Hydrothermal Evolution of the Thiourea−Cerium(III) Nitrate System: Formation of Cerium Hydroxycarbonate and Hydroxysulfate

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Introduction

Rare earth compounds have always been the focus of much interest for their important applications on luminescent lighting, displays, and IR windows.[1] The most frequently studied materials are usually oxides and sulfides. In comparison, as a different type of rare earth compounds, the hydroxide salts have been studied only in terms of crystal structure and thermal analysis.[2] Hydrothermal techniques are effective not only for synthesizing useful materials but also for investigating the formation mechanism of desired compounds in solution.[3,4] Recently, ionic conducting rare earth composite oxides were prepared by a hydrothermal method.[5] Much longer ago, lanthanide basic salts were reported to form in oxide−hydroxide sulfate systems at 400−500 °C during the study of hydrothermal equilibria.[6] However, no photoluminescence properties were reported.

In our work on the low-temperature synthesis of La_2O_2S phosphor, monoclinic $LaOHSO_4$ was produced from an aqueous solution of thiourea and lanthanum nitrate at temperatures above 300 °C.[7] Although the formation mechanism of lanthanum oxysulfide was made clear, the chemical process of the hydroxysulfate remained obscure. Optical measurement of the hydroxysulfate showed extremely poor photoluminescence. Because cerium(III) is more abundant in band gaps than lanthanum(III), the cerium(III) compounds are expected to yield better photoluminescence performance. This work reports an investigation on the reaction mechanism of the thiourea−cerium nitrate(III) system under controlled hydrothermal conditions and examines the photoluminescence properties of compounds obtained from the solutions.

Experimental Section

The reagents used in the experiments are of analytical purity. A typical solution is prepared by dissolving 0.8 g of $Ce(NO_3)_3 \cdot 6H_2O$ and 0.42 g of $CS(NH_2)_2$ into 20 mL of distilled water. Hydrothermal treatment of the solutions was performed in a sealed 25 mL stainless steel vessel. Solutions with the same concentration and volume were treated for 6 h under set temperatures ranging from 50 to 250 °C. Then the vessel was cooled to ambient temperature and opened to collect the product. Separated solid products were washed with distilled water several times and dried in a vacuum at 60 °C for 1 h. The solutions were examined by Raman spectroscopy at room temperature on a Spex-1403 spectrometer. The radiation source was a 100 mW 514.5 nm argon ion laser. The solid samples were characterized by X-ray diffraction (XRD) on a Dandong X-ray diffractometer equipped with graphite-monochromatized Cu Kα radiation. FT-IR spectra were recorded on a Magna IR 750 spectrometer. Scanning electron microscopy (SEM) of crystallites was taken on an X-650 scanning electron microanalyzer. X-ray photoelectron spectra (XPS) were recorded on a MKII electron spectrometer.

By combining the analytical results of solutions and solids, we could understand the evolution of the system under hydrothermal conditions. To examine the PL of the synthesized single phases, we recorded the PL spectra using an 850 fluorescence spectrophotometer.

Results and Discussion

As the temperature is increased, the solution undergoes a significant change due to the decomposition of thiourea and the transformation of anions. The Raman spectra of solutions treated under typical temperatures are shown in Figure 1. There is no perceptible chemical change at temperatures below 140 °C. The peak at 732 cm^{-1} corresponds to the $CS(NH_2)_2$ molecule,[8] and the chemical shift at 1048 cm^{-1} is ascribed to the NO_3^- anion.[9] After the solution was heated at 160 °C, the $CS(NH_2)_2$ peak disappeared almost completely, implying the decomposition of $CS(NH_2)_2$. Furthermore, the characteristic smell of H_2S perceived upon opening the reaction vessel confirms that H_2S is a product of the decomposition. The solution is alkaline with pH 8.5−9, presumably because of dissolved NH_3. Due to the alkalinity, the HS^- and HCO_3^- ions should be present in the solution in addition to H_2S (aq). Therefore, the decomposition reaction could be represented as the following equation:

$$CS(NH_2)_2\,(aq) + 3H_2O \rightarrow 2NH_4^+\,(aq) + HS^-\,(aq) + HCO_3^-\,(aq)$$

A solid is produced from the solution at 160 °C. It is indexed as orthorhombic $CeOHCO_3$ with cell parameters of $a = 5.016$ Å, $b = 8.561$ Å, and $c = 7.311$ Å. The XRD pattern of the single phase is shown in Figure 2a. The SEM of the crystallites reveals them to be shuttle-like. FT-IR spectra demonstrate the presence of absorption peaks of the OH^- group at 3495 cm^{-1} and of the CO_3^{2-} group near 1400 cm^{-1}. The $CeOHCO_3$ may be produced by the four-body collision involving the Ce^{3+}, HCO_3^-, and OH^- ions. However, considering that multi-charged positive ions tend to give acid solutions and form $MOH^{(n-1)+}$ groups,[10] the cerium(III) would be the $CeOH^{2+}$ in the alkaline system. Moreover, the CO_3^{2-} ion, unlike the HCO_3^- ion in the reaction, only requires a two-body collision that appears to be a more realistic reaction, although the concentration of the HCO_3^- ion is greater than that of the CO_3^{2-} ion in solution. The HCO_3^- ion could replenish the CO_3^{2-} ion

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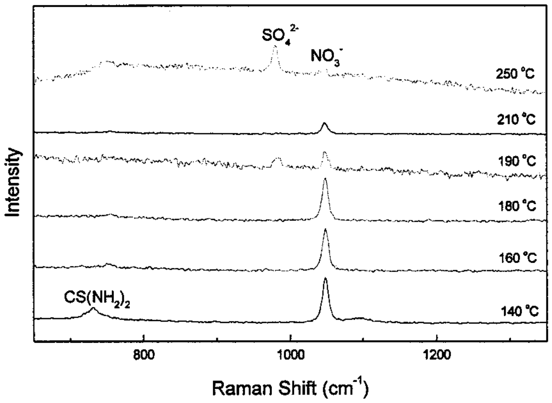

Figure 1. Raman spectra of the thiourea−cerium(III) nitrate systems hydrothermally treated at different temperatures.

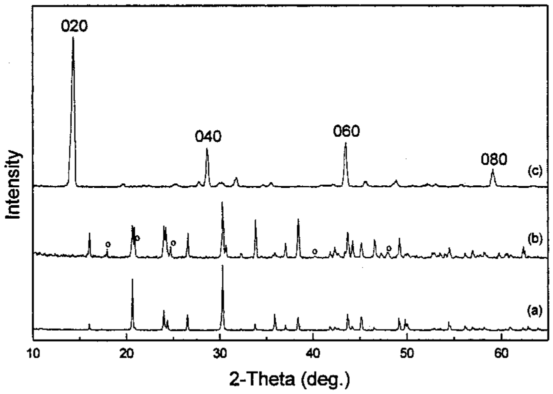

Figure 2. XRD patterns of solid products obtained under hydrothermal conditions: (a) orthorhombic $CeOHCO_3$ produced at 160 °C; (b) orthorhombic $CeOHCO_3$-dominated powders obtained at 190 °C ("o", hexagonal $CeOHCO_3$); (c) monoclinic $CeOHSO_4$ produced at 250 °C.

while the latter anticipates the formation of $CeOHCO_3$.

$$Ce^{3+}\ (aq) + OH^{-}\ (aq) \rightleftharpoons CeOH^{2+}\ (aq)$$

$$HCO_3^{-}\ (aq) + OH^{-}\ (aq) \rightleftharpoons CO_3^{2-}\ (aq) + H_2O$$

$$CeOH^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightarrow CeOHCO_3\ (s)$$

When the solution was treated at 190 °C, SO_4^{2-} was derived, as indicated in the Raman spectrum. The chemical shift of the SO_4^{2-} anion at 980 cm^{-1} in solution is very close to those in solid samples.[11] Similar to the oxidizing lanthanum nitrate,[12] cerium nitrate is an oxidant here and oxidizes the sulfide ion to a higher valence state. It is noteworthy that the NO_3^{-} peak in the Raman spectrum shrinks after an increase in temperature, which implies a decrease in the nitrate anion concentration and, in turn, confirms the nitrate-anion-consuming reaction. As the oxidant, the nitrate ion will be reduced to a lower valence state, more often a nitrogen oxide than the elemental nitrogen. However, the species of nitrogen oxide produced is still unidentified. For example, if the reduced product were elemental N_2 (g), the redox reaction would be expressed as

$$8NO_3^{-}\ (aq) + 5HS^{-}\ (aq) \rightarrow 5SO_4^{2-}\ (aq) + 3OH^{-}\ (aq) + 4N_2\ (g) + H_2O$$

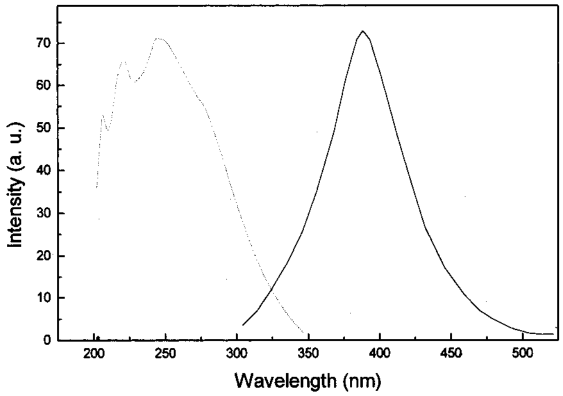

Figure 3. PL spectra of monoclinic $CeOHSO_4$: (a) emission spectrum (solid line) and (b) excitation spectrum (faint, dotted line).

Despite the introduction of the sulfate anion in solution at 190 °C, solid sulfate was not produced simultaneously, but a small amount of orthorhombic $CeOHCO_3$ turned into hexagonal $CeOHCO_3$, as shown in Figure 2b. It seems that the temperature is not high enough to meet the requirement of the solid sulfate formation. When the temperature rises to 210 °C, the SO_4^{2-} peak is absent from the Raman spectrum of the solution. Meanwhile, a new phase, monoclinic $CeOHSO_4$ with the refined cell parameters of $a = 4.503$ Å, $b = 12.513$ Å, $c = 7.137$ Å, and $\beta = 111.060°$, is produced and dominates the solid products. The phenomenon may be explained by the rapid consumption of SO_4^{2-} anions during the formation of hydroxysulfate under suitable conditions. The XRD pattern of the highly crystallized single phase at 250 °C is given in Figure 2c. The Raman spectrum reveals that the mother liquor still contains SO_4^{2-} anions after the solid has become solely hydroxysulfate. Unlike orthorhombic $CeOHCO_3$ crystals, monoclinic $CeOHSO_4$ crystals exhibit unusually strong (0*k*0) diffraction and are flakelike in shape. The XPS of the new phase is recorded. The strong peaks at 886 and 904.4 eV are related to the Ce 3d binding energy for the Ce^{3+} cation; the single peak at 168.7 eV corresponds to the S 2p binding energy in the SO_4^{2-} anion.[13] Sharp peaks of the SO_4^{2-} group at 1070 and 1150 cm^{-1} also appear in the FT-IR spectrum. According to the facts that the SO_4^{2-} anion coexists with $CeOHCO_3$ in the system at lower temperature (190 °C) and the solid product becomes solely $CeOHSO_4$ at higher temperature (250 °C), there most probably is a transformation from $CeOHCO_3$ to $CeOHSO_4$. It may be the quickness of the transformation reaction at suitable temperatures that makes it difficult to collect enough mixture for detection by XRD analysis.

$$CeOHCO_3\ (s) + SO_4^{2-}\ (aq) \rightarrow CeOHSO_4\ (s) + CO_3^{2-}\ (aq)$$

Meanwhile, there is a possibility that $CeOHSO_4$ is produced in a way similar to that of $CeOHCO_3$. This reaction should not be disregarded rashly because it occupies a larger reaction area than does the preceding solid−liquid reaction. Furthermore, the two-body collision is favored by the ample supply of SO_4^{2-} (aq) produced at higher temperatures.

$$CeOH^{2+}\ (aq) + SO_4^{2-}\ (aq) \rightarrow CeOHSO_4\ (s)$$

To assess the possibility of orthorhombic $CeOHCO_3$ and monoclinic $CeOHSO_4$ as phosphor materials, we recorded their

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PL spectra. These two compounds exhibit distinctly different PL properties. The luminescence band of $CeOHCO_3$ is near 374 nm, and the optimum excitation wavelength is 306 nm, but the intensity is extremely weak. In contrast, $CeOHSO_4$ displays considerably stronger ultraviolet fluorescence. As shown in Figure 3, the optimum excitation wavelength ranges from 243 to 248 nm, and the broadened luminescence band is centered on 388 nm. The PL intensity of the new compound is about 400 times that of $CeOHCO_3$. The dissimilar band structures of the two kinds of crystals with the different symmetrries are believed to be responsible for their different PL behavior.

In summary, the evolution of the thiourea−cerium(III) nitrate system was investigated under hydrothermal conditions. Chemical reactions in the solutions were discussed. The aqueous solution produces $CeOHCO_3$ under lower temperature but affords $CeOHSO_4$ at higher temperature. Therefore, simply changing the temperature controls the phase. Of the two synthesized single phases, the monoclinic $CeOHSO_4$ is more interesting because of its ability to emit 388 nm ultraviolet fluorescence. This compound may also be useful in catalysis.[14,15]

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Additions and Corrections

2000, Vol. 39

Seiji Komeda, Martin Lutz, Anthony L. Spek, Masahiko Chikuma, and Jan Reedijk*: New Antitumor-Active Azole-Bridged Dinuclear Platinum(II) Complexes: Synthesis, Characterization, Crystal Structures, and Cytotoxic Studies

Page 4232, right column, line 29. The word “diastereoisomers” is changed to “enantiomers”.

Page 4233, right column, line 10. The word “diastereoisomers” is changed to “enantiomers”.

Page 4233, right column, lines 11 and 12. The word “diastereomers” is changed to “enantiomers”.

Page 4234, left column, line 1. The word “diastereomers” is changed to ”enantiomers”.

Page 4236, left column, line 27. The word “diastereomers” is changed to “stereoisomers”.

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