

Photophysics of Ceramic Luminophores. Zeolite-Based Luminophores of the Types $\text{Zn}_2\text{SiO}_4\text{:Mn}$ and $(\text{CdO})_2\text{B}_2\text{O}_3\text{:Mn}$

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The emission spectra (at $T = 10\text{ K}$ and 296 K) and the excitation spectra (at $T = 295\text{ K}$) of zeolite-based luminophores of the types $\text{Zn}_2\text{SiO}_4\text{:Mn}$ and $(\text{CdO})_2\text{B}_2\text{O}_3\text{:Mn}$ show the characteristics of Mn^{2+} in tetrahedral and octahedral surroundings, respectively, as well as additional features due to impurities and/or structural defects of the host crystal. The ZnSiO_4 -type phosphor exhibits photostimulated emission, which can be assigned to trap states of the silicate host.

1. Introduction

In order to prepare ceramic glazes it is a well-known task to find materials whose optical properties are not changed considerably by the firing process. Beside their colors, for particular applications the luminescence properties of these materials are of interest. As shown by Kiss *et al.* [1] luminescence centers Mn^{2+} can be doped into zeolites by ion exchange. These zeolites act both as diluents and as cages for the Mn^{2+} centers preventing the Mn^{2+} from oxidation during the firing process. Slightly varying with the kind of zeolite the resulting ceramic luminophores $\text{Zn}_2\text{SiO}_4\text{:Mn}^{2+}$ ($= L_{\text{Zn}}$) and $(\text{CdO})_2\text{B}_2\text{O}_3\text{:Mn}^{2+}$ ($= L_{\text{Cd}}$) exhibit luminescence depending on the dopant concentration and the temperature. Purpose of this letter is to report the typical luminescence properties of the systems L_{Zn} and L_{Cd} and to discuss the experimental results.

2. Experimental

The luminophore $L_{\text{Zn}}(L_{\text{Cd}})$ has been prepared from the zeolites by adding the corresponding amount of $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ in aqueous solution, drying, admixing of zinc oxide (cadmium oxide) and silicic acid (boric acid), followed by heating to $\sim 1060^\circ\text{C}$ ($\sim 760^\circ\text{C}$). By X-ray analysis it could be shown that L_{Zn} has the same structure as $\alpha\text{-Zn}_2\text{SiO}_4$ (Willemite), which contains two non-equivalent sites of Zn [2]. Each of these is surrounded tetrahedrally by four oxygen atoms. In Willemite Zn can be exchanged by

Mn [3]. From this we infer that in L_{Zn} the Mn^{2+} ions also occupy sites of tetrahedral symmetry. The solid L_{Cd} is composed of several crystalline phases. A comparison with JCPDS data [4] indicates that the main components have the stoichiometries $2\text{CdO} \cdot \text{B}_2\text{O}_3$, $3\text{CdO} \cdot 2\text{B}_2\text{O}_3$, and $2\text{CdO} \cdot 3\text{B}_2\text{O}_3$, respectively. The site symmetry of the Mn^{2+} ions in L_{Cd} could not be determined by X-ray analysis.

3. Results and Discussion

Figs. 1 and 2 show the emission spectra and excitation spectra of samples of L_{Zn} and L_{Cd} . The green

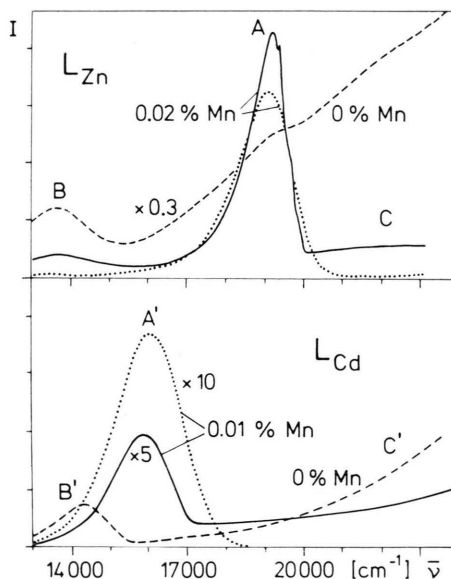


Fig. 1. Emission spectra of L_{Zn} and L_{Cd} , $\lambda_{\text{exc}} = 254\text{ nm}$.
.....: $T = 295\text{ K}$, -----: $T = 10\text{ K}$.

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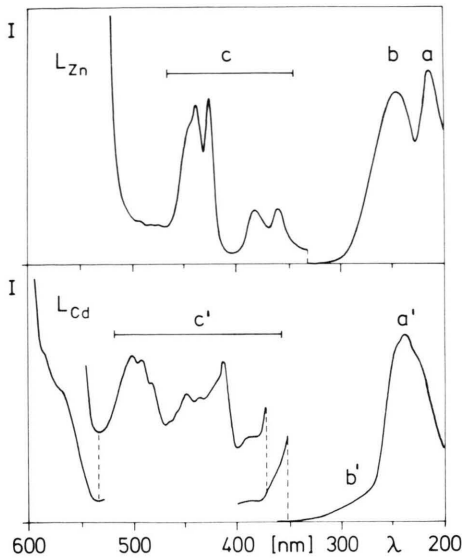


Fig. 2. Excitation spectra of L_{Zn} and L_{Cd} with $\lambda_{det} = 526$ nm and 626 nm, respectively. $T = 295$ K.

luminescence of L_{Zn} is typical for the transition ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ of tetrahedrally coordinated d^5 ions, *cf.* Fig. 1, upper part. As compared with Mn^{2+} in similar surroundings [5, 6] the emission of L_{Zn} ($\bar{\nu}_{max} \approx 19,000$ cm^{-1}) is red shifted and the structure of the emission band falls off with increasing Mn content. This effect is probably due to an interaction between Mn pairs yielding a splitting of each corresponding 4T_1 pair with an energetically lowered emitting component. The band at $\bar{\nu} = 19,420$ cm^{-1} and the shoulder at $\bar{\nu} = 19,840$ cm^{-1} in the 10 K-spectrum can be assigned to zero-phonon transitions ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$ in Mn^{2+} at the two different Zn sites, respectively, and the broad bands at the low energy side belong to vibronic transitions [7]. The low intense emission bands B ($\bar{\nu} \sim 14,000$ cm^{-1}) and C ($\bar{\nu} \gtrsim 20,000$ cm^{-1}) are observed also for L_{Zn} without Mn^{2+} . B is probably due to an emission by Fe^{3+} impurities [8]. C can be assigned to the emission of phases rich in SiO_2 [9]. The excitation spectrum, *cf.* Fig. 2 upper part, confirms the assignments described above and yields information on the energy of the involved Mn^{2+} states. Peak a can be assigned to the band-band transition in the Willemite and peak b corresponds to the $Mn^{2+} \rightarrow$ conduction-band charge-transfer-excitation. From the spectral data a band-band gap of $\Delta E_V \sim 5.51$ eV and a $Mn^{2+} -$ valence-band gap of $\Delta E_V - \Delta E_{Mn} \sim 0.43$ eV can be

derived, *cf.* Fig. 3. The structured part c of the excitation spectrum belongs to $d \rightarrow d$ transitions of the Mn^{2+} ions. A comparison with the T_d -Orgel diagram yields a ligand field strength of $10 Dq \sim 5500$ cm^{-1} .

The red-orange luminescence of L_{Cd} at $\bar{\nu} \sim 17,000$ cm^{-1} and the excitation spectrum of L_{Cd} are typical for Mn^{2+} in octahedral surroundings with $10 Dq \sim 7500$ cm^{-1} indicating that the Mn^{2+} ions occupy Cd sites. The intense emission band A' can be assigned to the transition ${}^4T_1({}^4G) \rightarrow {}^6A_1({}^6S)$. From the excitation spectrum a band-band gap of $\Delta E_V \sim 4.86$ eV and a $Mn^{2+} -$ valence-band gap of $\Delta E_V - \Delta E_{Mn} \sim 0.44$ eV can be estimated, *cf.* Fig. 3. Analogous to the bands B and C in L_{Zn} there appear at low temperatures also in L_{Cd} additional emission bands B' and C' which are not due to Mn^{2+} -centers.

For L_{Zn} a photostimulated green emission could be observed [10]. The sample has been excited with 254 nm light for several minutes. If it is irradiated some seconds afterwards by light of lower energy (632.8 nm line of a He-Ne-Laser) a luminescence at $\lambda = 526$ nm appears. Its intensity I_{sti} decreases with the time t as $I_{sti}(t) \sim t^{-n}$, *cf.* Fig. 4. Between $T = 10$ K and 295 K the exponent n varies from $n = 1.00$ to 0.48. Fig. 5 shows the intensity $I_{sti}(t=1s)$ of two samples as functions of the time interval Δt between the excitation (with $\lambda_{exc} = 254$ nm) and the stimulation ($\lambda_{sti} = 632.8$ nm). The properties of the photo-stimulated luminescence can be described by an energy level system with metastable defect states below the conduction band, as shown at the right-hand side of Fig. 3, see also Ref. [11]. By irradiation with light of $\lambda_{exc} = 254$ nm, electrons of the manganese centers can be excited from the Mn^{2+} ground state into the conduction band, and then they can be cap-

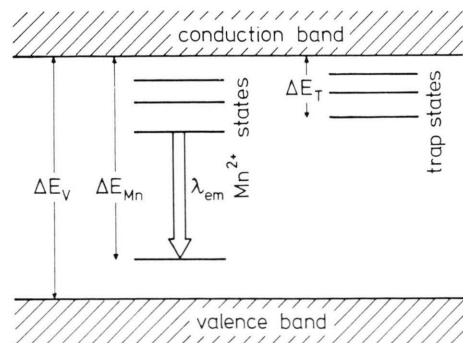


Fig. 3. Proposed energy level diagram of the luminophores, schematically.

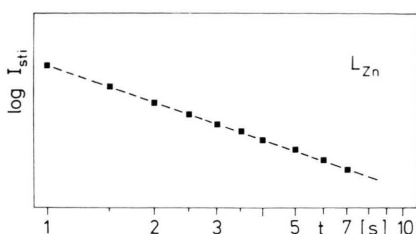


Fig. 4. Intensity I_{sti} of the photostimulated emission of L_{Zn} versus the time t . $\lambda_{sti} = 632.8$ nm. $\lambda_{em} = 526$ nm. $T = 295$ K.

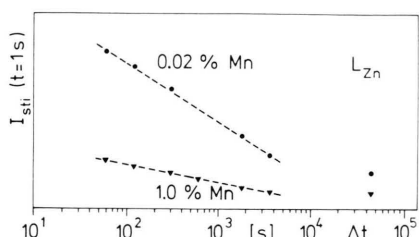


Fig. 5. Intensity I_{sti} (1 s after photostimulation) versus the time interval Δt between excitation ($\lambda_{exc} = 254$ nm) and stimulation ($\lambda_{sti} = 632.8$ nm) for different Mn concentrations. $T = 295$ K.

tured partly by metastable traps, whose energy is lower by $\Delta E_T \lesssim 1.96$ eV ($\cong \lambda_{sti}$) than the lower band edge of the conduction band. A population of these traps is also possible by an excitation of electrons of the valence band. If the system is subsequently exposed to light of λ_{sti} the trapped electrons can be transferred *via* the conduction band to manganese centers, which have a positive hole in their ground state level. After a non-radiative deactivation into the emitting state of such a Mn^{2+} ion, the green luminescence occurs. The fact that the photostimulated emission can be observed even several hours after the excitation indicates a high degree of localization and stability of the holes and of the traps. The traps are probably a feature of the Willemite structure. The reduction of the simulated emission intensity (at constant t^{-n} -dependence of the decay) with increasing manganese content can be explained by a loss of stability of the trap states as a consequence of increasing approach of traps and manganese centers. A prolongation of the time interval Δt or an increase of temperature intensify the thermal depopulation of the shallow traps and, thus, the exponent n in the t^{-n} -dependence is reduced.

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