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AN OPTICALLY ACTIVE PHASE IN Er DOPED Ge₂O-PbO GLASSES

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Substantial increase of the effective optical second-order susceptibility near the critical temperature points corresponding to the structural transformation in GeO₂-PbO glasses near the 708 K was established. The increasing Er³⁺ content in the glass favors an increase of the photoinduced second harmonic generation (SHG). This temperature of the increase correlates well with the differential scanning calorimetry (DSC) measurements.

Key words: GeO₂-PbO glasses, second-order susceptibility, photoinduced second harmonic generation (SHG), differential scanning calorimetry (DSC).

Germanate glasses are interesting materials for photonics applications [1]. Particularly GeO₂-PbO glasses are interesting because they combine high photomechanical stability and chemical durability with temperature stability and excellent transmission in the infrared region (up to 4,5 μm). Besides the low phonon energy (around 700 cm⁻¹) compared to borates (around 1400 cm⁻¹) and phosphates (around 1200 cm⁻¹) the glasses indicate low nonradiative relaxation rates and makes up-conversion easily observable. The rare earth ions are known to affect an optical properties (SHG) of a glass. The results of measurements of a dependence of SHG in GeO₂-PbO glasses on Er³⁺ content are reported in this paper together with thermal measurements of this glasses.

The samples were prepared by method described in [2]. DSC (Differential Scanning Calorimetry) measurements were done with Netzsch Simultaneous Thermal Analyzer STA409C. The apparatus was calibrated with melting temperatures and enthalpies of pure metals: Ga, In, Sn, Bi, Zn, Ag and Au. Samples in corund pans were heated from ambient temperature up to 1 150 K and then cooled down. The heating and cooling rate was 10 K per minute. Inert gas, Ar of 5 N purity, was supplied to a furnace to prevent the samples from oxidation.

The method of the SHG measurement is, in details, given elsewhere [7, 8].

On the Er₂O₃ doped GeO₂-PbO glasses DSC traces reveal two transitions, both for 0,5 and 1,0 wt% of Er₂O₃ (see Fig. 1). The first one, at about 710 K, is a glass transition. The second one, at 859 K and at 875 K, for 0,5 and 1,0 wt% of Er₂O₃ respectively, is connected with the melting of the glass. There are no exothermic peaks on this curves which may be related to nano-crystalization. The glass transitions are reversible what can be seen comparing the heating and cooling parts of the DSC curves. The glass with smaller Er₂O₃ amount (0,5 wt%) has much more structure strains, which are relaxed, in temperatures below the proper glass transition. No similar effect was

observed for the glass with 1,0 wt % of Er_2O_3 . We will focus attention on part of DSC curves at which glass transitions are seen, shown on Fig. 1.

As is seen from this figure the onset temperature for the glass transition is slightly lowered with an increase of the Er^{3+} ions contents in the glass but the temperature of an inflection point, i.e. temperature at which rate of the transition has its maximal value, is almost the same for both samples. A heat capacity change is significantly greater for the glass with 0,5% of the Er_2O_3 what confirms a higher level of the structure strains in this case.

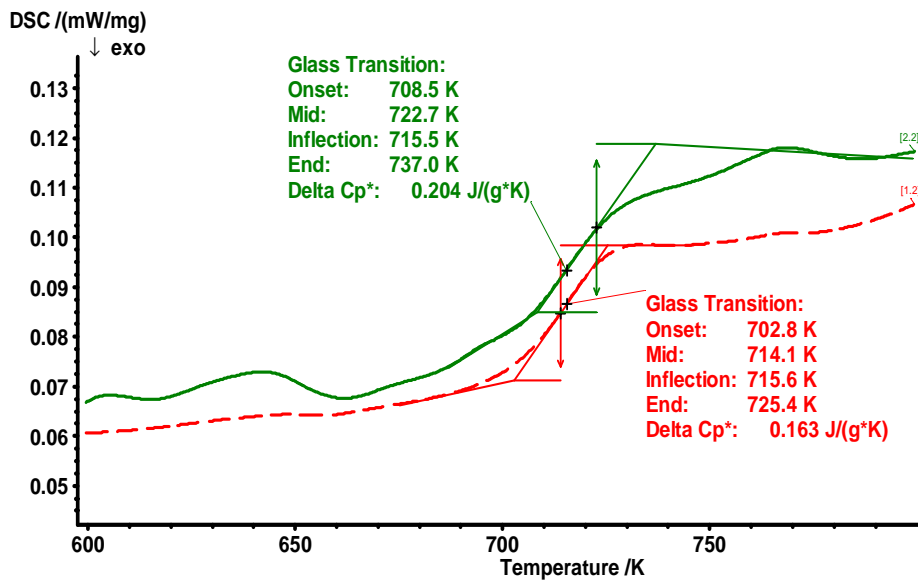


Fig. 1. DSC curves in the glass transition region for the Er_2O_3 doped GeO_2 - PbO glasses: 0,5 wt% solid line; 1,0 wt% dashed line

The performed optical measurements at different temperatures have revealed that maximal efficiency of optical poling exists at this temperature. Typical pump power dependences for the SHG are presented in the Fig. 2.

If we compare the DSC traces with a temperature dependence of a second order susceptibility increase it is seen (see figure no.3) that substantial increase starts at the temperature almost strictly matching to the onset of the glass transitions. The onset temperature for the sample with the higher amount of Er ions is five K lower and the second order susceptibility increase for this sample is not only much greater then for the second one but also begins at lower temperature.

Following the thermal measurements we could conclude that in the glass transition range of temperatures optical poling is especially effective in breaking a macroscopic scale inversion symmetry in the glass. On the other hand however temperature treatment

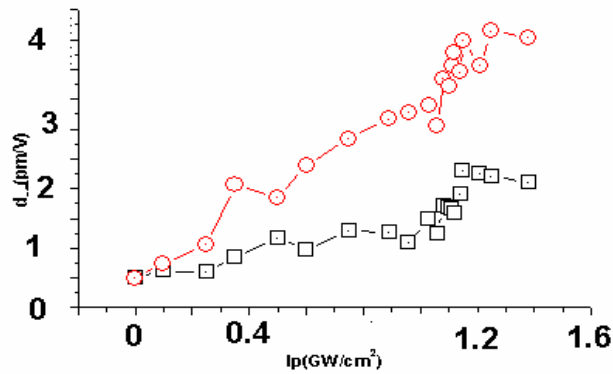


Fig. 2. Pump-dependent features of the effective second-order susceptibility: Squares – 1% in weigh. Units of Er^{3+} ; rings – 0,5% in weight units of Er^{3+} . Recorded at temperature 708 K

of Er_2O_3 doped GeO_2 - PbO glasses do not lead to permanent introduction of anisotropy due to nanocrystallisation as is observed in some other Er^{3+} doped glasses [4]. Similar nanocrystal precipitation is recorded in TeO_2 -based, SGH generating glasses [5].

So the optical poling of the glasses has shown substantial increase at temperatures near the critical points detected by the DSC and for the samples with the higher amount of the Er the effect is larger (see Fig. 2 and 3). This may be a consequence of additional polarizability introduced by the Er ions, as it was shown during investigations of the rare earth doped glasses [6]. The SHG temperature dependence clearly shows that the region of the critical point is more prominent for the optical poling. However it exists only near the mentioned temperature. It may indicate also on a substantial contribution of the photoinduced anharmonic to the process, how it was shown during non-coherent photoinducing SHG [7, 8] under infrared photoexcitation and role of the rare earth will here play crucial role [9].

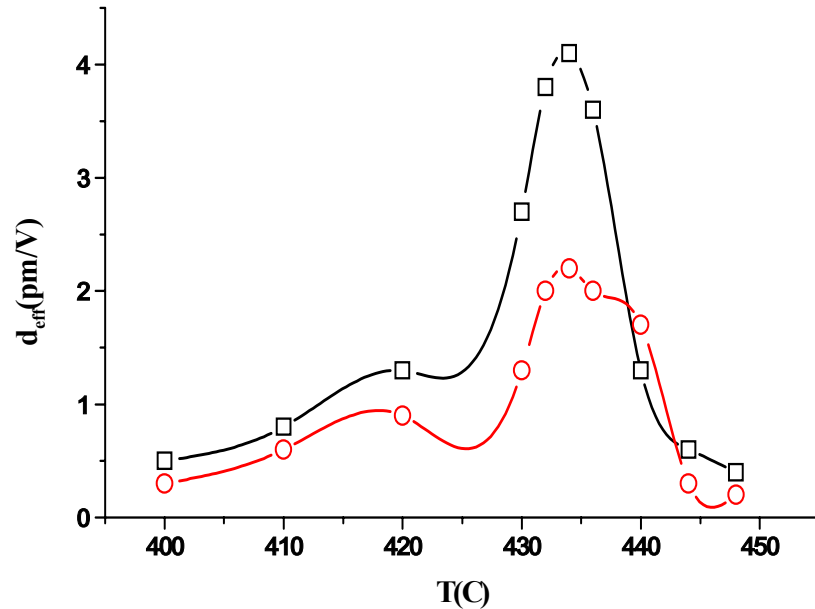


Fig. 3. Temperature dependence of the effective second order susceptibility obtained during the optical poling by two coherent beams 1,54 and 0,77 μm

Comparison of the obtained data leads us to conclusion that the charge transfer may play important role in the effect observed [10]. Deviations from this temperature leads to substantial diminishing of the effects. For the practical application in a future it would be useful to perform the cooling in the external electrostatic field to conserve the corresponding non-centrosymmetry, as it is usually performed during the thermal poling [11–12].

Another aspect of the phenomenon observed may be related to partial crystallization with the increase of the Er content [13–14]. However, following the structural analysis and DSC measurements role of this effect should be minimal.

The observed effect may be used for obtaining proper glass properties, particularly for the glasses possessing high conductivity, to use them as light modulators and deflectors in the IR spectral range.

We have shown that the efficiency of the optical poling of the Er doped germanate glasses substantially increases near the critical temperatures corresponding to 708 K. Increasing Er content favors additional enhancement of the effect. This may be a consequence of high polarizability of the Er states favoring larger polarizabilities. The DSC data have shown that the role of the crystallization effects is not crucial here and more probable seem to be participation of the high temperature anharmonic phonons.

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ОПТИЧНО АКТИВНІ ФАЗИ В СТЕКЛАХ Ge₂O-PbO, ЛЕГОВАНИХ Er**М. Піасецкі, П. Бронгель, І. Кітик**

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З'ясовано, що для стекол Ge₂O-PbO в області критичної температури ($T = 708$ К), яка відповідає структурним змінам, простежують значне підвищення оптичної сприйнятливості другого порядку. Збільшення вмісту іонів Er³⁺ у склі сприяє збільшенню фотоіндукованої генерації другої гармоніки. Спостерігають кореляцію між отриманим значенням температури та даними вимірювань диференційної скануючої калориметрії.

Ключові слова: стекла GeO₂-PbO, оптична сприйнятливість другого порядку, фотоіндукована генерація другої гармоніки, диференційна скануюча калориметрія.

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