



ELSEVIER

Contents lists available at [SciVerse ScienceDirect](http://www.sciencedirect.com)

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Synthesis and luminescent properties of red-emitting phosphors: $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ doped with Mn^{4+}

Mariusz Kubus^a, David Enseling^b, Thomas Jüstel^{b,*}, H.-Jürgen Meyer^{a,**}

^a Abteilung für Festkörperchemie und theoretische Anorganische Chemie, Institut für Anorganische Chemie, Eberhard-Karls-Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

^b Fachhochschule Münster, Labor für Angewandte Materialwissenschaft, Stegerwaldstrasse 39, D-48565 Steinfurt, Germany

ARTICLE INFO

Article history:

Received 27 September 2012

Received in revised form

6 December 2012

Accepted 27 December 2012

Available online 4 January 2013

Keywords:

 $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ Mn^{4+}

Crystal structure

Photoluminescence

Synthesis

ABSTRACT

A simple method for the synthesis of red emitting Mn^{4+} activated phosphors is presented. The crystal structure of $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ was determined by single crystal X-ray diffraction and was isotopic with $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$ (space group $R\bar{3}$). Luminescent properties of $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ doped with manganese(IV) at different concentration levels were studied. The optimal Mn^{4+} concentration with respect to the emission intensity was found to be 5 mol% for $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and 3 mol% for $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Manganese at different oxidation states is an efficient activator ion for photo- and cathodoluminescence in many solid state compounds. However, in most of applied phosphors manganese is present in the oxidation states (II) or (IV), due to the high efficiency [1]. Manganese(IV) is used as an activator in a large number of luminescent materials, for example in (i) oxides: $\text{Y}_3\text{Al}_5\text{O}_{12}$ [2], YAIO_3 [3], $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ [4], $\text{MAl}_{12}\text{O}_{19}$ (where M is Ca, Sr, or Ba) [5], LiGa_5O_8 [6], Mg_2TiO_4 [7], (ii) nitrides: GaN [8], or (iii) fluorides: Na_2SiF_6 [9], K_2GeF_6 [10]. If a trivalent ion such as aluminum(III) is substituted by manganese(IV), the additional charge is often compensated by co-doping with a divalent ion, e.g. Ca^{2+} or Mg^{2+} [11]. Most of the Mn^{4+} phosphors are synthesized at a high temperature, which requires special equipment and thus causes rather high costs [9].

Novel synthesis methods as well as the study of the photoluminescence properties of hexafluoro complexes doped by manganese(IV) are in the focus of the interest of many research groups at academia and industry due to their potential application in solid state light sources [12]. Red emitting phosphors derived from alkaline hexafluorides, such as $\text{K}_2\text{SiF}_6 \cdot \text{Mn}^{4+}$, exhibit high

PL quantum efficiency and a suitable color point for fluorescent light sources with a high color rendering for red colors [13]. The most common method to synthesize fluorides doped by Mn^{4+} is the direct method, i.e. the chemical etching of Si wafers or Ge shots in aqueous HF solution upon an addition of potassium permanganate [1,9,10,14]. Another method of synthesizing doped fluorides is based on the dissolution of an appropriate hexafluoride compound KMF_6 (M=Si, Ti, and Ge) with K_2MnF_6 and its subsequent re-crystallization [15,16]. Hexafluorosilicates doped with Mn^{4+} may be as well precipitated from a solution of e.g. hexafluorosilicic acid in HF and K_2MnF_6 by the addition of the appropriate metal sources. K_2MnF_6 used as a source of Mn^{4+} is mostly synthesized through reduction of permanganate by the Bode's method [17] or with diethylether [18].

Beyond the already described hexafluorides, also hydrates of the hexafluorides can be doped by manganese(IV). Hexafluorides $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ belong to the group of compounds with the general formula $\text{M}^{\text{II}}\text{SiF}_6 \cdot 6\text{H}_2\text{O}$ (wherein e.g. M^{II} is Co, Ni, or Mn) and are isotopic to $\text{NiSnCl}_6 \cdot 6\text{H}_2\text{O}$ (space group $R\bar{3}$) [19].

To our best knowledge, this work on the luminescent properties of hexafluoride-hexahydrates doped by different concentrations of manganese(IV) is reported for the first time. The crystal structure of $\text{ZnGeF}_6 \cdot 6\text{H}_2\text{O}$ was investigated by single-crystal X-ray diffraction. The purity of all obtained materials was confirmed by powder X-ray diffraction and thermoluminescent properties were determined by photoluminescence spectroscopy.

* Corresponding author. Fax: +49 2551 9 62502.

** Corresponding author. Tel.: +49 7071 29 76226; fax: +49 7071 29 5702.

E-mail addresses: tj@fh-muenster.de (T. Jüstel).

Juergen.Meyer@uni-tuebingen.de (H.-J. Meyer).

2. Experimental

K_2MnF_6 was synthesized according to the method described in the literature [18]. 2.5 g KHF_2 (99.99%, Merck) was dissolved in HF (38%, Merck), after 20 min of mixing 2 g $KMnO_4$ were added and the solution was cooled in an ice bath. After 10 min of stirring, 15 drops diethylether were added and the precipitate (K_2MnF_6) was filtered off and washed with glacial acetic acid and acetone. The obtained yellow powder was dried on air.

The synthesis of $ZnSiF_6 \cdot 6H_2O:Mn^{4+}$ was carried out in a polyethylene beaker. H_2SiF_6 (34%, Sigma-Aldrich) was dissolved in an aqueous HF solution together with varying concentrations of K_2MnF_6 (5, 3 and 0.5 mol% of Mn^{4+}). Then, to the above solutions ZnF_2 (99%, Sigma-Aldrich), dissolved in HF, was added. The mixture was cooled until $ZnSiF_6 \cdot 6H_2O:Mn^{4+}$ precipitated. The obtained powder was filtered off and dried on air.

$ZnGeF_6 \cdot 6H_2O:Mn^{4+}$ was synthesized by the same procedure. The appropriate amount of GeO_2 (99.99%, Fluka) was dissolved in aq. HF and K_2MnF_6 (0.5, 3, or 5 mol% of Mn^{4+}) was added. Next, ZnF_2 dissolved in HF was added and the mixture was cooled down. The obtained precipitate was filtered off and dried on air. The single crystal of $ZnGeF_6 \cdot 6H_2O$ was obtained by slow evaporation of the described mixture.

The powder diffraction patterns of all samples were recorded with a powder diffractometer (Stoe STADI-P, Ge monochromator) using $CuK_{\alpha 1}$ radiation. Excitation and emission spectra were recorded on an Edinburgh Instruments FSL920 spectrometer equipped with a 450 W Xe arc lamp, mirror optics for powder samples and a cooled ($-20^\circ C$) single-photon counting photomultiplier from Hamamatsu (R2658P). The correction file for the emission spectra was obtained from a tungsten incandescent lamp certified by the NPL (National Physics Laboratory, UK). For thermal quenching measurements a cryostat "MicrostatN" from Oxford Instruments in the present spectrometer was employed. Liquid nitrogen was used for cooling.

3. Results and discussion

The XRD pattern of a typical sample and the corresponding calculated pattern of $ZnSiF_6 \cdot 6H_2O$ are shown in Fig. 1. Fig. 2 displays the XRD pattern of $ZnGeF_6 \cdot 6H_2O:Mn^{4+}$ (5%). All synthesized

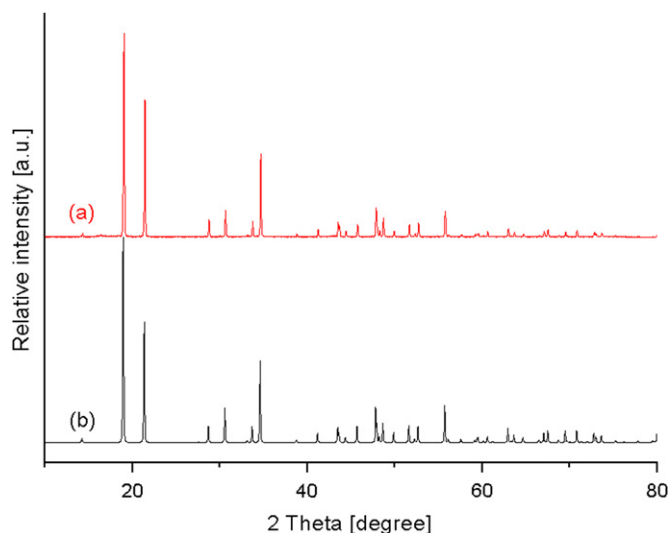


Fig. 1. Experimental XRD pattern of $ZnSiF_6 \cdot 6H_2O:Mn^{4+}$ (5%) (a) and the corresponding pattern calculated from single crystal data [ICSD file no. 34757] (b).

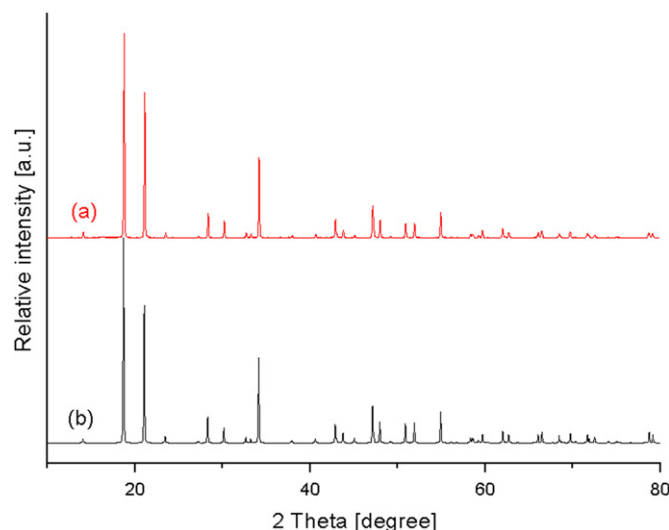


Fig. 2. Experimental XRD pattern of obtained $ZnGeF_6 \cdot 6H_2O:Mn^{4+}$ (5%) (a) and the corresponding pattern calculated from single crystal data obtained by our group (b).

Table 1

Crystal data and structure refinement for $GeF_6 \cdot Zn(OH_2)_6$.

Empirical formula	$H_{12}F_6GeO_6Zn$	
Formula weight	360.06 g mol ⁻¹	
Crystal system	Trigonal	
Space group	$R\bar{3}$ (no. 148)	
Unit cell dimensions	$a=b=948.7(3)$ pm	$\alpha=\beta=90^\circ$
	$c=982.1(3)$ pm	$\gamma=120^\circ$
Volume	0.7655(4) nm ³	
Z	3	
Temperature	220(2) K	
Density (calculated)	2.343 g/cm ³	
Absorption coefficient	5.389 mm ⁻¹	
F(0 0 0)	528	
Crystal shape	Colorless needle	
Crystal size	0.44 × 0.14 × 0.14 mm ³	
Theta range for data collection	3.23–25.93°	
Index ranges	−11 ≤ h ≤ 11, −11 ≤ k ≤ 11, −12 ≤ l ≤ 12	
Reflections collected	2669	
Independent reflections	331 [R(int)=0.0558]	
Data/parameters	331/31	
Goodness-of-fit on F ²	1.100	
Final R indices [I > 2σ(I)]	R1 = 0.0288, wR2 = 0.0662	
R indices (all data)	R1 = 0.0318, wR2 = 0.0674	
Largest diff. peak and hole	0.459 and −0.500 e/Å ³	

substances were crystalline and of single-phase, which means additional phases could not be detected.

$ZnSiF_6 \cdot 6H_2O$ and $ZnGeF_6 \cdot 6H_2O$ have the same structure as $NiSiF_6 \cdot 6H_2O$ [20]. $ZnGeF_6 \cdot 6H_2O$ consists of octahedral $[Zn(H_2O)_6]^{2+}$ and $[GeF_6]^{2-}$ units, which are interconnected by hydrogen bonds. The arrangement of the polyhedra is related to CsCl-type structure [21,22]. Crystallographic data for $ZnGeF_6 \cdot 6H_2O$ are given in Table 1, the octahedral $[Zn(H_2O)_6]^{2+}$ and $[GeF_6]^{2-}$ units are shown in Fig. 3. Atomic coordinates and equivalent isotropic displacement parameters for $ZnGeF_6 \cdot 6H_2O$ are reported in Table 2. The positions of the H-atoms were found from a difference Fourier map and refined freely. The crystal structure of $ZnGeF_6 \cdot 6H_2O$ was refined with the space group $R\bar{3}$ (no. 148) and unit cell dimensions $a=948.7(3)$, $c=982.1(3)$ pm for $Z=3$. The Si or Ge ions have point symmetry of -3 .

Due to presence of water molecules in the crystal structure, the compounds are not stable at higher temperatures. That means

Download English Version:

<https://daneshyari.com/en/article/5400685>

Download Persian Version:

<https://daneshyari.com/article/5400685>

[Daneshyari.com](https://daneshyari.com)