Functional Materials 9, No.3 (2002) 

# Optical properties of $Mn^{2+}$ activated $Zn_2SiO_4$ and $Mg_2SiO_4$ solid solutions

*A.V.Shamshurin, N.P.Efryushina, S.L.Tamazlykar', A.V.Repin*

A.Bogatsky Physical-Chemical Institute, National Academy of Sciences of Ukraine, 86 Lustdorfskaya Road, 65080 Odesa, Ukraine

*Received July 23, 2001*

Optical characteristics of $Zn_2SiO_4$–$Mg_2SiO_4$ system samples activated by $Mn^{2+}$ ions have been studied. The sample properties are interpreted from the standpoint of the crystal field theory. The experimental level energy values are in good agreement with calculated ones.

Исследованы оптические характеристики образцов в системе $Zn_2SiO_4$–$Mg_2SiO_4$, активированных ионами $Mn^{2+}$. Интерпретированы их свойства с точки зрения теории кристаллического поля. Наблюдалось хорошее соответствие между экспериментальными и вычисленными значениями энергии уровней.

Willemite ($Zn_2SiO_4$:$Mn^{2+}$) is among efficient silicate luminophors for special screens, in particular, for those of grid-free electron beam memory devices [1, 2]. The band positions in its luminescence spectrum (the $^4T_1(^4G)\rightarrow{}^6A_1(^6S)$ transition) and the excitation one are defined by the split character of $d^5$ configuration terms of the activator ions in the ligand field [3]. The excited level energy values of Mn(II) ion ($^4T_1(^4G)$, $^4T_2(^4G)$, $^4A_1(^4G)$, $^4E(^4G)$, $^4T_2(^4D)$, $^4E(^4D)$, $^4T_1(^4P)$) depend on the crystal field (CF) parameters $B$, $C$, and $D_q$. The ligand type being the same, the distance between the central ion and ligand and its coordination are of importance. This strong influence can be illustrated by the fact that in willemite, the Mn(II) ion emits in the green spectral region ($\lambda_{max} = 530$ nm) while in $Mg_2SiO_4$, in the red one ($\lambda_{max} = 635$ nm). The excitation spectra of those samples described in [3, 4] show a poor band resolution, so that not all bands are identified; the crystal field parameters are not calculated. The purpose of this work is to study the optical characteristics of $Zn_2SiO_4$–$Mg_2SiO_4$ system samples activated by $Mn^{2+}$ ions and to interpret their properties from the standpoint of the crystal field theory.

The system choice is due to that ionic radii ($R$) of $Zn^{2+}$, $Mg^{2+}$, and $Mn^{2+}$ are close to each other (thus, formation of a series of solid solutions is possible) as well as to different structures of their crystal lattices what is expected to influence the formation of different emission centers and a regular variation of their optical properties. The compounds to be studied are high-melting (m.p. 1509°C for $Zn_2SiO_4$ and 1890°C for $Mg_2SiO_4$), so that it is hardly possible to obtain the solid solutions directly from silicates and using standard apparatus. The luminophors were synthesized by ceramic (solid-phase) method using sintering of $ZnCO_3$, $MgCO_3$, $MnCO_3$, and $SiO_2$ mixtures, the chromophor impurity content in all materials being less than $1\cdot10^{-3}$ %. Zinc fluoride (up to 5 % by mass) was used as flux. The calcination was performed in two stages, at 750°C for 1 h and then at 1100 to 1200°C for 1.5 to 2 h. The dispersity of reagents is of considerable importance in the synthesis, as well as a $SiO_2$ excess of 3 to 6 % as compared to the stoichiometry. The synthetic procedure of silicate crystal luminophors is described in detail in [5].

The sample phase composition was examined by X-ray phase analysis (RPA). The