

INFLUENCE OF THE MELT COMPOSITION ON CHROMIUM SOLUBILITY AND $\text{Cr}^{3+} / \text{Cr}^{4+}$ RATIO IN FORSTERITE

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Forsterite (Mg_2SiO_4) is the major component of important rock forming mineral olivine. Besides, chromium-doped forsterite is well-known laser crystal. Depending on growth conditions chromium can be present in forsterite crystal in different valent and structural states. Laser performance in forsterite was obtained on both Cr^{4+} and Cr^{3+} ions [1]. Increase in concentration of optically active centers and their share in total chromium content is actual problem for improvement of laser characteristics of forsterite crystals. A change of oxygen fugacity at crystal growth is one of the possible ways of influence on laser properties of chromium-containing forsterite. Based on the results of optical absorption spectroscopy, authors of Refs. [2, 3] came to conclusion that the share of Cr^{3+} centers in forsterite crystal increases with increase of Cr concentration in the melt. In the present work, it is investigated the influence of Cr concentration in the melt on solubility of chromium in a forsterite crystal and relationship between Cr ions of different valency.

Forsterite single crystals were grown from the melt by Czochralski method at oxygen fugacity $\lg f_{\text{O}_2} \cong -1.7$. Concentration of chromium in the melt (C_L) varied from $1.5 \cdot 10^{-2}$ up to 1.4 wt %. Chromium distribution along a crystal was determined by microprobe analysis. The information on the valent state and structural localization of Cr ions was obtained from optical absorption and EPR spectra. Absorption spectra were investigated in the range 275-1250 nm. Change in the concentration of centers was estimated through change of absorption coefficients of bands with peaks at 295 and 470 nm for Cr^{3+} centers as well as at 740 and 1085 nm for Cr^{4+} centers.

Fig.1 shows the dependence of C_S on C_L , where C_S is initial concentration of chromium in a crystal. In the range of low concentrations of chromium ($C_L \leq (1-2) \cdot 10^{-2}$ wt %), the distribution coefficient of chromium between crystal and melt ($K = C_S / C_L$) can be considered as constant and equal to 0.2 (the dependence $C_S = 0.2 C_L$ is shown in Fig.1 by solid line). In the range of higher concentrations of chromium in the melt, the rise of C_S slows down (see a dotted line in Fig.1) hence K decreases. The deviation from the Henry's law is apparently connected with the formation of chromium-containing complexes in the melt, which prevent entering the chromium into the crystal.

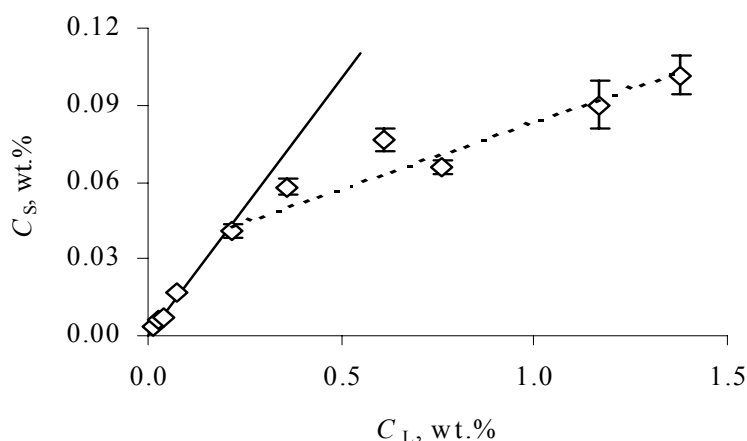


Fig.1. Dependence of Cr concentration in crystal (C_S) from Cr concentration in melt (C_L)

Absorption spectroscopy has shown that change of absorption coefficients in the bands caused by $\text{Cr}_{\text{Mg}}^{3+}$ and $\text{Cr}_{\text{Si}}^{4+}$ centers is proportional to the change of total chromium content in the crystal (Figs. 2 a, b). These data testify that the $\text{Cr}_{\text{Mg}}^{3+} / \text{Cr}_{\text{Si}}^{4+}$ ratio does not vary with increasing total Cr concentration in crystal. Concentration dependences of $\text{Cr}_{\text{Mg}}^{3+}$ and $\text{Cr}_{\text{Si}}^{4+}$ centers versus Cr content in the melt follow more or less precisely the dependence of C_S on C_L .

The analysis of EPR spectra has allowed revealing the $\text{Cr}_{\text{Si}}^{4+}$

centers and different $\text{Cr}_{\text{Mg}}^{3+}$ centers, namely, $\text{Cr}_{\text{Mg(M1)}}^{3+}$ and $\text{Cr}_{\text{Mg(M2)}}^{3+}$ located in structurally nonequivalent magnesium sites M1 and M2 as well as the associates of these ions with magnesium vacancies. From data published in Refs [4, 5] follows that optical absorption of three-valent chromium ions is

caused by Cr^{3+} (M2)'' centers that are associates of two $\text{Cr}_{\text{Mg(M2)}}^{3+}$ ions with (M1) magnesium vacancy. Alteration of the concentration of Cr^{3+} (M2)'' and $\text{Cr}_{\text{Si}}^{4+}$ centers along C_s according EPR data is described by linear dependences Fig. 2 (c, d) and correlate with the absorption spectroscopy data (Fig. 2 a, b). In conclusion, the obtained results have not confirmed findings of Refs. [7, 8] regarding the

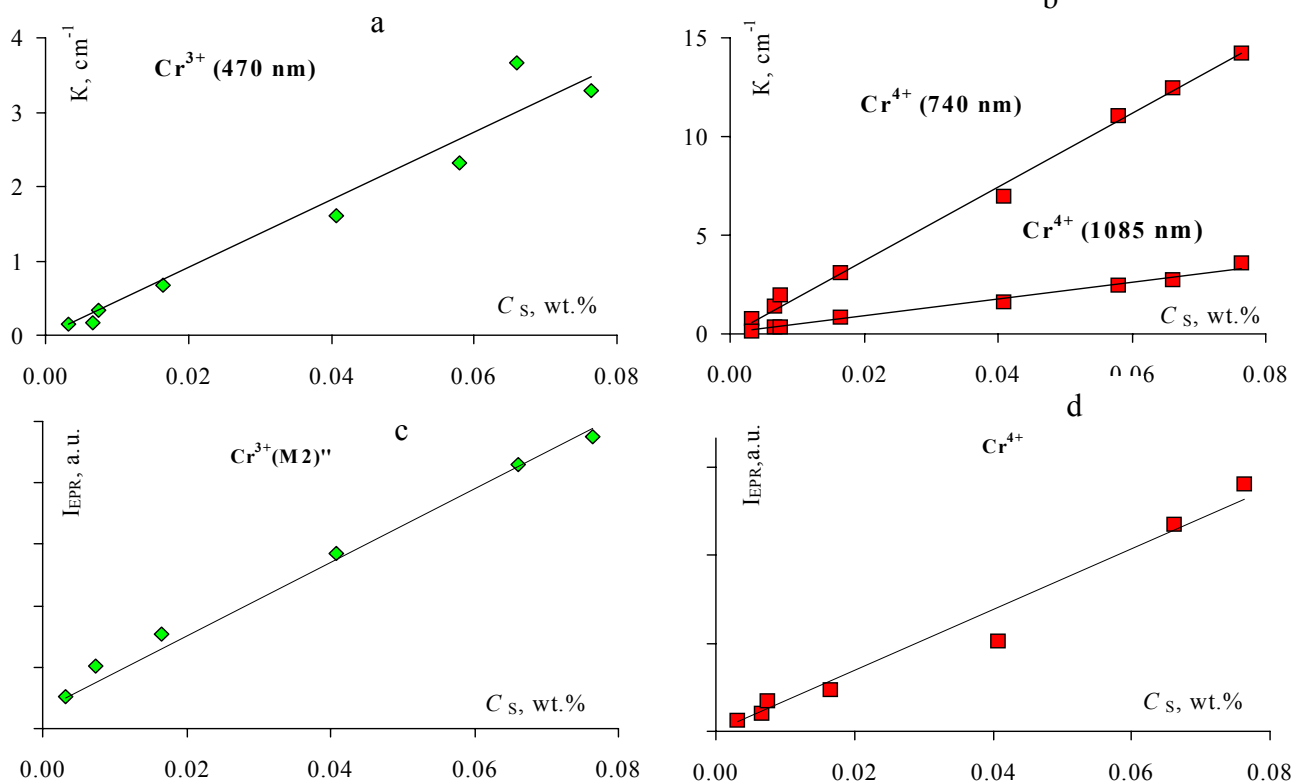


Fig.2. Dependences of optical absorption (a, b) and integrated intensity of EPR signal (c, d) for Cr^{3+} and Cr^{4+} ions on Cr concentration in forsterite crystals

rise of $\text{Cr}^{3+} / \text{Cr}^{4+}$ ratio along with increasing the chromium concentration in the melt.

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