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High-T non-stoichiometry of titanomagnetite re-examined – New experimental data

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Titanomagnetite (Tmt; solid solution between magnetite and ulvöspinel (Usp)) can depart from stoichiometry at high temperature, depending on T, X and fO_2 . However, existing studies [1-5] cover only a limited T-X-range: Most data have been retrieved at 1300-1275°C [1, 2, 3, 5], but at 1100-1200°C only few compositions with $X_{Usp} \leq 0.75$ were examined [1, 4]. There are serious disagreements about the concentrations of the cationic vacancies and no data are available on Mg and Al-bearing Tmt, which are particularly relevant for natural basaltic systems.

To obtain Tmt with maximum vs. minimum vacancy concentrations, we are synthesising assemblages of Tmt with either ilmenite-hematite_{ss} or with wüstite_{ss} in the system Fe-Ti-O±Mg±Al at 950-1300°C, 1 bar and oxygen fugacities in the range FMQ -4 to +5. The run products are drop-quenched into water and examined with a combination of several methods with the aim of quantifying the concentration of the cationic vacancies. We are currently focussing on two methods:

a) Precise determination of the **unit cell parameter of Tmt**. In agreement with [3], 1300°C samples show, especially at high X_{Usp} , significantly lower a_0 in Tmt coexisting with Ilm_{ss} vs. those coexisting with Wü, pointing to cationic vacancies in the first case. Preliminary results suggest that Tmt equilibrated with Ilm_{ss} at 950 and 1100°C in the Fe-Ti-O system are nearly stoichiometric.

b) **Annealing at 950°C of high-T run products** sealed in evacuated silica glass ampoules in order to heal the cationic vacancies. The vacancy relaxation results in the formation of Ilm_{ss} exsolution lamellae and rims [5]. The original vacancy concentration can be calculated from the shift of the molar proportions (image analysis) and chemical compositions (EMP) of the coexisting Tmt and Ilm_{ss}. Again, preliminary results suggest near-stoichiometry for Mg- and Al-free Tmt in equilibrium with Ilm_{ss} at 1100°C.

References

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Solid solutions in the titanite structure field

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Solid solubility and structural phase transitions in the compounds $CaTi(Ge_xSi_{1-x})O_5$, $(Ca_xSr_{1-x})TiGeO_5$, and $Ca(Ti_xZr_{1-x})GeO_5$ have been studied in order to gain insights into the driving forces of structural phase transitions in these transition metal compounds. The room temperature structures of $CaTiGeO_5$ and $SrTiGeO_5$ are isomorphous with the low-temperature structure of titanite, $CaTiSiO_5$ whereas $CaZrGeO_5$ is triclinic. High temperature X-ray diffraction measurements have been carried out to characterize a series of compositions along the binary joins between room temperature and 773 K. Structural phase transitions are identified based on the determination of spontaneous strain associated with them.

In $CaZrGeO_5$ a phase transition from the low temperature triclinic structure to a monoclinic structure with A2/a-symmetry occurs at approximately 493 K. The transition $P2_1/a - A2/a$, which is typical for the $CaTi(Ge_xSi_{1-x})O_5$ and $(Ca_xSr_{1-x})TiGeO_5$ solid solutions, is not observable above ambient temperature for Zr-concentrations in excess of 10%. The addition of Zr apparently destabilizes the ordered $P2_1/a$ phase. Thus the critical temperature drops from 588K in the end member composition $CaTiGeO_5$ to approximately 480K in the compound $Ca(Ti_{0.95}Zr_{0.05})GeO_5$.

Spontaneous strain associated with the $P2_1/a - A2/a$ transition in $CaTi(Ge_xSi_{1-x})O_5$ has been used to estimate the order parameter evolution as a function of temperature. Near tricritical behaviour is observed for the endmember compositions and the compounds $CaTi(Ge_{0.95}Si_{0.05})O_5$ and $CaTi(Ge_{0.1}Si_{0.9})O_5$ whereas the intermediate compositions approach second-order behaviour.

The phase transition in $SrTiGeO_5$ occurs at 560 K with a linear increase of Tc towards the intermediate phase $(Ca_{0.5}Sr_{0.5})TiGeO_5$. Between $(Ca_{0.5}Sr_{0.5})TiGeO_5$ and the endmember composition $CaTiGeO_5$ Tc stays constant.