

# Low-temperature technology and physical processes in green thin- film phosphor $\text{Zn}_2\text{GeO}_4\text{-Mn}$

*V. Bondar, S. Popovich, T. Felter, J. Wager*

This article was submitted to  
2001 Materials Research Society Spring Meeting, San Francisco,  
CA., April 16-20, 2001

**U.S. Department of Energy**

Lawrence  
Livermore  
National  
Laboratory

**May 6, 2001**

## DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
And its contractors in paper from  
U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
Telephone: (865) 576-8401  
Facsimile: (865) 576-5728  
E-mail: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for the sale to the public from  
U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: (800) 553-6847  
Facsimile: (703) 605-6900  
E-mail: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory  
Technical Information Department's Digital Library  
<http://www.llnl.gov/tid/Library.html>

## Low-temperature technology and physical processes in green thin-film phosphor $\text{Zn}_2\text{GeO}_4\text{-Mn}$

V. Bondar, S. Popovich, T. Felter<sup>1</sup>, J. Wager<sup>2</sup>

Lviv National University, Department of Physics, 50 Dragomanov Str., 79005, Lviv, Ukraine.

<sup>1</sup> Lawrence Livermore National Laboratory, PO Box 808, L - 356, Livermore, CA, 94550

<sup>2</sup> Department of Electrical and Computer Engineering, Oregon State University, Corvallis, Oregon 97331-3211, U. S. A

### ABSTRACT

Thin-film  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  phosphors with lower temperature of crystallization, and potentially compatible with industrial technologies were investigated. The technology of thin films synthesis has been developed, as well as their structure and crystal parameters have been investigated. Photoluminescence excitation spectra, photoconductivity, temperature dependencies and ESR-spectra determined by manganese ions were studied. The mechanism of luminescence in this phosphor has been proposed. Cathodo- and electroluminescent parameters of thin film structures based on  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  are presented.

### INTRODUCTION

The manganese dopant is one of the most efficient centers of luminescence in phosphors. Together with high efficiency, one more advantage is the color of ion emission, which varies dependent on crystal lattice: yellow in  $\text{ZnS:Mn}$ , green in  $\text{Zn}_2\text{SiO}_4\text{:Mn}$ , or blue-green in  $\text{ZnGa}_2\text{O}_4\text{:Mn}$ . Oxide phosphors are more stable in comparison to sulfide ones and therefore are prospective for flat panel displays applications. However, the usage of oxides thin-film phosphors in many cases is limited because of their high crystallization temperature. That is why series of recent works [1, 2, 3] was directed on the development of phosphors with lowered crystallization temperature. In this work we have developed the technology of synthesis of thin-film  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  phosphors with lower temperature of crystallization, which can be compatible with industrial technologies, as well as investigated the crystal structure of thin films and luminescent processes caused by manganese dopant.

### EXPERIMENTAL

$\text{Zn}_2\text{GeO}_4\text{:Mn}$  films were deposited by rf-magnetron sputtering [4] of a pressed target manufactured from the presynthesized powder corresponding to stoichiometric composition of  $\text{Zn}_2\text{GeO}_4\text{:Mn}_2\text{O}_3$ . The quality control of thin films dependent on deposition conditions was made by absorption edge position, refraction index, and transparency of the films in visible region obtained from optical measurements. The film structure was investigated using an HZG-4A X-ray powder diffractometer ( $\text{Cu}_{K\alpha}$  radiation,  $\theta$ - $2\theta$  scan mode, step  $0.05^\circ$ ,  $t=10$  s per point). The Rietveld profile refinement method of analysis of experimental XRD data was used [5, 6]. Specified parameters were unit cell parameters and a texture parameter [7]. The X-band ( $\nu \approx 9.4$  GHz) ESR spectra were registered using a computer controlled commercial AE-4700 radio

frequency spectrometer with 100 kHz magnetic field modulation at room temperature. The microwave frequency was controlled by means of diphenylpicrylhydrazyl (DPPH) g-marker ( $g=2.0036\pm 0.0001$ ). Cathodoluminescence spectra at e-beam energy excitation between 1 and 6 KeV and current density  $1 \text{ mA}\cdot\text{cm}^{-2}$  were measured at 300 K. Photoluminescence excitation spectra and photoconductivity were measured in wavelength range from 200 to 400 nm and temperature range from 120 to 360 K with MDR-4 monochromator. As excitation sources the hydrogen (LDD-400) or xenon (DKSEL-1000) lamps were used. Measured excitation, emission and photoconductivity spectra were corrected accordingly to spectral distribution of emission and spectral sensitivity of measuring system.

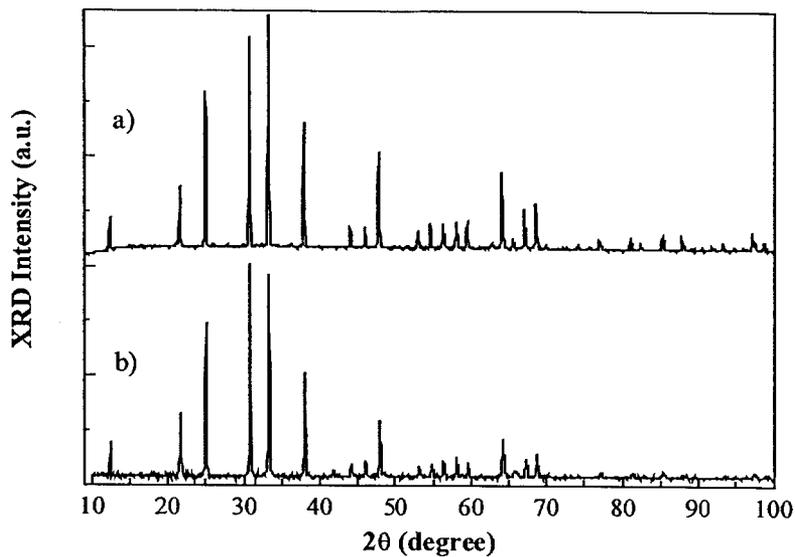
## RESULTS AND DISCUSSION

Films after the deposition by rf-magnetron method showed amorphous structure. After temperature treatment the structure becomes more perfect, the films are crystalline and correspond to the structure type of R3b with lattice constants  $a = 14.206\text{\AA}$ ,  $b = 9.5146\text{\AA}$ , (table.1, figure 1). The powder phosphor has the texture axis (100) and texture coefficient 1.09, whereas the films have a dominating texture axis (001) and texture coefficient 0.91.

**Table 1.** Crystal parameters of thin film

Crystal parameters of thin film	$\text{Zn}_2\text{GeO}_4$	$\text{Zn}_2\text{GeO}_4\text{-Mn}$ , target	$\text{Zn}_2\text{GeO}_4\text{-Mn}$ , film
Cell dimension (a, $\text{\AA}$ )	$14.2333 \pm 0.0002$	$14.2365 \pm 0.0002$	$14.2060 \pm 0.0002$
Cell dimension (c, $\text{\AA}$ )	$9.5256 \pm 0.0002$	$9.5281 \pm 0.0001$	$9.5146 \pm 0.0001$
Cell volume ( $\text{\AA}^3$ )	$1671.14 \pm 0.07$	$1671.70 \pm 0.07$	$1662.22 \pm 0.07$
Texture axis	[100]	[100]	[001]
Texture parameter, $\tau$	1.0	$1.09 \pm 0.03$	$0.91 \pm 0.03$

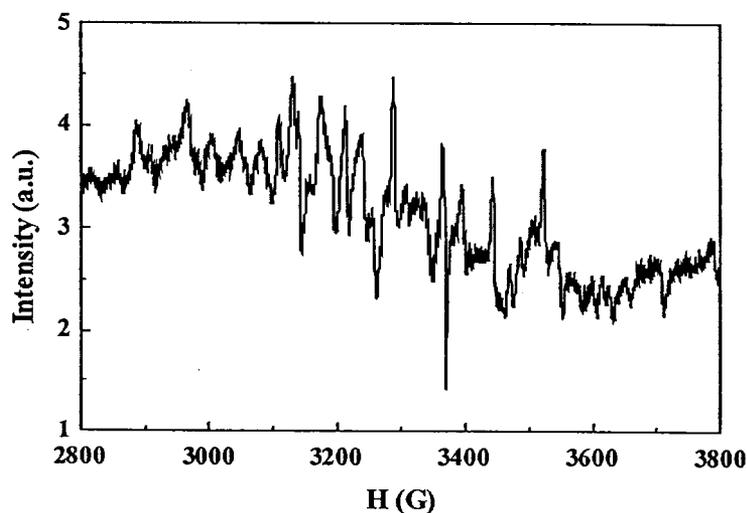
It was found that the parameters  $a$  and  $c$  of a crystal lattice of a film as compared to the powder phosphor decrease from  $14.2365\text{\AA}$  to  $14.206\text{\AA}$  and from  $9.5281\text{\AA}$  to  $9.514\text{\AA}$ , correspondingly, and the volume of the unit cell decreases approximately on  $8\text{\AA}^3$  (table.1). This decreasing of lattice constants may be caused by two the most probable reasons: either by formation of a defect anionic sublattice due to substitution of germanium atoms in tetrahedral sites for manganese atoms with smaller valence than germanium which results in formation of oxygen vacancies, or by increasing of covalent component of the Me-O chemical bond at isomorphic substitution of zinc for manganese, which results in decreasing of the corresponding atomic distances.



**Figure 1.** X-rays diffraction patterns of powder (a) and thin-film (b) phosphor  $Zn_2GeO_4:Mn$

The concentration dependence of a luminescence of  $Zn_2GeO_4:Mn$  phosphor was investigated. It was found that the maximal luminescence yield is observed at concentration of manganese 2 wt.%. At higher concentrations the decreasing of intensity of emission caused by concentration quenching was observed.

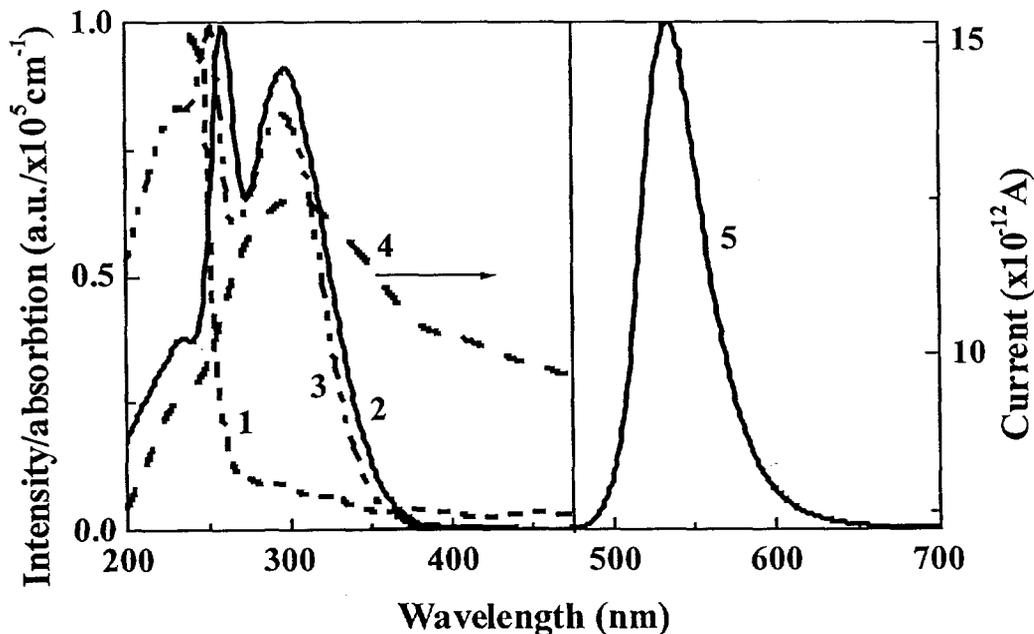
In investigated phosphors  $Zn_2GeO_4:Mn$  ( $C_{Mn} = 0.8$  wt. %) at 300K the composite ESR spectrum is observed, which consists of the broad ( $\Delta H_{pp} \approx 800$  G) line with  $g_{eff} = 2.0$  and about of 30 narrow lines of different intensity on it (figure 4). The broad line with  $g_{eff} = 2.00$  in polycrystalline samples may be interpreted as the unresolved fine structure (FS) of ESR spectrum in the disordered systems from isolated ions  $Mn^{2+}$  ( ${}^6S_{5/2}, {}^3d_5$ ), or as the ESR spectrum from clusters of 2 or more ions bounded with dipole-dipole magnetic interaction. Narrow lines of different intensity around  $g_{eff} = 2.00$  (figure 2) may be interpreted as allowed and forbidden transitions of the FS central component of isolated ions  $Mn^{2+}$ .



**Figure 2.** ESR spectrum of  $Zn_2GeO_4:Mn$  phosphor

As-deposited thin films are characterized by relatively weak luminescence with a maximum in the red area of spectrum, which evidently is associated with amorphous state of a film and not yet formed crystal neighborhood of dopant manganese ion that is confirmed by X-ray diffraction measurements. After annealing at temperature of 650-750°C the luminescence intensity grows, and the spectrum is transformed to a narrow band green emission at 535 nm, which corresponds to  ${}^4T_1({}^4G) - {}^6A_1({}^6S)$  transitions of  $Mn^{2+}$  ions in tetrahedral neighborhood.

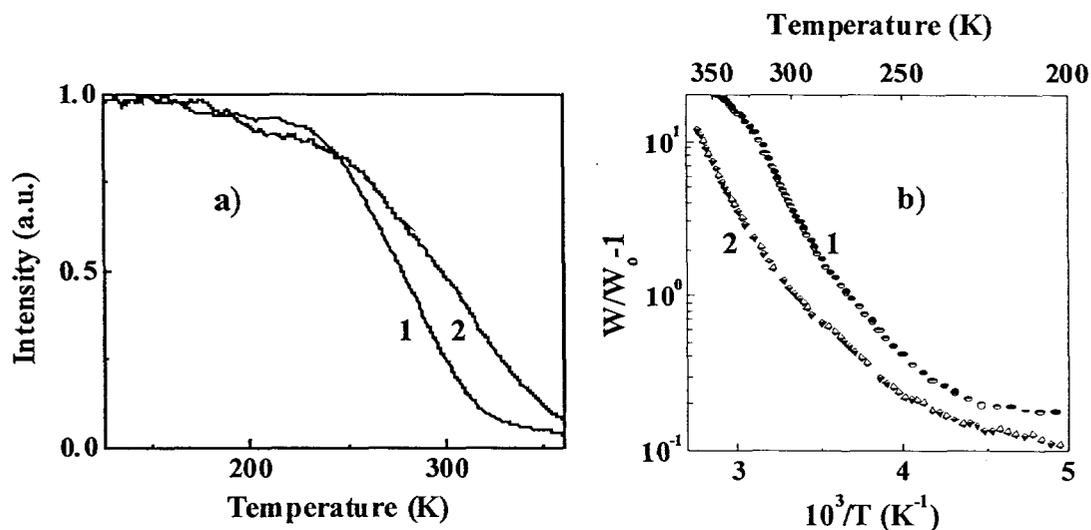
In order to investigate mechanism of emission of  $Zn_2GeO_4:Mn$  its luminescent properties were studied at photoexcitation. Excitation spectrum of  $Zn_2GeO_4:Mn$  green emission band shows maxima at 260 and 300 nm at room temperature (figure 3, curve 2). Lowering the temperature to 130 K shifts the high-energy maximum to 250 nm, whereas the low-energy maximum stays the same (figure 3, curve 3). Position of the high-energy maximum is in the region of absorption edge (figure 3, curve 1) and evidently is related to band-to-band transition with  $Zn_2GeO_4$  bandgap energy of 4.9 eV at 300K. Photoconductivity of  $Zn_2GeO_4:Mn$  films has maximum at 310 nm (figure 3, curve 4).



**Figure 3.** Absorption (1) and photoluminescence excitation (2, 3) spectra at 535 nm; photoconductivity (4) and photoluminescence (5) spectra of  $Zn_2GeO_4:Mn$  thin-films at 300K (1, 2, 4, 5) and 130K (3)

The temperature dependence of a green luminescence of  $Zn_2GeO_4:Mn$  films is characteristic with thermal quenching at  $T > 250K$  (figure 4, a). It should be noted that thermal dependencies of photoluminescence do not show substantial dependence on excitation region – band-to-band (259 nm) or near-edge (300 nm). Consequently, the mechanism of thermal quenching in both cases is similar. Activation energy determined from Mott's dependency is 0.20-0.24 eV (figure 3, b) in the temperature range of 250-280K and 0.40-0.44 eV at temperatures higher than 290K. The existence of two regions in temperature dependence indicates on the two components in temperature quenching process: low-temperature and high-temperature. The first one may be

caused by quenching of excitation, and the second one - due to internal quenching in  $Mn^{2+}$  ion.



**Figure 4.** Temperature dependence of luminescence at 535 nm of thin-film phosphor  $Zn_2GeO_4:Mn$  under excitation at 250 (curve 1) and 300 nm (curve 2) - (a), and the same dependencies in  $(W/W_0-1)$  vs.  $10^3/T$  coordinates - (b) .

Based on the results obtained, the most probable excitation mechanism of  $Zn_2GeO_4:Mn$  luminescence at 535 nm may be band-to-band energy transfer to nonradiative recombination center, which in turn transfers energy in a resonant way to  $Mn^{2+}$ - center. As intermediate center responsible for resonant energy transfer to  $Mn^{2+}$ - center may be the center responsible for the maximum at 300 nm in photoconductivity and excitation spectra. Its optical distance  $E_{opt} = 0.8$  eV from the bottom of valence zone and thermal depth  $E_{therm} = 0.2$  eV differ, however it does not contradict to the ideas of difference between thermal and optical energy levels in phosphors [8]. The optical activation energy can be several times higher than thermal one, and this difference tends to increase with increasing of crystal ionicity level.

Comparison of thermal dependency of  $Zn_2GeO_4:Mn$  luminescence investigated in present work and that of  $ZnS$  shows that thermal quenching of  $ZnS:Mn$  [9] starts already at temperatures of 100K, whereas  $Zn_2GeO_4:Mn$  shows the beginning of quenching at 250 K. Therefore, the temperature parameters of  $Zn_2GeO_4:Mn$  may be considered as good for practical use.

The thin-film phosphors  $Zn_2GeO_4:Mn$  for FED are characterized by luminescent efficiency of 2.4 lm/W at 2 keV electron excitation. The high stability is one more relevant advantage of developed thin-film phosphors for FED.  $Zn_2GeO_4:Mn$  showed considerably higher (in 5 times) stability at electron excitation – 20-30 Coulombs/cm<sup>2</sup> (dose of electron irradiation resulting in 50% decrease of luminescence intensity) at long-term testing compared to sulfide phosphors.

On a basis of  $Zn_2GeO_4:Mn$  the sulfurless electroluminescent structures “Corning/ ITO/ ATO/  $Zn_2GeO_4:Mn/SiON/Al$ ” with green color of emission have been fabricated. These structures showed high brightness (14ft-L at 40 V over threshold at 60 Hz), good efficiency (~0.2 lm/W), excellent color coordinates (CIE<sub>x</sub> = 0.302, CIE<sub>y</sub> = 0.668), robustness (withstand up to 300 V without burning out), and excellent aging characteristics (no measurable aging was observed after continuous excitation). These parameters are the relevant advantage as contrasted to conventional sulfide electroluminescent displays.

## CONCLUSIONS

The technologies of fabrication of thin film phosphors  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  using rf-magnetron method are developed. The obtained  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  thin films show cathodoluminescence in green region of spectrum with peak at 535 nm, which can be assigned to the  ${}^4\text{T}_{1g} \Rightarrow {}^6\text{A}_{1g}$  transition of the  $\text{Mn}^{2+}$  ions. Presence of the  $\text{Mn}^{2+}$  ions in the low- and high-symmetry sites of the  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  film structures is confirmed by ESR spectroscopy. It was found that photoluminescence excitation and photoconductivity spectra are characteristic with two regions of excitation: band-to-band and near-edge. Also the two stages of thermal quenching of luminescence were observed, which are explained as quenching of excitation and intrinsic quenching in  $\text{Mn}^{2+}$  center. The mechanism of  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  luminescence associated with resonant excitation energy transfer via nonradiative recombination center to  $\text{Mn}^{2+}$  emission center. Based on  $\text{Zn}_2\text{GeO}_4\text{:Mn}$  thin films cathodo- and electroluminescent structures with high luminescent parameters have been created.

## ACKNOWLEDGEMENT

This work has been supported by Ministry of the Science and Education of Ukraine (LSU Project Fz41B). The work of TEF has been performed under the auspices of the US DOE. by LLNL under Contract No. W-7405-ENG-48.

## REFERENCES

1. T. Minami, in *Proc. of 4-th Intern. Conf. on the Science and Technology of Display Phosphors* (Bend, Oregon, 1998), pp. 195-198.
2. A. N. Kitaii, in *Proc. of 4-th Intern. Conf. on the Science and Technology of Display Phosphors* (Bend, Oregon, 1998), pp. 199-202.
3. J. S. Lewis and P.H. Holloway, *Journal of the Electrochemical Society* **147** (8), 3148-3150 (2000)
4. V. Bondar, M. Vasylyv, Ukrainian patent No. 18151 A, (July 1997).
5. V. Lysoivan, S. Gromilov, *Aspects of accuracy in polycrystalline diffractometry* (Nauka, Novosibirsk, 1989 (in Russian)), p. 243.
6. V. K. Pecharski, L. D. Axelrood and P. Yu. Zavali, *Crystallography* **32** (6), 874-877 (1987).
7. A. Segmuller, *J. Vac. Sci. Technol. A* **9** (4), 2477-2480 (1991).
8. Vu. Kuang, M. V. Fok in *Luminescence centers in crystals* (Trudy FIAN, **79**, Nauka, Moskov, 1974 (in Russian)), pp. 39-63.
9. H. Hanzawa, M. Kobayashi, O. Matsuda, K. Murase and W. Giritat, *Phys. Stat. Sol. (a)* **175**, 715 (1999).