INFLUENCE OF COMPOSITION AND P_{O2} ON CHROMIUM DISTRIBUTION BETWEEN FORSTERITE CRYSTAL AND MELT
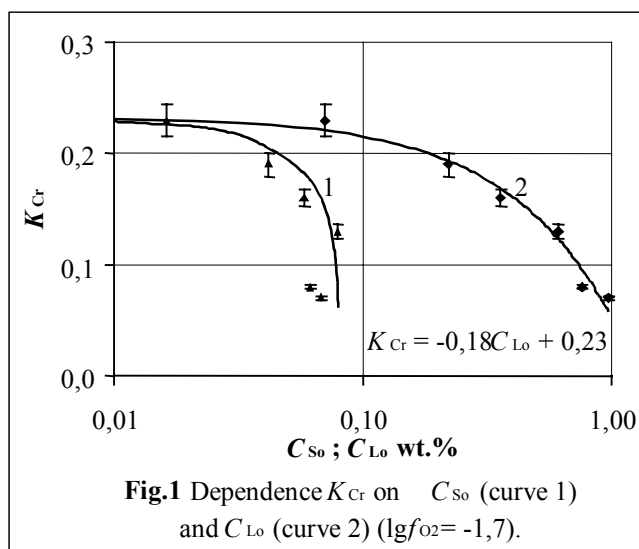
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The dependencies of distribution coefficient of chromium (K_{Cr}) between forsterite single crystal and its melt upon the initial chromium concentration in the melt, oxygen fugacity of growth atmosphere as well as upon additional doping by other elements (Li, Na, Al) were investigated.
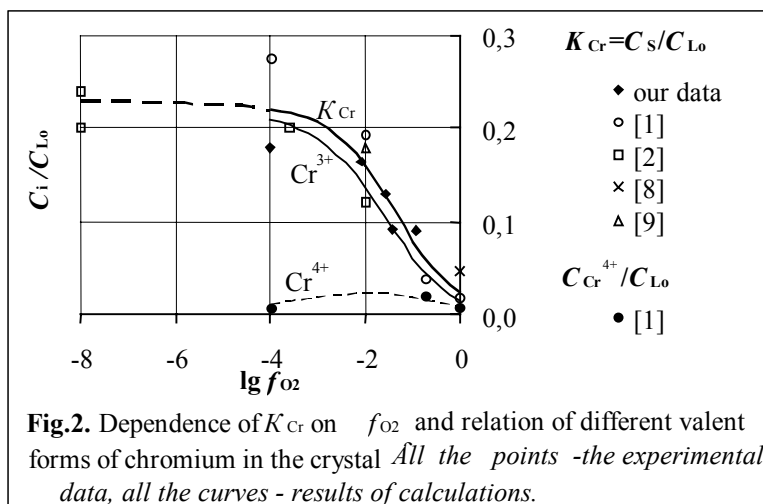
Forsterite single crystals were grown from the melt by the Czochralski method. Chromium concentration in the crystals was measured by microprobe analysis, lithium concentration – by atomic emission spectrometry with inductively coupled plasma. K_{Cr} was calculated by extrapolation of the dependence C_S/C_{Lo} on crystallized fraction of initial melt g to zero (C_S – chromium concentration in the crystal, C_{Lo} – initial chromium concentration in the melt).

Fig. 1 shows the dependencies K_{Cr} on C_{Lo} and C_{So} (C_{So} was found by the extrapolation C_S to g=0). One can see that K_{Cr} decreases more than three times when the initial chromium concentration in the melt increases from 0.07 to 0.97 wt.%. The extrapolation of the dependence K_{Cr} upon C_{Lo} to $C_{Lo}{\to}0$ gives the limiting value K_{Cr} equal 0.23. K_{Cr} can be considered as the constant only for $C_{Lo} \leq 0.1\text{-}0.2$ wt.%. The further increase of

$$K_{Cr} = -0,18C_{Lo} + 0,23$$

Fig.1 Dependence K_{Cr} on C_{So} (curve 1) and C_{Lo} (curve 2) ($\lg f_{O2}$= -1,7).

dopant concentration in the melt retards the growth of chromium content in crystal and C_{So} becomes saturated what leads to decrease of K_{Cr}. Probably, the reason for this effect is the formation of chromium clusters in the melt. This makes further insertion of chromium into the crystal difficult.

To study an influence f_{O_2} on K_{Cr} the series of single crystals grown in the high purity Ar atmosphere as well as in the mixtures of N_2 and O_2 with oxygen content from 0.85 to 12 vol.% was explored. The initial chromium concentration in the melt was 0.12±0.02 wt.%. Our results together with data from literature are shown on Fig. 2 and display that K_{Cr} decreases sharply at $f_{O_2}>10^{-4}$. Three different models were examined for description such behavior of K_{Cr} making allowance for EPR-data [1] for determination of Cr^{4+}–content in the crystals. In all the models we assume that chromium is present in the crystals in range $-4<\lg(f_{O_2})<0$ only in the form of Cr^{3+} and Cr^{4+} ions, as determined

Fig.2. Dependence of K_{Cr} on f_{O2} and relation of different valent forms of chromium in the crystal *All the points -the experimental data, all the curves - results of calculations.*

earlier [1,2]. Evidence on valence state of chromium in the forsterite melt is absent. It has been known that Cr^{3+} and Cr^{6+} ions are in equilibrium in oxidizing conditions in the more complex silicate melts [3]. The possible variants of coexistence in the melt Cr^{3+} and Cr^{4+} ions (model 1), Cr^{3+} and Cr^{6+} (model II), Cr^{3+}, Cr^{4+} и Cr^{6+} (model III) were analyzed.

The experimental data can be closely approximated only at the assumption that Cr^{6+} ions exist in the forsterite melts (models II and III). According to these models when f_{O_2} increases, Cr^{6+} ions accumulate in the melt, and at the same time the concentration of Cr^{3+} ions in the melt (and, as consequence, also in the crystal) decreases. The concentration of Cr^{4+} ions only slightly varies with f_{O_2} change. As a result the total chromium content in the crystals and K_{Cr} decrease sharply when f_{O_2} increase.

Partial distribution coefficient for Cr^{3+}–ions (K_{Cr}^{3+}) evaluated within models II and III equals 0.2; K_{Cr}^{4+} for model III equals 0.1. Ions Cr^{2+} could appear in crystals by $f_{O_2} < 10^{-4}$ [2]. A value of K_{Cr}^{2+} can be evaluated by means of dependence of distribution coefficients of divalent impurities between forsterite single crystal and its melt upon their ionic radii. We investigated this dependence earlier in [4]. The value of K_{Cr}^{2+} equals ~ 0.5. Thereby, with increasing Cr valence its distribution coefficient decreases.

The Cr^{3+} ions have a main influence on total K_{Cr} because these ions predominate in the crystals. The solubility of the Cr^{3+} ions with the charge more than that of replaceable ions of Mg^{2+} can be increased by additional doping by ions which charge is less than that of the replaceable cations of the host crystal. To select the most suitable charge compensator we performed the computer simulation of the forsterite crystal structure using minimization of static energy of the crystal lattice using the GULP program [5]. The parameters of the interatomic potentials were taken from [6,7]. The calculations were made within the framework of an ionic model taking into account covalent effects by means a three-body O-Si-O bond-bending potential and electron polarization of oxygen ions.

We compared the solution energies of Cr^{3+} ions for different mechanisms of charge compensation using magnesium vacancies v''_{Mg}, monovalent ions in magnesium sublattice (Li'_{Mg}, Na'_{Mg}) and trivalent ion in silicon sublattice (Al'_{Si}). According to our calculations, the Cr^{3+} solubility decreases in the following row of charge compensators: $Li'_{Mg} > Na'_{Mg} > v''_{Mg} > Al'_{Si}$.

K_{Cr} was measured for the crystals doped only by chromium as well as by both chromium and lithium. The initial chromium concentration in the melt was 0.06±0.01 wt.%, the initial lithium content in the melt was varied in the range 0.01 – 0.42 wt.%. All the crystals were grown in the high purity argon atmosphere since the crystals grown in such condition (lg f_{O_2} ~ -4) contain mainly Cr^{3+} [1]. First K_{Cr} increases as the lithium content in the melt increases and then becomes saturated (fig. 3). The value of K_{Cr} in case of the conjugate isomorphism with lithium can be increased about 1.5 times in comparison with that in the case of the individual impurity. The saturation of K_{Cr} dependence on lithium content occurs when the atomic ratio Li/Cr in the crystal is close to 1.
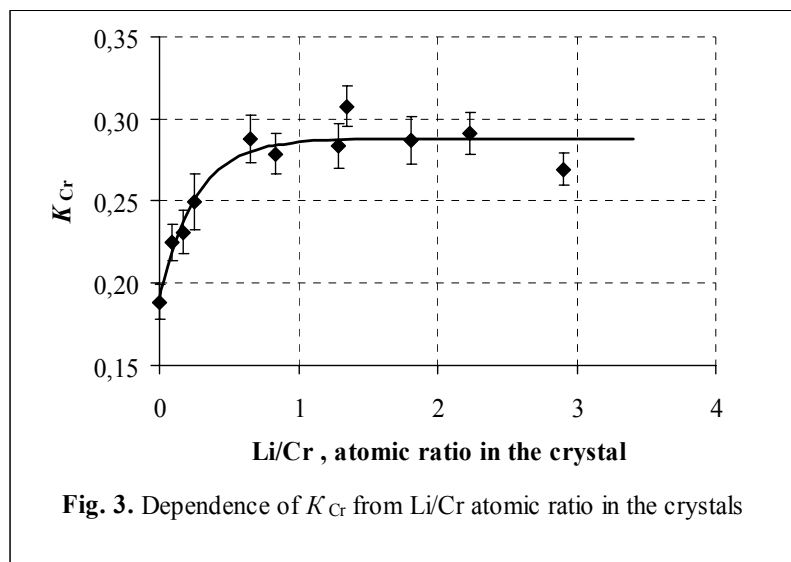

Fig. 3. Dependence of K_{Cr} from Li/Cr atomic ratio in the crystals

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