EPR STUDY OF NEUTRON IRRADIATED Ge-S GLASSES

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The results of EPR measurements on neutron irradiated Ge-S glasses doped by Mn are presented. It has been found that the integrated neutron flux from $1.1 \times 10^{15}$ n. cm$^{-2}$ to $1.5 \times 10^{17}$ n. cm$^{-2}$ has no detectable effect on the nearest neighbour surroundings of Mn$^{2+}$ probing ions but increases the intensity of all EPR lines. A new EPR line was detected in Mn-doped Ge-S glasses irradiated with the highest neutron dose of $1.5 \times 10^{17}$ n. cm$^{-2}$.

1. INTRODUCTION

It is well known that glassy semiconductors generally do not exhibit an intrinsic signal of electron paramagnetic resonance [1]. However, EPR gives valuable information on the structure at atomic level. In order to obtain them the probing ions are used. The EPR spectrum of a probing ion will reflect the properties of its nearest neighbour surroundings — the symmetry and the character of bonds. Manganese is the most frequently used dopant because the EPR spectrum of its Mn$^{2+}$ ion ($^6S_{5/2}$) can easily be detected even at room temperature.

The influence of the radioactive radiation on various materials is the subject of a systematic research, but this is not the case of the disordered materials. There are few papers devoted to the investigation of radiation hardness of disordered structures [2–5]. It should be noted that the measurements of such physical parameters of irradiated samples like heat conductivity, dc and ac electrical conductivities, etc. do not provide information about the changes at atomic level.

Our experiments were led by the idea to detect changes due to the neutron irradiation of investigated glasses in the EPR spectra of the probing ions. Unlike other glassy semiconductors even the pure Ge-S system exhibits a rather high density of unpaired spins [6], but measured signals do not give structural information.

2. EXPERIMENTAL

The samples studied in this work, Ge$_{40}$S$_{60}$ + 0.01 at.% Mn and Ge$_{25}$S$_{75}$ + 0.01 at.% Mn, were chosen from both glass-forming regions of the system Ge-S [7, 8]. These glasses were prepared from elemental materials of at least 5N purity by direct melting in quartz ampoules evacuated to $10^{-3}$ Pa and sealed. Both syntheses and homogenization were performed in a rocking furnace at approximately 1250 K for 4 hours, and thereafter the melt was quenched in air.
The structure of prepared glasses was examined by several methods, by means of X-ray powder diffraction, differential thermal analysis (DTA) and scanning electron microscopy. The samples were glassy, no crystalline regions occurred.

The samples were irradiated in a nuclear reactor by fast neutrons with an energy of 2 MeV. The following integrated neutron fluxes were chosen: $\theta = 1.1 \times 10^{15}$ n.cm$^{-2}$, $9.8 \times 10^{15}$ n.cm$^{-2}$, $2.8 \times 10^{16}$ n.cm$^{-2}$ and $1.5 \times 10^{17}$ n.cm$^{-2}$. The temperature during the irradiation was 350 K. Tests with samples after neutron irradiation have shown that samples also remain glassy after the irradiation.

The EPR measurements were performed using a Varian E-4 spectrometer operating in the X-band with 100 kHz field modulation in the temperature range from 298 to 77 K. The glassy samples were crushed and several pieces of them were put into an EPR sample tube.

Fig. 1. Typical EPR spectrum for neutron irradiated Ge$_{40}$S$_{60}$ + 0.01 at.% Mn glasses at 77 K: a) and b) $g = 2.0$ and $g = 4.3$ signals, respectively.

Fig. 2. a) EPR spectrum for Ge$_{25}$S$_{75}$ + 0.01 at.% Mn glasses at 77 K, b) EPR spectrum for neutron irradiated Ge$_{25}$S$_{75}$ + 0.01 at.% Mn glasses at 77 K.