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Nickel speciation in multi-oxydes components silicate glasses: new UV-VIS-NIR spectroscopic results and geochemical implications

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Silicate glasses are usually considered as good analogues for natural melts and thus frequently synthesized to study their structural properties.

The optical spectra of Nickel are well constrained in crystal phases [1]. Only recent studies permit real advances of Ni speciation in glasses [2, 3]. In alkali and alkaline-earth silicate glasses, $Ni^{2+}$is always found as predominantly $^{[5]}Ni^{2+}$ with some minor $^{[4]}Ni^{2+}$, whereas in borosilicate and borate glasses with the same network modifying cations, Nickel could be observed as $^{[4]}Ni^{2+}$, $^{[5]}Ni^{2+}$ and/or $^{[6]}Ni^{2+}$, depending on the glass composition and especially on the proportion and nature of alkali/ alkaline-earth cations.

The short-range structure of a new large compositional range of Ni-doped (1000 ppm) multi-oxides silicate glasses has been investigated by UV-VIS-NIR spectroscopy. The glasses were synthesized to study the separate and combined influences of alkali (K, Na), alkaline-earth elements (Ca, Mg) and Al on Ni speciation.

First, our spectral results on non-magnesian system confirm a high $^{[4]}Ni^{2+}$ content in silico-potassic (11.5 to 28.7 wt.% K_2O) glasses compared to the predominance of $^{[5]}Ni^{2+}$ ($\pm$ $^{[4]}Ni^{2+}$) in purely silico-sodic glasses (15 to 27.5 wt.% Na_2O) and a mixing of variable proportions of $^{[4]}Ni^{2+}$ and $^{[5]}Ni^{2+}$ in mixed chemical compositions (Si-K-Ca and Si-Na-Ca with each element varying independently from $\sim$10 to $\sim$25 wt.%). Mixed Si-K-Ca glasses (fixed $\sim$10 wt.% K_2O and 9.1 to 26.4 wt.% CaO) show significant $^{[5]}Ni^{2+}$ spectral band appearance with the increase of Ca concentration. At constant Ca ($\sim$10 wt.% CaO) and variable K (14.3 to 29.7 wt.% K_2O), $^{[4]}Ni^{2+}$ spectral band intensities remain predominant. Na rich silicate glasses always favor $^{[5]}Ni^{2+}$while, for high K concentration, Ni^{2+} is mainly found as $^{[4]}Ni^{2+}$. This behaviour of Ni^{2+} as a function of glass composition is coherent with $^{[4]}Ni^{2+}$ being predominant in presence of large charge compensating, low field strength cations such as K. In that case, Ni^{2+} is found in network forming position but does not take that role because of its low charge as compared to network forming cations such as Si^{4+}. With higher field strength cations such as Ca or Na, $Ni^{2+}$is mostly found as network modifier. $Al^{3+} \leftrightarrow Si^{4+}$ substitution (15 wt.% Al_2O_3) in alkali-alkaline earth systems show clear decrease of $^{[4]}Ni^{2+}$ spectral band intensities revealing preferential use of Na^+ and Ca^{2+}+ Na^+ to charge compensate oxygen anions associated to Al^{3+}. This reveals the importance of the competition between cations for the charge compensating effect.

$^{[6]}Ni^{2+}$ in glasses has only been observed in borate ones with low alkali content [4]. Our results on the structural investigation of pseudo-basaltic magnesian glasses (CMNAS system with 7 to 20 wt.% MgO) show first evidences of combined presence of $^{[6]}Ni^{2+}$, $^{[5]}Ni^{2+}$ and $^{[4]}Ni^{2+}$ in purely silicate glasses. The presence of the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(P)$ electronic transition on the optical spectra of the investigated glasses allow identification of $^{[6]}Ni^{2+}$. The intensity of the band corresponding to this transition increases at the expense of the $^{[5]}Ni^{2+}$ band in relation with the increase of the MgO content of the glass.

The discovery of the MgO addition effect on Ni coordination with the appearance of $^{[6]}Ni^{2+}$ gives new insights on the olivine-liquid partitioning of Ni. According to our results, the resulting effect would be an increase affinity of Ni for a melt with high MgO content, considering the glass to be a snapshot of the liquid structure. This could explain, the partition coefficient ($D_{Ni}^{ol/liq}$) decrease coupled with the increase of the MgO content of the equilibrium melt observed in several experimental studies [5].

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