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Divalent chromium in alkaline earth silicate systems

Only a few Cr^{2+}-containing oxides, e.g. Cr_2SiO_4 [1], and spinels e.g. $(Mg, Cr^{2+})Cr_2O_4$ [2], are known. Their preparation requires high temperatures and a strongly reducing atmosphere. Some other compounds could only be obtained at non-equilibrium conditions. From the rules for multicomponent system, the addition of acid SiO_2 and the oxides MgO, CaO, SrO and BaO with different basicity and radii of the metal ions seemed to be favourable for the preparation of Cr^{2+}-containing oxides. Cr^{2+} should be more basic than Cr^{3+}, and should have an ion radius greater than Cr^{3+}, which might be advantageous for the substitution of the alkaline earth atoms. In alkaline earth oxide–silica–chromium oxide systems the higher oxidation states of chromium are stable at high CaO, SrO and BaO contents, and low temperatures. Lower oxidation states of chromium therefore could be expected at low content of alkaline earth oxide and high temperatures. The temperature for the occurrence of liquids however decreases in the order MgO > CaO > SrO > BaO especially at a low content of alkaline earth oxide and chromium oxide [4].

Mixtures of reagent grade MeO (Me = Mg, Ca, Sr, Ba), Cr_2O_3 and SiO_2 (from silicic acid) were thoroughly ground under acetone and pre-reacted in air for about 1 h at 1100° C. Small portions of the powder samples were put in fused silica crucibles, equilibrated at high temperatures in vertical molybdenum wound tube furnaces and quenched in water after about 20 min. A short time for equilibration seemed to be essential, because of reaction with the silica crucible and also of the fast volatilization of CrO, which both would change the composition. The strongly reducing atmosphere was attained by a slow current of H_2 which was saturated with H_2O vapour in a temperature controlled water bath.

Cr^{2+} could be identified by the blue colour of the quenched samples depending on the composition, temperature and oxygen partial pressure [3]. It could be most easily obtained in quenched liquids at the conditions listed in Table I.

TABLE I

System	Temperature (° C)	log $P(O_2)$/atm	Approximate composition (mol %)		
			MeO	"CrO"	SiO_2
$MgO–Cr_2O_3–SiO_2$	1530	−12	42	4	54
$CaO–Cr_2O_3–SiO_2$	1405	−13	36	4	60
$SrO–Cr_2O_3–SiO_2$	1390	−13	31	5	64
$BaO–Cr_2O_3–SiO_2$	1350	−13.5	25	5	70

A decrease of the H_2O content in H_2 had little influence on the temperature of Cr^{3+} reduction. Hydrogen, which had passed through concentrated H_2SO_4 lowered the temperature only to ~ 1505° C in the MgO containing system. Therefore, the conditions described above were chosen for this investigation with approximately constant H_2O content of the gas mixture and temperatures up to 1660° C. The change of colour at the $Cr^{3+} \rightarrow Cr^{2+}$ reduction from green to an intensive blue occurred within a few minutes and could be used as an indicator to check the oxygen partial pressure.

Though there are many silicate phases with alkaline earth atoms of different sizes, Cr^{2+} seems to form no significant solid solution with alkaline earth silicates, but decreases the liquidus temperature in the presence of these compounds. In SrO and BaO containing systems the blue liquid was even separated from the green Cr^{3+} containing liquid. Liquids with high Cr^{2+} content are very mobile and could creep out of the crucible, as was also observed in former investigations [1]. The only solid phases with sufficient amount of Cr^{2+} detectable by X-ray diffraction were $MgCr_2O_4$, where a lattice distortion is subject to Cr^{2+} [2], $CaCr_2O_4$, where an atmosphere-dependent phase transition implies solid solubility and probably also $SrCr_2O_4$. Light blue solids were observed in the presence of the composition Ca_3SiO_5, Sr_3SiO_5 and Ba_3SiO_5, indicating some solid solution. The X-ray diagrams of those samples however had very poor quality, even after prolonged annealing of the samples.

The electron spectra of the Cr^{3+} containing samples exhibit two absorption bands at 20 800 to 23 300 cm^{-1} for the transition $^4A_{2g} \rightarrow {}^4T_{1g}$ and at 15 400 to 17 300 cm^{-1} for the transition $^4A_{2g} \rightarrow {}^4T_{2g}$ (see also [5]). Due to a decreasing ligand field stabilization, the wave numbers of the absorption bands decrease in the order $MgCr_2O_4$, $(Mg, Cr^{2+})Cr_2^{3+}O_4$, α-$CaCr_2O_4$, Cr_2O_3, β-$CaCr_2O_4$, $SrCr_2O_4$ and Cr^{3+} in glass. Cr^{2+} in an octahedral field requires one single band for the spin allowed transition $^5E_g \rightarrow {}^5T_{2g}$. This transition was observed by reflection spectroscopy at about 15 900 cm^{-1} with a small shift to 15 400 cm^{-1} for the MgO containing glass. This value can be compared with the transition at 6670 cm^{-1} for tetrahedral co-ordinated Cr^{2+} in $(Mg, Cr^{2+})Cr_2O_4$ [2] with the approximate relation, $Dq\,(\text{tet}) \simeq 4/9\, Dq'(\text{oct})$, of crystal field theory. Additional weak absorption bands at 19 600 cm^{-1} for the CaO and BaO containing glass could not be assigned without knowledge of structural details.

The high-spin d^4 configuration of Cr^{2+} must be treated like d^9 of Cu^{2+} and should have a similar influence on crystal chemistry. The Jahn–Teller distortion might be one reason for the limited solid solution of Cr^{2+} in the compounds of this investigation. Also the crystal field stabilization favours Cr^{3+} in solids, it should be less important for Cr^{2+} in molten silicates. The stabilization energy for Cr^{3+} in solids has about twice the value than for Cr^{3+} (~ 57/~ 27 kcal mol^{-1} for octahedral co-ordinated chromium and ~ 13/~ 7 kcal mol^{-1} for tetrahedral co-ordination [5, 6]).

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