USE OF IR AND RAMAN SPECTROSCOPY FOR STUDYING THE FORMS OF DISSOLUTION OF H, N AND O VOLATILES IN GLASSES - MELTING PRODUCTS OF THE EARLY EARTH'S MANTLE

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A series of experiments was carried out in the system Fe-bearing melt + fused metallic Fe phase + Si_3N_4 (1, 3, 5, 7% wt) + H_2 conducted at high pressure 4 GPa, high temperature 1550°C, and low oxygen fugacity $\Delta \lg fO_2$ from 2 to 4 below the iron-wustite buffer equilibrium $\Delta \lg fO_2(IW)$. We have characterized the nature and quantified the abundance of N- and H-compounds dissolved in a model silicate melt ($NaAlSi_3O_8$ 80% wt + FeO 20% wt).

To elucidate the mechanisms of mutual solution of H and N as a function of oxygen fugacity fO_2we have used the IR and Raman spectroscopies of glasses as quenching products of the reduced melts. IR measurements are carried out on a vacuum Fourier-transform IR (FTIR) spectrometer «Bruker IFS-113v» combined with an optical attachment "IR Microscope A590" allowing to focus on various inclusions the radiation transmitted through researched samples into a spot from 50 up to 400 μm in diameter. The transmission spectra were recorded in the frequency region from 350 to 5000 cm^{-1} with the resolution of 2 cm^{-1} and noise level not worse than 0.1 %. Raman spectra were recorded in a back-scattering geometry with a Jobin Yvon Triple Raman spectrograph T-64000 equipped with a CCD detector cooled by liquid nitrogen. The exciting 514.5 nm radiation of a Spectra Physics Ar^+-laser was focused on sample surface into a 2 μm spot. The band positioning accuracy in the Raman spectra was better than 1 cm^{-1}.

IR Spectroscopy of Glasses

To measure the IR transmission spectra of glasses as quenching products of reduced melts, we have prepared thin plane-parallel plate samples, optically polished on both sides, with the cross-section area ranging from 1 to 200 mm^2 and thickness 80÷140 μm.

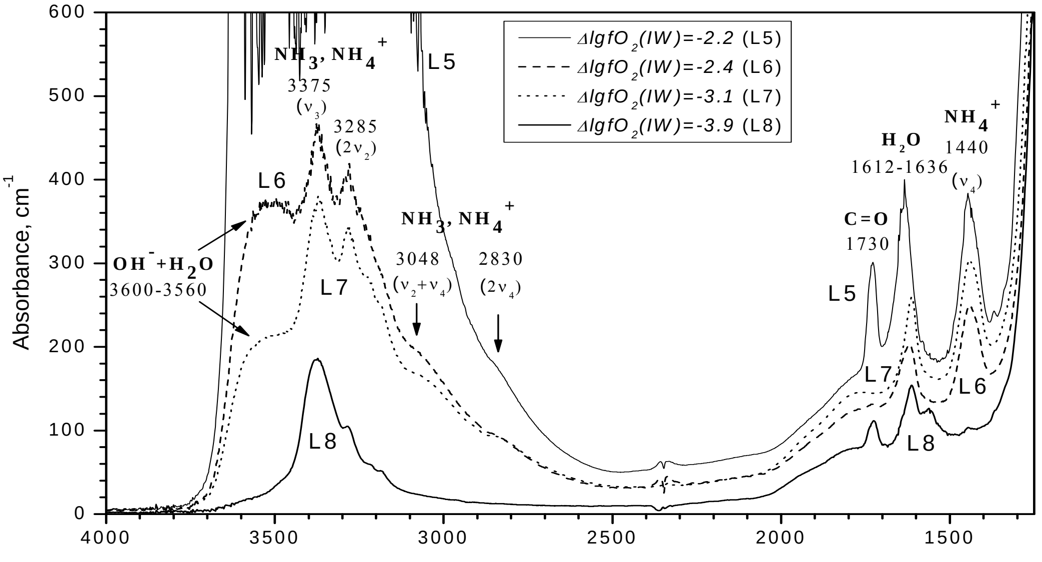

Fig.1. IR spectra of N–H-bearing glasses in the range of 1000-4000 cm^{-1}: $\Delta \lg fO_2(IW) = -2.2$ (run L5, h = 114 ± 3 μm); $\Delta \lg fO_2(IW) = -2.4$ (run L6, h = 96 ± 3 μm); $\Delta \lg fO_2(IW) = -3.1$ (run L7, h = 111 ± 2 μm); $\Delta \lg fO_2(IW) = -3.9$ (run 8L, h = 94 ± 2 μm), where h is the thickness of plane-parallel plates

Fourier transform IR spectra of N–H-bearing glasses for samples L5, L6, L7, and L8 (1, 3, 5, 7% wt Si_3N_4, respectively) in the range of 4000-1000 cm^{-1} are shown in fig. 1. A remarkable feature of these spectra is the occurrence of a few bands showing evidence for the presence of N–H- and OH-type bonds in glasses.

O-H bonds. A wide absorption band at the frequencies of 3560, 3572, and 3580 cm^{-1} for $\Delta lg fO_2(IW) = -2.2, -2.4$, and -3.1, respectively (fig. 1) is a result of stretching vibrations of the OH^- groups and H_2O molecules [1,2]. As fO_2 decreases in the experiments, the absorption band intensity falls down, and at $\Delta lg fO_2(IW) = -3.9$ the band is no more seen in the spectra. A sharp peak at 1612-1636 cm^{-1} is known to fit the bending vibrations of H_2O molecules [3].

N-H bonds. The IR absorption bands of glasses for $\Delta lg fO_2(IW) = -2.2, -2.4, -3.1$, and -3.9 at 1440 cm^{-1}, for $\Delta lg fO_2(IW) = -2.2, -2.4$ and -3.1 at 2830cm^{-1}, for $\Delta lg fO_2(IW) = -2.4$ and -3.1 at 3048 cm^{-1}, for $\Delta lg fO_2(IW) = -2.4, -3.1$, and -3.9 at 3285 and 3375 cm^{-1} (Fig. 1) lie within the wavenumber range typical for the compounds containing N–H bonds [4,5]. IR spectroscopy of silicate materials, having NH_4 group in their structure, e.g. tobelite $[NH_4]Al_2[AlSi_3O_{10}](OH)_2$, reveals the absorption bands in the frequency region of 1400-3300 cm^{-1}. These bands belong to normal vibrational modes of a free ammonium ion NH_4^+ of T_d symmetry, where v_2 are symmetric bending vibrations, v_3 are antisymmetric stretching vibrations, v_4 are antisymmetric bending vibrations [6-8]. In our experiments the peaks we observe at 3375 (v_3), 3285 ($2v_2$), 3048 (v_2+v_4), 2830 ($2v_4$), and 1440 (v_4) cm^{-1} fit these vibrations very well. It is assumed that in N–H-bearing glasses produced in our experiments the absorption bands detected in the IR spectra are related to the vibration motions of both NH_4^+ and NH_3 molecules.

C-O bonds. The IR spectroscopy of glasses reveals a sharp peak at 1730 cm^{-1} for $\Delta lg fO_2(IW) = -2.2$ and -3.9 (fig. 1). It is located in the region of C-O bond vibrations. According to [9], it is supposed that this peak belongs to the C=O bond in glass. Carbon is not a component of initial mixture for the experiments. So it is assumed to be a diffusion product of some amount of C from graphite heater through the Pt ampoule during the experiments.

Raman spectroscopy of glasses

Raman spectra of L5-L8 glasses reveal a series of peaks in the range 1500-4000 cm^{-1}, which may be ascribed to the bonds N–H, N–N, N-Si, C-H, H-H, and O–H. The characteristic Raman spectrum of sample L6 ($\Delta lg fO_2(IW)= -2.4$) is shown in fig. 2 as an example.

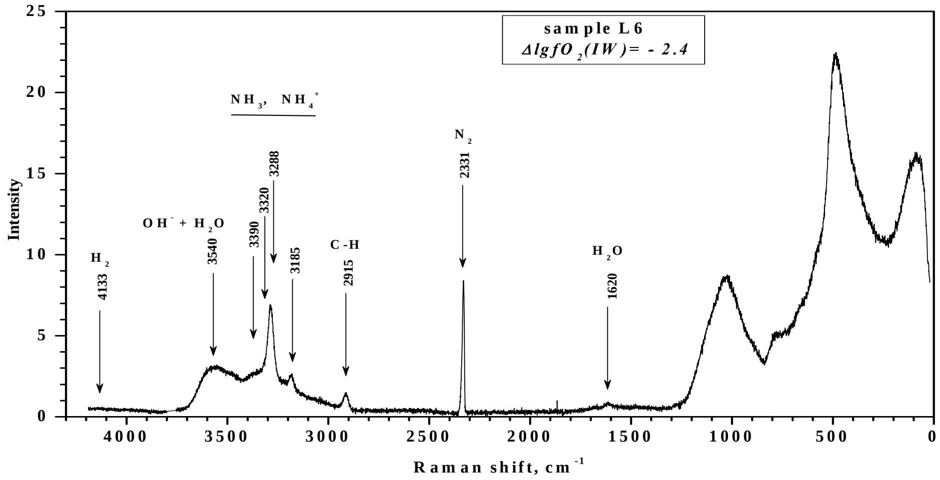

Fig.2. Raman spectra of N–H-bearing glasses in the range of 0-4200 cm^{-1}: $\Delta lg fO_2(IW) = -2.4$ (run L6)

O–H bonds. The position and shape of a wide asymmetric band at 3540 cm^{-1} is similar to that found in water-bearing alumosilicate glasses [10, 11]. This band fits the vibrations of O–H bonds in H_2O molecule or in OH^- groups in the structure of silicate melts. A decrease in the intensity of this band with decreasing fO_2 was detected. A weak peak at ~1620 cm^{-1} observed in glass samples corresponds to a deformational vibration of H_2O molecules dissolved in glass [3].

H–H bonds. A weak 4133 cm^{-1} band (fig. 2) belongs to the molecular hydrogen H_2 dissolved in glass [11].

N–H bonds. It is assumed that a sharp double peak at 3288; 3320 cm^{-1} for all fO_2 values during the experiments and the peaks at 3185 and 3390 cm^{-1} may belong to the NH_3 molecule in glass, and probably, to the ammonium NH_4^+ cation. According to [12, 13], the Raman spectra of NH_3 molecule are characterized by a sharp peak at 3334 cm^{-1}. With lowering fO_2, a wide OH^- peak at 3540 cm^{-1} disappears, the intensity of the peak at 3288 cm^{-1} increases, and new peaks at 3320 and 3390 cm^{-1} (NH_3, NH_4^+) appear in the Raman spectra of glasses.

N–N bonds. A sharp and narrow peak at 2331 cm^{-1} belongs to the fundamental vibration of molecular nitrogen N_2 in glass. Similar N_2 peak in glasses was detected in [14] after the study of nitrogen solubility in the melt at 3 GPa and 1300-1700°C.

C-H bonds. Raman spectroscopy of glasses reveals a small sharp peak at 2915 cm^{-1}, lying in the region of C–H bond vibrations. By analogy to [2], it is suggested that this peak corresponds to the vibrations of CH_4 molecule dissolved in glass.

N–Si bonds. The Raman band at 1030-1120 cm^{-1} rapidly shifts towards lower frequencies as the nitrogen content increases and the FeO content decreases in glass. We think that lowering peak frequencies in the region of 1030-1120 cm^{-1} reflects the occurrence of nitrogen in the melt structure with the formation of N–Si-type bond, as it has been established by [15] in the study of Si_3N_4 solubility in the melts of $CaO–Na_2O–SiO_2$ composition. It should be noted that there are no Raman bands characteristic of Si_3N_4 [16, 17] in glasses, that points to the absence of such a molecule in the melt.

Thus, the results of IR and Raman studies of glasses on interaction of H and N with reduced silicate melt equilibrated with the metallic Fe phase point to a double mechanism of nitrogen dissolution in the melt: as the complexes NH_4^+ and NH_3 with the N-H type bond, and the N_2 molecule. Besides the compounds with the N-H bonds, the dissolved hydrogen exists in the melt also in the form of hydroxyl OH^-, molecular hydrogen H_2 and water H_2O. With fO_2 decreasing hydrogen and nitrogen content in glasses increases, while their molar ratio H/N decreases. This testifies to an exclusive role of hydrogen in this process and an appreciable change in the mechanism of H and N dissolution: lowering fO_2 at $\Delta \lg fO_2$(IW) from -2 to - 4 is accompanied by an increase in the content of N-H complexes (NH_3, NH_4^+) and a decrease in the amount of oxidized OH^- and H_2O species. It is suggested that at rather low fO_2 values the main form of N dissolution is the NH_3 group.

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