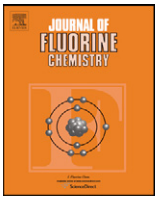
Journal of Fluorine Chemistry 132 (2011) 1095–1101

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor



Synthesis and luminescent properties of rare-earth-doped CeO_2–CaF_2 solid solutions via chemical solution routes

Shinobu Fujihara *, Hiroki Sato

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

ARTICLE INFO

Article history:
Received 11 April 2011
Accepted 20 June 2011
Available online 5 July 2011

Keywords:
Calcium fluoride
Cerium oxide
Trifluoroacetic acid
Solid solution
Luminescence

Dedicated to Professor Alain Tressaud in honor of his receipt of the 2011 ACS Award for Creative Work in Fluorine Chemistry.

ABSTRACT

CeO_2–CaF_2 solid solutions were synthesized by a chemical solution method starting from metal acetates, trifluoroacetic acid as a fluorine source, and anhydrous ethanol as a solvent. Precursor gels, which were obtained by drying the resultant ethanolic solution at 110 °C, were heat-treated at a temperature in the range 400–1000 °C in air to obtain powdery products. Elemental analysis by energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy revealed that heating products actually contained cerium, calcium, oxygen, and fluorine. According to X-ray diffraction analysis, possible reaction pathways under high-temperature treatments were considered as initial formation of fluorides (CeF_3 and CaF_2), subsequent oxidation of Ce^{3+} to Ce^{4+} in air, and final conversion to fluorite-type Ce–Ca–O–F solid solutions. Doping of Eu^{3+} or Sm^{3+} ions in the solid solutions led to occurrence of their characteristic photoluminescence due to intra-configurational f–f electronic transitions. Photo-excitation was achieved by irradiation with near ultraviolet light mainly through charge transfer from O^{2-} to Ce^{4+} in the solid solutions and subsequent energy transfer to the doped ions. Spectral structures of photoluminescence suggested the occupation of Eu^{3+} or Sm^{3+} in Ce^{4+} sites with inversion symmetry in the solid solutions.

1. Introduction

Luminescence of rare-earth ions arising from their intra-configurational f–f transitions is of technological importance because it has been widely applied to phosphors for color displays and fluorescent lamps [1–3]. Alkaline earth and rare-earth fluorides and oxyfluorides have been intensively studied as host materials for doping rare-earth ions because of their unique physical properties reflecting chemical bonding between metal cations and fluoride ions. It is known that relative intensities of emission lines from the excited rare-earth ions are determined primarily by their local environment in host crystals. For example, emissions from trivalent europium (Eu^{3+}) ions are governed by the probability of electronic transitions from the lowest $^5D_0$ excited state to the $^7F_{0–6}$ ground states, depending on site symmetries of host crystals.

Calcium fluoride (CaF_2) has a cubic fluorite-type structure and is optically transparent in a wide wavelength range from ultraviolet (UV) to infrared (IR). Doping in a CaF_2 host crystal has been investigated for divalent or trivalent rare-earth ions [4–7]. However, photo-excitation efficiency of rare-earth ions doped in CaF_2 is generally low due to the absence of chemical species effectively absorbing the excitation light. In contrast, cerium oxide (CeO_2) having a similar cubic fluorite-type structure is well known as an excellent UV absorber because of its band-gap energy located at the near UV region [8]. Doping of rare-earth ions in CeO_2 leads to efficient photo-excitation through electronic transition in the host crystal and subsequent energy transfer to the rare-earth ions [9]. Consequently, it is an interesting undertaking to synthesize mixed-anion solid solutions between CeO_2 and CaF_2 and investigate luminescence properties of rare-earth ions doped in them.

In this work, chemical solution routes were employed to synthesize rare-earth-doped CeO_2–CaF_2 solid solutions starting from metal acetates and trifluoroacetic acid (CF_3COOH; TFA). In our series of previous studies, TFA was proven to work as an excellent fluorine source through thermal decomposition of metal trifluoroacetate precursors at temperatures around 300 °C [10–12]. Chemical composition, structure, and optical properties of Eu^{3+}- or Sm^{3+}-doped CeO_2–CaF_2 solid solutions are reported here and the relationship between them is discussed. Also the results are compared with those obtained for Ce–Ca-based oxyfluorides prepared with a coprecipitation method which has been reported by Sronek et al. [13,14].

---

* Corresponding author.
E-mail address: shinobu@applc.keio.ac.jp (S. Fujihara).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.06.026

2. Experimental

$Ce(CH_3COO)_3 \cdot H_2O$ (99.99% purity; Kanto Chemical Co., Inc., Japan), $Ca(CH_3COO)_2 \cdot nH_2O$ (99.9%; Wako Pure Chemical Industries Co., Ltd., Japan), $Eu(CH_3COO)_3 \cdot 3H_2O$ (99.9%; Soekawa Chemicals Co., Ltd., Japan), and $Sm(CH_3COO)_3 \cdot 4H_2O$ (99.95%; Soekawa) were dissolved separately in a mixed solvent comprised of anhydrous ethanol (99.5%; Imazu Chemical Co., Ltd., Japan) and trifluoroacetic acid (98%; Wako). A mixing ratio of the solvent was fixed at ethanol:TFA = 47:3 in volume. The respective cation concentration was fixed at 0.2 mol/dm^3. The resultant metal acetate solutions were mixed further in cation ratios of $Ce{:}Ca = (100 - x){:}x$, $Ce{:}Ca{:}Eu = (100 - x - y){:}x{:}y$, or $Ce{:}Ca{:}Sm = (100 - x - z){:}x{:}z$ in mol%. The solutions were stirred for 24 h at room temperature and then dried at 110 °C to be converted into precursor gels. The gels were pulverized in an alumina mortar and placed in an alumina crucible. The gels were then heated to a temperature in the range 400–1000 °C at a heating rate of 10 °C/min and kept there for 2 or 10 h in air. The heated gels were pulverized again to obtain powder samples.

Elemental analysis of the powder samples were carried out by X-ray photoelectron spectroscopy (XPS; JEOL, type JPS 9000MX). An anion ratio of oxygen to fluorine in the samples was determined as follows. Reference samples were prepared by mixing CeO_2 (99.99%; Kanto) and CaF_2 (99.9%; Wako) in ratios varying from 0 to 100 mol% CeO_2 with every 10 mol%. Contents of the respective elements were determined by measuring XPS peak heights. A calibration curve was made by plotting a fluorine content against a calcium content in the reference samples. A cation ratio of calcium to cerium was determined by energy dispersive X-ray spectroscopy (EDX) equipped in a scanning electron microscope (Hitachi, type S-4700). The phase identification of the powder samples was performed with an X-ray diffractometer using Cu Kα radiation (Bruker AXS, type D8-02). Lattice constants of the samples were determined by a least square method from X-ray diffraction (XRD) patterns recorded with tungsten powders as an internal standard. Photoluminescence (PL) spectra were measured at room temperature with a spectrofluorophotometer (Shimadzu, type RF-5300PC) using a xenon lamp (150 W) as a light source. A filter was used to remove a second-order peak of the excitation light in the PL measurement.

3. Results and discussion

3.1. Composition and structure of CeO_2–CaF_2 solid solutions

It is of fundamental significance to know the composition and bonding states of elements in the mixed-anion solid solutions of the CeO_2–CaF_2 system. Fig. 1 shows XPS spectra of the samples, which were obtained by heating the "$Ce{:}Ca = (100 - x){:}x$" gels ($0 \le x \le 50$) at 600 °C for 10 h in air, for the Ce 3d, the Ca 2p, the O 1s, and the F 1s region. The Ce 3d spectrum is generally comprised of two multiplets corresponding to the spin-orbit split $3d_{5/2}$ and $3d_{3/2}$ separated by approximately 18 eV [15]. Since the 4f state couples with the core hole in the final state of photoemission, a remarkable splitting in the $3d_{5/2}$ and $3d_{3/2}$ core photoemission spectrum is observed for rare-earth systems [16]. The fine structure of the $3d_{5/2}$ and $3d_{3/2}$ multiplets can be used to judge the valence state of cerium. In mixed-valence cerium compounds, three different final states ($4f^0$, $4f^1$, and $4f^2$) arise from the 4f-level relaxation around the core hole. The corresponding XPS peaks are denoted by v_0 (Ce^{3+}, $4f^2$), v (Ce^{4+}, $4f^2$), v' (Ce^{3+}, $4f^1$), v'' (Ce^{4+}, $4f^1$), and v''' (Ce^{4+}, $4f^0$) for $3d_{5/2}$ and u_0 (Ce^{3+}, $4f^2$), u (Ce^{4+}, $4f^2$), u' (Ce^{3+}, $4f^1$), u'' (Ce^{4+}, $4f^1$), and u''' (Ce^{4+}, $4f^0$) for $3d_{3/2}$ [17,18]. In the sample with $x = 0$, there exist six peaks of v (882 eV), v'' (889 eV), v''' (899 eV), u (901 eV), u'' (907 eV), and u''' (917 eV), indicative of the presence of Ce^{4+}. No peaks related to Ce^{3+} (v_0, v', u_0, and u') are observed in the spectrum. This observation is also the case with the other samples ($10 \le x \le 50$). Under the heating condition at 600 °C for 10 h in air, cerium is oxidized from Ce^{3+} in the gels to Ce^{4+} in the solid-solution samples. This change will be discussed later.

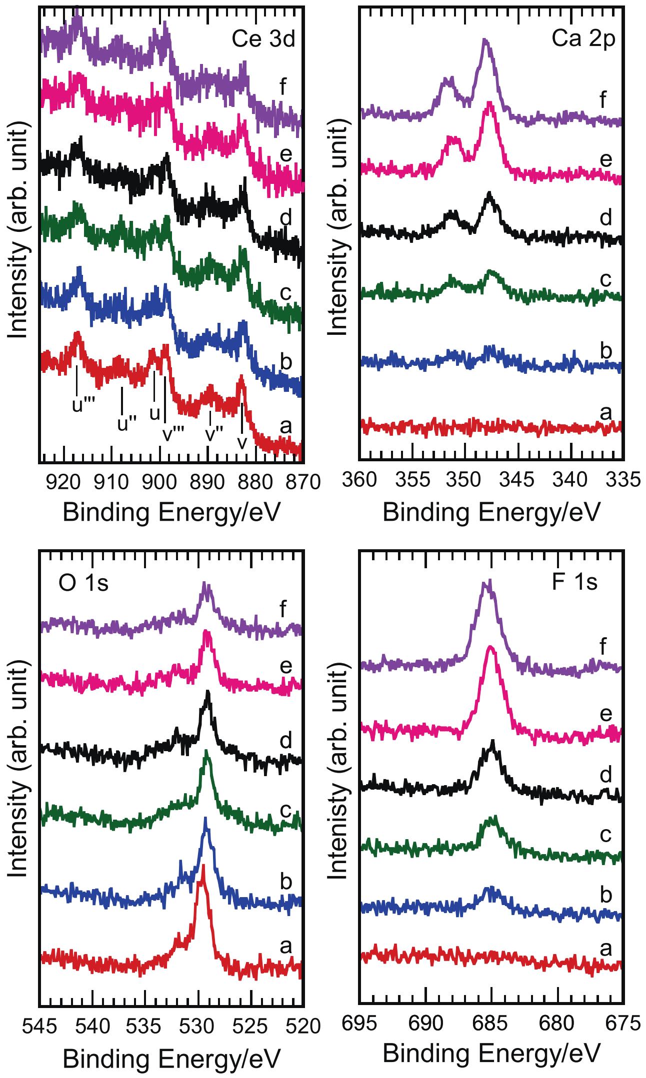


Fig. 1. XPS spectra of the samples, which were obtained by heating the "$Ce{:}Ca = (100 - x){:}x$" gels ($0 \le x \le 50$) at 600 °C for 10 h in air, for the Ce 3d, the Ca 2p, the O 1s, and the F 1s region; (a) $x = 0$, (b) 10, (c) 20, (d) 30, (e) 40, and (f) 50.

In the Ca 2p region, peaks due to Ca 2p electrons are observed at 347.6 and 351.2 eV for the samples with the x values between 10 and 50. The position and the relative intensity of these peaks correspond to those of CaF_2 reported in the literature [19]. Moreover, the intensity of the Ca 2p peaks becomes higher with increasing the x values. These results indicate that the amount of the calcium ions bonded to fluorine increases continuously in the "$Ce{:}Ca = (100 - x){:}x$" samples.

The O 1s peak is observed at 529 eV for all the samples. The peak position is consistent with that of CeO_2 [20]. The samples then contains the Ce–O bonds rather than the Ca–O bonds. The intensity of the O 1s peak becomes lower with increasing the x values. The F 1s peak is observed at 685 eV for the samples with the x values between 10 and 50. The position of the F 1s peak is reportedly at 684.5 and 684.6 eV for CaF_2 and CeF_3, respectively [21,22]. It is therefore difficult to judge the bonding state of fluorine only from the F 1s spectra. Nonetheless, the intensity of the F 1s peak