Morphological aspects and optical properties of Ag$_4$P$_2$O$_7$

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**ABSTRACT**

The structural, morphological and optical properties of silver pyrophosphate (Ag$_4$P$_2$O$_7$) powders were investigated in detail. This material was synthesized by chemical precipitation (CP), conventional hydrothermal and microwave-assisted hydrothermal. The crystallization of hexagonal Ag$_4$P$_2$O$_7$ phase presented a dependence with both temperature and synthesis approach. A system composed of doughnut/hexagonal-shaped microparticles was evidenced for the powders obtained by CP. The hydrothermal treatments modified these particle shapes. Ultraviolet–visible spectra revealed a band gap controlled by indirect electronic transitions. Broadband photoluminescence spectra with maximum emissions in blue region were detected, suggesting the participation of several intermediary energy levels in the band gap.

1. Introduction

In Physics, color is defined as a visual sensation received by the brain, as a result from the detection of light interacted (absorbed, reflected and/or transmitted) with an object [1]. The human eyes have capacity of perceiving a small part of the spectrum of electromagnetic waves, i.e., an interval from 380 to 780 nm (visible light spectrum) [2]. Commercially, there is an enormous interest of multinational companies specialized in light-emitting devices of finding new luminescent materials with adjustable visible light emissions for the improvement of lasers, light-emitting diodes, lamps, displays and so on.

In recent years, photoluminescence (PL) emissions of different silver-based semiconductors have been widely studied for these technological purposes [3,4]. However, few studies have been focused on the physical and chemical properties of silver pyrophosphate (Ag$_4$P$_2$O$_7$). In our knowing, Takahashi et al. [5] were the first to investigate this oxide by analyzing its ionic conductivity properties. It was only from 1986, when Koizumi et al. [6] published their research on high-pressure polymorphs in Ag$_4$P$_2$O$_7$ single crystals, that the structural features of this material began to be explored [7,8].

In the present study, Ag$_4$P$_2$O$_7$ powders were synthesized via different approaches: chemical precipitation (CP), conventional hydrothermal (CH) and microwave-assisted hydrothermal (MH).

The influence of structural and morphological aspects on the PL response at room temperature was also explored.

2. Materials and methods

2.1. Synthesis

Potassium pyrophosphate (K$_3$P$_2$O$_7$, 99%, Aldrich), silver nitrate (AgNO$_3$, 99.8%, Vetec) and ammonium hydroxide (NH$_4$OH, 30%, Synth) were chosen as chemical starting precursors. For the CP reaction, NH$_4$OH was dripped into 0.02 M AgNO$_3$ solution heated at 90°C until a transparent solution formed. Thereafter, 0.025 M K$_4$P$_2$O$_7$ solution was added into the previously prepared mixture, which was maintained for 30 min under stirring. The obtained precipitates were centrifuged, washed with deionized water/acetone, and dried at 60°C for 2 h. This experimental procedure was also adopted in CH and MH, except that after mixing both AgNO$_3$ and K$_4$P$_2$O$_7$ solutions, the resulting solution was immediately transferred into an autoclave (stainless – CH and Teflon – MH). The hydrothermal treatment was performed at 100, 120 and 140°C for 1 h.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a XRD-6000 diffractometer (Shimadzu, Japan) with CuKα radiation ($λ = 0.154184$ nm) by using a scanning rate of 0.2°/min and step size of 0.02°. Raman spectra were registered on a Senterra
Raman scattering microscope (Bruker Optik, Germany) equipped with a laser of 532 nm and operated at 2 mW. The infrared (IR) spectrum was acquired on an Equinox 55 Fourier-transform infrared spectrometer (Varian, USA) operated in diffuse-reflection mode. PL spectra were analyzed at room temperature on a Fluorolog-3 FL3-122 spectrofluorometer (Horiba Jobin Yvon, Japan) equipped with a xenon lamp (450 W).

3. Results and discussion

Fig. 1 (A-B) shows the XRD patterns of as-synthesized powders. In a first observation, Ag₄P₂O₇ formed by the CP reaction presented a typical diffractogram belongs to hexagonal phase, as reported in other published studies [6,7,9]. In this case, CP performed at 90°C for 30 min provided a thermodynamically favorable condition for the gradual decomposition of silver diamine complex, [Ag(NH₃)₂]⁺. The Ag⁺ ions released in solution were bound to those of P₂O₇⁴⁻, forming the Ag₄P₂O₇ phase (Eqs. (1)–(4) and Fig. S1 in Supplementary Data (SD)):

\[
2\text{NH}_4\text{OH}^{\text{aq}} + 2\text{AgNO}_3^{\text{aq}} \rightarrow \text{Ag}_2\text{O}^{\text{s}} + 2\text{NH}_4\text{NO}_3^{\text{aq}} + \text{H}_2\text{O}^{\text{l}} \quad (1)
\]

\[
\text{Ag}_2\text{O}^{\text{s}} + 4\text{NH}_3^{\text{aq}} + \text{H}_2\text{O}^{\text{l}} \rightarrow 2[\text{Ag(NH}_3)_2]^{\text{aq}}^{\text{+}} + 2\text{OH}^{\text{aq}} \quad (2)
\]

\[
[\text{Ag(NH}_3)_2]^{\text{aq}}^{\text{+}} \rightarrow \text{Ag}^{\text{aq}}^{\text{+}} + 2\text{NH}_3^{\text{aq}} \quad (3)
\]

\[
4\text{Ag}^{\text{aq}}^{\text{+}} + [\text{P}_2\text{O}_7]^{\text{aq}}^{\text{+}} \rightarrow \text{Ag}_4\text{P}_2\text{O}_7^{\downarrow} \quad (4)
\]

A curious behavior was detected for the powders conditioned to the CH environmental, which were influenced by the temperature processing. At 100°C, a preferred crystallographic orientation phenomenon was identified because of strong XRD peaks found at 26.0° and 39.6°, corresponding to (0 0 1 2) and (0 0 1 8) planes, respectively. This behavior can be ascribed to slow transferring energy (thermal conduction and convection) imposed by the CH, whose reaction system takes much longer to achieve the target temperature. Therefore, the crystallites in the material had sufficient time to orient themselves in certain crystallographic planes. This preferred orientation was not observed at 120°C. When the temperature was increased at 140°C, a phase transition from Ag₄-P₂O₇ to silver phosphate (Ag₃PO₄) was perceived (* in Fig. 1 (A)). This Ag₃PO₄ phase was formed due to hydration of P₂O₇⁴⁻ [7].

Adopting these same temperatures in MH, in which the microwaves were the energy source, XRD patterns showed peaks related to hexagonal phase. No signal of preferential orientation was observed; however, small traces of Ag₃PO₄ was evidenced for the powders hydrothermalized at 140°C (* in Fig. 1 (B)). These results denote that the microwave irradiation promoted a fast and homogeneous heating of the solution (dipolar polarization and ionic conduction), accelerating the decomposition of [Ag(NH₃)₂]⁺ to release Ag⁺ ions [10]. Although these events were very fast, the system was not able to stabilize only the Ag₄P₂O₇ phase at 140°C.

Infrared spectroscopy was used as a tool to extract any structural information of Ag₄P₂O₇ as well as to probe the possible molecules adsorbed. In IR spectra (Fig. 1 (C-D)), four absorption bands assigned to P₂O₇⁻ were distinguished at around 546 (ν₃POP), 705 (ν₂POP), 907 (ν₁POP) and 1117 cm⁻¹ (ν₃PO₃) [11]. The bands from 2800 to 3350 cm⁻¹ are arising from N—H and O—H bonds, as a consequence of ammonia and water molecules adsorbed on the powders. The other band of water adsorbed was seen at 1667 cm⁻¹. It is
important to emphasize that the powders synthesized at 140 °C in CH presented a band at 1014 cm⁻¹ provoked by PO₄³⁻ [10]. To corroborate with the structural data of as-synthesized powders, the Raman spectroscopy was also performed. All Raman spectra revealed characteristic Raman-active bands related to vibrational frequencies of P₂O₇⁴⁻ (Fig. S2 in SD).

Exploring the morphological behavior via SEM images, a system composed of doughnut/hexagonal-shaped microparticles was

Fig. 2. SEM images of Ag₅P₂O₇ powders synthesized by (A) CP and CH at 100 °C (B), 120 °C (C) and 140 °C (D) for 1 h.

Fig. 3. Excitation and emission PL spectra of Ag₅P₂O₇ powders synthesized by (A) CP and (B-D) CH. Insets show the respective Egap.
observed for Ag₄P₂O₇ synthesized by the CP. These particle shapes also presented surface defects (irregularities), Fig. 2(A). The temperature was the driving force to promote the break of [Ag(NH₃)₂]⁺ and induce the supersaturation of the solution. Hence, the morphological control was affected in CP by a competitive effect between nucleation and growth. Due to the slow release of Ag⁺ ions in a saturated medium of P₂O₇³⁻, some nuclei were being formed while other particles were evolving to a grow stage. When submitted to CH at 100 and 120 °C, these microparticles grew, but they presented a morphological fragility (easily breakable), Fig. 2(B-C). These morphological changes can be arising from a dissolution-recrystallization process in a classical crystallization pathway [12]. As provided by XRD, the temperature of 140 °C favored only the growth of rhombic dodecahedron-shaped Ag₄PO₄ microparticles, Fig. 2(D) [10].

A similar behavior of these microparticles was noted in MH; however, several surface defects were verified in the microparticles submitted at 120 °C. In addition, at 140 °C was registered a mixture of hexagonal-shaped Ag₄P₂O₇ microparticles and rhombic dodecahedron-shaped Ag₄PO₄ microparticles in a same system (Fig. S3 in SD), in agreement with XRD patterns.

The optical band gap energy (Egap) was estimated via UV–vis spectroscopy by employing the Kubelka-Munk method [13] for indirect transitions [14]. The Egap values slightly oscillated from 3.36 to 3.41 eV, the only exception was the powder treated at 140 °C in CH (2.44 eV) because the single Ag₃PO₄ phase (Fig. 3 and Fig. S4 in SD).

In relation to excitation spectra was identified maximum points from 376 nm (3.3 eV) to 400 nm (3.1 eV). When compared to Egap results, the electronic transitions were arising from intermediary energy levels in the band gap (deep- and shallow-level defect states) due to distortions on P-O bonds of P₂O₇³⁻ [3,15]. This information can be confirmed by PL emission spectra, which exhibited a broadband profile. The maximum emissions were verified in violet/ blue regions, indicating a superior contribution of shallow-level defect states (Fig. 3 and Fig. S4 in SD).

4. Conclusion

Ag₄P₂O₇ powders were successfully prepared via CP, CH and MH approaches. Single hexagonal Ag₄P₂O₇ phase was obtained by CP and hydrothermal treatments performed at 100 and 120 °C. The break of [Ag(NH₃)₂]⁺ contributed to the appearance of doughnut/hexagonal-shaped microparticles. These microparticles grew and became easily broken in CH and MH. The maximum blue PL emissions were related to additional levels caused by shallow-level defect states.

Conflict of interest

None declared.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.04.038.

References