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Crystallization kinetic of supercooled $CaO\text{-}Fe_2O_3\text{-}SiO_2$-melts by application of the high temperature ultraviolet/visible reflection spectroscopy (up to 1550 ˚C)

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0.0.1 Introduction

The spectroscopic investigation of silica based melts and their chemical structure is important for both earth science and technological applications (metallurgical and glass industry).

This work is about the reflectivity of liquid und supercooled silicates in the ultraviolet and visible spectral range under the reflection angle 0˚. For these considerations, we have developed a spectroscopic reflection method (impulse-flash-technique). By use of this method, we can record crystallisation processes of an supercooled glassy matrix to a crystalline equilibrium phase at high temperatures (transition of a mirror reflection to a diffuse reflection). We investigated the system $CaO\text{-}Fe_2O_3\text{-}SiO_2$ with Fe_2O_3-contents above 40 % (mass percent) in the initial temperature range 1400 ^{o}C to 1550 ^{o}C (liquid state) and supercooling temperature down to 1260. . . .1100 ˚C with an oxygen partial pressure of $p(O_2)$=0.21 bar.

The reflection spectra have been analysed quantitatively and they have been related to the molecular structure of the liquid and glassy solidified systems, charge-transfer- and d-d-transitions of the pair Fe^{3+}/O^{2-}.

For Fe^{3+}-O^{2-}-complexes (where the ion considered as an O^{2-}-ion appears in a bound form), very strong absorptions are found in the UV-range that are related to the photochemical process of the intermediate metal cation reduction by means of a light quantum $hc\nu$ (h=Planck´ constant, c= vacuum light velocity, ν=wave number), charge transfer transitions (CT-bands):

Fe^{3+}-O^{2-} + $hc\nu \quad \rightarrow Fe^{2+}$-$O^{-}$.

The d-d-electron transitions in the different Fe^{3+}-O^{2-}-complexes (tetrahedral or octahedral symmetry) are measured. All d-d-transitions of the $3d^5$-cations are ‘Laporte´-forbidden transitions (forbiddance of transitions with same parity and forbiddance of the transitions between states with different multiplicities) and should be measurable with only low intensities. In order to justify that the Laporte rule does not have any effect on this work, we can give two quantum mechanical reasons:

As a consequence of thermal movements of the complexes at higher temperatures, fuzzy bond distances, disharmonious oscillations and fluctuations arise . The asymmetric composition of the complexes (involving terminal and non-permanent O^{2-}-ions of the network as ligands) causes dipole moments of the complexes that are non-equal to zero. Consequently, the Laporte-forbiddance is not applicable, especially at high temperatures.

A pair interaction of the d^5-cations leads to the annihilation of the multiplicity forbiddance and therefore, to a strong increase of the intensities [increased absorptions and amplified reflections)]. This mechanism becomes effective if the d^5-cations are not separated by more than one atom of the anion. In the investigated silicate systems, we do not have any “depleted circumstances”. In fact even the opposite is valid. In liquid or supercooled silicates, we have extremely high Fe^{3+}-concentrations respectively. Therefore we have to assume strong Fe^{3+}- Fe^{3+}-pair interactions that are enhanced by thermal fluctuations.

The experimental method

The main topic is the high temperature cell developed by us. The used coaxial optical fibre system consists of two fibres. The first fibre bundle (sender fibre for the transmission of the light flash from the high energy lamp) is distributed cylindrically on a cladding (with diameter of approximately 5 mm). The second fibre bundle (receiver fibre for forwarding the reflected light flash to the detector) is arranged coaxially. The ray coming from the source of the light flash is transmitted by the cladding and focused on the silicate surface by a quartz lens. The ray reflected by the silicate surface is focused on the coaxial fibre bundle (with the diameter 2 mm) by the same quartz lens. The angle deviation is not allowed to exceed 2° so that the reflected ray hits the coaxial fibre bundle.

The central part of high temperature reflection cell is a Pt70Rh30-plate (0.3 mm plate thickness, 20 mm width, and 35 mm length) that is clamped into massive copper jaws. The plate is heated up to a well-defined temperature by a high-capacity power generator. The Pt70Rh30-plate can be durably heated up to 1600 ˚C. The liquid silicates or supercooled melt on the Pt70Rh30-plate in a controlled manner and form a closed film with thickness between 2 and 4 mm and a surface of about 5 to 10 cm^2. The temperature is determined by use of a radiation pyrometer (with a precision of about $\pm$ 20 ^{o}C).

Without the covering with the fluxes, this Pt70Rh30-plate has an almost ideally mirroring surface with a reflectance of approximately 94 % (measured with respect to an ideally reflecting aluminium standard) that does not depend on the wave number (50000 to 15000

cm^{-1}). After the registration of a reference spectrum, the silicate sample is measured on the same surface and under the same geometric conditions.

For taking reflection spectra a light flash of high energy (0.6 J/flash, duration of an impulse approximately 10^{-6} s, efficiency of an impulse above 10^3W/mm^2) is fired. These flash impulses are focused on the silicate surface with an optical fibre, through the quartz lens. The distance between the lens and the silicate surface is approximately 20 cm. In the wave number range between 50000 and 14000 cm^{-1} maximally 80 impulses per second (= scan rate) can be fired. Consequently, maximally 80 spectra per second can be taken. This spectroscopic technology (spectrometer type MCS 522) has been produced by Fa. Jenoptik/Zeiss, Jena/Germany. The spectrometer system is suited for recording crystallisation processes that can be resolved in the range of seconds.

0.0.2 Summary of results and discussion

The molten silicate is quenched within 1 s from the one-phase liquid state (1500 to 1400 ˚C) to the multi-phase solid state (temperature range between 1200 and 1000 ˚C). First, the silicate solidifies glassy. Subsequently the crystallisation process starts. A specular surface is transformed diffuse reflecting surface, which grows as a function of time. The reflectance [measured with respect to an (almost) ideally mirroring Pt70Rh30-surface] strongly decreases with time. From the recorded time dependent function “reflectance as function of time” for a constant supercooling temperature interval the crystallisation degree can be estimated.

In a fast reaction, the $Fe^{3+}(O^{2-})_4$-complex which is more stable in the liquid state firstly transforms to the $Fe^{3+}(O^{2-})_6$-complex whose d-d-transition $^6A_1 \rightarrow {}^4A_1, {}^4E(G)$ is located in the wave number range around $\sim$23000 cm^{-1}. Probably, this restructuring reaction is simply an oscillation process between the potentially existing close-by oxide ligands and the Fe^{3+}-Ion which can take place without a diffusion step. Within the rearrangement in the supercooled state, the d-d-band intensity increases initially during the time interval τ ($t \leq \tau$).The reason is that the oxide ligands of the newly-formed complex are located at equilibrium distances. Starting from this state, the nucleation proceeds for the times $t \geq \tau$. The induction time τ can be analysed quantitatively by applying the nucleus formation theory for homogenous nucleus formation.

A slower decomposition reaction starts subsequently. During this reaction, the stepwise formation of the equilibrium phases $(Fe_2O_3)_2 \cdot (CaO)_3 \cdot (SiO_2)_3 + (CaO)_3 \cdot (SiO_2)_2 + Fe_2O_3$ from the glassy state is carried out.