The Effect of Nano-Particle Formation on Radiation Resistance of Phosphate Glasses Potentially Suitable for Nuclear Waste Immobilization

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Abstract

The effect of nano-particles on the radiation resistance of glasses potentially suitable for nuclear waste immobilization was investigated. The glasses were investigated by means of EPR, UV-visible optical spectroscopy, RBS and TEM. EPR spectra of the samples implanted with Ti^+,Cr^+, Mn^+,Co^+ and Cu^+ to $F \leq 10^{16}$ cm^{-2} contain the lines typical of “isolated” Ti^{3+}, Cr^{3+}, Mn^{2+}, $Co^{2+}$and Cu^{2+} ions in oxide glasses.

Intoduction

It is known that glasses are used for immobilization of radioactive wastes. Nuclear waste contain different chemical elements forming as fission products of uranium or as corrosion products from the storage tank walls (Fe,Ni,Cr, etc). Heavy ion implantation is a convenient laboratory technique for the studying radiation resistance of materials of interest for radioactive waste encapsulation. The analysis of EPR data for more than 100 oxide glasses implanted with different ions at various energies and fluences has shown that molecular ion O_2^- is dominant defect in all the samples [1]. The O_2^- ions are formed due to the displacement of oxygen atoms as a result of elastic collisions with implanted ions. The O_2^- ions can form clusters aggravating radiation resistance of glass.We use the concentration of O_2^- ions as the extent of the damage of implantation layer. Corrosion elements can aggregate yielding metallic particles because of collisions with moving O_2^- ions or form with O_2^- ions oxides and other compounds.

This work aims to study the effect of nano-particles on the radiation resistance of glasses potentially suitable for nuclear waste immobilization. The ion implantation of transition metals (TM) into glasses is one of a powerful technique for the elaboration of nanoparticles. Chemical states of transition elements implanted into glasses are dominant factors which determine the composition and the structure of particles. There are three possible groups of such particles: metallic colloids, metal oxides and composites including TM and elements of glass-network. We studied the evolution of states of TM of first transition raw, the formation TM clusters and nano-particles depending on the fluence and post-implantation heat treatment.

The objects of our investigation were oxide glasses implanted with ions of first transition raw and with non-transition elements which set this raw in a frame (for comparison). Recently the investigations of nanometer-sized particles embedded in glasses have received considerable attention because of possible practical applications in different fields.

Experimental

The molar chemical compositions of glasses used in this work are $65P_2O_5$-$10B_2O_3$-$10Al_2O_3$-15MgO (P-1) , $36P_2O_5$-$20Al_2O_3$-44 Na_2O (P-2) and $60P_2O_5$-$3B_2O_3$-$10Al_2O_3$-12MgO -10CaO-5ZnO (P-3). Polished plates were prepared and irradiated with Ca^+, Ti^+, V^+, Cr^+,Mn^+, Co^+, Cu^+, Zn^+, Ge^+,As^+ ions at energy E=150 keV and fluences (F) ranging from 2x 10^{15} to 5x10^{17} ions/cm^2. The glasses were investigated by means of EPR, UV-visible optical spectroscopy, RBS and TEM.

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Results and discussion

The O_2^- ions are formed due to the displacement of oxygen atoms as a result of elastic collisions with implanted ions. It has been shown [1] that the decrease in concentration of O_2^- ions is related with an increase in a projection range of implanted ions. Fig.1 shows the decrease in concentration of O_2^- ions with increasing atomic mass of implanted ions at $F=10^{16}$ cm^{-2} andfor two glasses. According to RBS data the projection range decreases with increasing atomic mass of implanted ions at $F=10^{16}$ cm^{-2} for both glasses. The number of O_2^- ions in P-1 glass is smaller than in P-2 sample under the same implantation conditions because of the same reason. At $F=10^{17}$ cm^{-2} the concentration of O_2^- ions deviates from both curves in the case of transition metals.

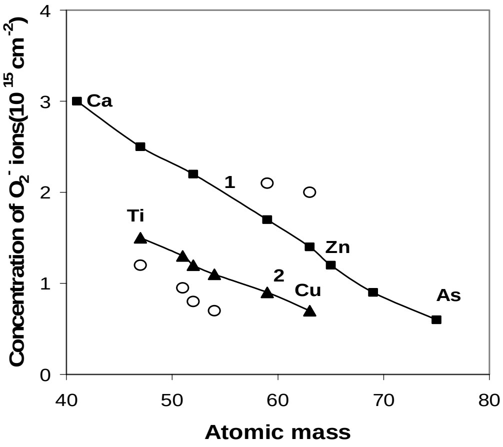

Fig.1. The dependence of concentration of O_2^- ions on atomic mass of implanted ions for P-2 sample (1) and for P-1 glass (2) at fluence $F=10^{16}$ cm^{-2}. Transparent circles are for both glasses at $F=10^{17}$ cm^{-2}

EPR spectra of the samples implanted with Ti^+,Cr^+, Mn^+,Co^+ and Cu^+ to $F \leq 10^{16}$ cm^{-2} contain the lines typical of “isolated” Ti^{3+}, Cr^{3+}, Mn^{2+}, $Co^{2+}$and Cu^{2+} ions in oxide glasses.

For example in Fig.2 EPR spectrum of P-1 sample implanted with Cr^+ at F= $3x10^{16}$ ions/ cm^2 is shown. The spectrum contains two well known lines: peak at g~5.2 and line with g=1.975, observed for isolated ions Cr^{3+} in many oxide glasses[2], i.e. at low fluences TM ions enter glass network to their typical positions. As follows from Fig.1, the concentration of O_2^- ions depends on atomic mass for TM and for non-transition elements equally.

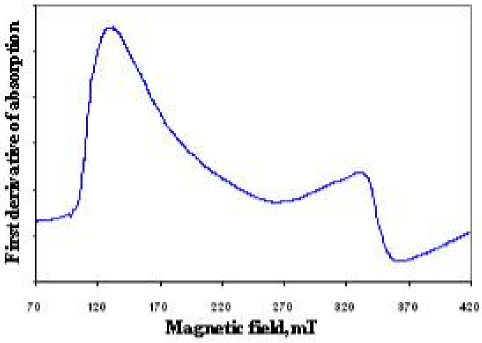

Fig.2. EPR spectrum of P-1 sample implanted with Cr^+ at $F=3x10^{16}$ ions/cm^2

At higher fluences a single line with g~1.97 was observed and attributed to Cr^{3+} clusters coupled by exchange interactions [2]. For the sample implanted with Cr^+ to fluence F= $5x10^{17}$ ions/cm^2 the almost symmetric line at g~1.98 with width ΔH_{pp} ~250 G was observed at 360K. In Fig. 3 temperature dependence of the width and relative intensity for this line is presented. The line exhibits the anomlous temperature dependence. Its intensity increases in temperature range from 473 to~335K, is almost constant between 335 and 320K, and drasticly decreases below 315K. This line is very weak at room temperature. Linewidth is constant in the range from 473 to 325K, and below 320K rapidly growths. Such a behavior is characteristics of crystalline Cr_2O_3 which is antiferromagnetic compound with T_N=306K [3].

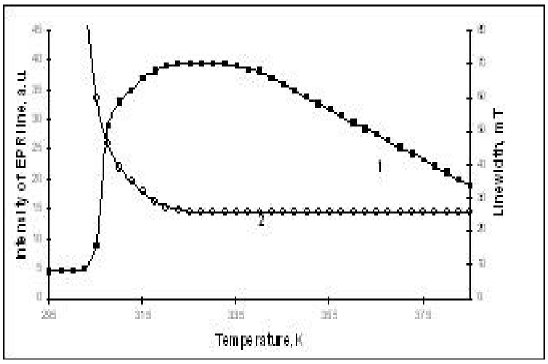

Fig.3. Temperature dependence of the linewidth (2) and relative intensity (1) for line at g~1.98 of the sample P-1 implanted with Cr^+ to fluence F= $5x10^{17}$ ions/cm^2

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This fact indicates the precipitation of Cr_2O_3 particles in P-1 glass.

Similar dependence has been observed for the line at g=2 of Mn^{2+} in phosphate glasses implanted with Mn^+ at fluence F=2x10^{17} ions/cm^2. This dependence is due to phase transition from paramagnetic state to antiferromagnetic one with T_N=116 K typical of fcc crystal MnO [4], i.e. particles of crystalline MnO participate in glasses.

It has been reported earlier [5] that VO_2 crystals exhibiting phase transition metal- insulator are formed in ultra-phosphate glasses implanted with V^+ ions at high fluences.

Fig 4. shows EPR spectrum of the glass P-1 recorded at 4.2 K. The spectrum consists of a broad (ΔH_{pp}~1000 G) slightly asymmetric signal with base-line crossing at g=4.4±0.05.

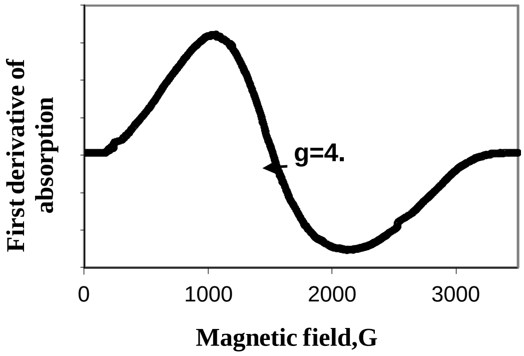

Fig.4. EPR spectrum of the glass P-1 implanted with Co^+ ions at at F= 3x10^{15} ions/cm^2 and recorded at 4.2 K

The g ~ 4.4 is close to g-value typical of octahedral environment of Co^{2+}, and large width of the line indicates the strong distortion of this environment. Because of short spin-lattice time EPR of Co^{2+} is observed in octahedral coordination only at low temperatures [6].

Fig.5. presents the spectrum of the P-1 sample implanted with Co^+ at F=8x10^{15} ions/cm^2 recorded at 4.2 K. This spectrum contains two lines: the line at g=4.4 with ΔH_{pp} ~ 600 G and the line at g=2.30 ±0.02 and ΔH_{pp}=150±20 G. The concentration of Co^{2+} ions contributing to the g=4.4 line is (5± 0.5)·10^{15} ions/ cm^2 (6.5x10^{15} cm^{-2} in accordance with data of RBS). The concentration of paramagnetic species responsible for the g=2.3 line is (8±1)x10^{13} cm^{-2}. The intensity of this line increases after heat treatment in H_2 .Its width is independent on temperature within errors of measurement. This line was detected at 77K but was not found at 100 K. We assume that the g=2.3 signal in ion implanted layer can be due to Co^{1+} ions, since its intensity increases after heat treatment performed under reduced conditions (H_2 atmosphere).The lines with g=2.17-2.31 have been observed at temperatures 4.2-90K in many reduced crystals doped with Co and have been attributed to Co^{1+} ions [7].

For the sample P-2 this line was observed neither 4.2 nor 77K.

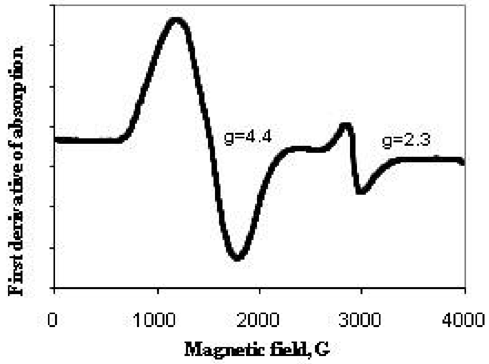

Fig.5.EPR spectrum of P-1 glass implanted with Co^+ at F=8x10^{15} ions/cm^2 recorded at 4.2 K

A situation varies at higher fluences. Bright field microphotographs obtained from TEM using planar samples reveals that spherical particles are formed in P-2 substrate by high-fluence ion implantation glass. The particle size increases with increasing fluence from 3÷4 nm at F=5x10^{16} to 5 ÷10 nm at F=3x10^{17}ions/ cm^2.

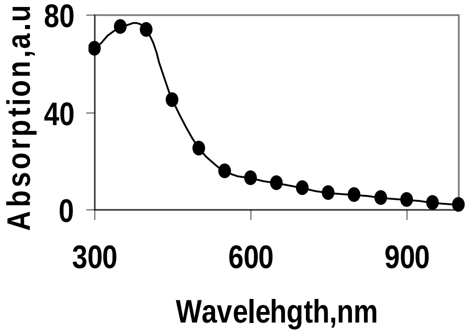

Fig.6. Optical spectrum of P-2 sample implanted to F=3x10^{17}ions/ cm^2

The weak peak at ~350 nm is due to plasmon resonance of metallic Co [8].This result allows one to assume the formation of colloid particles of metallic Co [8]. Metallic Co is ferromagnetic. According to [9], metallic Co exhibits a signal FMR with g=2.22 observed at room temperature.

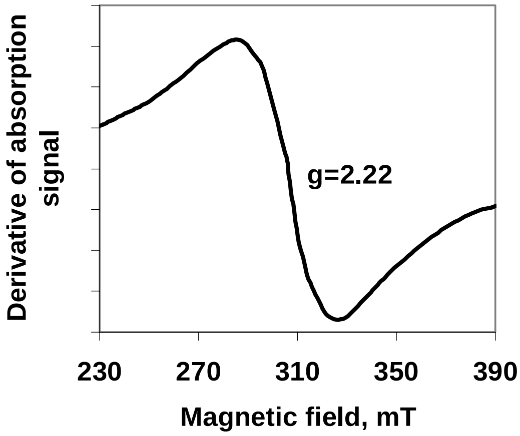

Fig. 7. FMR line of the sample P-2 implanted with Co^+ at $F=2x10^{16}$ cm^{-2} and recorded at room temperature.

The line with g = 2.2 broadens with decreasing temperature of the measurement from room temperature to 77K for the P-2 sample Such a behavior can be associated with the formation of superparamagnetic particles. The broadening of the line of superparamagnetic particles with decreasing temperature can be explained by the decrease in thermal fluctuations and an ordering of the magnetic directions [10]. The appearance at 4.2K of additional shoulder at 265 mT (fig.8) for P-2 sample implanted at high fluences indicates the increase in magneto crystalline anisotropy [8].

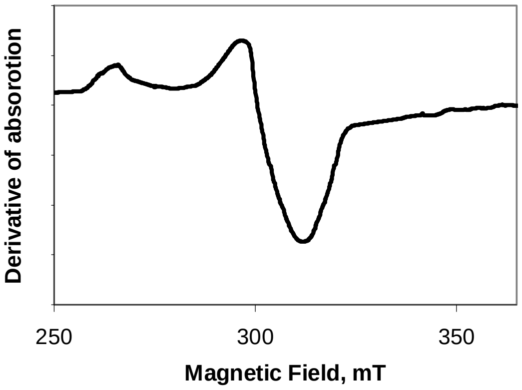

Fig. 8.

In phosphate glasses implanted with Cu^+ at $F<10^{16}$ cm^{-2} EPR and optical spectra are typical of oxide glasses. The absorption band at 560 nm (Fig.9) was found for these samples implanted with Cu^+ to $F \geq 10^{17}$ and can be attributed to surface plasmon resonance of Cu metallic nano-particles [11]. No EPR signal was observed for these samples.

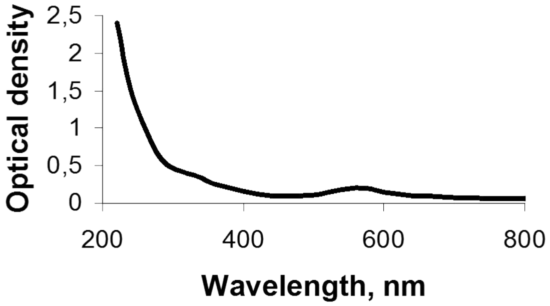

Fig. 9. The optical absorption spectrum of P-2 glass implanted with Cu^+ to $F=2x10^{17}$ cm^{-2}.

Conclusion

Data of EPR and optical spectroscopy show that in phosphate glasses implanted to fluences $F \leq 10^{16}$ cm^{-2} TM ions can be in “isolated”states. The oxides TM of nano-meter size are formed at high fluences and heat treatment .In this case concentration of O_2^- decreases in comparison with the samples implanted by the same elements at lower fluences since oxygen enters nano-particles. Thus we considered several examples of the identification of compounds nanoparticles owing the presence of phase transitions in these compounds.

In the cases Co and Cu metallic nano-particles are formed. Then the increase in concentration of O_2^- ions is observed.

Thus, the formation of nano-particles of TM oxides improves radiation resistance of glasses whereas the formation of metallic colloidal particles aggravates a situation.

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