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Raman and optical reflection spectra of germanate and silicate glasses

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Abstract

Germanate and phosphosilicate glasses made in oxygen surplus conditions were studied by Raman and optical reflection methods. We found that the optical reflection spectra of the germanate glasses are quite similar to the one those of a GeO_2 crystal with the α-quartz structure. The reflection of phosphosilicate glasses is very close to silica glass-related spectra. Hence, the determining influence of the tetrahedral structure on reflection spectra is revealed. The Raman spectra of germanate samples are similar to those reported the one known in the literature. Octahedral entities, namely bands similar to stishovite vibration modes, were difficult to detect in phosphosilicate glasses through Raman spectroscopy.

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1. Introduction

The Glassy state could be presented as a set of chaotic density fluctuations corresponding to the polymorphism of the crystalline state of a material. In the case of germania and silica glasses, there is a major structural motif is the tetrahedron. Tetrahedral structure allows a wide range of density fluctuations by the creation of rings of different dimensions [1]. In the case of the corresponding crystals the properties of electronic states are not very sensitive to the density, provided that the main structural motif is the tetrahedron. Despite a density difference between α-quartz and coesite, the positions of the intrinsic absorption thresholds coincide [2]. Moreover, the intrinsic optical reflection spectra of silica glass and α-quartz exhibit some similar features, although their bands have slightly different intensities and widths [3].

There is an increasing interest in the possible existence of octahedra as minority motives in the short-range order of germanate and silicate glasses [4]. Experimental evidences of the existence of the rutile-type structure was obtained in the case of germania glass [4]. Two positions of the intrinsic absorption threshold [4] were observed, one at 6 eV coinciding with that of the α-quartz-like structured GeO_2 crystal, another at 4.5 eV coinciding with that of the rutile-like structured GeO_2 crystal. It is now well recognized that alkali plays a role of catalyst for the creation of octahedral structures in the case of germanium dioxide [5,6]. The threshold at 4.5 eV could be obtained on strongly oxidized samples, while in samples melted under normal or reducing conditions, the absorption of oxygen deficient centers obscures the intrinsic threshold position [7,8].

The situation with silicon dioxide is far from clear. The intrinsic absorption threshold of stishovite single monocrystal is situated at 8.75 eV [2] being higher than that for α-quartz. This shows different structures of the electronic states related to tetrahedral and octahedral structures in silicon dioxide. In silica glass, which has an absorption threshold energy of 8.2 eV for the purest samples [8], a possible threshold related to the sixfold-coordinated silicon cannot be observed. So, the existence of motives with

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sixfold-coordinated cations may be mainly assumed in the germanate glasses properties.

The problem of the existence of sixfold-coordinated germanium was discussed in a series of articles dedicated to the problem of the so call 'germanate anomaly', where a negative conclusion was made, (see [9] and references therein). It is useful to underline that Raman investigations never revealed any similarity between the glass spectra and the rutile GeO_2 crystal [9]. However, we have a direct proof of the existence of GeO_6 through the rutile-like absorption threshold of alkali germanate glasses [4].

In the case of silica it is known [10] that phosphosilicate crystals (SiP_2O_7) include a lot of sixfold-coordinated silicon atoms. The aim of this work is to detect sixfold-coordinated germanium and silicon in the corresponding alkali- or phosphorus-doped glasses using Raman and optical reflection spectroscopy. As materials under investigation, we have chosen glasses and crystals where sixfold-coordinated silicon or germanium evidently exists [4,10].

2. Experimental

The studied germanate glass samples were melted under oxidizing conditions. The same samples were previously analyzed in [4] for the intrinsic absorption threshold and in [8] for the intrinsic luminescence. Four compositions $15Na_2O \cdot 85GeO_2$, (labeled 15Na) $25Na_2O \cdot 75GeO_2$, (labeled 25Na), $33Na_2O \cdot 67GeO_2$, (labeled 33Na) and $8La_2O_3 \cdot 92GeO_2$, (labeled La) were prepared.

The phosphosilicate glass sample was produced by Demskaya and Prokhorova [11] by melting a phosphorus-doped synthetic silicon dioxide powder, obtained after the hydrolysis of tetraethoxysilane and phosphorus acid. The composition $3P_2O_5 \cdot 7SiO_2$ was chemically stable. The sample had a milky aspect, showing a strong light-scattering.

Raman spectra where obtained using a triple-grating micro-Raman spectrometer (T64000 Jobin Yvon) in a confocal configuration. The samples were excited by the 514.5 nm line of an Ar^+ laser.

The reflection spectra were taken on a 0.5 m Seya–Namioka vacuum monochromator, consisting of a concave toroidal grating cut in glass, a hydrogen flow windowless discharge light source with a W filament as a hot cathode, a toroidal concave mirror made of crystalline quartz (grating and mirror are without metallic covering) and a vacuum chamber for the sample.

3. Results

3.1. Germanate samples

Raman spectra. In Fig. 1, the Raman spectra of the studied germanate samples are in good agreement with those reported in the literature [9,12], except for the La sample. To our knowledge, the Raman scattering from La_2O_3-doped germanate has never been measured before.

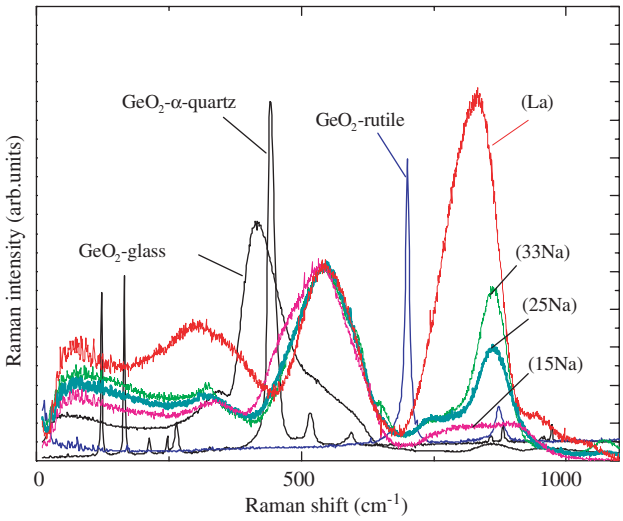

Fig. 1. Raman spectra of the studied germanate samples.

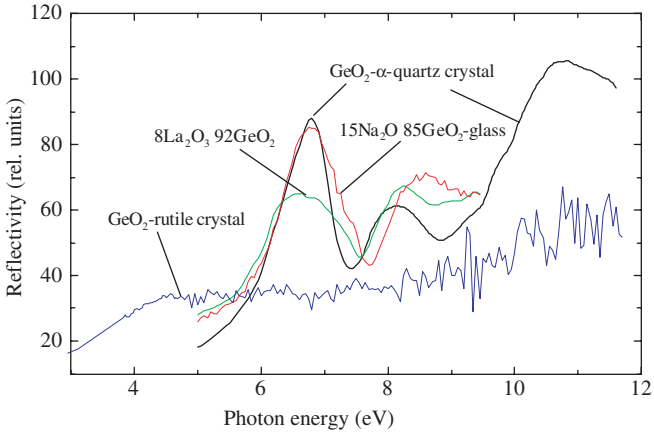

Fig. 2. Optical reflection spectra of the studied germanates.

Optical reflection spectra. The optical reflection spectra of some germanate samples are presented in Fig. 2. The reflectivity spectra of doped germanate glasses exhibit a band at 6.6 eV, the same as in GeO_2 α-quartz crystal and in GeO_2 glass [13]. No reflection band below 6 eV has been obtained in alkali germanate glasses although the intrinsic absorption threshold starts around 4.6 eV, as in the case of GeO_2 crystal with rutile structure [4]. The reflection spectrum of the rutile-like GeO_2 crystal shows a rather flat band around 5 eV, but we did not detect any other band at 6.6 eV.

3.2. Silicate and phosphosilicate samples

Raman spectra. In Fig. 3, the Raman spectra of different silicates are presented. Phosphosilicate is an example of glass containing sixfold-coordinated silicon atoms. However, it is evident that Raman spectrum of $3P_2O_5 \cdot 7SiO_2$