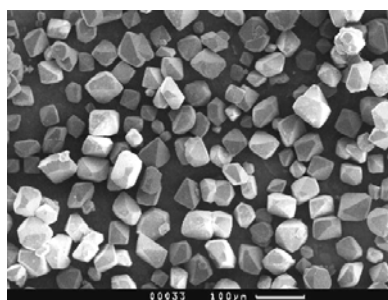


# STATE OF MANGANESE IONS IN MATRIX OF CORUNDUM SYNTHESIZED IN SUPERCRITICAL WATER FLUID

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Kinetics and mechanism of  $\alpha$ - $\text{Al}_2\text{O}_3$  (corundum) formation from  $\text{Al}(\text{OH})_3$  (hydrargillite) in supercritical water fluid at the presence of manganese ions was investigated. In these conditions of transformation of hydrargillite the powder of small single crystals of corundum doped with manganese was obtained [1, 2] (Fig. 1). It is found that the corundum synthesized in medium of supercritical water with the  $\text{Mn}^{2+}$  ion or  $\text{MnO}_4^-$  anion contain one-type composite defects containing ions  $\text{Mn}^{4+}$  (discovered by photoluminescence method, Fig. 2),  $\text{Mn}^{3+}$  (discovered by diffuse reflection spectroscopy method, Fig. 3) and  $\text{Mn}^{2+}$  (observed by EPR method) alongside with hydroxyl groups and oxygen vacancies. The appearance of manganese ions with a different charge in corundum structure is determined by oxidation-reduction properties of supercritical water fluid. It has been supposed that in the synthesized corundum during doping with the manganese is formed a composite defect, consisting from exchange-bonded manganese ions and charged oxygen vacancy:  $\text{Mn}^{4+}\text{-V}_\text{O}\text{-Mn}^{2+}$ . The manifestation peculiarities by manganese ions in corundum of spectral properties are caused by possibility of electron transfer between manganese ions and oxygen vacancy. In this case the charge state of manganese ions varies and oxygen vacancies into F-centres are converted. It is revealed that the corundum doped with manganese exhibits ferromagnetic properties at room temperature. On the basis of the obtained results it is concluded that formation of well-faceted crystals of corundum uniformly doped with manganese occurs owing to solid phase mobility, which arises in the conditions of reversible



dehydroxilation at interaction of solid phase with water fluid.

Fig.1

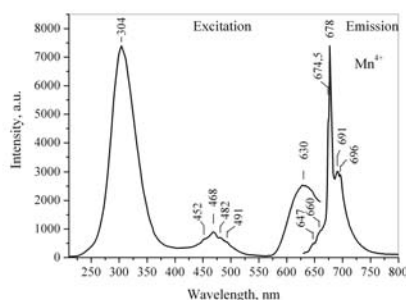


Fig.2

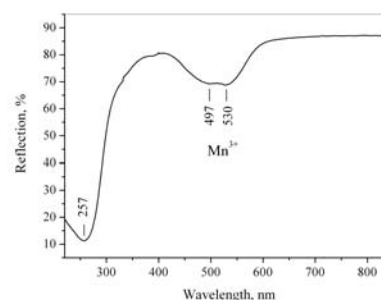


Fig.3

Fig. 1. SEM image of fine crystalline Mn doped corundum synthesized from hydrargillite in SCW at 410°C and 32 MPa.

Fig. 2. The luminescence band (with basic maximum at 678 nm) of  $\text{Mn}^{4+}$  ions in corundum doped with manganese and its excitation spectrum.

Fig. 3. The diffuse reflection spectrum of corundum doped with manganese.

[1] Danchevskaya M.N., Yu.D. Ivakin, S.N. Torbin, G.P. Panasyuk, V.N. Belan, I.L. Voroshilov. Scientific basic technology of fine-crystalline quartz and corundum. High Pressure Research, 2001, v.20, pp. 229-239.

[2] Ivakin Yu. D, Danchevskaya M.N., Torbin S. N., Ovchinnikova O. G. Synthesis of luminophores – powders in supercritical fluid. Joint 20<sup>th</sup> AIRAPT – 43<sup>rd</sup> EHPRG Conference on Science and Technology of High Pressure - Karlsruhe (Germany) from June 26 till July 2, 2005.