

SYNTHESIS, ISOMORPHIC CAPACITY AND CRYSTAL CHEMISTRY $Zn_{2-2x}M_{2x}SiO_4$ (M = Mn, Ni, Mg, Cu)

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Zinc orthosilicate with willemite structure, activated by manganese ions, Zn, SiO₄: Mn, is an effective luminescent substance of green luminescence. The structure of Zn_sSiO_t is characterized by the presence of two crystallographically nonequivalent positions of the metal atom. The formation of substitution solid solutions in such structures can be associated with the non-statistical filling of nonequivalent positions with dopant metal atoms. The study of isomorphic capacity of substitution solid solutions $Zn_{2,2y}M_{2y}SiO_4$ (M = Mn, Ni, Mg, Cu) obtained by solid-phase synthesis was performed using powder diffraction data analysis, followed by calculation of the parameters of the unit cells. The effective Shannon radii and the volumes of the coordination polyhedra [ZnO₄] were chosen as the size factors for estimating the length of solid solutions. The homogeneity range of the solid solution $Zn_{2,2x}M_{2x}SiO_4$ (M = Mn, Cu, Ni, Mg) increases sequentially: 13 at.% in $Zn_{2-2x}Mn_{2x}SiO_4$, 15 at.% in $Zn_{2-2x}Ni_{2x}SiO_4$ and 50 at.% in $Zn_{2-2x}Mg_{2x}SiO_4$ and $Zn_{2-2x}Cu_{2x}$. SiO_4 . Changes in the crystal chemical parameters of $Zn_{2-2x}M_{2x}SiO_4$ (M = Mn, Ni, Mg, Cu) were analyzed and compared. Due to the presence of a rigid anionic group [SiO₄]⁴, unchanged during the formation of solid solutions, there is no significant change in the linear and volume coefficients of thermal expansion. It was found that small changes in the unit cell parameters of $Zn_{2,2v}M_{2,2}SiO_4$ with increasing concentrations of Ni²⁺, Mg²⁺ and Cu²⁺, having a smaller radius compared to Zn²⁺, are associated with a predominant substitution of zinc in a position with a smaller volume of coordination polyhedron. While the thermal expansion of the structure as a whole is due to the deformations of the larger polyhedron. The absence of the possibility of shear deformations of the crystal lattice due to the crystallization of Zn_2SiO_4 in the hexagonal syngony leads to the fact that as the relative difference in the effective radii of interchangeable cations decreases, the homogeneous regions of the $Zn_{2,2x}M_{2x}SiO_4$ solid solutions increases in the range of dopants M = Mn, Ni, Mg, Cu.

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