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High temperature crystallization of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ microscopic powders by activated fluidization processes

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ABSTRACT

A high temperature fluidized bed reactor (HTFBR) has been developed to crystallize $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ microscopic powders between 900 and 1200°C. Because of high interparticle forces existing in such Geldart's group C powders, it was necessary to activate their fluidization. Following previous results, two activated processes of fluidization were used, addition of coarse particles to fine powders and vibrated fluidization. In order to evidence the advantages of the fluidized bed technology over more conventional treatments in static mode, a comparative study of the main particle characteristics after heat treatment in a crucible and in the HTFBR was performed. The X-Ray Diffraction patterns, the size distribution and the FEG SEM morphology of particles before and after thermal treatments were compared for the three processes. The crystallinity of the samples treated was equivalent for the three methods. Massive sintering phenomena occurred in the crucible from 1000°C whereas the original granulometry of particles was maintained in the HTFBR till 1100°C. The interest of activated fluidization processes to post treat microscopic particles is thus fully demonstrated.

KEYWORDS: Gas solid fluidization, Microscopic powders, Vibrated fluidized bed, High temperature crystallization, Particle morphology, Sintering

I. INTRODUCTION

Phosphor materials play a key role in manufacturing emissive displays, paint pigments and high quality fluorescent lamps. Spray pyrolysis (SP) is one of the most efficient processes for the large scale production of microscopic phosphor particles. High temperature thermal post treatments are mandatory to enhance the final properties of phosphors prepared by this technique. Indeed, the increase of crystallite size of the host lattice regardless of the surface area is essential to enhance the luminescent intensity of SP phosphor particles [1]. The size of the crystallites mainly depends on the temperature and the duration of the post heat treatment [2-4].

This post heat treatment is classically carried out in a static mode, for either a few grams of particles in a crucible at the lab scale or in moving belt furnaces at the industrial scale. The crystallization of most phosphor particles requires very high temperatures e.g. between 900 and 1200°C. The extreme temperatures associated with a static mode treatment often lead to sintering of particles. Sintering is the bonding of adjacent surfaces of particles, by heating most often below the melting point of the main constituent [5].

The manganese doped willemite powder $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ is an efficient green phosphor widely used in fluorescent lamps or emissive flat displays. It exhibits good luminescence features under VUV (vacuum ultra violet) excitation and is in consequence employed in emissive flat plasma display panels (PDPs) [3-4]. Keeping the original granulometry of microscopic phosphor particles is of main importance since in particular the compacting on flat displays and the spatial resolution will be improved.

In this framework, gas-solid fluidization appears to be an interesting alternative solution, since this technology involves intense mixing of particles by the gas flow, which could limit sintering phenomena. It naturally leads to isothermal conditions, which could improve the homogeneity of the final phosphor products. Fluidization is easy to scale up and can reach high productivities, especially if organized in a continuous mode [6]. However, the main problem is that fluidization of microscopic powders belonging to Geldart's group C particles [7] usually leads to slugging and channeling phenomena. The interparticle forces, especially Van der Waals ones, are so considerable that they prevent fluidization [8]. In order to improve this situation, fluidization can be activated by various means, for instance using mixtures of fine and coarse powders [9, 10], by applying mechanical stirring [11], or exposing the bed to vibrations [12-14]. We have studied the fluidization behaviour of various microscopic powders (in particular $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ of interest here), at ambient temperature and pressure in previous works [15,16]. Different fluidization technologies were tested, such as mechanical stirred fluidization, vibrated fluidization and addition of easy-to-fluidize large particles. Stirred fluidization was not satisfactory. Convenient fluidization conditions were found for $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ either by adding 50 wt % of porous alumina of 245 μm in mean diameter to microscopic powders or by horizontally vibrating the column [15]. These results then opened the possibility of thermally post treating such microscopic powders in a fluidized bed (FB).

In the present work, a high temperature fluidized bed reactor (HTFBR) is used to post treat $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ microscopic powders synthesized by SP [3, 4]. In order to reveal any advantage of the FB process over the conventional static mode heat treatment, a comparative study of the main particle characteristics after heat treatment in a crucible and in the HTFBR is performed. Following previous results [15], two activated fluidization processes are studied: addition of coarse particles to fine powders and vibrated fluidization. The crystallinity, the size distribution and the outer morphology of the $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ particles before and after thermal treatment are analysed.

II. EXPERIMENTAL

Figure 1 illustrates the experimental HTFBR used, consisting first of a cylindrical alumina column; its internal diameter and its height were 0.05 m and 1.2 m, respectively. A porous alumina plate provided a homogeneous gas distribution. A long wide box underneath acted as a pre-heater for the fluidizing gas. Water cooled flanges located at the bottom and top parts of the column ensured the tightness of the reactive zone. The reactor was externally heated by a three-zone electrical furnace able to operate at temperatures up to 1300°C. Three regulating thermocouples were placed on the outer reactor wall. Fluidized bed temperatures were monitored using a movable-central thermocouple which indicated the axial profile of temperature in the reactor. A fast response differential pressure gauge controlled the pressure drop existing between the bottom part of the reactor (under the distributor) and its top part. For security reasons, an absolute pressure gauge measured the total pressure under the distributor.

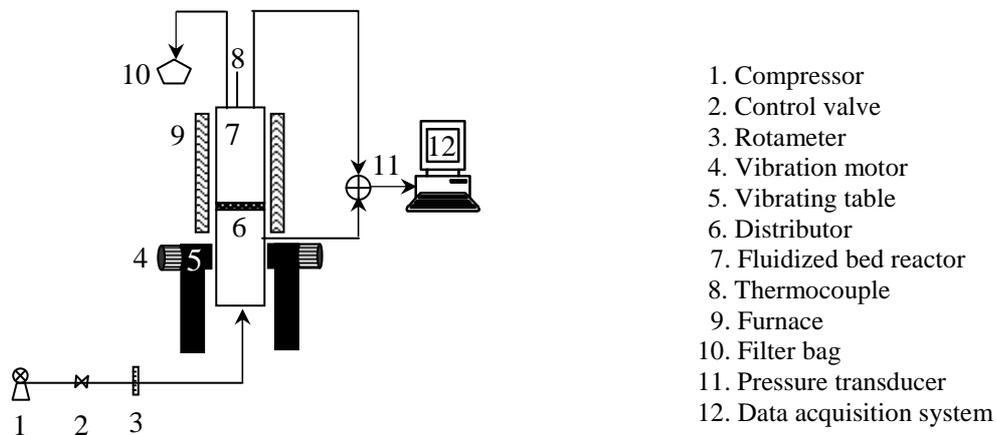


Fig.1: Schematic representation of the high temperature fluidized bed reactor (HTFBR)

The experiments were performed at ambient pressure. The differential pressure drop and fluidized bed temperature were monitored continuously using a computerized data acquisition system. Dry air was used as the fluidizing gas. Its flow rate was controlled by a calibrated rotameter. A bag filter was located after the reactor exit to collect the elutriated particles.

Vibrated fluidization experiments were performed by fixing the fluidized bed column on a vibrating table as illustrated in Figure 1 and detailed elsewhere [15]. The experiments which involved adding large particles to fine powders were carried out in the HTFBR without exerting any external action.

For the static mode treatment, a closed furnace of $40 \times 40 \times 40 \text{ cm}^3$ was used, made up of 4 heating elements allowing a maximum temperature of 1500°C to be reached. The sample was heated in a crucible of 6 cm in length, 2 cm in width and 1 cm in height which was placed on the bottom of the furnace under confined air atmosphere.

In all thermal treatments, the temperature was raised at a constant rate of 10°C/min. When the thermal regime was reached, the crystallisation/densification process was maintained for 30 minutes as determined from previous results [3, 4]. The operating temperatures were fixed at 900, 1000, 1100 and 1200°C.

Concerning the operating procedure, for vibrated fluidized bed experiments, a mass of 300 g of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ was introduced into the HTFBR, corresponding to an initial fixed bed height of 20 cm. When coarse powders were used as fluidization promoters, pre-mixed weights of 140 g of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ and 140 g of group B porous alumina were introduced into the reactor. A constant flow rate of air fluidized the bed during its heating. When vibrated fluidization experiments were

performed, vibrations were started at the same time as the heating. In all cases, the fluidization ratio U/U_{mf} was fixed to 1.1, so as to limit elutriation. In all static crystallization runs, the crucible was filled with 5 g of $Zn_2SiO_4:Mn^{2+}$.

The manganese doped zinc silicate powders of interest have been prepared by SP by Joffin [3], from a mixture of zinc and manganese nitrates and of a colloidal solution in relevant proportions. The theoretical density of the material is equal to 4.24 g/cm^3 [3]. The molar concentration of manganese is equal to 10%. This amount was selected in order to enhance the sintering ability of particles. Their mean volume diameter is of $2.2 \mu\text{m}$. They are hydrophilic. In addition, a Hausner Ratio of 1.6 classifies them as highly cohesive powders [17]. Indeed we have verified that interparticle forces are so high that conventional fluidization is not possible.

Before and after each thermal treatment, the particles in the crucible and in the FB were characterized by the following techniques:

-The powder X-ray diffraction (XRD) patterns were analyzed by a Seifert XRD3000 diffractometer using $\text{Cu-K}\alpha$ radiation in conventional operating conditions and $\theta = 2\theta$ configuration to analyze the crystalline phase. The JCPDS database and PowderCell diffraction pattern simulation software were used classically for identifying the phase diffraction peaks. The Scherrer crystallite size was classically estimated by the Halder, Schoenig and Wanger method [18].

-Laser scattering size analyses of particles after air-dispersion were performed with a MasterSizer Malvern S set up. Each measurement corresponds to an average value calculated over 3 runs.

- The powder morphology was observed by Field Emission Gun Scanning Electron Microscopy (FEG SEM) on a JEOL 6700F.

III. RESULTS AND DISCUSSION

For the two activated fluidization techniques, the optimal fluidization conditions obtained at ambient temperature [15] were applied in this study at high temperature. Preliminary pressure drop measurements between 900 and 1200°C have allowed verifying that satisfactory fluidization conditions were also obtained at high temperature; they lead to quite perfectly isothermal beds. Thus convenient conditions were then met to post treat the $Zn_2SiO_4:Mn$ powders, as we will see below.

III.1. Crystallinity

Zinc silicate owns several crystalline structures, in particular the α phase called willemite. When the material is Mn doped, this phase leads to green luminescence properties [19]. The domain of thermal stability of this α phase is preceded at lower temperature by that of the β phase whose luminescence properties are less interesting [3]. Roobsky et al. [19] and Joffin [3] have shown that the β phase begins to form near 700°C and disappears beyond 900°C , whereas the α phase appears from 850°C and is favored by thermal treatment beyond 900°C . As Zn_2SiO_4 is stable up to 1430°C , the presence of Mn induces the appearance of a liquid phase from 1250°C , whose proportion increases with the doping level [20]. For the present work, Mn being present in high proportions in the material, it is likely that sintering phenomena occur from 1200°C or even below. These are the reasons why the thermal treatments were performed here between 900 and 1200°C .

Figure 2 shows XRD patterns obtained before and after treatment at different temperatures in crucible and vibrated FB. The results obtained in FB activated by coarse particles are not presented

because they are similar to those in vibrated FB. Mn in partial substitution of Zn does not give any diffraction ray.

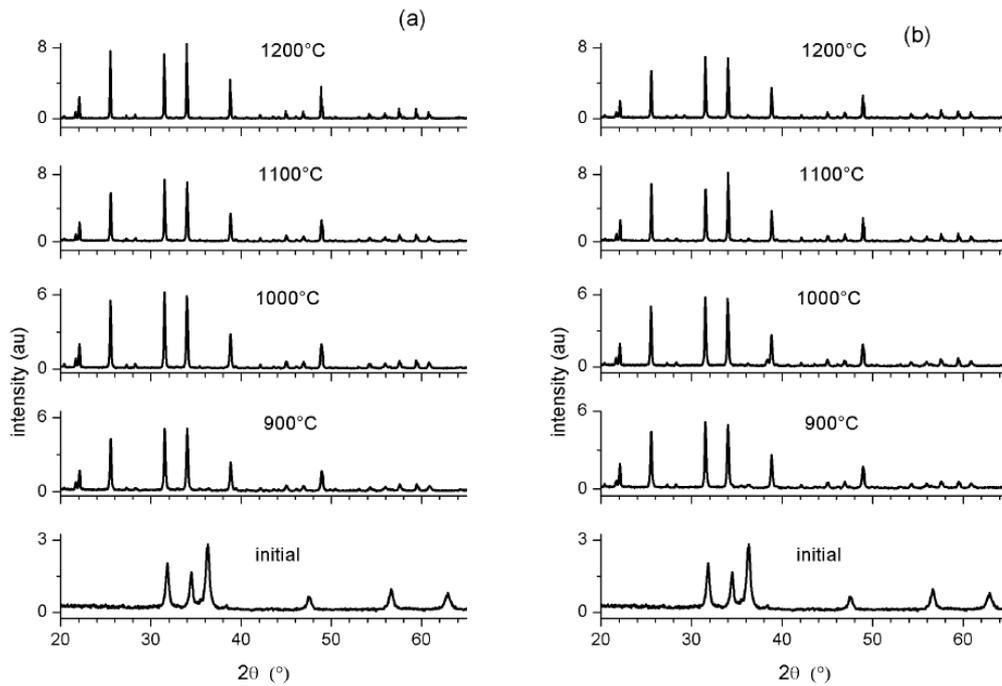


Figure 2: XRD patterns of the initial and final powders before and after treatment (a) in crucible and (b) in vibrated FB at the various temperatures

Before thermal treatment, the diffraction of particles only exhibits poorly crystallized ZnO; the silica is amorphous and does not diffract. The results confirm the necessity to thermally post treat these SP particles to enhance their optical properties.

Indeed only the α -Zn₂SiO₄ peaks are present after treatment at 900°C for the whole processes. In all cases, the solid phase reactions are complete at 900°C since at higher temperature, there is no more phase transformation. However, the peaks of the α -Zn₂SiO₄ sharpen when increasing temperature, indicating an increase of the average crystal size. For each spectrum, the six most intense diffraction peaks were analysed to estimate the Scherrer crystallite size. In all cases, the Scherrer average diameter increases with temperature, and varies in the same range of values, from 43 to 84 nm between 900 and 1200°C. So, for all the tested conditions, the crystallization of the powders in FB is as efficient as in crucible.

Joffin [3] has shown that the luminescence properties of particles increase with the annealing temperature and that they are optimal at 1200°C due to the better crystallinity of powders. An important interest then exists to post treat such powders at the highest possible temperature regarding sintering phenomena.

III. 2. Particle size distribution

Table 1 gives the particles volume median diameter obtained by laser granulometry after post heat treatment with the various processes for the four temperatures tested. Figure 3 details the granulometry distribution of particles before and after treatment at 1100°C in crucible and in the two FB processes.

Table 1: Volume median diameter (in μm) of the powders treated by the various techniques

Temperature ($^{\circ}\text{C}$)	Crucible	Vibrated FB	FB with coarse particles
900	1.5	1.9	-
1000	14.2	2.1	-
1100	766.6	1.7	1.9
1100 (reproducibility)	-	1.8	-
1200	1088.4	80.5	5.2

It appears that the mean particle diameter remains lower than $2\ \mu\text{m}$ after thermal treatment at 900°C by the whole techniques. At this temperature, the original granulometry of powders is then fully maintained.

However, in crucible, this mean diameter rapidly increases with temperature to reach $766\ \mu\text{m}$ at 1100°C and $1088\ \mu\text{m}$ at 1200°C . In figure 3, two populations of particles can be observed in crucible at 1100°C , one minor around $10\ \mu\text{m}$ and the most important one near $1\ \text{mm}$. Massive sintering phenomena occur then in crucible from 1000°C , leading to a loss of the original morphology of powders, as confirmed below by FEG SEM analyses.

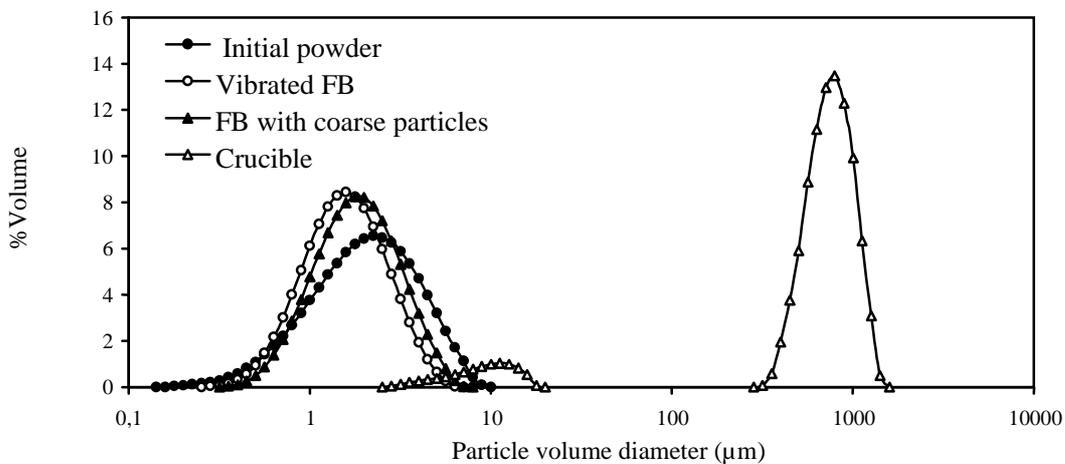


Figure 3: Particle diameter distribution after thermal treatment at 1100°C

On the opposite, up to 1100°C , the two FB processes are efficient to maintain the original morphology of particles. The comparison of the two experiments performed at 1100°C in the vibrated HTFBR demonstrates the reproducibility of results provided by this process. But some sintering phenomena occur at 1200°C , leading to a mean volume diameter of $5\ \mu\text{m}$ in the FB activated by adding easy-to-fluidize particles and of $80.5\ \mu\text{m}$ in vibrated FB. The extremely high temperature applied, very close to the melting point, and the high percentage of Mn in the material certainly explain these results. But even for these extreme conditions, sintering is clearly less intense in FB than in crucible. Fluidization activated by adding group B particles seems to be slightly more efficient to limit these phenomena than vibrated fluidization for the conditions tested.

III.3. Surface morphology

The FEG SEM morphology of particles before and after post heat treatment at 1100°C by the various processes studied is presented in figure 4. Initial particles are full spheres constituted of nanometric aggregates. After treatment in crucible, FEG SEM analyses clearly show the occurrence of inter-particle sintering phenomena, i.e. the formation of interparticle bridges and a loss of the spherical morphology of individual powders. So evident sintering phenomena could not be detected on samples post treated in the HTFBR. As can be seen in figures 4 (c) and (d), the sphericity and the individuality of powders were maintained after treatment in the two FB processes.

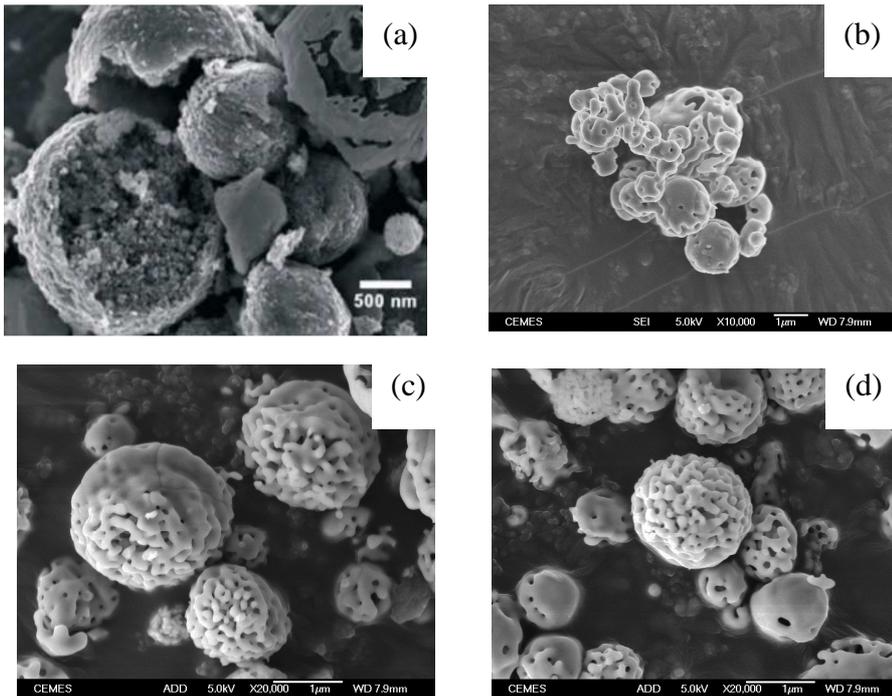


Figure 4: FEG SEM views of the $Zn_2SiO_4:Mn^{2+}$ powders (a) before and after treatment at 1100°C (b) in crucible, (c) in FB activated with coarse particles and (d) in vibrated FB

IV. CONCLUSIONS

Microscopic porous $Zn_2SiO_4:Mn^{2+}$ powders have been treated at ambient air pressure between 900 and 1200°C in order to crystallize them. Three heat treatment processes have been studied: (i) a conventional static bed process in a crucible, (ii) a fluidization process activated by adding coarse powders, (iii) another fluidization process activated by column vibrations. This activation of fluidization was necessary because of the high interparticle forces existing in such Geldart group C powders. The choice of these methods of activation proceeds from previous results obtained at ambient temperature and confirmed at high temperature.

The crystallinity by X-ray diffraction, the size distribution by laser scattering in dry mode and the outer morphology by scanning electron microscopy of particles, before and after thermal treatments, have been analysed and compared for the three processes tested. The crystallinity of the samples treated was equivalent for the three methods of thermal treatment. It increased with

temperature and was then optimal at 1200°C. Massive sintering phenomena started to occur from 1000°C in crucible, whereas they only appear at 1200°C in the fluidization processes. For the conditions tested, fluidization activated by coarse particles appeared to be slightly more efficient in limiting sintering phenomena than vibrated fluidization at 1200°C. It has been shown [3] that the luminescence properties of particles are proportional to the annealing temperature. An important interest then exists to thermally post treat these particles in fluidized bed.

More precisely, these results open up promising perspectives to post treat microscopic powders in reproducible and uniform conditions in an easy-to-scale-up technology, i.e. the fluidization process, for crystallisation purposes, their reduction, carbidization, grafting and coating by chemical vapor deposition (CVD).

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