Raman spectroscopy of germanate and germanosilicate glasses and melts

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The germanate glasses and melts of $X\%Na_2O$* ($100\text{-}X$)%GeO_2 (X = 0, 10, 20, 30) composition, were studied by high-temperature Raman spectroscopy. The main band near 420 cm^{-1} corresponding to symmetric stretching vibrations of Ge-O-Ge bridges in the polymerized network, disappears with addition of the Na_2O to GeO_2, and a new intense peak near 530-540 cm^{-1} appears. This band assigned to vibrations of three-membered rings from tetrahedral GeO_4. A shoulder near 600 cm^{-1} to the right side of the band is assigned to vibrations of connected GeO_6 octahedral units. The new band near 870 cm^{-1} is observed in the glass spectrum with 20% Na_2O content. An increase of Na_2O content to 30% causes an appearance a new band near 790 cm^{-1}. These bands are attributed to the vibrations of GeO_4 with one and two nonbridging oxygen atom, respectively (by analogy with Q^1 and Q^2 units in silicate melts). The change in spectra during the glass-melt transition is a result of the conversion of germanium ions from six-fold to four-fold coordination with simultaneous formation of nonbridging oxygen atoms.

The spectra of germanosilicate glasses and melts of $33\%M_2O\cdot 67\%SiO_2$ + $x\%GeO_2$ composition (x = 0, 20) are characterized by bands near 1090-1110 cm^{-1} and 935-955 cm^{-1}, corresponding to vibrations of nonbridging bonds of Q^3 и Q^2 silicate groups, respectively. A band at high frequencies about 870 cm^{-1} at 20°C и 855 cm^{-1} at 1100°C is assigned to vibrations of GeO_4 tetrahedral with one nonbridging oxygen atom. The band near 555 cm^{-1} is observed in the low-frequency region and corresponds to symmetrical valence vibrations of Si-O-Si (Ge) bridging bonds. A decrease of the band intense near 935-955 cm^{-1} with addition of GeO_2 to $Na_2Si_2O_5$, indicates that germanium atoms are glass-forming cations in glass and melt of this composition, and the addition of GeO_2 leads to an increase of a degree of polymerization. The comparison of germanosilicate glass and melt spectra shows some increase of the band intense near 935-955 cm^{-1} at high temperature, and it corresponds to some increase of Q^2 content.

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Interaction of Hg and other metals with marine macroaggregates

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Macroaggregates (macrogels), appearing episodically in the Gulf of Trieste (northern Adriatic Sea), are formed by agglomeration of dissolved organic matter, mostly heteropolysaccharides of phytoplanktonic origin. Since macrogels are organic structures with large binding surfaces, they are thought to be important horizontal and vertical carriers of different and toxic substances. Therefore, once formed they offer a great opportunity for studying their complexation with metals. Although macrogels can persist in a marine environment for quite a long time, they are subjected to microbial and photochemical degradation. Macroaggregates, collected in the Gulf of Trieste (northern Adriatic Sea), were fractionated into matrix (water insoluble fraction) and interstitial water (water soluble colloids) using filtration and centrifugation. The colloidal fraction was subsequently ultrafiltered in a 'cascade fashion' through membranes with a nominal pore size of 30, 10 and 5 kDa and fractions were analyzed for carbohydrate, C_{org}, N_{tot}, $P_{tot.,}$ metal (Hg, Ba, Cd, Co, Cr, Mn, Ni, U, V, Zn) and metaloid (Se and As) contents, and used for FTIR. The highest carbohydrate content and the lowest C/N ratio were associated with a higher molecular weight (MW) fraction (>30 kDa) suggesting that aminopolysaccharides and glycoproteins can be important constituents of this fraction. Analyses of ultrafiltrates revealed that Hg and other metals have a tendency to bind to a larger (>30 kDa) macromolecules while Se has a tendency to bind to a medium MW (10-30 kDa) macromolecules. The laboratory based degradation experiment, which included the indigenous microbial population, revealed an extensive degradation of organic matter especially in the smallest (5-10 kDa) fraction. Increasing Metal/C_{org}. (atomic) ratios, except for As, at the end of the experiment suggest the preservation of suitable binding sites for most observed metals and metalloids in degraded products.