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ScienceDirect

Ceramics International 38S (2012) S567–S569

CERAMICS INTERNATIONAL

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Luminescence of $(H_3O)Al_3(SO_4)_2(OH)_6$:Cu synthesized under hydrothermal condition

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Abstract

Copper doped hydronium alunite; $(H_3O)Al_3(SO_4)_2(OH)_6$:Cu was successfully synthesized under hydrothermal conditions. The blue cathodoluminescence (peak at about 414 nm) was observed from the $(H_3O)Al_3(SO_4)_2(OH)_6$:Cu when the copper ratio x was 1 and above, where x was the molar ratio of Cu:Al:S = x:3:2 ($0 \leq x \leq 15$) in the starting materials. The luminescence intensity increased with increasing x up to 3, and then decreased. The monovalent copper ion (Cu^+) was detected by XPS measurements for all the doped samples. In addition, the divalent copper (Cu^{2+}) was detected for the samples with $x \geq 6$. Therefore, the origin of the blue luminescence is considered to be monovalent Cu^+ ion. Excess doping of Cu^+ ($x \geq 6$) is thought to cause a concentration quenching of the luminescence. The obtained $(H_3O)Al_3(SO_4)_2(OH)_6$:Cu is expected to find use in the blue luminescent phosphor under electron beam irradiation.

Keywords: A. Powders: chemical preparation; B. X-ray methods; C. Optical properties; E. Functional applications

1. Introduction

Alunite, $KAl_3(SO_4)_2(OH)_6$, is one of the most abundant sulfate mineral group, containing potassium and aluminum with hexagonal crystal system (space group of R-3m). The general formula of the alunite is represented as $AM_3(SO_4)_2(OH)_6$, where A can be K^+, Na^+, Rb^+, Tl^+, Ag^+, NH_4^+, H_3O^+, Ca^{2+}, Pb^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Ce^{3+}, and M can be Al^{3+}, Fe^{3+} or minor Cu^{2+}, Zn^{2+} [1,2]. Generally, natural alunite has a potassium deficiency which is commonly compensated by the hydronium ion (H_3O^+) [2,3]. Completely substituted H_3O^+ for K alunite is often called hydronium alunite ($(H_3O)Al_3(SO_4)_2(OH)_6$) which is not produced naturally.

Copper ion is well known as a luminescent center in the various host matrixes. The wavelengths of the luminescence are changed by the matrixes, such as 375 nm ($NaMgF_3$), 415 ($KMgF_3$), 465 ($LiBaF_3$) [4], 413 (CaS), 472 (MgS), 478 (SrS), 585 (BaS) [5], 410, 450, 480, 510 and 540 (silica zeolite) [6], 510 (silicate glasses) [7], 360 and 420 (NaCl) [8,9], 387 (Li_2SO_4:Cu) [10].

In this paper, we demonstrated a synthesis of a novel luminescent material based on the copper ion doped hydronium alunite prepared through a hydrothermal process. Furthermore, a dependence of the luminescence intensity on the copper ratio in the starting material was investigated. The origin of the luminescence was discussed from the results of cathodoluminesence and X-ray photoelectron spectroscopy.

2. Experimental

Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) and elemental sulfur (S) were used as starting materials. The nitrates were dissolved in distilled water. The molar ratio of Cu:Al:S was set to x:3:2 ($0 \leq x \leq 15$). The concentrations of aluminum and copper nitrate water solutions were 0.250 and 0.083x mol/l, respectively. The mixture of solutions of 10 ml and elemental sulfur was sealed into a pressure vessel with a quartz inner tube which has the volume of 26 ml. The vessel was heated with a rate of 1.5 °C/min in an electric furnace, maintained at 240 °C for 60 min and then cooled to room temperature in the furnace. The obtained products were filtered and dried at 80 °C for 4 h. The powder X-ray diffraction (XRD) patterns were obtained using a Rigaku MultiFlex diffractometer (Cu Kα radiation) with a

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doi:10.1016/j.ceramint.2011.05.099

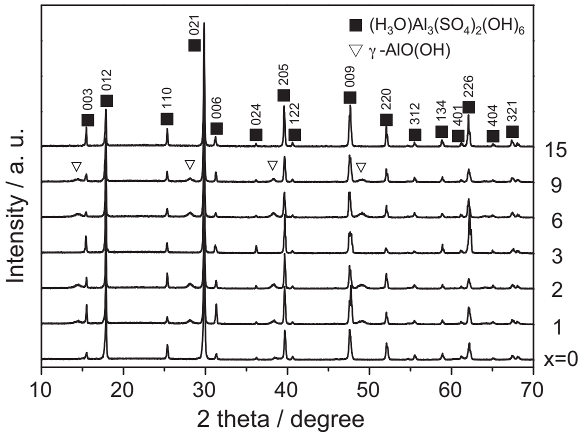

Fig. 1. XRD patterns of the obtained products. Most of the peaks were attributed to the hydronium alunite.

graphite monochromator. The cathodoluminescence (CL) was measured at room temperature using a system consisted of a grating monochromator, optical fiber and a liquid-nitrogen-cooled CCD detector (HORIBA, MP-32M-0MT). The accelerating voltage and electron beam current were 20 kV and 1.5 nA, respectively. In order to determine the valency of the copper ion, X-ray photoelectron spectroscopy (XPS) profiles were measured using JEOL JPS-9010TR with the Mg Kα line running at 10 kV and 10 mA as an excitation source. The XPS binding energy was calibrated using C (1s) at 284.6 eV.

3. Results and discussion

A white powder product was precipitated on the bottom of quartz inner tube at $x = 0$ after hydrothermal synthesis. When the x was 1 and above, the colors of the precipitates were changed to bluish white. The deepness of the blue color increased with increasing x.

Fig. 1 shows XRD patterns of the obtained precipitates. The XRD revealed that all the products have the crystal structure of hydronium alunite (ICDD; 016-0409). In the cases of $x = 1, 2, 6$ and 9, a few peaks due to boehmite (γ-AlO(OH), ICDD; 074-1895) were detected.

Fig. 2 shows SEM images of the products which were gold-sputter-coated in order to avoid the charge-up effect. Two kinds of shapes were observed for the products. One was irregular and the other was truncated cubic. The irregular shape products are considered to be boehmite. The crystallographic outer shape called "pseudocubic" [11] is thought to reflect a crystal structure of the hydronium alunite. An edge length of the pseudocubic products for $x \leq 3$ varied in the range of 70–100 μm, while that of the products for $x \geq 6$ were about 30 μm.

Fig. 3 shows cathodoluminescnence spectrum of the product prepared at $x = 3$ without gold-sputtering. The product exhibited a blue luminescence peak at a wavelength of about 414 nm. Fig. 4 shows the dependence of the luminescence intensity on the Cu ratio x of the starting material. Pure hydronium alunite ($x = 0$) did not show any luminescence. Therefore, the origin of the blue luminescence is considered to be Cu ion in the hydronium alunite. The luminescence intensity increased with increasing x, reached its maximum value at $x = 3$ and decreased gradually.

Fig. 5 shows the X-ray photoelectron spectra of the Cu 2p electrons. The peaks at 933 and 953 eV indicate the monovalent copper ion (Cu^+). On the other hand, 934 and 954 eV indicate the divalent copper ion (Cu^{2+}). Additional satellite peaks at 944 and 963 eV caused by the existence of the Cu^{2+} were obtained [12]. When the copper ratio x in the starting material was changed from 1 to 3, the peaks attributed to the Cu^+ increased. The satellite peaks caused by Cu^{2+} were detected and increased with increasing $x \geq 6$. The x range where Cu^{2+} satellite peaks appeared ($6 \leq x \leq 15$) agreed well with that where the small pseudocubic crystals were observed. Therefore, it is suggested that the suppression of the crystal growth was caused by the existence of Cu^{2+}. From the result of the blue luminescence intensity dependency on x shown in Fig. 4, the intensity increased with increasing x up to 3. Consequently, the origin of the blue luminescence is considered to be Cu^+ ion. The peaks for Cu^+ increased with increasing $x \leq 9$. A concentration quenching of luminescence from Cu^+ at 387 nm for Li_2SO_4:Cu phosphor was reported [10]. Therefore, it is thought that the

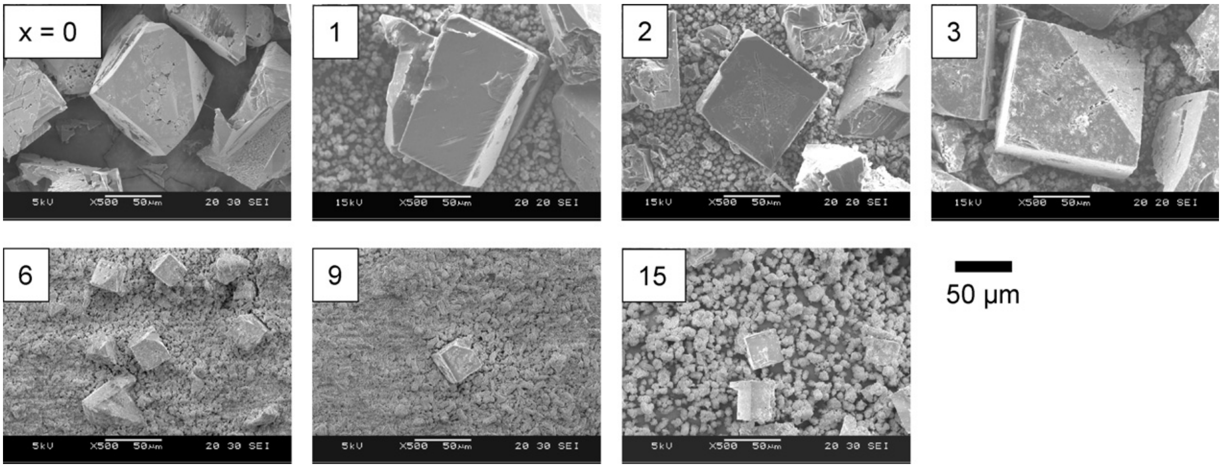

Fig. 2. SEM images of the obtained products.

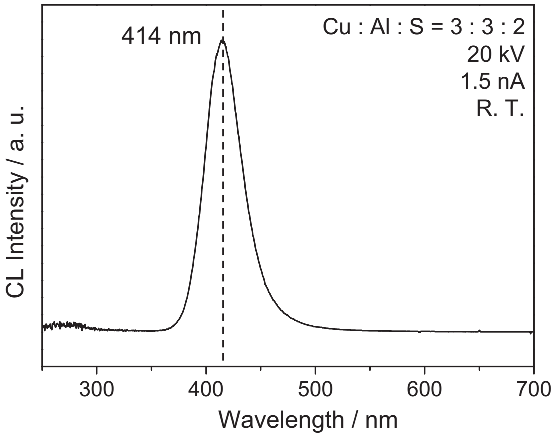

Fig. 3. Cathodoluminescence spectrum for the obtained product prepared at a copper ratio $x = 3$ in the starting solution.

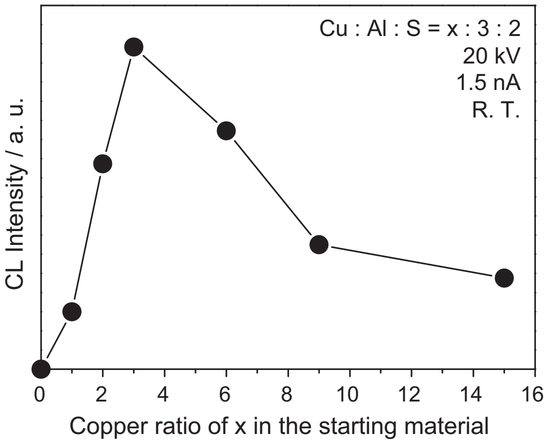

Fig. 4. Dependence of the luminescence intensity on the copper ratio in the starting material.

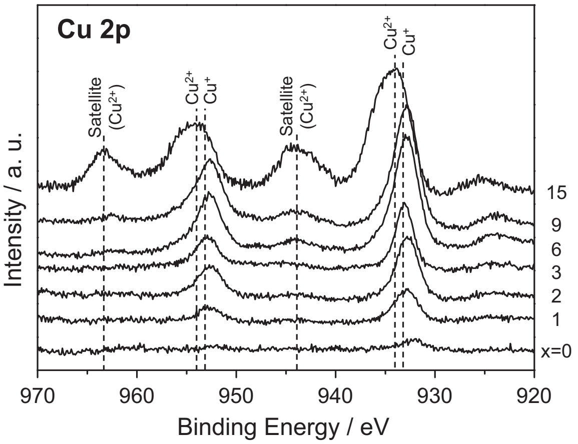

Fig. 5. X-ray photoelectron spectra of the products. The peaks attributed to the Cu^+ ion were mainly observed ($1 \leq x \leq 3$). The satellite peaks caused by Cu^{2+} were also detected for $x \geq 6$.

decrease in the luminescent intensity above $x = 3$ in Fig. 4 also indicates the concentration quenching. Kurobori et al. reported that the intensity of the blue luminescence at 420 nm for the Cu^+ ion depended on the presence of OH^- ions in the NaCl crystal, although an isolated Cu^+ ion exhibited the luminescence at 360 nm [8,9]. In this work, the luminescence peak wavelength for Cu^+ ion is also thought to be shifted from 360 to 414 nm by the presence of OH^- and/or H_3O^+ ions in the hydronium alunite.

It is expected to find applications in blue phosphors under electron beam irradiation. The blue luminescence intensity can be controlled by changing the copper concentration of the starting materials.

4. Conclusions

Copper doped hydronium alunite was successfully synthesized under hydrothermal conditions. The product exhibited the blue luminescence peak at the wavelength of about 414 nm. XPS measurement revealed that the luminescence was caused by the Cu^+ ion. The intensity of the luminescence was controlled by the concentration of copper ion in the starting material solution. The obtained material can be applied to a blue phosphor excited by electron beam.

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