Controlling Europium Oxidation State in Diopside Through Flux Concentration

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This explores the connection between the H_3BO_3 flux concentration and the coexistence of Eu^{2+} and Eu^{3+} dopants within $CaMgSi_2O_6$ crystals (diopside). The samples were synthesised using a solid-state synthesis method under varying atmospheric conditions, including oxidative (air), neutral (N_2), and reductive (H_2/N_2 mixture) environments. Additionally, some materials underwent chemical modification by partially substituting Si^{4+} with Al^{3+} ions. Depending on the specific synthesis conditions, the materials predominantly displayed either the orange-red luminescence of Eu^{3+} (under oxidising conditions) or the blue luminescence of Eu^{2+}. However, the comprehensive results confirmed the co-existence of Eu^{3+}/Eu^{2+} luminescence in both cases. In the case of materials obtained under oxidazing atmosphere the intensity of the trace Eu^{2+} emission increased with increasing of flux concentration independently on the materials modification, while in the case of materials obtained under reductive atmosphere the changes of Eu^{3+} emission intensity depended on the presence or absence of Al^{3+} ions (the intensity increased in the case of unmodified materials and decreased in the modified ones with increasing of concentration of flux). The emission of the materials obtained under neutral atmosphere was characterized by the Eu^{3+} and Eu^{2+} luminescence and the evolution of the Eu^{2+} emission intensity, with increasing of flux concentration, was similar behavior as in the case of samples obtained in air. All these effects were qualitatively explained considering the double role of the flux in the studied system: as an agent that facilitate the diffusion of chemical species during solid state process and as a charge compensating agent.

Acknowledgements: This work was supported by the National Science Center (NCN) Poland under project PRELUDIUM-17, no. UMO-2019/33/N/ST4/00425.

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