Preparation for Spherical particles of Praseodymium doped Perovskite Red Phosphor by Hydrothermal Reaction

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Abstract. Spherical particles of 0.5mol\% Pr\textsuperscript{3+}-doped CaTiO\textsubscript{3} were prepared by hydrothermal reaction on dissolved CaCl\textsubscript{2}, Pr(NO\textsubscript{3})\textsubscript{3}, and ammonium citratoperoxotitanate (IV) complex precursor solution with molar ratio of Ti/CA=1:2 and calcination in ambient atmosphere. The obtained particle exhibited red photoluminescence at 610nm. It is found that several particles have hollow structure. It is required that further investigation is needed to clarify the formation mechanism of these spherical hollow paricles.

1. Introduction

Pr\textsuperscript{3+}-doped perovskite-type titanates like CaTiO\textsubscript{3}[1-3], SrTiO\textsubscript{3}[4-6], and BaTiO\textsubscript{3}[7,8] have been considered as attractive phosphors for field-emission display[4,9] since these materials exhibit closely ideal red emission. Previous studies with regard to Pr\textsuperscript{3+}-doped CaTiO\textsubscript{3} prepared by solid-state reaction or liquid phase reaction proposed that their red emission ascribe to the f-f transition of Pr\textsuperscript{3+} occurs via the band-gapand inter-valence charge transfer photo-excitation processes[10,11].

From the standpoint of powder preparation for the desired morphology and chemical uniformity, liquid phase process have many benefit. However, titanium tetrachloride or titanium isopropoxide, which are usually utilized as liquid titanium compounds, are susceptible to hydrolysis. Therefore, the preparation are required to conduct in a dry inert atmosphere. Recently, Professor Kakihana and his group developed water-soluble titanium complex (ammonium citratoperoxotitanate (IV)) and reported that the chemical formula is (NH\textsubscript{4})\textsubscript{8} [Ti\textsubscript{4}(C\textsubscript{6}H\textsubscript{4}O\textsubscript{7})\textsubscript{4}(O\textsubscript{2})\textsubscript{4}] \cdot 8H\textsubscript{2}O based on the results of single crystal x-ray diffraction [12].

Though it is known that the synthesis of uniform precipitate is relatively difficult by hydrothermal reaction due to the difference in hydrolysis rate of dissolved metal compound, citric acid as chelate ligands can act to yield a polyester network in which metal ion are dispersed uniformly [13]. Thus, hydrothermal reaction on precursor solution with dissolved citric acid as a chelating agent is a promising method for preparation of uniformprecipitates under specific conditions.

In this article, 0.5mol\% Pr\textsuperscript{3+}-doped CaTiO\textsubscript{3} red phosphor was prepared by hydrothermal synthesis on dissolved CaCl\textsubscript{2}, Pr(NO\textsubscript{3})\textsubscript{3}, and water-soluble titanium complex precursor solution and calcination in ambient atmosphere. We investigated the crystal structure, morphology, and photoluminescence of the powder obtained.
2. Experimental

Water-soluble Ti complex solution was prepared according to paper of Professor Kakihana’s group [12]. $5 \times 10^{-3}$ mol of Ti powder was dissolved into 20ml of 30% H$_2$O$_2$ and 5ml of 28% NH$_3$ solution to obtain a yellowish peroxy titanous acid solution with pH≈11. When the excess of H$_2$O$_2$ is decomposed, prescribed amount of citric acid (CA) was dissolved into this peroxy titanous acid solution with continuous stirring. After evaporative drying, yellow gel formed. This gel was dissolved into ion exchange water to make a water-soluble Ti complex solution with Ti concentration of 0.25mol/L.

Thereafter, CaCl$_2$ and Pr(NO$_3$)$_3$ solutions were added to the Ti complex solution and finally the precursor solution was prepared with molar ratio of Ti:Ca:Pr=1:1:0.005. The PTFE vessel introducing 20ml of transparent precursor solution was sealed in a stainless lined autoclave and hydrothermally heated at 423K for 24h. After the autoclave was cooled to room temperature, the precipitate was centrifugally separated and dried at 383K for 18h. Finally, the precipitate was calcined at 1023K for 1h in ambient atmosphere and then sample powder was obtained.

The X-ray diffraction (XRD) analysis of the obtained powder before and after calcination was carried out using CuKα radiation by Rigaku Ultima IV Multipurpose X-ray Diffraction system equipped with D/teXUltra-high-speed, position-sensitive detector. The morphology and chemical composition of the powder were investigated using Hitachi SU8020 field-emission scanning electron microscopy equipped with Horiba EMAX Evolution X-Max SDD detector. The photoluminescence measurement were performed at room temperature using Shimadzu RF-6000 spectrofluorophotometer with L42 long pass filter.

3. Results and discussion

Figure 1(a) shows XRD pattern of powder prepared from the precursor solution dissolving citric acid (CA) with Ti/CA=1:5 ratio and calcined at 1023K for 1h. XRD analysis revealed that perovskite (CaTiO$_3$) and anatase (TiO$_2$) phases dominate in the structure indicating calcium and titanium ions are inhomogeneously distributed in the powder.

Figure 1(b) shows the SEM image of the as-prepared powder. The powder involved a spherical particle of 2-3μm in diameter. EDS analysis revealed that chemical composition of the spherical particle is 3.0at% Ca, 31.3at% Ti and 65.7 at% O. Considering Ca ion distributed other region in the powder, the excess amount of CA in the precursor solution lead to inhibit co-precipitation reaction with Ca ion stabilizing water-soluble Ti complex. Therefore, it is indicated that the controlling for hydrolysis rate of Ti complex govern the chemical homogeneity of precipitate obtained by hydrothermal reaction.

![Figure 1](image1.png)
Then, we conducted the preparation using the precursor solution with Ti/CA=1:2 ratio to stimulate the co-precipitation reaction with Ca\(^{2+}\) and Ti\(^{4+}\). XRD revealed that the powder has amorphous-like structure after hydrothermal reaction at 423K for 24h and calcination at 1023K for 1h resulted in the formation of perovskite single phase as shown in Figure 2.

![Figure 2](image)

**Figure 2.**

SEM observation demonstrated that the powder contain considerable amounts of spherical particles with 2-3\(\mu\)m in diameter as shown in Figure 3 (a). EDS analysis confirmed that these spherical particles have chemical composition of 14.3at% Ca, 23.8at% Ti, and 61.9 at% O. These spherical particles exhibited red photoluminescence at 610nm, which is corresponded to the ones by previous works [14].

![Figure 3](image)

**Figure 3.** SEM images of (a) obtained spherical and (b) spherical hollow particles by hydrothermal reaction on the precursor solution with Ti/CA=1:2 at 423K for 24h and calcination at 1023K for 1h

We discovered spherical hollow particle in the powder during SEM observation as shown in Figure 3(b). Recently, one-pot synthesis for porous hollow La\(_2\)O\(_2\)CO\(_3\) microspheres using hydrothermal treatment of glucose and La(NO\(_3\))\(_3\) \(\cdot\)6H\(_2\)O, and subsequent calcination was reported [15]. The authors proposed the formation process of the hollow sphere as follows. Firstly, carbonaceous polysaccharide microspheres binding La\(^{3+}\) were formed via hydrothermal treatment of glucose/water/melt salt. Then, the sequential removal of carbon cores, densification, cross-linking, and phase transformation of La in the layer via calcination result in the formation of the hollow spheres. Though polysaccharide like glucose isn’t contained in our precursor solution, we speculated that formation process like mentioned above is proceeded during our hydrothermal reaction.
Figure 4 shows XRD patterns of obtained powders by calcination at 1023K for 1h after hydrothermal reaction at 423K for 6, 12, 18, and 24h. It is demonstrated that Ca rich phase dominated in the powder in the early stage of hydrothermal reaction and CaTiO$_3$ ratio was increased as time course. These results indicated that hydrolysis reaction of metal ion isn’t proceeded simultaneously even in present condition and chemically homogeneous particle are formed inducing resolve and precipitation reactions. However, we considered that further investigations are needed to clarify the formation mechanism of Pr$^{3+}$ doped CaTiO$_3$ spherical hollow particles.

4. Conclusion

The hydrothermal synthesis on dissolved CaCl$_2$, Pr(NO$_3$)$_3$, and ammonium citratoperoxotitanate complex precursor solution with Ti/CA=1:2 at 423K for 24h caused to form precipitates which have amorphous-like structure and spherical morphology. The precipitates calcined at 1023K for 1h have perovskite single phase structure exhibiting red photoluminescence at 610nm. We proposed the formation mechanism of Pr$^{3+}$ doped CaTiO$_3$ spherical hollow particles. However, further investigation is required.

References

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