Development of new solution method using citric acid and ethylenediamine for borate compounds

Yuma MATSUMOTO,* Koji TOMITA,** Yoshika SEKINE*** and Masato KAKIHANA***

*School of Earth and Environmental Sciences, Tokai University, 4–1–1 Kitakaname, Hiratsuka, Kanagawa 259–1292
**Department of Chemistry School of Science, Tokai University, 4–1–1 Kitakaname, Hiratsuka, Kanagawa 259–1292
***Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2–1–1 Katahira, Aoba-ku, Sendai 980–8577

A new solution method that can be used to synthesize borate compounds was developed using citric acid and ethylenediamine. The conventional polymerizable complex method (polyester method) has a significant advantage in terms of homogeneity of the precursor, and it has been utilized in the synthesis of numerous oxide ceramics. However, it is very difficult to synthesize borate compounds by the conventional polymerizable complex method because boron reacts with the glycol that is necessary for the polymerization as polyester and is volatilized from the solution. In this paper, functional borate compounds such as YBO3:Eu4+, InBO3, and K3Ta3B2O12 were synthesized by the conventional polyester-type polymerizable complex method as well as the new solution method. In the polyester method, citric acid was dissolved in propylene glycol and the component metal salts were then dissolved in the solution. In the method that we propose in this paper, citric acid and ethylenediamine were dissolved in distilled water, and component metal salts were added to the solution. All solutions were heated at 403 K with stirring for the polymerization reaction to proceed, yielding polymer resins. The resins were heated to 723 K and powder precursors were obtained. The precursors were calcined under various temperature conditions. In the case of YBO3:Eu4+, the formed product was Y2O3 by the polyester method due to volatilization of boron. On the other hand, single-phase YBO3:Eu4+ was synthesized by the new method. YBO3:Eu4+ synthesized by the method showed higher photoluminescence intensity than samples synthesized by a solid-state reaction method and the complex gelation method. Synthesis of single phase InBO3 and K3Ta3B2O12 was also successfully demonstrated by the method using a very small excess amount of H3BO3.

Key-words: Solution method, Polymerizable complex method, Photocatalyst, Phosphor

1. Introduction

There are roughly three types of methods to synthesize ceramics, solid phase methods (solid-state methods), liquid phase methods (solution methods) and gas phase methods. In a solid-state method, ceramics are synthesized by pulverizing and mixing various solid raw materials, and subsequently calcining the mixtures. However, calcination for long times at high temperatures is needed in this method since it requires volume diffusion of the composition metal ions. Furthermore, this method is not suitable for doping small amounts of elements, because there is not sufficient homogeneity at the ion size level. The gas phase method has various disadvantages, including difficulties in mass production as well as typically high cost. In contrast, in the case of solution methods, since the starting materials are dissolved and mixed in liquids, homogeneous mixing becomes possible at the molecule/atom level. This allows for ease of grain boundary diffusion/surface diffusion resulting in lower temperatures and shorter times for the calcination conditions, which is a significant advantage. These conditions also make solution methods suitable for industrial mass-production.

There are various solution methods available, such as the co-precipitation method, the sol–gel method, the complex gelation method and the polymerizable complex method. Kakihana compared these solution methods and clarified the characteristics and disadvantages of each method.1) In the co-precipitation method, multiple metals that comprise the composition form precipitates in the reaction solution simultaneously. However, conditions for precipitation reaction of each element are different because each has a different solubility product resulting in inhomogeneity of the precipitate. In the sol–gel method, multiple metals generate gel precursors by heating metal alkoxides to cause hydrolysis. However, it is very difficult to adjust the hydrolysis rate of each element in the composition. Therefore, inhomogeneous precursors are obtained when the reaction condition is not appropriate. In the complex gelation method, each metal ion forms a complex with a complexant agent such as citric acid. By removing the solvent, such as water, the complexes and remaining complexant species forms a gel in which the bonds of each component are weak hydrogen bonds. These weak bonds cannot prevent segregation of metal ions resulting in inhomogeneity of the precursors. Therefore, it is very difficult to obtain a homogeneous precursor by the solution methods mentioned above.

The polymerizable complex method was developed by Kakihana et al. solves these problems. The polymerizable complex method uses citric acid to form metal complexes and to form a polyester precursor with glycol (polyester method). There is no precipitation involved in this process, which is a big advantage in terms of homogeneity of the precursor compared to the co-precipitation and sol–gel methods. However, the polyester method has a problem for the synthesis of compounds containing boron in this process, boron volatilizes out of the system.

©2011 The Ceramic Society of Japan

[Received March 2, 2011; Accepted April 7, 2011]
reacting with the glycol that is used in the polyester method.\(^{31}\) Our aim in this work was to synthesize materials containing boron by developing a new solution method that uses ethylenediamine instead of glycol to form a polyamide precursor with citric acid (CE method).

While there are a variety of ceramic materials that contain boron, in this study, we synthesized three different materials, K\(_3\)Ta\(_3\)B\(_2\)O\(_{12}\), InBO\(_3\) and YBO\(_3\):Eu\(^{3+}\). K\(_3\)Ta\(_3\)B\(_2\)O\(_{12}\) is a photocatalyst for water splitting, discovered by Ikeda et al.\(^{3-5}\) It has been reported that this photocatalyst generates H\(_2\) at a rate of 2.39 mmol/h without a co-catalyst, which is typically required for photocatalytic water-splitting reactions. InBO\(_3\) shows high activity as a photocatalyst for water splitting and is also used as a phosphor. InBO\(_3\) shows strong luminescence when doped with rare-earth ions as an activator.\(^{10-15}\) YBO\(_3\):Eu\(^{3+}\) is a well-known red phosphor used in plasma displays and fluorescent lamps; it has been the subject of extensive research in recent years.\(^{6-9}\) In this study, these three materials containing boron were synthesized by the CE method.

2. Experimental

2.1 CE method and polyester method

KNO\(_3\), Y(NO\(_3\))\(_3\), EuO\(_3\) and In\(_2\)O\(_3\) were used as starting materials of the corresponding metals. The chloride ion reacts with boron, and the boron volatilizes. Therefore, in order to remove chloride ions, TaCl\(_3\) was suspended in H\(_2\)O and dissolved by adding NH\(_3\) aq. Methanol was then added and a white precipitate was obtained. This precipitate was filtered and again dissolved in H\(_2\)O and NH\(_3\) solution to form a transparent peroxotantalic acid complex solution. Since Eu\(_2\)O\(_3\) and In\(_2\)O\(_3\) are not soluble in water, they were suspended in H\(_2\)O to be dissolved by heating at 363 K along with stirring for one day. These solutions were evaporated once and dissolved again in distilled water. Each metallic starting material and H\(_2\)BO\(_3\) were then dissolved in distilled water and citric acid was added. Here, 0–5 mol % excess H\(_2\)BO\(_3\) was added for the synthesis of InBO\(_3\), and 0–40 mol % excess H\(_2\)BO\(_3\) was added for the synthesis of K\(_3\)Ta\(_3\)B\(_2\)O\(_{12}\). Ethylenediamine was added here in the CE method. Propylene glycol was added here in the polyester method. The molar ratio of the total metal ions (M), citric acid (CA) and ethylenediamine (en) was M:CA:en = 1:5:20. The molar ratio in the polyester method was M:CA:PG = 1:5:20 (PG = propylene glycol). The mixture solutions were heat-treated using a hot stirrer at 403 K to form resinous precursors. The precursors were thermally decomposed at 723 K and powder precursors were obtained. The precursors were calcined for 5 h in air at different temperatures.

2.2 Solid state method

Y\(_2\)O\(_3\) and H\(_3\)BO\(_4\) along with Eu\(_2\)O\(_3\) were mixed well for 30 min in an agate mortar. The mixture was calcined in air for 5 h at 1073 K.

2.3 Complex gelation method

Y(NO\(_3\))\(_3\) and H\(_3\)BO\(_4\) were dissolved in distilled water. Eu\(_2\)O\(_3\) was dissolved in a nitric acid aqueous solution which was added to the Y(NO\(_3\))\(_3\) and HBO\(_4\) solution. Citric acid was added here as a complexant agent. The molar ratio of the total metal ions (M) and citric acid (CA) was M:CA = 1:5. The complex solution was heated and evaporated using a hot stirrer at 373 K. After evaporation, the formed gel was thermally decomposed at 723 K and a powder precursor was obtained. This powder precursor was calcined at 1073 K for 5 h in air.

2.4 Characterization

The IR spectrum of the resin prepared from only citric acid and ethylenediamine without the metals was obtained using an infrared spectrophotometer. Simultaneous differential thermogravimetry (TGA) measurements of the precursors obtained with the CE method was carried out. The phase purity of the calcined products was checked using XRD. The fluorescence spectrum of the synthesized YBO\(_3\):Eu\(^{3+}\) was measured with a fluorometer.

3. Results and discussion

IR was used to check for the formation of amide bonds in the prepared resinous precursor. Results of the IR measurement are shown in Fig. 1. Peaks specific to citric acid and ethylenediamine were not detected in the IR spectrum of the resinous precursor. In the IR spectrum, peaks appeared at 3300 and 1650 cm\(^{-1}\). Since peaks at 3300 and 1650 cm\(^{-1}\) are identified as N–H, O–H absorption and C=O absorption in the amide bond respectively, suggesting formation of amide bond.

TG and DTA data for the precursors of each sample prepared by the CE method are shown in Figs. 2 and 3 respectively. There were no major differences in the TG and DTA results among the samples. Weight loss due to heating from room temperature to 473 K is caused by evaporation of the adsorbed water due to the endothermic reaction, and this appeared in the DTA results. The strong exothermic reaction and large weight loss between 673 and 873 K are caused by calcination of organics. The gradual weight loss between 873 and 1073 K is caused by volatilization of nitrate and carbonate ions originating from the starting materials and organics. Small heat generation is observed at 1073 K in the DTA curves of YBO\(_3\):Eu\(^{3+}\) and InBO\(_3\) indicating crystallization of each phase.

XRD patterns from the YBO\(_3\):Eu\(^{3+}\) synthesized by the polyester method and the CE method are shown in Fig. 4. The peaks from the sample synthesized by the polyester method correspond to Y\(_2\)O\(_3\) peaks. This means that boron was volatilized from the solution, by reacting with propylene glycol. Volatilization of boron was not observed in the CE method and single phase YBO\(_3\):Eu\(^{3+}\) was obtained. It should be noted that stoichiometric amount of boric acid was used here.

In order to clarify the homogeneity of the prepared samples by the CE method, the luminescence intensities of the YBO\(_3\):Eu\(^{3+}\) synthesized by the solid-state method, the complex gelation method and the CE method were compared. XRD patterns from the YBO\(_3\):Eu\(^{3+}\) synthesized by the three methods are shown in Fig. 5. The sample prepared by the solid-state method was a mixed phase of Y\(_2\)O\(_3\) and YBO\(_3\) as seen from the XRD peaks. In
the sample synthesized by the complex gelation method, $Y_2O_3$ peaks were not observed, rather, $YBO_3$ peaks were observed. However, this was not single phase YBO$_3$:Eu$^{3+}$, because some unknown peaks were also observed. Single phase YBO$_3$:Eu$^{3+}$ was obtained only by the CE method as seen from Fig. 5. These results show that the precursor obtained by the CE method has excellent homogeneity, compared with the precursors obtained by the solid-state and the complex gelation methods. Emission spectra of the synthesized YBO$_3$:Eu$^{3+}$ by the three methods are shown in Fig. 6. The emission intensity of the sample obtained by the CE method was stronger than that from the samples obtained using the solid-state and complex gelation methods. It is considered that concentration quenching by cross-relaxation among Eu atoms was suppressed by the homogeneous dispersion of the Eu dopant due to the excellent homogeneity of the precursor for the CE method sample. Therefore we conclude that the CE method yields excellent homogeneity, similar to the polyester method.

The synthesis of InBO$_3$ and $K_3Ta_3B_2O_12$ was carried out next using the CE method in order to explore the possibility of synthesis of other borate materials. XRD patterns from the InBO$_3$ synthesized by the CE method are shown in Fig. 7. A mixed phase of InBO$_3$ and In$_2O_3$ was obtained for all heat-treatment temperatures. As the temperature was raised from 1073 K, the In$_2O_3$ peaks decreased and InBO$_3$ peaks increased in intensity. However, as the temperature was raised up to 1423 K, the InBO$_3$ peak decreased and the In$_2O_3$ peaks increased. The reason for this is considered to be volatilization of boron due to the high calcination temperatures. Since the In$_2O_3$ peak was detected at all calcination temperatures, we synthesized InBO$_3$ by the CE method using a slightly excess amount of H$_3BO_3$. Single phase InBO$_3$ was successfully synthesized when 5% excess amount of H$_3BO_3$ was used. In this case, the boron that volatilizes at high temperatures was likely compensated. The reported synthesis procedure by the two step precipitation method used 10 times
the amount of H$_3$BO$_3$ with respect to the stoichiometric ratio. Compared to that method, the CE method succeeded in synthesizing single phase InBO$_3$ using a very small excess amount of H$_3$BO$_3$, significantly reducing the volatilization of the boron.

The XRD patterns from the K$_3$Ta$_3$B$_2$O$_{12}$ synthesized by the polyester method and the CE method are shown in Fig. 8. The sample synthesized in the stoichiometric ratio by the polyester method resulted in KTaO$_3$, according to the XRD peaks, due to the volatilization of most of the boron. The sample synthesized in the stoichiometric ratio by the CE method resulted in a mixed phase of K$_3$Ta$_3$B$_2$O$_{12}$ and K$_3$Ta$_{10.5}$O$_{30}$. Although the volatilization of boron was suppressed, a part of the boron present was still volatilized. By using 40 mol % excess amount of H$_3$BO$_3$, the synthesis of single phase K$_3$Ta$_3$B$_2$O$_{12}$ was successfully accomplished.

4. Conclusion

We succeeded in developing the CE method using citric acid and ethylenediamine. Using the CE method, borate materials that cannot be synthesized by the conventional polyester method, such as YBO$_3$:Eu$^{3+}$, InBO$_3$, and K$_3$Ta$_3$B$_2$O$_{12}$, were successfully synthesized in the single phase with a very small amount of excess H$_3$BO$_3$. Since absorptions peculiar to the amide bond were detected by IR measurements of the resinous precursor obtained using the CE method, amide bond seems to be formed in the precursor. However, we need more evidences about polymerization to determine that the precursor forms polyamide. The resinous precursor had superior homogeneity, and the synthesized YBO$_3$:Eu$^{3+}$ phosphor by the CE method showed higher fluorescence emission compared with the material obtained using the solid-state method and the complex gelation method. The synthesis of InBO$_3$ and K$_3$Ta$_3$B$_2$O$_{12}$ was also successfully demonstrated using the CE method, indicating that this method can be used for the synthesis of various inorganic materials containing boron.

Acknowledgements This work was partially supported by Grant-in-Aid for Scientific Research (A) (no. 22246081) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

References