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Luminescence of divalent europium-doped calcium carbonate and oxalate

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Abstract

Divalent europium-doped calcium carbonate and oxalate were synthesized by means of co-precipitation, solid state reactions, and thermal decomposition processes under strictly controlled experimental conditions. Preliminary studies of the synthesized phosphor materials showed that $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} have similar spectra, e.g. they both have broad band excitations and emissions with peaks at 350 and 450 nm, respectively. Their luminescence properties are excellent to meet the requirement for an optical brightening agent (OBA) which is widely used in, for example, the paper industry. Furthermore, these materials can be made at ambient to 500°C which means a considerable lower cost compared with today's commercial blue phosphors that need annealing temperatures above 1000°C. Blue luminescent $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} are therefore attractive alternatives for today's OBAs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Divalent europium; Calcium carbonate; Calcium oxalate; Luminescence; Optical brightening agent

1. Introduction

Divalent europium is an important activator for luminescent materials which have been extensively studied for years. One of the best known Eu^{2+} activated phosphors is the blue luminescent BAM ($BaMg_xAl_yO_z$:Eu^{2+}) used for fluorescent lamps, which has almost 100% efficiency. The phosphors have an outstanding performance but they are expensive. However, there are some applications in which very low prices are of primary concern.

In the paper industry, for example, fluorescent dyes that absorb UV and emit in blue color are widely used as optical brightening agents (OBA) in order to whiten otherwise yellowish paper and enhance the brightness [1]. An important part of the cost of paper constituents is the OBAs, and however, the prices of these organic materials are a fraction of those inorganic phosphors. Yet there are demands for better OBAs in terms of degradation upon light, heat, chemical exposition during the period of storage, and unresolved environmental issues. Many inorganic phosphors are much more stable than the organic OBAs and also convert UV to blue light, therefore they are attractive as a replacement for organic OBAs. Furthermore, most of the inorganic phosphors are white powders that are insoluble in water, weak acid or base which can be readily used as fillers and pigments for paper and paper coatings [2].

Calcium carbonate is primarily used as fillers and pigments in the paper industry, therefore, it is our intention to find a calcium carbonate phosphor that absorbs UV and emits blue light. Alkaline earth carbonate is best known for its thermal luminescence properties [3]. Luminescence of alkaline earth carbonates doped with rare earth and some other metals have been reported [4,5]. However, the literature contains no data concerning the properties of divalent europium in alkaline earth carbonates.

Here we report the preliminary studies of two new blue luminescent $CaCO_3$:Eu^{2+} and the closely related CaC_2O_4:Eu^{2+} phosphors.

2. Experimental

Direct preparation of $CaCO_3$:Eu^{2+} via aqueous solution is not easy since Eu^{2+} can be easily oxidized into the more stable trivalent state. Several attempts of co-precipitation using high purity $EuCl_2$ and various calcium, carbonate, and hydrocarbonate ions containing compounds easily resulted in a trivalent europium-doped $CaCO_3$ material, despite that the reaction conditions were carefully controlled, and all reactants were degassed and handled in air-tight glassware. The resulting $CaCO_3$:Eu^{3+} can be

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identified with its orange emission under UV excitation. An alternative to the carbonate co-precipitation reaction is to use oxalate co-precipitation since oxalates have a very low solubility and they do not decompose in slightly acidic solutions. The desired carbonates can be obtained by further decomposition of anhydrous precipitates at 450 to 550°C in air. The co-precipitation process can be simplified into the following reaction equations:

$$CaCl_2 + H_2C_2O_4 + EuCl_2 \rightarrow CaC_2O_4{:}Eu^{2+}(\downarrow) \xrightarrow{\Delta} CaCO_3{:}Eu^{2+} \qquad (1)$$

However, it was difficult even in the reaction (1) to avoid oxidation. A modified version of the reaction, viz. co-precipitation was found more favorable, e.g. a slightly acidic $CaCl_2$ solution containing 0.5–5 mol.% Eu^{3+} ions was slowly passed through a zinc reductor into a hot concentrate $H_2C_2O_4$ solution which resulted in well crystallized CaC_2O_4:Eu^{2+} precipitates. The process requires only ambient condition but produces a high quality material. Yet a solid state reaction was also found successful. In the solid state approach, 0.5–5 mol.% $EuCl_2$ was first well mixed with anhydrous $CaCl_2$. Excessive anhydrous solid oxalic acid and/or ammonium oxalate was then added into it. The well grounded mixture was then heated at 200–300°C in an air-tight flask, resulting in CaC_2O_4:Eu^{2+} and sublimated oxalic acid, which can be easily removed after reaction. High purity Ar gas was used throughout the handling of chemicals and the reaction process. The final $CaCO_3$:Eu^{2+} was obtained by decomposition of the corresponding oxalate without severely damaging the divalent oxidation state of europium.

X-ray powder diffraction showed the CaC_2O_4 to be monoclinic α-type mixed with monohydrate ($CaC_2O_4 \cdot H_2O$) whewellite due to the re-absorption of crystalline water in air, while calcinated $CaCO_3$ was of pure calcite type. Dynamic thermogravimetric analysis in N_2 atmosphere revealed a loss of crystalline water of $CaC_2O_4 \cdot H_2O$ at 115°C and a complete decomposition into carbonate took place at 500°C. Luminescence properties were studied with an EAI (Edinburgh Analytical Instruments) FS900/FL900 spectrofluorophotometer equipped with an Oxford Optistat^{CF} cryostat.

3. Results and discussion

Since the carbonate is a decomposition product of the oxalate salt, the properties of CaC_2O_4:Eu^{2+} are therefore discussed first. Luminescence studies showed that the phosphor had a broad band excitation and emission with peaks at 350 and 450 nm, respectively (Fig. 1). The spectra locations are excellent for use as an OBA. It is well known that CaC_2O_4 has a yellowish white color. Our synthesized CaC_2O_4:Eu^{2+} powders, however, have a pure 'white' color due to the effect of blue emission which enhances the visual sensation of white color.

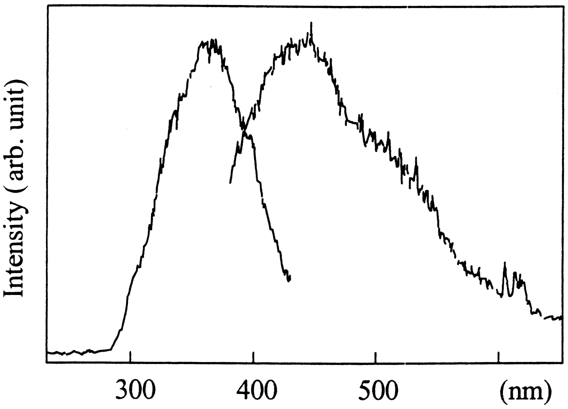

Fig. 1. Excitation and emission spectra of CaC_2O_4:Eu^{2+}.

The excitation and emission bands of $CaCO_3$:Eu^{2+} are located almost at the same region as those of CaC_2O_4:Eu^{2+}. Both emission and excitation spectra are somewhat broadened with stronger features in the shoulders (Fig. 2).

For the divalent europium-doped phosphors, the emission of Eu^{2+} is due to the parity-allowed $4f^7$–$4f^65d$ transition, which is strongly influenced by the crystal field. Thus the emission color of Eu^{2+}-doped phosphors varies from UV to red, over a wide spectral range. There has been a few reports on red emission of CaO:Eu^{2+} [6,7], which is a result of the extremely large splitting of the two excited energy levels (E_g and T_{2g}) in a very strong field of cubic crystal. The red emitting CaO:Eu^{2+} can be obtained through decomposition of $CaCO_3$:Eu^{2+} at high temperature in a reducing atmosphere. We expected different luminescence properties of Eu^{2+} in $CaCO_3$ and CaC_2O_4 compared to that of CaO since the crystal fields of carbonate and oxalate are much weaker than that of the oxide. Nevertheless, it is interesting to see that the spectra of $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} are so similar and that

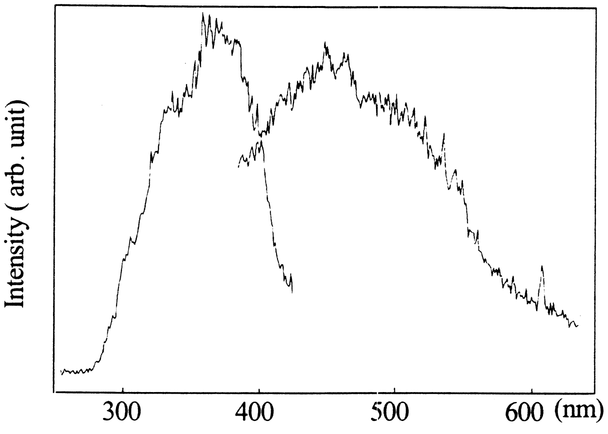

Fig. 2. Excitation and emission spectra of $CaCO_3$:Eu^{2+}.

they show blue emissions like many Eu^{2+}-doped oxidic materials, viz. aluminates, silicates and phosphates.

One should be cautious in the interpretation of the excitation spectra of both $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} because they seem to have only one broad band. Eu^{2+} should have two excitation bands corresponding to the E_g and T_{2g} excited energy levels as those observed in CaO:Eu^{2+}. In many other systems, however, the excitation spectra are very broad (from near UV extend to 200 nm or even higher energy) and often consist of several featureless peaks which are difficult to interpret. Nevertheless, some systems have shown one broad excitation band and those compounds often have a weak crystal field [8–10]. $CaCO_3$ crystal has a rhombohedral structure where the calcium ion is sandwiched between two CO_3^{2-} planes in an inversed S_6 symmetry. A Eu^{2+} ion in such a cation site could experience a weak ligand-field interaction that shows in the excitation only a broad band with shoulders that are difficult to deconvolute. Because the calcium carbonate is a product of a decomposition reaction it may contain a lot of structural defects. This cannot be ruled out when looking for reasons for the broad excitation band. The situation of whewellite ($CaC_2O_4 \cdot H_2O$) is different. In this lattice the calcium ions have two different sites where in both of them calcium is surrounded by eight oxygen atoms that form a distorted antiprism. Seven of the oxygen atoms are from five oxalic groups and one from the crystalline water. The coordination could also indicate a weak crystal field resulting in similar excitation band as that of $CaCO_3$:Eu^{2+}. Unfortunately, we were not able to testify to such an assumption due to the limitations of our instrumentation, i.e. the spectrum intensity decreases drastically at wavelengths shorter than 300 nm, therefore, any spectra features at wavelengths from 200 to 300 nm were difficult to resolve.

Preliminary decay studies on the $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} phosphors also showed similar values. The decay time curves were single exponential having time constant of about 0.1 μs at both room temperature and 80 K. Divalent europium-doped phosphors usually have fast decays of 1 to 2 μs and become much faster at elevated temperature. A decay time of 0.2 μs also has been reported [11]. Our recorded decay times for $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} were faster which may indicate a considerable role of defects or killer centers in the synthesized products owing to the difficulties in preparation. Further efforts are needed to improve the performance and quality of the phosphors.

4. Conclusions

Two new blue luminescent phosphors, namely $CaCO_3$:Eu^{2+} and CaC_2O_4:Eu^{2+} have been synthesized and characterized. Their excitation and emission properties are excellent to meet the requirements for OBAs. The high potential of these phosphors is their much lower synthesis temperature, from ambient to 500°C, as compared with today's commercial blue phosphors that need annealing temperature above 1000°C. This means considerably lower costs but properties that are highly desirable, for example in the paper industry, can be achieved.

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