

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 ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$) and tri-sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), 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 $A_1(\text{R}) + E(\text{R}) + 2F_2(\text{IR}+\text{R})$. The $\nu_1(A_1)$ and $\nu_2(E)$ 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 ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and tri-sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$), 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 identified 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 $A_1(\text{R}) + E(\text{R}) + 2F_2(\text{IR}+\text{R})$. The $\nu_1(A_1)$ and $\nu_2(E)$ 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.