C_{12}H_{24}Cl_3O_{12}Pr_2 \cdot 3(Cl)$, containing ninefold praseodymium atoms with three chlorine atoms bridging them. Naturally, the coordination of glycol molecules via oxygen atoms means that the replacement of these ligands by ethanol is very possible in the systems under investigation.

The next step was to investigate the solutions by spectroscopic method. The examples of the obtained spectra are shown in Fig. 2.

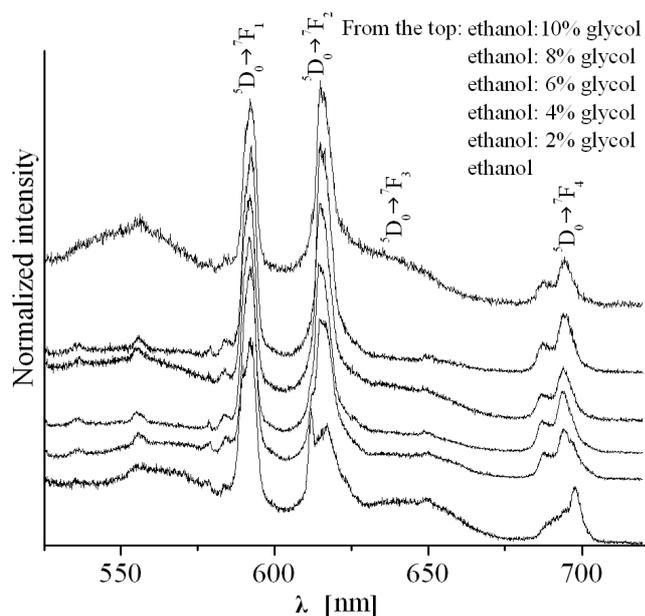


Fig. 2. Emission spectra of sol-gel glasses prepared by means of 1% europium (III) chloride in ethanol and mixtures of solvents ethanol: ethylene glycol, measured at 293 K. The legend lists glycol contents in the same order as they appear in the figure (the top curve corresponds to the solution of 10% mol of glycol in ethanol curve, the bottom one — to pure ethanol solution; the succeeding spectra are shifted for clarity).

Europium compounds were chosen for spectroscopic measurements because both 7F_0 ground state multiplet and 5D_0 emitting level are non-degenerated. This is why this ion is particularly useful as an optical probe [12].

The emission spectra of sol-gel containing europium chloride obtained at 293 K are shown in Fig. 2. When the ratio ethanol: ethylene glycol in the initial solution of $EuCl_3$ is changing, one observes changes in the intensity of ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions, which give information on the site symmetry of Eu^{3+} ion. The relative intensities of ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions indicate the lowering of symmetry of active center in glasses with an addition of ethylene glycol. Thus the electric-dipole ${}^5D_0 \rightarrow {}^7F_2$ transition probability is the greatest. The

change of site symmetry of Eu^{3+} ion is already observed when the concentration of glycol is about 2% mol. In the case of 10% mol ethylene glycol, the intensity of ${}^5D_0 \rightarrow {}^7F_2$ is almost equal to that of ${}^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition.

Also the comparison of the spectra of liquid solutions (not shown here) with those of glasses clearly shows that the symmetry of the surrounding of lanthanide ion remains practically undisturbed after the formation of gel, and further glass. When adding ethylene glycol to the initial solution, the ${}^5D_0 \rightarrow {}^7F_4$ band is split, i.e. the symmetry is lowered by the penetration of glycol molecules into the solvation sphere of the europium cation. Exactly the same lowered symmetry is also well observed in the glass phase.

The lowering of the symmetry controlled by the content of the glycol additive can have an important practical meaning because it leads to a changed number and order of the electronic levels and, consequently, affects the efficiency and energy of the observed optical absorption and emission lines.

Finally, we applied the positron annihilation technique to test the microscopic structure of the glasses and the effect of addition of both ethylene glycol and lanthanide salts to the reaction mixture. The examples of the results — here in the form of normalized time spectra — are shown in Fig. 3.

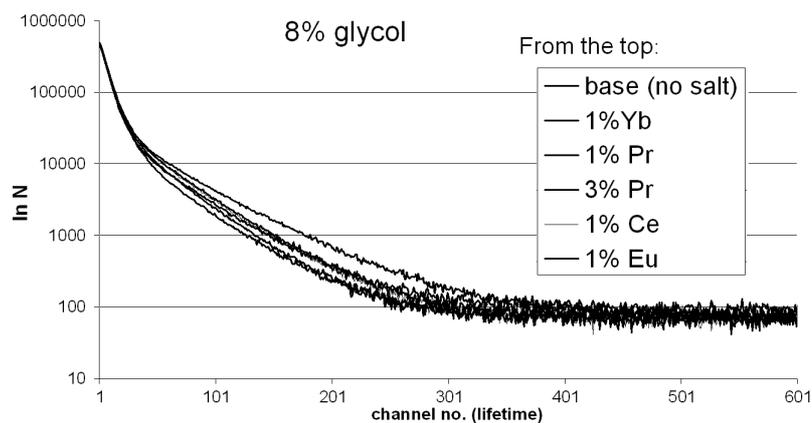


Fig. 3. The examples of the time-spectra of positron annihilation in selected glasses investigated in this work. The legend contains electrolytic additives in the same order as they appear in the figure (the base corresponds to the top curve, 1% Eu — to the bottom one). The differences caused by minor addition of lanthanide chlorides are clearly seen.

So far glasses were investigated by annihilation of positrons mainly for determining their porosity and texture [13–15] — the factors important for macroscopic optical properties of materials. In particular, this technique was able to evaluate both the mean number and size distribution of nanopores and showed how these properties change with the temperature treatment of glasses and their exposition to different atmospheres during preparation.

The most striking feature of the annihilation results is a very strong influence of the lanthanide salts added on the spectrum. One should remember that the lanthanides contents were, typically, only 1% mol — much too low to affect the spectrum meaningfully only because of the average increase in the electron density.

The annihilation spectra were primarily resolved into four components, but further it has been found that three of them are sufficient. Moreover, and more important, when resolving the spectra into three components only, one obtains more illustrative and clear results. In fact, only the long-living component was interpreted, here denoted by subscript “3”, while it corresponds to the microscopic, local structure of glasses, which was our main area of interest in this work. The results are summarized in Figs. 4 and 5.

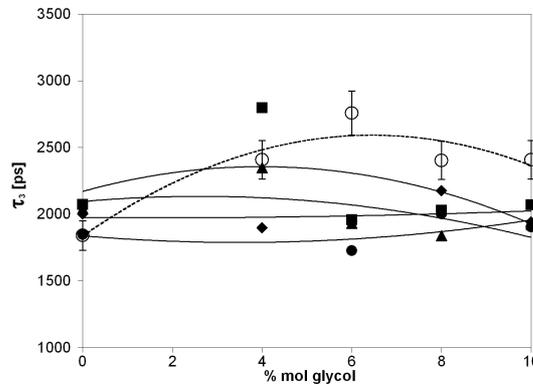


Fig. 4. The dependence of lifetime of the long-living component of annihilation spectra on glycol content in the initial solution. Symbols: ▲ — Eu 1%, ■ — Yb 1%, ◆ — Pr 1%, ● — Pr 3%, ○ — matrix (no lanthanide added).

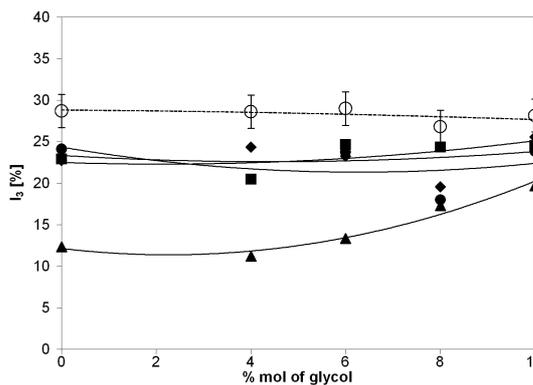


Fig. 5. The dependence of intensity of the long-living component of annihilation spectra on glycol content in the initial solution. For symbols see caption of the preceding figure.

In the most simplified but reasonable interpretation, the intensity of the short-lived components should increase (and — consequently — that of the long-lived component should decrease) when the mean electron density of the system increases. The range of salt concentrations is, however, too low in our samples to cause an observable changes in intensities, i.e. any observed changes of intensities must be caused by structural effects only.

Thus, the main conclusions that can be drawn from annihilation data are as follows:

1. An addition of glycol to ethanol has almost no effect on the annihilation spectra.
2. An addition of minor amount of lanthanide salts (*ca.* 1% mol) decreases the intensity of the long-living component by about 1/5, but a further addition of lanthanide has no visible effect (compare the data for 1 and 3% Pr).
3. By average, an addition of lanthanides decreases the lifetime of the long-lived component also by 1/5.

In the light of the spectroscopic and acoustic results, the first of these notes does not seem strange. While glycol molecules can replace those of ethanol in the solvation shell of lanthanide cation almost without changing its symmetry and size, the interaction of the solvate with its surrounding (liquid or glassy) should not depend too much on the solvent composition.

Two further conclusions can be understood as follows. The long-lived component of the annihilation spectrum (i.e. mainly annihilation of *o*-positronium) is formed mainly in cavities and/or defects of the glass structure, the addition of lanthanide salts decreases both their number (seen as the decrease in I_3) and the average size (decrease in τ_3), in the same proportions. This suggests that solvates occupy the largest cavities of the glass structure and are not accommodated in the bulk structure of the liquid before its solidification. By extrapolation, one can suggest that also in the liquid state, mixtures of ethanol with ethylene glycol are open-work, containing empty spaces of different sizes, among them also as big as the six-coordinate solvate of a lanthanide with ethanol+glycol. Let us note also that for systems without glycol, τ_3 seems to be not influenced by the addition of lanthanide salts, different than I_3 . This could mean that for pure ethanol solutions the addition of salt decreases the number of empties in glass structure, but not the distribution of their sizes. This conclusion needs an independent confirmation and will be the subject of our future studies.

The existence of such local non-homogeneities can have a key importance in designing the optical properties of lanthanide doped glasses: local and subtle deviation from a high symmetry can lead to materials that will be effective emitters of light desired wavelength. Combined with the symmetry decrease caused by the insertion of ethylene glycol molecules into the solvation sphere of lanthanide ion, as found by spectroscopy and additionally proved by acoustic method, this feature

of the now investigated materials can open wide opportunities of modification of their optical properties and, consequently, possible application in optoelectronics.

Acknowledgments

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