CHAPTER 4

CONCLUSIONS AND SUGGESTIONS

4.1 Conclusions

4.1.1 Microwave irradiation method

Microwave irradiation method as a heating method has been found and developed for a number of applications in chemistry and ceramic processing. Compared with the usual methods, microwave synthesis has the advantages as very simple, very short reaction time, inexpensive, small particle size, narrow particle size distribution and high purity. It can be applied for the synthesis of other nanomaterials.

4.1.2 Synthesis of $LaPO_4$ by microwave irradiation method

In this research, hexagonal $LaPO_4$ nanorods were successfully synthesized from Lanthanum (III) Chloride heptahydrate ($LaCl_3 \cdot 7H_2O$) and tri-sodium phosphate ($Na_3PO_4 \cdot 12H_2O$), as starting reagent, in DI water by microwave radiation method. The variety of the pH value of the precursor solutions and the mechanism on the formation of $LaPO_4$ nanocrystalline were studied and discussed. The products were characterized by XRD, FT-IR, SEM, TEM, UV-vis NIR and PL spectroscopy. The XRD patterns revealed pure hexagonal structured $LaPO_4$ phase by comparing with its

JCPDS database. By decreasing the pH value of the precursor solutions from 6 to 1, the crystalline $LaPO_4$ and particle size were improved and larger. Thus the condition at 180 W and 60 min was selected to study the effect of pH value of the precursor solutions. FT-IR spectra presented the vibration modes as $A_1(R) + E(R) + 2F_2(IR+R)$. The $\upsilon_1(A_1)$ and $\upsilon_2(E)$ corresponding to the symmetric stretching and bending modes are Raman active. Their morphologies analyzed by SEM and TEM showed the nanoparticles, short nanorods and long nanorods, which were controlled by the pH value of the precursor solutions. The $LaPO_4$ product was prepared at pH 1 are the longest nanorods. Whereas, the products prepared at higher pH value were became short nanorods and nanoparticles, respectively. It was concluded that pH is a key factor to control the $LaPO_4$ morphologies, by changing from nanoparticles to 1-D nanorods, due to the increase in the H^+ concentration of the solutions. The optical properties of the product were observed by UV-vis NIR and PL spectroscopy. From UV-vis NIR spectroscopy, the direct band gap of $LaPO_4$ nanorods is 3.64 eV (340 nm) with large red shift. The maximum emission is 410 nm in the violet range, optimized by PL spectroscopy.

4.1.3 Synthesis of $CePO_4$ by microwave irradiation method

In this research, hexagonal and monoclinic $LaPO_4$ nanocrystals were successfully synthesized from Cerium (III) Nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and tri-sodium phosphate ($Na_3PO_4{\cdot}12H_2O$), as starting reagent, in DI water by microwave radiation method. Nitric acid (HNO_3) was used to adjusting pH value of the precursor solutions to 1-5 in DI water, as solvent. The solution was continuously heated by a microwave oven at a time at 180 W for 60 min. The products were analyzed using XRD, FTIR, SEM, TEM, UV-NIR and PL spectroscopy. The pH value of the precursor solutions and the mechanism on the formation of $LaPO_4$ nanocrystalline were studied and discussed. The XRD patterns were indentified to correspond with the pure monoclinic $CePO_4$ phase for the product synthesized in the solution pH of 1, and hexagonal $CePO_4$ phase for the pH of 2, 3, 4, and 5, comparing with its JCPDS database. By decreasing the pH value of the precursor solutions from 5 to 1, the crystalline $CePO_4$ (shape peak) and rod size were improved and larger. Thus the condition of 180 W and 60 min was selected to study the effect of pH value of the precursor solutions. FT-IR spectra presented the vibration modes as $A_1(R) + E(R) + 2F_2(IR+R)$. The $\upsilon_1(A_1)$ and $\upsilon_2(E)$ corresponding to the symmetric stretching and bending modes are Raman active. No vibration of NO_3^- anions were detected in these spectra, proving that the as-synthesized $CePO_4$ nanostructures has very high purity, confirmed by the XRD results. Their morphologies were analyzed by SEM and TEM, which showed nanoparticles (pH 3-5), short nanorods (pH 2), long nanorods (pH 1.5) and nanowires (pH 1) - controlled by the pH values of the precursor solutions. These were summarized that the pH values of the precursor solutions are a key factor to control the $CePO_4$ morphologies, by changing from nanoparticles to 1-D nanorods and nanowires, due to the increase in the H^+ concentration of the solutions led the maximum chemical potentials and optimum ionic motion of the ion in the solution. The optical properties of the product were observed by UV-vis NIR and PL spectroscopy. UV-vis NIR spectroscopy revealed the $^2F_{5/2} \rightarrow {}^2D_{3/2}$ and $^2F_{5/2} \rightarrow {}^2D_{5/2}$ transition in the spectra. The direct band gap of $CePO_4$ nanorods is 4.1 eV. Using PL spectroscopy, the maximum emission is 419 nm in the violet range.

4.2 Suggestions

1. Synthesis of $LaPO_4$ and $CePO_4$ nanostructures by microwave irradiation method should be compared to the conventional heating process.

2. The other effects such as base, solvent, mole ratio of Ln (La,Ce) and phosphate and reaction time should be studied as well.

3. Synthesis of other novel rare earth phosphate complexes, such as $GdPO_4$, $EuPO_4$, and etc., by microwave irradiation method should be studied as well.