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Control of morphology of Zn_2SiO_4 by hydrothermal preparation

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Pure and Mn-doped willemite, Zn_2SiO_4 of different morphologies and particle sizes were prepared with and without NH_4OH under different hydrothermal conditions. Pure willemite was synthesized at a temperature as low as 165 °C using autogeneous pressure. The nature of the anion, silica source and the $NH_4OH:Zn^{2+}$ ratio played an important role in the size and morphology of the willemite phase. The presence of SO_4^{2-} anions resulted in mainly equiaxed grains. Such powders are expected to be good for consolidation and in the processing of phosphors.

1. Introduction

Manganese doped willemite, Zn_2SiO_4, is mainly used as a green phosphor in lamps and cathode ray tubes. Over the last decade, to prepare this material, some researchers have developed new chemical methods instead of the traditional solid state reaction method to improve the quality and light output of the phosphors. The new chemical processing techniques include sol–gel [1], coprecipitation [2] and hydrothermal [3, 4]. Matijevic and coworkers [5–8] have been using controlled precipitation techniques to synthesize monodispersed powders in simpler systems. Morimo and Matae [1] used a sol–gel method to prepare Zn_2SiO_4 phosphors and compared it with that made by the solid state or dry method. Their results showed that the ultraviolet (u.v.) excited emission intensity of the sol–gel derived material was three times larger than that by the dry method when the concentration of Mn^{2+} was about 2 mol %. Chang *et al.* [2] used a coprecipitation method and showed that the cathodoluminescence intensity depended not only on the concentration of Mn^{2+} and coactivator As^{5+} on the surface layer of particles, but also depended on the particle size. The low temperature of synthesis in the hydrothermal process and the advantage of easy doping would seem to favour this process over the calcination method, [9–12] for making willemite. Thus, hydrothermal processing becomes a prospective route for preparation of this phosphor [3, 4]. Toshiyuki has already used the hydrothermal method and prepared columnar [3] and spherical Mn doped Zn_2SiO_4 for phosphors. However, this author [3, 4] did not investigate the uniformity of Mn^{2+} distribution in the structure. Most relevant in this connection, he did not investigate the possible control of morphology under hydrothermal conditions. Thus the objective of this study was to determine the influence of different pressure (P) and temperature (T) conditions and chemistry of the starting materials on the morphology of willemite phase, including the Mn^{2+} doped one made under hydrothermal conditions.

2. Experimental procedure

Starting mixtures were made with different zinc sources, such as nitrate, sulfate, oxide, phosphate, carbonate or chloride, and different silica sources, such as gel, sol or quartz. A single phase willemite gel was prepared by mixing Zn nitrate and tetraethoxysilane, in ethanol and hydrolysing the components with water and nitric acid. Table I lists the starting materials and the different hydrothermal conditions used for willemite synthesis. The starting materials were sealed in Parr bombs and heated in an oven at different temperatures. For the synthesis of Mn doped willemite, it was necessary to control the pO_2 in the hydrothermal vessel and prevent oxidation of Mn^{2+}. This was accomplished by including excess $Mn(OH)_2$ powder in a separate Teflon container within the hydrothermal vessel. After the hydrothermal treatment, the samples in bombs were cooled to room temperature. The solid samples were separated by centrifugation, washed with deionized water, and dried in an oven at 90 °C. All the samples were characterized by powder X-ray diffraction (XRD) using a Scintag X-ray diffractometer [12] with Ni filtered CuK_α radiation. Some of the samples were characterized for particle size and shape by scanning electron microscopy (SEM), using an ISI-DS 130 instrument, and the emission spectrum of Mn^{2+} doped willemite was recorded on a fluorescence spectrophotometer (Hitachi F-4010 instrument) using an excitation wavelength of 240 nm.

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TABLE I Starting materials and hydrothermal conditions for willemite synthesis

Starting materials	Hydrothermal conditions	
	Temperature (°C)	Time of treatment (h)
$Zn(NO_3)_2 \cdot 6H_2O$ + silica gel + NH_4OH	165	24
	225	5,48
$Zn(NO_3)_2 \cdot 6H_2O$ + silica sol + NH_4OH	200	24
	225	48
$Zn(NO_3)_2 \cdot 6H_2O$ + quartz + NH_4OH	225	48
$ZnSO_4 \cdot 7H_2O$ + silica sol + NH_4OH	200	24
	225	5,48
$ZnSO_4 \cdot 7H_2O$ + silica sol + $(CH_3)_4NOH$	200	24
$ZnSO_4 \cdot 7H_2O$ + $Mn(OH)_2$ + silica sol + NH_4OH	200	4
ZnO + silica sol	225	48
ZnO + silica gel	225	48
Zn_2SiO_4 single phase gel[a] + H_2O + $(NH_4)_2SO_4$	225	24
$Zn_3(PO_4)_2$ + silica sol + $(CH_3)_4NOH$[b]	200	24
	225	24
	240	24
$ZnCO_3$ silica sol + $(CH_3)_4NOH$[b]	200	24
	225	24
	240	24
$ZnCl_2$ + silica sol + $(CH_3)_4NOH$[b]	200	24
	225	24
	240	24

[a] Zn_2SiO_4 gel was prepared from Zn nitrate, tetraethoxysilane, ethanol, water and nitric acid.
[b] Willemite phase did not form in these runs.

3. Results and discussion

3.1. Effect of the mole ratio of NH_4OH:$ZnSO_4$ [$Zn(NO_3)_2$] on the morphology of willemite

Willemite was grown from both Zn nitrate and sulfate at 225 °C in the presence of ammonia. The lowest temperature for the willemite formation was found to be near 165 °C, which is similar to that reported by Toshiyuki [3]. Figs 1 and 2 show that both particle size and shape changed sharply with the NH_4OH:Zn salts ratios. Figs 3 and 4 give the SEM photographs of willemite prepared from Zn sulfate and nitrate, respectively. In both systems, when the ratio of NH_4OH:Zn salt is low (1.7), the particles formed are primarily spherical in shape; but when the ratio is high (3.9 or 4.9) acicular crystals are formed. When the NH_4OH:$ZnSO_4$ ratio is equal to 1.7, uniform quasi-spherical particles of 1.0 ~ 1.5 μm diameter form in

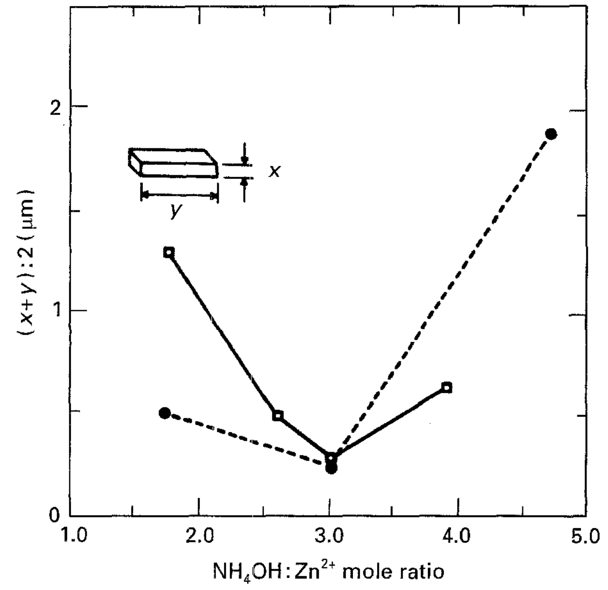

Figure 1 Change in willemite particle size as determined by $x + y$:2 (as defined in figure) ratio with a change in NH_4OH:Zn^{2+} mole ratio at 225 °C: (□) $ZnSO_4$, (●) $Zn(NO_3)_2$.

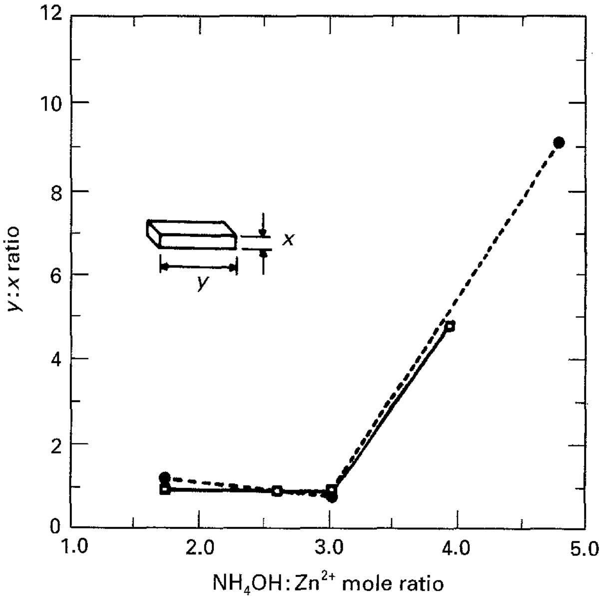

Figure 2 Change in willemite particle shape as determined by y:x (as defined in figure) ratio with a change in NH_4OH:Zn^{2+} mole ratio at 225 °C: (□) $ZnSO_4$, (●) $Zn(NO_3)_2$.

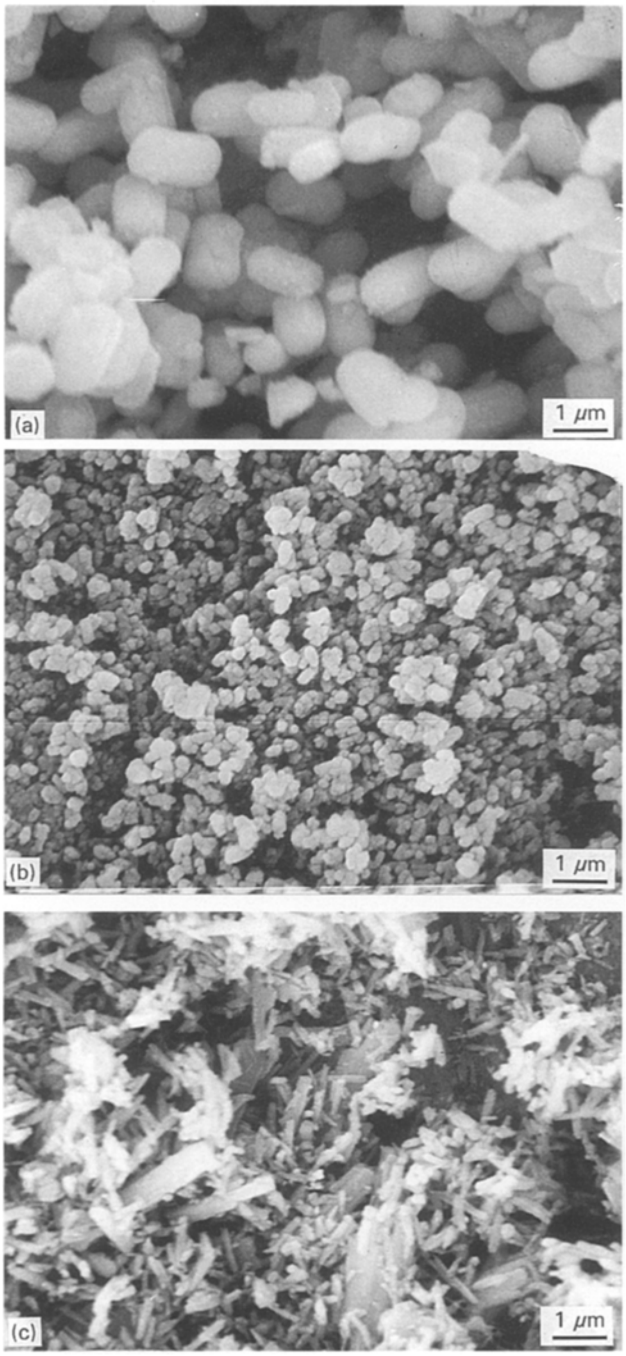

Figure 3 Scanning electron micrographs of willemite prepared hydrothermally from $ZnSO_4$ and silica sol: (a) $NH_4OH:Zn^{2+}$ mole ratio is 1.7 and treated at 225 °C 5 h; (b) $NH_4OH:Zn^{2+}$ mole ratio is 3.0 and treated at 225 °C 5 h; (c) $NH_4OH:Zn^{2+}$ mole ratio is 3.9 and treated at 225 °C 5 h.

the sulfate system. In the nitrate system, the particle shape is not as uniform as in the sulfate system at this $NH_4OH:Zn(NO_3)_2$ ratio. Particle size was also affected by the type of anion as discussed below. In the sulfate system, when the NH_4OH:Zn salt ratio is equal to 1.7, the particles are about 1.0 ~ 1.5 μm in diameter. However, the particle size decreased sharply with increasing $NH_4OH:ZnSO_4$ ratio from 1.7 to 3.0, the willemite particles became about 0.2 μm in diameter. In the nitrate system, a change in the NH_4OH:Zn salt ratio from 1.7 to 3.0 did not cause any change in the particle size. Although the precise mechanism by which the size and shape of the willemite particles are controlled, is not known, it may

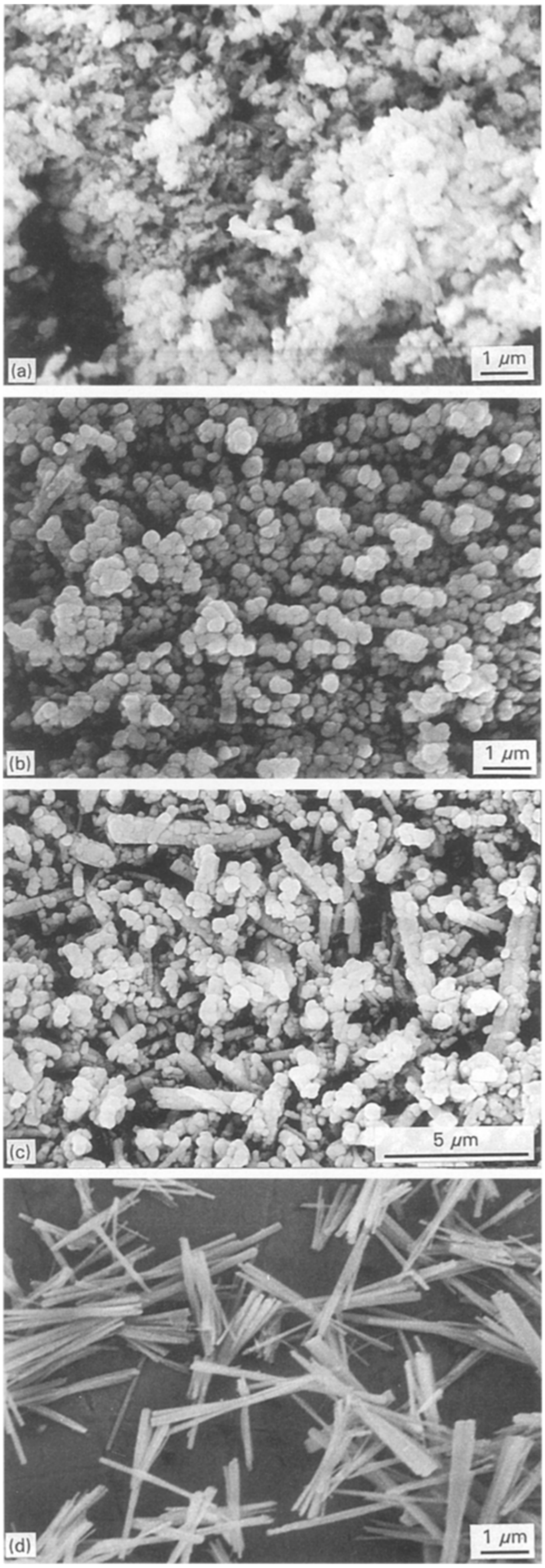

Figure 4 Scanning electron micrographs of willemite prepared hydrothermally from $Zn(NO_3)_2$ and silica sol: (a) $NH_4OH:Zn^{2+}$ mole ratio is 1.7 and treated at 225 °C 5 h; (b) $NH_4OH:Zn^{2+}$ mole ratio is 3.0 and treated at 225 °C 5 h; (c) $NH_4OH:Zn^{2+}$ mole ratio is 4.9 and treated at 225 °C 5 h (an unidentified second phase is present along with willemite); (d) same as Fig. 4c, but treated for 48 h to obtain single phase willemite.

be because of the Zn^{2+} complexation with anions and NH_3, as well as the control on silica solubility, i.e. starting silica phase.

3.2. Willemite morphology as affected by temperature in organic base.

The SEM micrographs of willemite powders, synthesized in tetramethyl ammonium hydroxide at different temperatures, are shown in Fig. 5. When the temperature of hydrothermal processing is at or below 225 °C, the powders have a spherical morphology. However, when the temperature is raised to 240 °C, the powders formed have acicular morphology. The average diameter of the spherical particles is about 0.5 μm and the XRD pattern of these powders, Fig. 6, shows a preferred (3 0 0) orientation. According to the standard pattern (No. 8–492) reported by the Joint Committee on Powder Diffraction Standards (JCPDS), the (1 4 0) plane is of 100% intensity, while the (3 0 0) plane is only of 35% intensity. Fig. 6 clearly shows a preferred orientation of (3 0 0) plane.

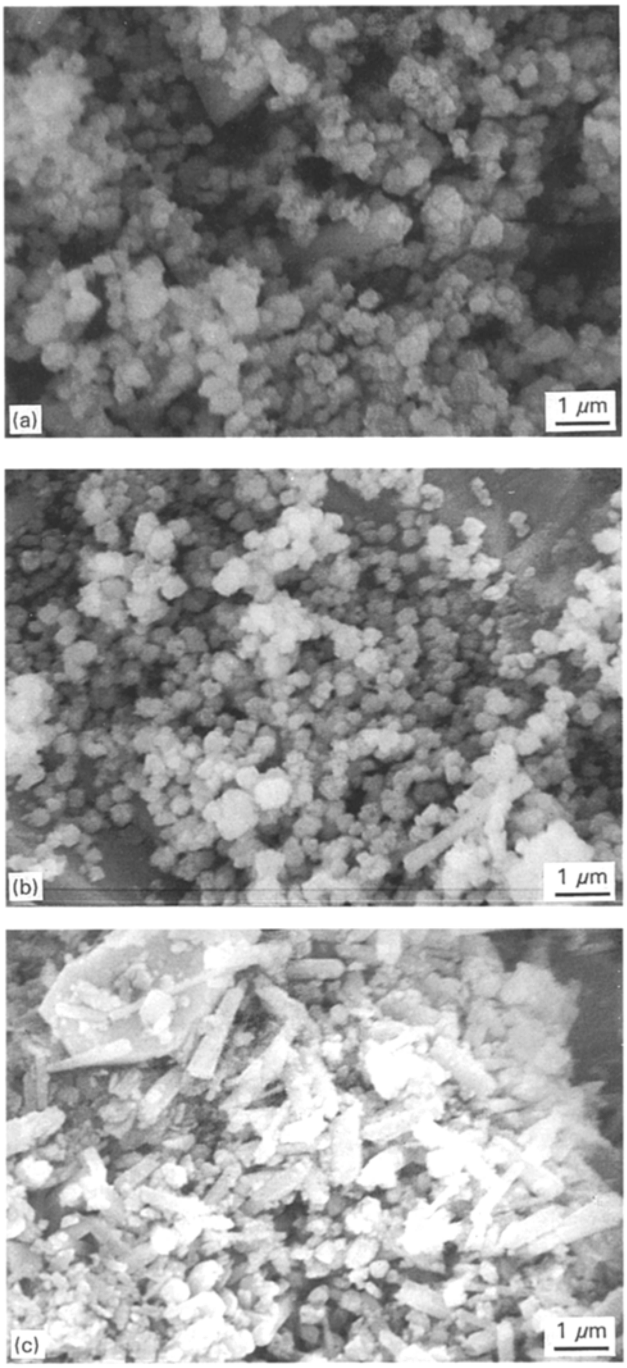

Figure 5 Scanning electron micrographs of willemite prepared hydrothermally from $ZnSO_4$, silica sol and $(CH_3)_4NOH$ under different conditions: (a) 200 °C 24 h; (b) 225 °C 24 h; (c) 240 °C 24 h.

3.3. The influence of Mn^{2+} on willemite morphology

Fig. 7 shows the morphology of Mn doped Zn_2SiO_4 phosphor, which was synthesized using NH_4OH hydrothermally from $Mn(OH)_2$ and $ZnSO_4$ (Table 1). The presence of Mn led to the formation of extremely fine particles which agglomerated, Fig. 7. Compare this morphology with that in Fig. 5a, which was made with the same $NH_4OH:ZnSO_4$ ratio, but with Mn absent. Fig. 8 shows the emission spectrum of Mn doped for Zn in willemite. The green emission from doped Mn^{2+} at 518 nm (λ max) can be clearly seen. When an acid leached kaolinite clay was used as the

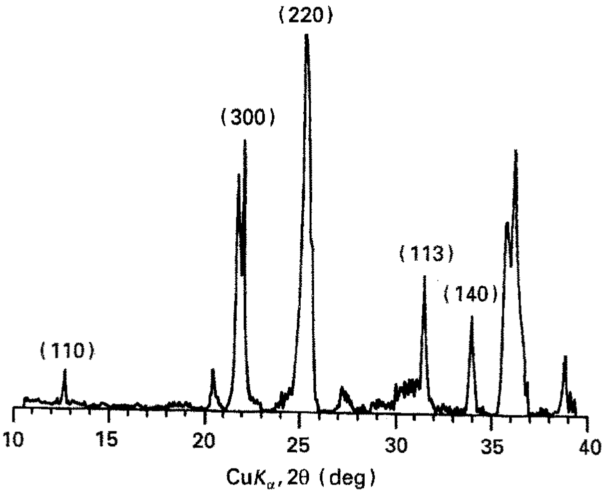

Figure 6 X-ray diffractogram of willemite synthesized hydrothermally from $ZnSO_4$ silica sol and tetramethyl ammonium hydroxide at 240 °C 24 h showing orientation along (3 0 0) plane.

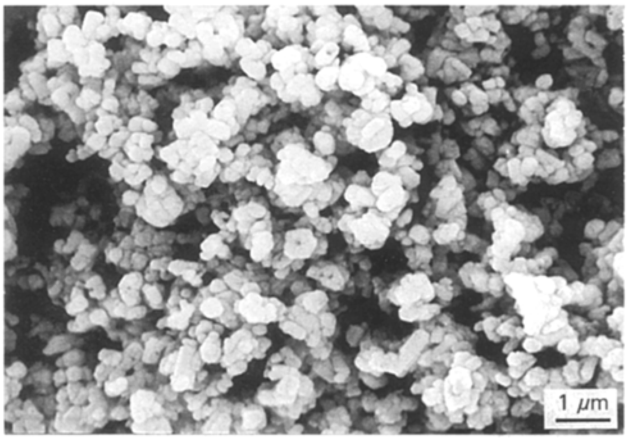

Figure 7 Scanning electron micrograph of Mn^{2+} doped willemite synthesized hydrothermally at 200 °C using $ZnSO_4$, $Mn(OH)_2$ and NH_4OH.

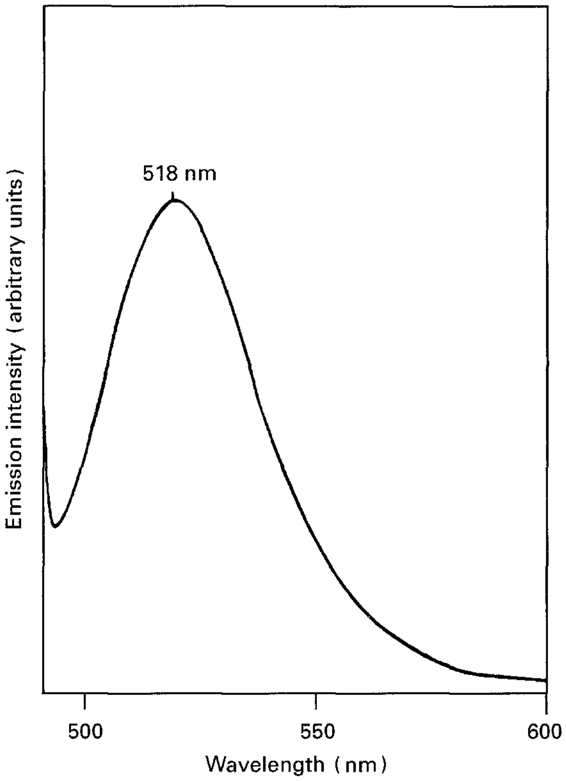

Figure 8 Emission spectrum of Mn^{2+} doped willemite.

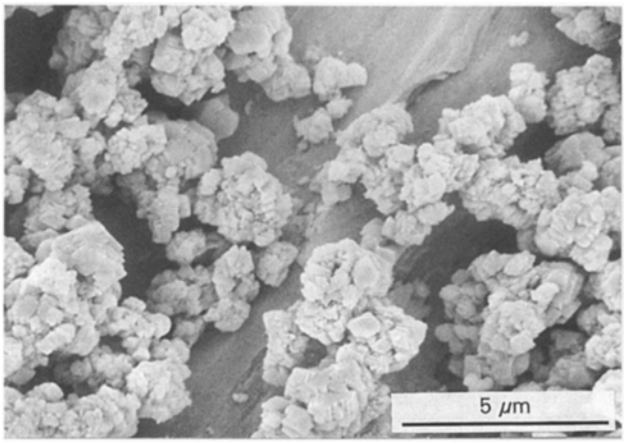

Figure 9 Scanning electron micrograph of hydrothermally synthesized willemite using ZnO and silica gel at 225 °C 48 h.

SiO_2 source, in the hope of obtaining platy epitaxial crystals, the same morphology, as above, was obtained.

3.4. The role of Zn solubility on willemite morphology

In order to test the role of the solubility of the Zn source on willemite morphology, ZnO was used as the starting material along with either silica sol or gel. At 225 °C, agglomerated small platy particles formed in these systems. Fig. 9 is the SEM micrograph of the synthesized powder using silica gel. Due to the lower solubility of coarse ZnO powder, the nucleation appears to be heterogeneous on the surface of the ZnO particles Fig. 9 [13]. Subsequent willemite particles appear to grow epitaxially on the surface of the original willemite particles from the total dissolution of ZnO and silica gel.

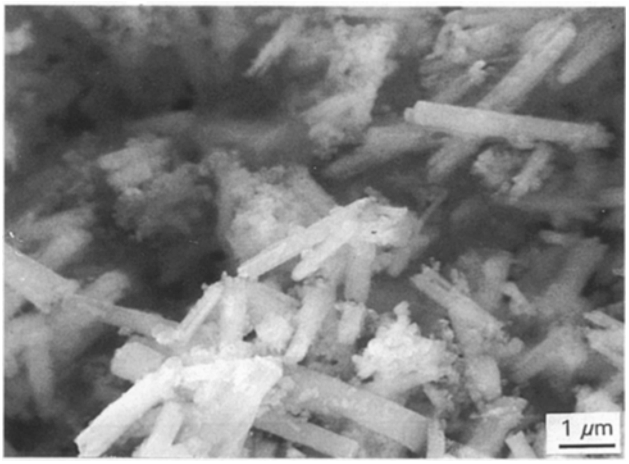

Figure 10 Scanning electron micrograph of hydrothermally prepared willemite using Zn_2SiO_4 gel and $(NH_4)_2SO_4$ at 225 °C 24 h.

3.5. The role of the single phase gel on willemite morphology

When a single phase gel was used as a starting material for the hydrothermal synthesis of willemite, the addition of $(NH_4)_2SO_4$ was necessary to form the phase at 225 °C. When the gel was treated at 225 °C in water without $(NH_4)_2SO_4$, the willemite phase did not form. The morphology of the willemite phase synthesized from the single phase gel is shown in Fig. 10. The concentration of SO_4^{2-} and pH in this system are the same as those in the $ZnSO_4$ and NH_4OH system (see above), but the willemite morphologies are different, Figs 3a and 10.

3.6. The role of PO_4^{3-}, Cl^- and CO_3^{2-} as starting Zn sources, in the synthesis of willemite

Willemite did not form from these Zn sources when treated hydrothermally with silica sol up to a temperature of 240 °C and using a starting pH of ~ 7.

4. Conclusions

The zinc source, $ZnSO_4$, was found to be the best for obtaining equiaxed or spherical Zn_2SiO_4 particles in ammonia under hydrothermal conditions irrespective of the silica sources. By controlling the $NH_4OH:Zn^{2+}$ ratio and the solubility of the SiO_2 source, different size particles can be obtained which have a quasi-spherical shape. Controlled pO_2 in the bomb is essential for Mn^{2+} doping in willemite, because Mn^{2+} is easily oxidized under hydrothermal conditions.

Acknowledgements

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