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SYNTHESIS OF EUROPIUM AND DYSPROSIUM ACTIVATED STRONTIUM MONO-ALUMINATE.

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ABSTRACT

The formation of SrAl_2O_4 by solid state reaction between SrCO_3 and Al_2O_3 has been studied. The firing conditions, namely the time, the atmosphere and the temperature, have been optimized so as to obtain pure well crystallized SrAl_2O_4 , allowing the further study of the influence of the atmosphere on the optoelectronic properties of the phosphor. To this end, fluorescent and thermoluminescent experiments have been carried out in order to characterize the defects responsible for the phosphorescent mechanism.

INTRODUCTION

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is a green emitting phosphor^[1]. Co-activated by Dy^{3+} , it shows a long lasting phosphorescence^[2,3].

Our aim was to study the influence of the firing conditions on the formation of the strontium aluminate structure as well as on its luminescent properties.

In order to improve these properties and to understand the mechanism of phosphorescence, one has to control the synthesis of the host lattice.

So we were first interested in the unactivated strontium aluminate and studied the influence of both temperature and atmosphere on its formation and on its optoelectronic properties.

To this end, we studied the thermal behavior of the precursor and made kinetic and thermodynamic studies of the formation reactions.

The optoelectronic properties have been characterized by fluorescence and thermoluminescence.

Thereafter, we doped the host lattice with europium, and then with europium and dysprosium, so as to observe to what extent the optoelectronic properties have been modified.

PROCEDURE

The thermal behavior has been studied by coupling a Differential Thermal Analyser (DTA), a ThermoGravimetric Analyser (TGA) and a Mass Spectrometer (MS).

Kinetic and thermodynamic studies have been carried out by firing a mixture of strontium carbonate and alumina, in a horizontal tubular furnace, controlling the firing time, temperature and atmosphere.

The influence of the temperature has been studied in the 600°C-1400°C range. We used different atmospheres : an inert one (Ar), an oxidizing one (O₂), a reducing one (Ar+H₂) and CO₂.

The doping was made by adding Eu₂O₃ and/or Dy₂O₃ to the initial mixture.

Fluorescence and thermoluminescence (TL) have been recorded versus the firing conditions.

THERMAL BEHAVIOR

The strontium carbonate undergoes two endothermic transformations (*fig.1*), the first of which (I) corresponds to its polymorphic transformation, the second (II) to its decomposition.

On the figure 2, presenting the mixture thermal behavior, one recognize the strontium carbonate polymorphic transformation (I). Prupit to this phenomenon stands a new peak, (0). X-Ray diffraction experiments allowed us to ascribe this peak, and the peak III, to the formation of strontium aluminates. Actually, two aluminates are synthesized, SrAl₂O₄ and Sr₃Al₂O₆, which stands next to SrAl₂O₄ in the complex SrO-Al₂O₃ system phase diagram.

KINETIC AND THERMODYNAMIC RESULTS

Kinetics

We fixed the temperature at different values and followed, by X-Ray diffraction experiments, the amount of the different compounds, with the time of calcination.

First of all, we can notice that SrAl₂O₄ is not the only product of reaction. Another aluminate precipitates : Sr₃Al₂O₆. This one seems however to react with the excess alumina beyond 1000°C.

Moreover, the system does not seem to evolve above 3 hours of calcination, time we will take for the thermodynamic study.

Thermodynamics

Here, we have followed the amount of each compound with the temperature, for 3 hours of heat treatment.

Both under flowing oxygen and hydrogenated argon, the reaction begins around 750-800°C, giving rise to the two aluminates noticed above (*fig.3 & 4*).

This study confirms the decrease of $\text{Sr}_3\text{Al}_2\text{O}_6$, beyond 1000°C under flowing oxygen (*fig.3*) and 900°C under flowing hydrogenated argon (*fig.4*).

Unfortunately, even at 1400°C, a small amount of $\text{Sr}_3\text{Al}_2\text{O}_6$ can still be detected by X-Ray diffraction. We were so led to anneal the as-synthesized aluminates so as to eliminate every side product.

These studies allow us to propose a preparation route, made up of two steps, a calcination followed by an annealing, leading to pure and well crystallized strontium monoaluminate, SrAl_2O_4 .

We were so able to study the influence of the atmosphere on the optoelectronic properties, that is on the response of both the fluorescence and the thermoluminescence. To this end, we made the calcination atmosphere varied, the annealing one being either the same as the calcination one, or hydrogenated argon.

LUMINESCENCE OF THE HOST LATTICE

Fluorescence

Concerning the host lattice we observed two different behaviors depending more or less on the reducing nature of the atmosphere.

As a matter of fact, under O_2 and CO_2 , the host lattice exhibits a blue emission band (*fig.5*), centered on 450nm, ascribed to host defects.

Under Ar, Ar+ H_2 and, whatever the calcination atmosphere, after a reducing annealing, beside the blue emission we observed a green emission, centered on 526nm (*fig.6*), similar to the Eu^{2+} one.

So, we came to the conclusion that there should be some traces of europium in the initial materials, even if we did not manage to detect them.

One emission center, emitting at 450nm, can be ascribed to the host lattice.

Thermoluminescence

Thermoluminescence is very useful to detect trap defects and the strontium monoaluminate exhibits lots of (fig.7).

It is interesting to notice that a reducing treatment increases the intensity of every thermoluminescent peaks. This can be ascribed either to an increase of the number of trap defects or to a change of the recombination center, if we assume that the fluorescence results can be transposable here.

EFFECT OF THE ACTIVATION ON THE LUMINESCENT PROPERTIES

All the materials presented here have been prepared by calcination under O_2 and annealing under $Ar+H_2$.

Europium activation

The europium doping increases the thermoluminescence intensity, especially those of the peaks at $-175^\circ C$ and $-75^\circ C$ (fig.8).

Thanks to the spectral analysis we know that, here, the recombination center is the divalent europium, the emission peaking at $526nm$.

So, we have a double effect :

- an increase of the number of the recombination center, leading to an increase of the mean intensity.
- a modification of the trap defects distribution as far as the increase of the intensity is not uniform.

Actually, the europium substitutes for the strontium. In the first step of the process, it is introduced in its trivalent state. So a charge compensation has to occur, probably creating trap defects, involved in the thermoluminescent curve shape modification.

Dysprosium co-activation

Compared with the europium activated strontium monoaluminate, the co-activation with dysprosium changes again the thermoluminescent curve shape (fig.9).

Here again we observe an increase of the thermoluminescence intensity.

We can notice the same effect concerning the peak at $-75^\circ C$, but what is much more interesting is the wide peak around the room temperature, responsible for the long lasting phosphorescence.

We assume that the dysprosium doping introduces a new mechanism our model is lying upon.

CONCLUSION

We have elaborated a process leading to pure well crystallized SrAl_2O_4 , allowing us to study the luminescent characteristics of this phosphor.

We pointed out the presence of two different recombination centers and of several trap defects, whose distribution varies with the doping.

We are now working on perfecting a model which will take into account all our experimental results and will be consistent with stable states of the activators, namely the europium and the dysprosium.

REFERENCES

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- ^[3] H. Yamamoto et al., Journal of luminescence **72-74**, 287 (1997)

FIGURES

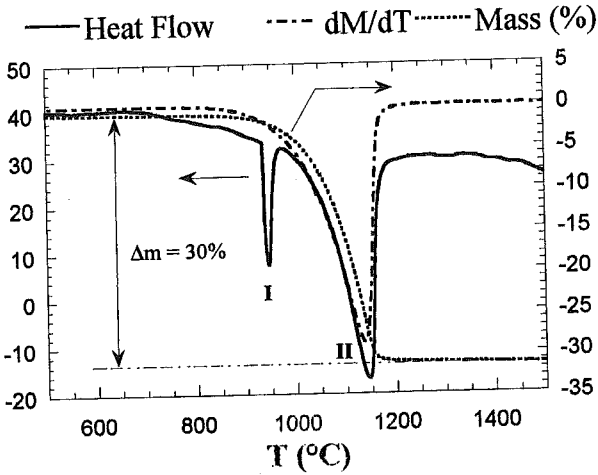


fig.1 : DTA-TGA of the strontium carbonate (SrCO_3)

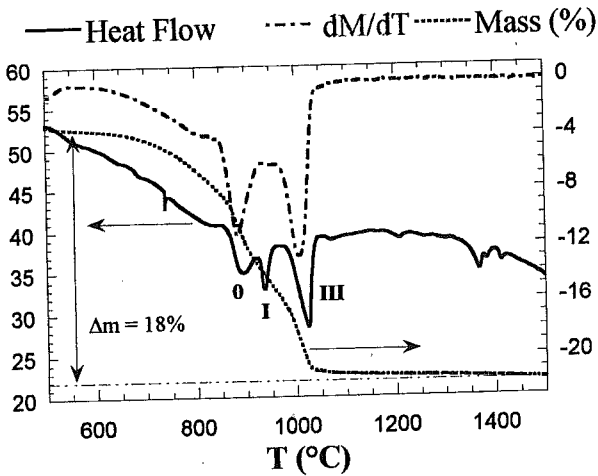


fig.2 : DTA-TGA of the mixture $\text{SrCO}_3 + \text{Al}_2\text{O}_3$

Mass ratio

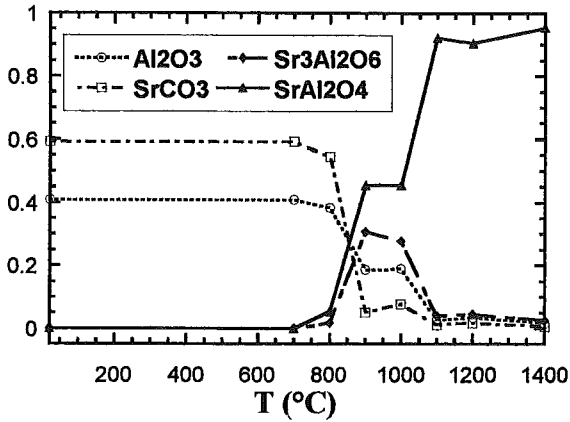


fig.3 : SrCO₃ + Al₂O₃ under O₂

Mass ratio

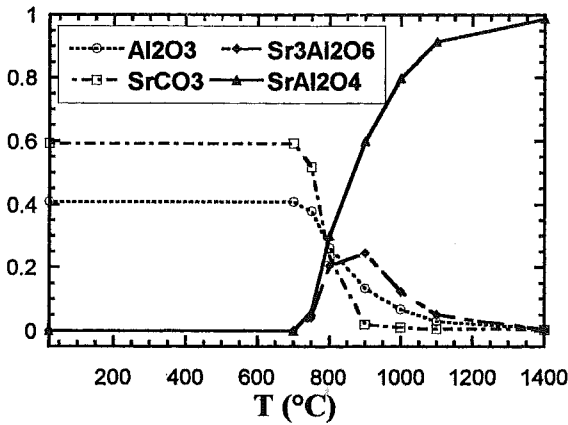


fig.4 : SrCO₃ + Al₂O₃ under Ar + H₂

Intensity (a.u.)

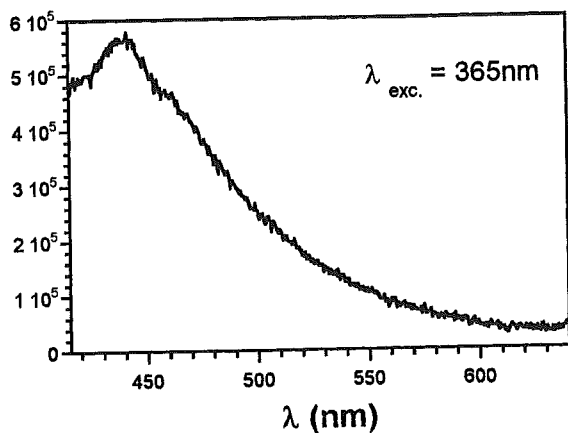


fig. 5 : Fluorescence emission spectrum of the host lattice synthesized under O_2
(same result under CO_2)

Intensity (a.u.)

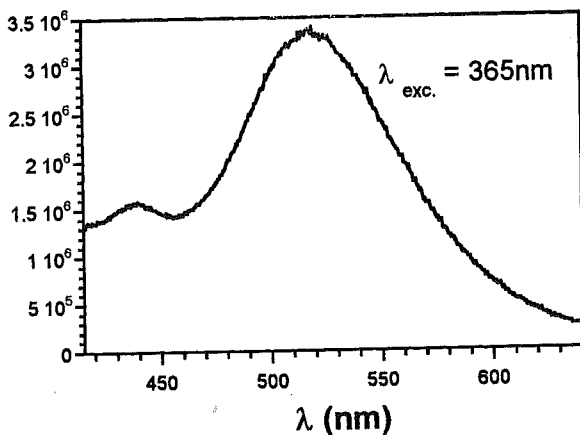


fig. 6 : Fluorescence emission spectrum of the host lattice synthesized under $Ar + H_2$
(same result under Ar)

I (A/mg)

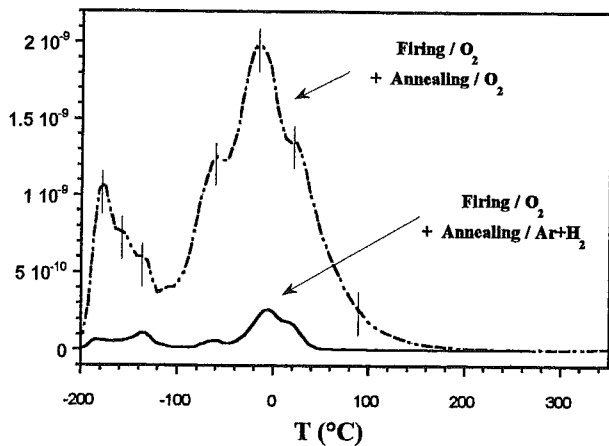


fig. 7 : Thermoluminescence curve of the host lattice

I (A/mg)

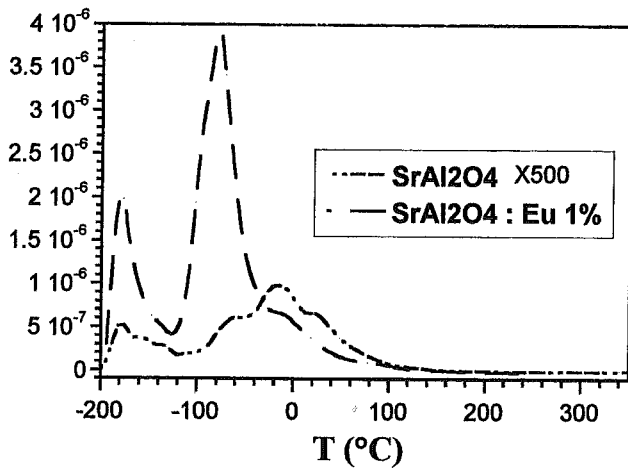


fig. 8 : Eu doping influence on the TL curves

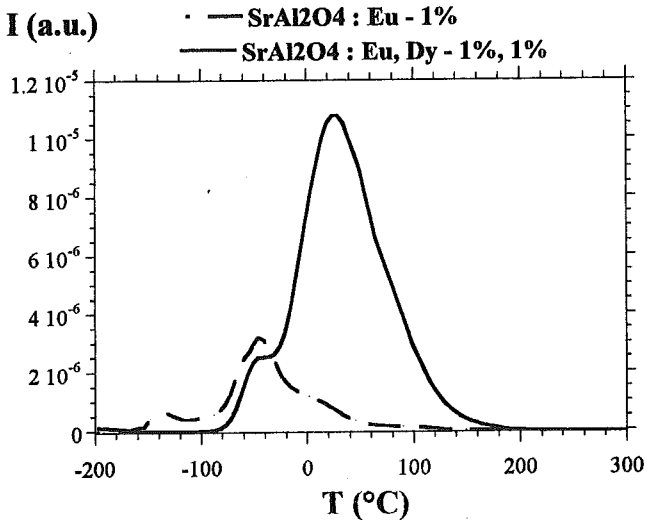


fig.9 : Dy co-activation influence on the TL curves