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Philibert Iacconi

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Christian Beauger, Philippe Grosseau, Bernard Guilhot, Denis Huguenin, Philibert Iacconi. Low temperature synthesis of ZnGa₂O₄ : Mn. C.R. Ronda, T. Welker. 6th International Conference on Luminescent Materials at the Joint Meeting of the Electrochemical Society/International Society for Electrochemistry, Aug 1997, Paris, France. Electrochemical Society, 97 (29), p. 235-245 - ISBN 1-56677-182-X, 1998, Electrochemical Society Series. <hal-00519581>

HAL Id: hal-00519581

<https://hal-mines-paristech.archives-ouvertes.fr/hal-00519581>

Submitted on 30 Aug 2011

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LOW TEMPERATURE SYNTHESIS OF $\text{ZnGa}_2\text{O}_4 : \text{Mn}$

C. Beauger¹, P. Grosseau², B. Guilhot², D. Huguenin³, P. Iacconi¹.

¹ LPES-CRESA Université de Nice-Sophia Antipolis
Parc Valrose, F-06108 NICE Cedex 2.

² SPIN-CRESA Ecole des Mines de Saint-Etienne
158, Cours FAURIEL, F-42023 S^t-Etienne, Cedex 2.

³ Rhône-Poulenc Recherches
52, rue de la Haie Coq, F-93308 Aubervilliers Cedex.

ABSTRACT

The dependence of the firing conditions on the crystal structure formation of ZnGa_2O_4 has been investigated. The effects of temperature and atmosphere were examined and gave evidence of the instability of the zinc gallate under a reducing atmosphere at temperatures above 600°C. A new preparation route has allowed to synthesize ZnGa_2O_4 at low temperature, right from 300°C, avoiding the decomposition of the matrix during the annealing. Moreover, a different behavior under excitation has been observed for the phosphor prepared via this new route compared with the compound obtained by solid state reaction. A model, based on the optical behavior observed, is presented.

INTRODUCTION

The phosphor industry has always been strongly involved in the search for new efficient emitting materials. In the meantime, very little has been made to adapt the nature of the precursor and the synthesis route to the formation of the suitable compound, with an accurate control of such characteristics as crystallization and oxidation state, stoichiometry, particle size or morphology.

As an example, manganese doped zinc gallate has been studied to highlight the difficulties to control simultaneously the manganese oxidation degree and the matrix stoichiometry. The emitting properties of Mn^{2+} doped ZnGa_2O_4 have already been described in the literature and the use of this phosphor in displays has been suggested. However few attention has been paid to the fact that the crystal structure is unlikely unstable under the reducing atmosphere used during the synthesis to maintain the doping agent in its divalent state.

Our intent is on one hand to demonstrate that the classical synthesis route cannot be used for the manufacturing of this compound and on the other hand to suggest an alternative solution, based on the firing of a nitrates based precursor, suitable for the preparation of zinc gallate at low temperature to avoid the thermal decomposition of the structure. We have investigated the influence of firing parameters such as the temperature and the atmosphere on the crystal formation as well as on its optical properties. The formation of a defect free compound emphasizes the advantage of this new route.

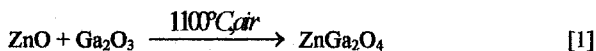
STATE OF THE ART

Under U.V. or electronic excitation, undoped zinc gallate is a blue emitting phosphor with an emission band peaking at 415 nm (1), whereas activation by manganese produces green luminescence centered at 505 nm (2). Its potentiality has been established for a use in Vacuum Fluorescent Displays (VFD) and Field Emission Displays (FED) (3) which require low gap semi-conducting emitting materials such as zinc sulfide, zinc oxide or zinc gallate. It is proposed as a substitute for zinc sulfide which emits corrosive gases under electron bombardment, limiting the life time of the device.

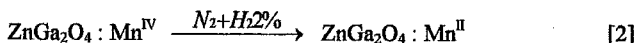
Zinc gallate crystallizes in the spinel structure with the formula AB_2O_4 , where A stands for a divalent cation, B for a trivalent one and O for oxygen. This structure is built on an oxygen framework creating tetrahedral and octahedral sites occupied by the cations. In normal spinel, A occupies the four-fold coordinated sites and B the six-fold coordinated ones whereas in the inverse structure, B occupies the four-fold coordinated sites and half of the six-fold coordinated sites, the other half being occupied by A cations. Most of the authors reported zinc gallate to be normal spinel (4-9).

The main characteristics that make $ZnGa_2O_4$ a good choice for the foreseen applications are its good electronic bombardment stability, high temperature resistance, emission wavelength range and low electronic gap (4.4 eV) (10)

Nowadays, the crystal structure is obtained by solid state reaction between oxides, at 1100°C in air (11), following the equation :



Doping is made by addition of manganese oxide or nitrate to the initial mixture. A subsequent annealing is necessary for the reduction of the manganese in its divalent state in order to obtain a green luminescent material.



The drawback of this process is due to the alteration of the matrix arising during the last thermal treatment. This step introduces electronic traps in the band gap which modify the electron capture mechanism from Mn^{2+} and leads to a modification of the optical response under excitation (2, 12).

This clearly demonstrates the necessity to improve the synthesis route of such a material.

EXPERIMENTAL

Powder samples were prepared by firing the nitrates mixture three hours at different temperatures, in a horizontal tubular furnace allowing to work under flowing atmosphere. Three different atmospheres were used: argon (inert), oxygen (oxidizing) and 2% hydrogenated argon (reducing). The crystal structure was checked by X-Ray Diffraction analysis using a D5000 SIEMENS diffractometer with $\text{Cu-K}\alpha$ radiation operating at 40kV, 30mA and 0.24° - $2\theta/\text{min}$ scanning rate.

The thermal decomposition behavior of the precursor has been analyzed from the recorded signal coming out from a ThermoGravimetric (TG) analyzer, a Differential Scanning Calorimetric (DSC) analyzer and a Fourier Transform Infra Red (FTIR) analyzer. The DSC is used to detect exo or endothermic phenomena, the TG permits to associate any weight variation with these phenomena and gases emitted during the heat treatment are analyzed by FTIR.

RESULTS AND DISCUSSION

Precursor thermal behavior

The precursor thermal decomposition has been studied between 20 and 600°C . The results observed under an oxidizing atmosphere are plotted in fig 1-a. Similar data have been recorded under inert atmosphere. In fig 1-b are presented the data obtained under a reducing atmosphere.

Up to 370°C , whatever the atmosphere is, one can observe three endothermic phenomena (I, II and III), the last two of them being associated with a noticeable weight loss. Gas analysis helped us to attribute peaks II and III respectively to a water and a nitrogen oxide loss, nitrogen oxide appearing first through its dimmer form N_2O_4 . The

first endothermic phenomenon which cannot be associated with any weight loss corresponds probably to the melting of the zinc nitrate which is expected around 40°C.

Beyond 370°C, the experiment performed under flowing hydrogenated argon differs by the appearance of two exothermic phenomena, at 430°C and 470°C, the first of which can be associated with a new weight loss. Till now, we did not manage to explain these two phenomena.

Crystal structure formation

The crystal structure formation study has been performed by looking at the intensity of the most intense X ray diffraction peak area measured on powder samples. The crystallization quality increases with this parameter.

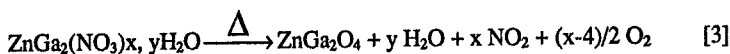
Once again, we have been able to distinguish two different behaviors depending on the nature of the firing atmosphere.

Whatever the atmosphere is, the zinc gallate crystallizes right from 300°C with a weight loss reaching 49% (fig. 2-a & 3).

Under inert and oxidizing atmosphere, this phase is stable at least up to 1200°C without any variation either in weight or in zinc rate (fig. 3 & 4).

Under the reducing atmosphere, one can observe the decomposition of the zinc gallate beyond 600°C (fig. 2-b) accompanied by a restart of the weight loss (fig. 3) and the formation of gallium oxide (Ga_2O_3). Furthermore, beyond 600°C, the ratio Zn/Ga decreases (fig.4) showing a zinc evaporation responsible for the new weight loss observed.

We are now able to establish the equation describing the formation of the zinc gallate by using the new precursor:



We have demonstrated the possibility to prepare crystallized zinc gallate at low temperature, the spinel structure being stable at least up to 1200°C under flowing oxygen or argon and decomposing itself beyond 600°C under flowing hydrogenated argon. This decomposition arises through a zinc loss and lead to the formation of gallium oxide.

Optical properties

We have prepared a 0.03% atomic manganese doped ZnGa_2O_4 by firing a zinc, gallium and manganese nitrates based precursor, first under argon at 800 °C for 3h and then under 2% hydrogenated argon at 600°C for 3h.

The emission spectrum of the manganese doped zinc gallate, excited at 254nm, shows a narrow band peaking at 505nm involving the 3d inner electronic shell of the Mn^{2+} (13) (Fig. 5). Green emission indicates that manganese occupies a four-fold coordinated site in the lattice (14).

We have compared the phosphor prepared with this new precursor with the classically prepared one as far as their opto-electronic properties are concerned. For this purpose, each of the two phosphors has been exposed to a U.V. source (254nm) and the manganese emission intensity at 505nm has been recorded as a function of time.

The new phosphor rapidly reaches the maximum intensity threshold while the classically prepared phosphor's response is much more time dependent (Fig. 6). This delayed luminescence observed in the phosphor prepared by a classical solid state route strongly limits its possible use as an emitting material for display devices with high scanning rate (like television or computer screen).

This phenomenon can be described by the following model (Fig. 7) :

Under U.V. excitation (254nm), Mn^{2+} can be excited via a charge transfer, occurring from the drop of an electron from the conduction band to one of the manganese excited electronic levels. The delay observed in the classical phosphor can be ascribed to the presence of defects introducing trapping levels in the matrix band gap. A broad peak recorded at 50°C on a thermoluminescence analysis has confirmed the existence of filled traps at room temperature in the classical compound. These defects are responsible for the establishment of a transient state meanwhile the excited electrons are filling the traps instead of participating to the manganese excitation process (Fig. 7-b). The observed delay shows that an efficient energy transfer takes place between these traps and the activator.

Concerning our defect free phosphor, the absence of defect suppresses this transient state since a very short time is required for the excited electron to reach the activator (Fig. 7-a). In this situation, the green emission is observed simultaneously with the excitation.

CONCLUSION

A complete analysis of the $ZnGa_2O_4$ crystal structure formation under reducing atmosphere has underlined the instability of this matrix at high temperature and gave evidence of the importance of the firing parameters on the control of both the manganese oxidation state and the matrix stoichiometry.

When manganese doped, the luminescent phenomenon observed in the phosphor prepared at high temperature is modified by the formation of electronic traps which compete with the direct Mn^{2+} excitation process.

By using a new precursor which can be described as a mixture of nitrates, it has been possible to prepare a Mn^{2+} doped $ZnGa_2O_4$ type phosphor at relatively low temperature to avoid the formation of electronic traps in the band gap. This defect free phosphor can be used as a green emitting material for display devices.

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FIGURES

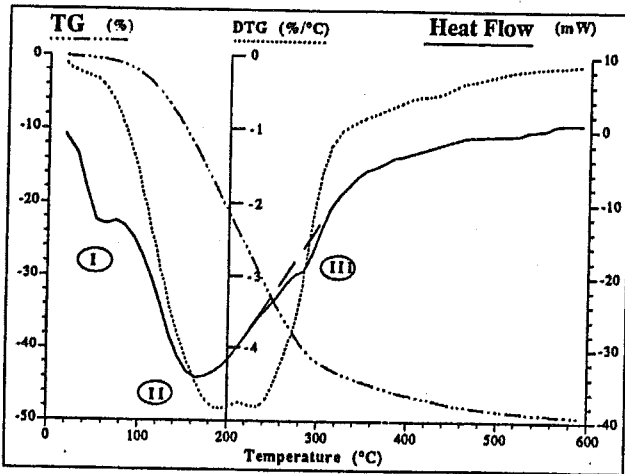


Fig. 1-a : TG-DSC of the precursor under O_2 .

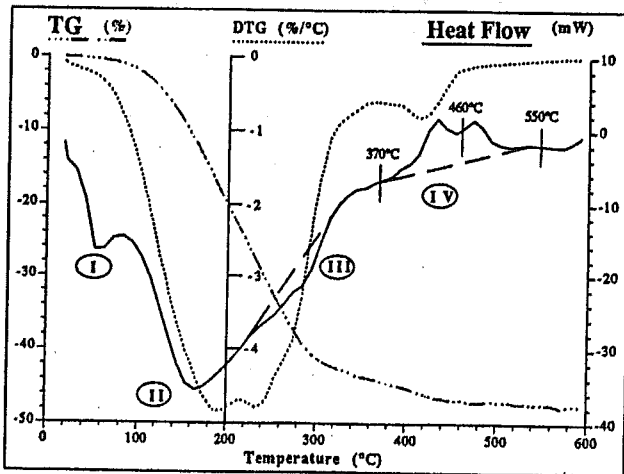
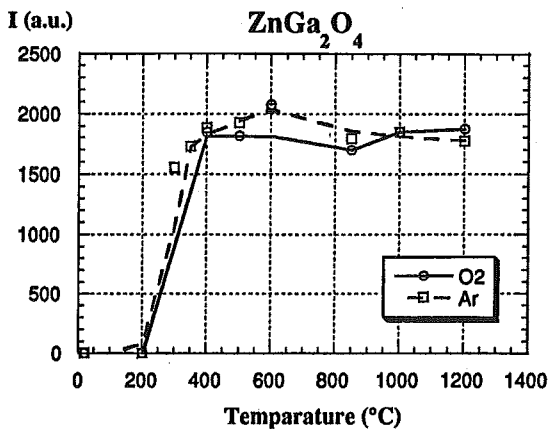
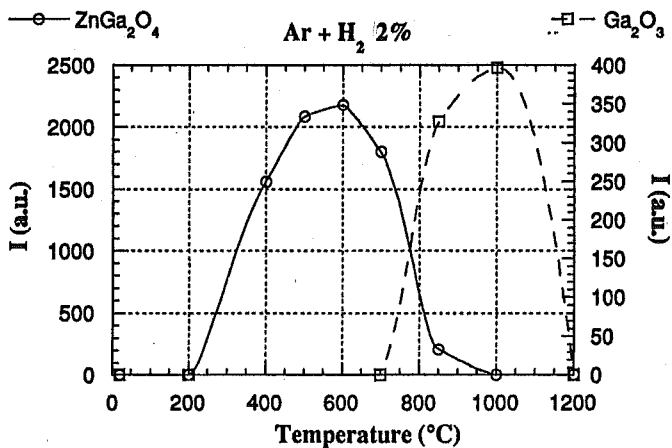


Fig. 1-b : TG-DSC of the precursor under $Ar+H_2$ 2%.



**Fig. 2-a : Most intense diffraction peak area.
(Samples fired under O₂ and Ar)**



**Fig. 2-b : Most intense diffraction peak area.
(Samples fired under Ar+H₂ 2%)**

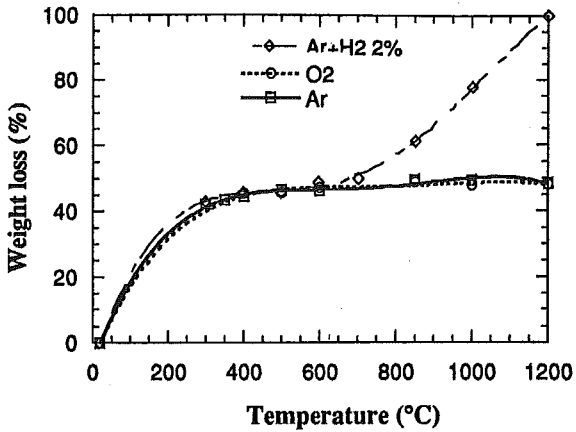


Fig. 3 : Weight loss as a function of firing temperature.

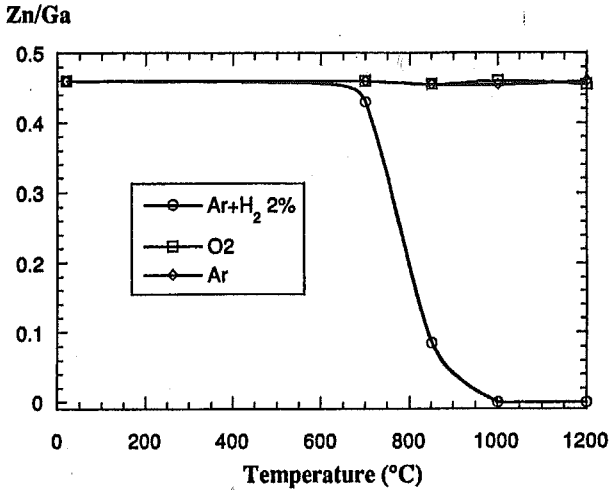


Fig. 4 : Zn/Ga ratio as a function of firing temperature.

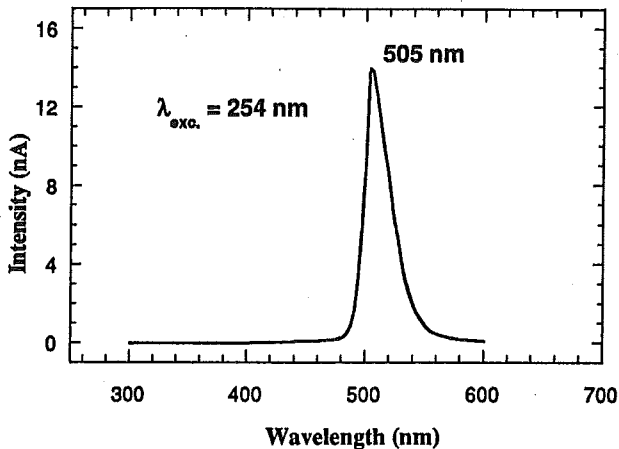


Fig. 5 : Emission spectra of a manganese doped zinc gallate

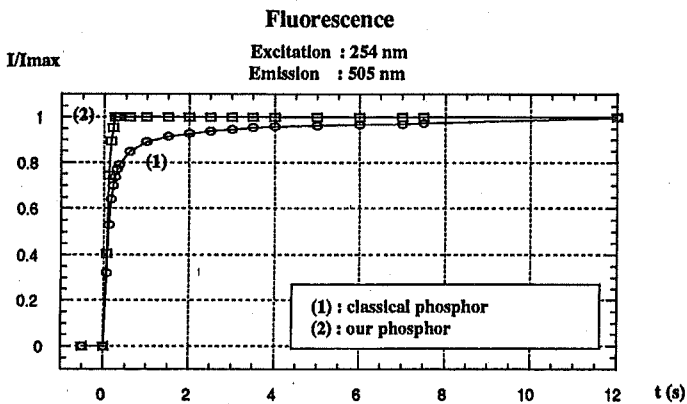


Fig. 6 : Response of the two phosphors to an U.V. excitation.

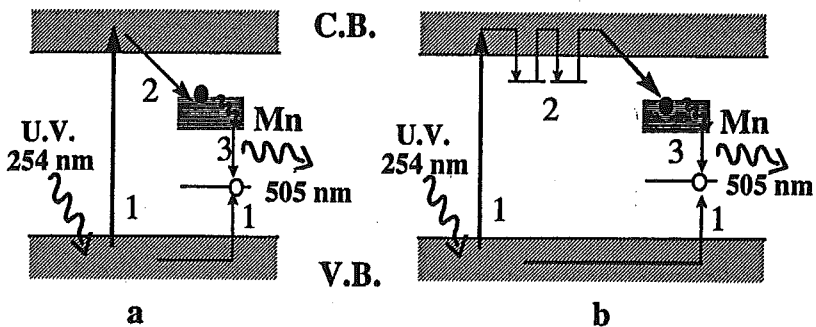


Fig. 7 : Model based on the opto-electronic behavior observed.