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Hydrothermal synthesis of α - $\text{Zn}_2\text{SiO}_4\text{:V}$ phosphor, determination of oxidation states and structural localization of vanadium ions



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ABSTRACT

The monophasic morphologically homogeneous phosphor α - $\text{Zn}_2\text{SiO}_4\text{:V}$ has been produced by the hydrothermal method. With the use of energy-dispersive analysis and X-ray powder diffraction analysis, it was established that the ratio of cations Zn:Si:V corresponded to the formula $\text{Zn}_2\text{Si}_{0.9}\text{V}_{0.1}\text{O}_4$. The charge state of vanadium ions was determined by the spectroscopic methods. Maxima of the bands in the luminescence spectra correspond to V^{5+} (523 nm) and V^{3+} (720 nm) centers. The small width of the EPR signal hyperfine structure components indicates the presence of single V^{4+} centers, their contribution is not greater than 0.1% of the total vanadium content. The presence of a broad structureless component in the EPR spectrum was explained by the fact that the main amount of the dopant ion was united in the areas containing V^{5+} , V^{4+} and V^{3+} ions. V^{4+} ions and V^{5+} ions with high probability occupy silicon positions in the lattice.

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1. Introduction

The zinc orthosilicate Zn_2SiO_4 was first described by Armand Levy, the French mineralogist and crystallographer, as willemite mineral in 1830 (called in honor of Willem I, the king of the Netherlands). Materials based on Zn_2SiO_4 are interesting due to their optical properties: natural crystals of willemite are used in jewelry, cobalt-doped silicates are synthesized as blue inorganic pigments [1,2], $\text{Zn}_2\text{SiO}_4\text{:Mn}$ is an industrial phosphor with yellow-green fluorescence for Field Emission Displays (FED), UV and Blue Chip Excited White LEDs, as well as for plasma display panels (PDPs) [3–5].

It was established that there exist several crystalline modifications of Zn_2SiO_4 , among which only the willemite structure, known also as α - Zn_2SiO_4 , is thermodynamically stable under standard conditions [6].

The trigonal frame structure of willemite is formed by the $[\text{SiO}_4]^{4-}$ and $[\text{ZnO}_4]^{6-}$ tetrahedra connected by shared oxygen atoms (Fig. 1).

The results of investigations of willemite doped with different ions are well presented in the literature. It is shown that Co^{2+}

[2,7,8], Ni^{2+} [8] and Mn^{2+} [9–14] ions occupy the zinc positions, and Ti^{4+} [15] and Cr^{4+} ions [16] occupy the silicon positions. Such substitution maintains the electrical neutrality of the compound and was predicted from the analysis of the ionic radii values [17]. The radii of the latter two ions differ considerably from the radius of replaceable silicon ion, and an even more essential difference is between the radii of Zn^{2+} and Pb^{2+} ; however the authors of [18] have obtained a compound with such substitution. Some works report the production of willemite doped with the Tb^{3+} [19,20] and Eu^{3+} [19–22] ions suggesting the possibility of heterovalent substitution in both cation sublattices. Thus, from analysis of the literature data it is seen that the structure of willemite is tolerant to polyhedra deformations occurring when zinc and silicon cations are replaced by the ions of sizes differing from those of the matrix ions. In this case, the charge state of the substituent ion should be changed to preserve electrical neutrality.

The experiments on implantation of the vanadium into the structure of willemite are of particular interest [23–27]. The luminescence spectra of $\text{Zn}_2\text{SiO}_4\text{:V}$ indicate that V^{5+} ions are present in the silicate; but the mechanism of charge compensation and the positions of substituent ions are not discussed. Synthesis of this silicate is a multistage process: ZnO:V precursor was produced from a mixture of ZnO and NH_4VO_3 under supercritical conditions in an autoclave with subsequent annealing; after that tetraethylorthosilicate (TEOS) and hydrofluoric acid were added to the

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