Optical Materials 59 (2016) 126–129

Contents lists available at ScienceDirect

Optical Materials

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

Room temperature red emitting carbodiimide compound $Ca(CN_2):Mn^{2+}$

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ARTICLE INFO

Article history:
Received 25 October 2015
Received in revised form 7 January 2016
Accepted 7 January 2016
Available online 11 January 2016

Keywords:
Carbodiimides
SSM reaction
Red luminescence
X-ray diffraction
Mn^{2+} photoluminescence

ABSTRACT

Carbodiimides are a growing group of compounds, which raised interest as hosts for luminescent materials. $Ca(CN_2)$ doped with 5, 10 and 50 mol% Mn^{2+} was synthesized by a solid-state metathesis reaction at rather low temperature. The unit cell volume of $Ca(CN_2)$ decreases with increasing the Mn^{2+} concentration. The emission spectra of the doped material show an emission band in the red spectral range originating from the $^4T_{1g}(^4G)–^6A_{1g}(^6S)$ transition.

1. Introduction

Inorganic materials, especially oxides, nitrides, sulfides, or chalcogenides, are used as host matrices for phosphors [1,2]. Depending on the area of application different luminescent activators are used, e.g. Ce^{3+}, Tb^{3+}, $Eu^{2+/3+}$, or $Mn^{2+/4+}$. Synthesis of the materials with europium or manganese ions usually requires a high temperature and special conditions for the oxidation state control of the photoluminescent centers. Emission of the activation centers, specially Mn^{2+} ions depends on the crystal-field strength of the host lattice and may vary from green (weaker crystal-field) to red (stronger crystal-field) [3,4].

An interesting group of inorganic compounds are carbodiimides and cyanamides, they are usually thermally and water stable materials, and have promising optical properties [5–9]. The properties of carbodiimides mainly originate from the strength of interatomic bonding of $(CN_2)^{2-}$ group, other functional groups, crystal structure and microscopic properties such as material porosity. Many transition-metal carbodiimides were prepared in solution, e.g. Co(CN_2), $Ni(CN_2)$ or $Cd(CN_2)$ [10–12], whereby the first embodiment of a carbodiimide comprising a magnetic transition metal ion was $Mn(CN_2)$. This compound was synthesized by solid state metathesis (SSM) reaction [13]. Using the same method, recently a large number of new carbodiimides and cyanamides were synthesized, from metal carbodiimides to mixed cationic and anionic compounds [14–16]. Most of rare earth carbodiimides were synthesized by the reaction of $Li_2(CN_2)$ with rare earth trihalides, but also the reaction with $Na_2(CN_2)$ gives new interesting compounds [17,18].

The triatomic $(NCN)^{2-}$ anion in carbodiimides and cyanamides can have different number of neighbor metal ions and the anions are often forming layers adjacent to cation layers [5,6].

In this paper, we report for the first time the room temperature luminescence of red emitting carbodiimide compound doped with Mn^{2+} ions. In literature, the photoluminescence properties of the alkaline earth carbodiimide $Sr(CN_2):Eu^{2+}$ was described as a compound which allows a rather large increase of Eu–N distance for $4f^65d^1$ excited state in comparison with the $4f^7$ ground state of Eu^{2+} ions [19,20].

2. Experimental

2.1. Synthesis

Reaction mixtures were prepared in an argon filled glove box starting from careful homogenization of $CaCl_2$ (Aldrich, 99%) and $Li_2(CN_2)$ (synthesis: ref. 18, Li_3N Alfa Aesar, 99.4%, $C_3N_3(NH_2)_3$ Aldrich, 99+%). Doped $Ca(CN_2):Mn^{2+}$ was prepared from a reaction mixture in which $CaCl_2$ was partially substituted with $MnCl_2$ (ABCR, 97%). The materials were placed into copper tubes, the tubes were fused by arc-welding and placed into silica ampoules,

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http://dx.doi.org/10.1016/j.optmat.2016.01.006
0925-3467/

which were evacuated and sealed. The synthesis directly in quartz ampules is also possible, metal tubes were used in order to avoid oxygen contamination. The samples were heated in a furnace up to 500 °C with a heating rate of 2 °C/min, held at this temperature for 2 days, and cooled to room temperature with rate 2 °C/min. The copper tubes were opened in a glove box, the products were washed several times with methanol and dried in vacuum at room temperature.

The purity of synthesized materials was checked by powder X-ray diffraction.

2.2. Characterization

XRD patterns of the powderised products were collected with a Stadi-P (Stoe, Darmstadt) powder diffractometer using Cu $K\alpha_1$ ($\lambda = 154.06$ pm, germanium monochromator) 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 °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).

3. Results and discussion

3.1. XRD measurements

Metal carbodiimides $Ca_{1-x}Mn_x(CN_2)$ with $x = 0, 0.05, 0.1$ and 0.5 were successfully obtained by a solid-state metathesis reaction between metal chlorides and $Li_2(CN_2)$ at 500 °C (Fig. 1). The reaction products were obtained as grayish crystalline powders, which slowly hydrolyze in humid air. The crystal structure of isostructural $Ca(CN_2)$ and $Mn(CN_2)$ compounds (space group $R\bar{3}mH$, no 166) contains cation layers alternating with layers of $(CN_2)^{2-}$ being orientated along the crystallographic *c*-axis direction (Fig. 1) [21]. The cations are situated in trigonal antiprismatic voids formed by the nitrogen atoms from the $(CN_2)^{2-}$ moieties.

Doped Mn^{2+} ions very likely occupy Ca^{2+} sites in the structure and hence the unit cell volume was expected to decrease with increasing Mn^{2+} concentration. The ionic radius of Ca^{2+} (1.00 Å, CN 6) is much larger than Mn^{2+} (0.67 Å, CN 6) [22]. The cell parameters of prepared materials were refined with the FullProf-WinPLOTR software [23,24]. Cell volume of the powder material $Ca(CN_2)$ without doping was 174.86(1) Å^3, for the doped material with 5, 10 or 50 mol% of Mn^{2+} the volume was 174.36(1), 172.33(3) and 172.88(6) Å^3, respectively. Almost the same cell volume for 10 and 50 mol% indicated border of the $Ca(CN_2)$ lattice flexibility. The solid solution of $Ca(CN_2)$ and $Mn(CN_2)$ was not formed and already for 10 mol% formation of the second phase was observed.

3.2. Photoluminescence

The photoluminescence of $Ca(CN_2)$ doped with Mn^{2+} ions was studied. The excitation spectrum of $Ca(CN_2):Mn^{2+}$ 5 mol% shows only a single band originating from host lattice excitation (Fig. 2).

The emission spectrum of $Ca(CN_2):Mn^{2+}$ 5 mol% was recorded upon 265 nm excitation causing the most intense emission for Mn^{2+} ions with maximum at 678 nm originated from $^4T_{1g}(^4G)$–$^6A_{1g}(^6S)$ transitions. The observed red emission indicated an octahedral coordination of the Mn^{2+} ions in this structure, resulting in a crystal field effect on the activator ions. The symmetry of the emission band without clearly separated multiple bands implies that there is solely one dominant crystallographic site for the Mn^{2+} ions.

Luminescent properties of the described carbodiimide can be compared to nitrides with strong crystal field ascribed to N^{3-} ions, e.g. $Mg_{1-x}Mn_xSiN_2$ ($0 \leqslant x \leqslant 0.05$; CN 4) with maximum of emission band at 626–655 nm [2], $M_2Si_5N_8:Mn^{2+}$ M = Sr, Ba (CN 8 and 10) with band at 606 and 567 nm, $Ca_2Si_5N_8:Mn^{2+}$ (CN 7) with band at 599 nm [25] or $CaAlSiN_3:Mn^{2+}$ with two bands at 548 and 627 nm (CN 5 and 4) [26]. The distance between metal and nitrogen atoms, for some of these compounds was 2.86–2.93 Å ($Sr_2Si_5N_8$), 2.92–2.98 Å ($Ba_2Si_5N_8$), 2.65–2.71 Å ($Ca_2Si_5N_8$) [25], and for $Ca(CN_2)$ (CN 6) was 2.46 Å [21] what together with covalent interaction for $(CN_2)^{2-}$ group has influence on the crystal field strength. The half-width for the emission band, about 115 nm can be compared with value for $CaAlSiN_3:Mn^{2+}$ (probably Ca^{2+} and Al^{3+} site occupied by Mn^{2+}) 100 nm [26] or $ZnSiN_2:Mn^{2+}$ (only Zn^{2+} site occupied by Mn^{2+}, CN 4) 130 nm [27].

The calculated CIE 1931 color coordinates of $Ca(CN_2):Mn^{2+}$ 5 mol% are $x = 0.55$ and $y = 0.32$ (Fig. 2). The values obtained of the presented red phosphor are comparable with the coordinates determined for $Zn_{0.99}Mn_{0.01}GeN_2$ with $x = 0.580$ and $y = 0.398$ [27].

The decay behavior of the $^4T_{1g}(^4G)$–$^6A_{1g}(^6S)$ transitions were investigated at room temperature (Fig. 3). The recorded decay curve was fitted by a biexponential function, where the fast decay

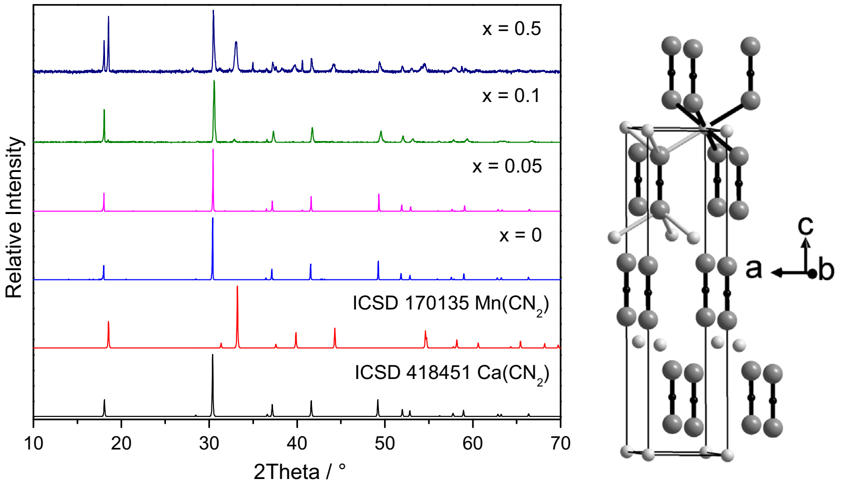

Fig. 1. XRD patterns of $Ca_{1-x}Mn_x(CN_2)$ with $0 \leqslant x \leqslant 0.5$ and ICSD-418451 pattern of $Ca(CN_2)$, and ICSD-170135 pattern of $Mn(CN_2)$ (left). Layers formed by $(CN_2)^{2-}$ ions in the structure of calcium or manganese carbodiimide (right). Metal atoms are light gray, N gray, C black; unit cell is outlined with solid black lines.