Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2015, **25**, 209–210

Mendeleev Communications

Synthesis and luminescent properties of $Al_{1-x}Tb_x(HCOO)_3$ and $Al_{2-2x}Tb_{2x}O_3$

Vladimir N. Krasilnikov,[a] Inna V. Baklanova[a,b] and Olga I. Gyrdasova*[a]

[a] *Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russian Federation*
[b] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620990 Ekaterinburg, Russian Federation. Fax: +7 343 374 4495; e-mail: gyrdasova@ihim.uran.ru*

DOI: 10.1016/j.mencom.2015.05.017

Formate $Al_{1-x}Tb_x(HCOO)_3$ ($0.0 \leqslant x \leqslant 0.15$) and the nanodispersed solid solutions $Al_{2-2x}Tb_{2x}O_3$ ($0.005 \leqslant x \leqslant 0.125$) have been synthesized and their luminescent properties have been estimated.

Aluminum sesquioxide is widely used in engineering and various technologies. Among its practical applications are abrasives, ceramics, sorbents, solid electrolytes and catalysts. Recently, attempts have been made to produce nanocrystalline phosphors based on Al_2O_3 doped with trivalent lanthanide cations (Ln^{3+}) as dense transparent ceramics, films and bulk samples.[1–3] Availability and low cost along with high heat conduction and chemical, mechanical and radiation stability are the attractive features of Al_2O_3, owing to which it favorably competes with the traditional matrix material Y_2O_3[4] and perspective Sc_2O_3.[5,6] At the same time, the main drawback of Al_2O_3 (corundum having a hexagonal lattice) is a low degree of substitution of Ln^{3+} for Al^{3+}.[1] This disadvantage can be overcome using an amorphous or cubic γ-modification of aluminum sesquioxide[7] as a matrix, which is more tolerant with respect to Ln^{3+} and can be produced by a low-temperature precursor method.

In this work, nanodispersed terbium-doped aluminum sesquioxide ($Al_{2-2x}Tb_{2x}O_3$) was synthesized using the mixed formate $Al_{1-x}Tb_x(HCOO)_3$ as a precursor, which was obtained by the overall reaction

$$(2-2x)Al(NO_3)_3 + 2x\,Tb(NO_3)_3 + 9\,HCOOH = \\ = 2Al_{1-x}Tb_x(HCOO)_3 + 3\,N_2 + 9\,CO_2 + 6\,H_2O. \qquad (1)$$

The samples of $Al_{1-x}Tb_x(HCOO)_3$, where x = 0.0, 0.005, 0.01, 0.025, 0.05, 0.075, 0.10, 0.125, 0.15, 0.20 and 1.0, were obtained using analytical-grade $Al(NO_3)_3\cdot 9H_2O$, $Tb(NO_3)_3\cdot 6H_2O$ and 85% HCOOH. To produce $Al_{2-2x}Tb_{2x}O_3$, $Al_{1-x}Tb_x(HCOO)_3$ was heated at 500 and 750 °C in air with exposures at each stage of annealing for 2 h.

According to X-ray phase analysis and vibration spectroscopy data,[†] the samples of $Al_{1-x}Tb_x(HCOO)_3$ at $x \leqslant 0.15$ were monophase substitutional solid solutions based on $Al(HCOO)_3$. The formation of the solid solutions was confirmed by the almost identical diffraction patterns and vibrational spectra of $Al(HCOO)_3$ and $Al_{1-x}Tb_x(HCOO)_3$. The sample of $Al_{0.8}Tb_{0.2}(HCOO)_3$ contained an impurity of the formate $Tb(HCOO)_3$. Thermal decomposition of $Al_{1-x}Tb_x(HCOO)_3$ in air with mass loss corresponding to the formation of oxide $Al_{2-2x}Tb_{2x}O_3$ occurred in one stage at ~450 °C. The powders of $Al_{2-2x}Tb_{2x}O_3$ produced by heating the precursor at 500 °C for 2 h were X-ray amorphous. The IR spectra of the powders exposed in air at room temperature for 2 h contained a very intense broad band at 3560 cm^{-1}, which indicates that the oxide formed as a result of precursor decomposition converted into hydroxide like $Al_{1-x}Tb_xO(OH)$ owing to its interaction with atmospheric water vapor. The X-ray diffraction patterns of the thermolysis products of $Al_{1-x}Tb_x(HCOO)_3$ ($x \leqslant 0.125$) at 750 °C point to the formation of terbium-substituted sesquioxide $Al_{2-2x}Tb_{2x}O_3$ with the γ-Al_2O_3 structure. The powders of $Al_{2-2x}Tb_{2x}O_3$ containing no more than 12.5 at% Tb were white. At terbium concentrations > 12.5 at%, they acquired a brownish color due to the presence of a reddish Tb_4O_7 oxide impurity. The morphology of $Al_{2-2x}Tb_{2x}O_3$ powders with x = 0.025 and 0.075

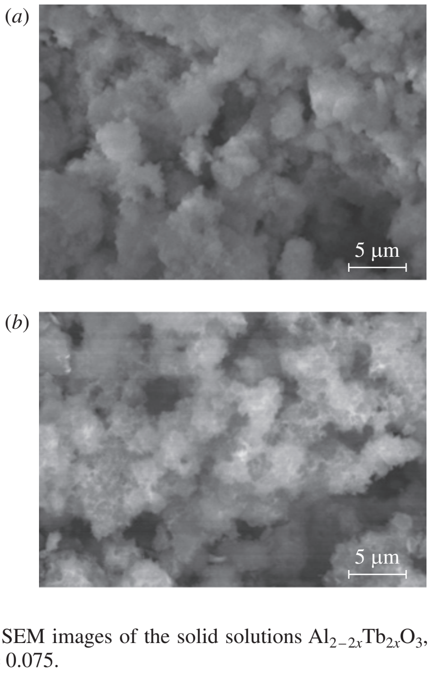

Figure 1 SEM images of the solid solutions $Al_{2-2x}Tb_{2x}O_3$, (*a*) x = 0.025 and (*b*) x = 0.075.

[†] The phase analysis of the synthesized samples was carried out on a STADI-P X-ray diffractometer in CuKα_1 radiation. Thermogravimetric analysis was performed on a TG–DTA SETARAM-92 analyzer with heating in air at a rate of 10 K min^{-1}. The shape and size of particles were determined by scanning electron microscopy on a JSM JEOL 6390LA instrument. The IR absorption spectra were measured on a Bruker Vertex 80 FTIR spectrometer in a range of 4000–400 cm^{-1} using powdered samples (pellets in CsI). The Raman spectra were obtained at room temperature on a RENISHAW-1000 spectrometer (λ = 633 nm, P = 25 mW). The absorption spectra in a range of 190–800 nm were recorded on a Shimadzu UV-2401 PC spectrometer (λ = 380 nm) using $BaSO_4$ as a standard sample. The emission spectra were measured on a Varian Cary Eclipse fluorimeter (75 kW xenon lamp).

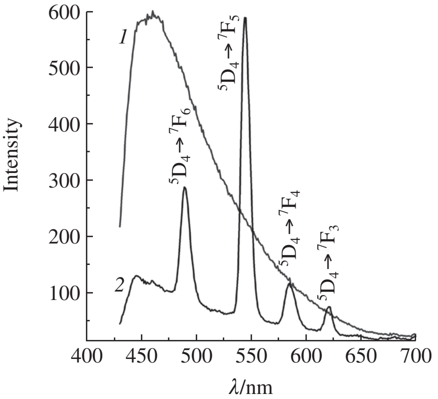

Figure 2 Emission spectra of $Al_{1-x}Tb_x(HCOO)_3$, (*1*) $x = 0$ and (*2*) $x = 0.075$.

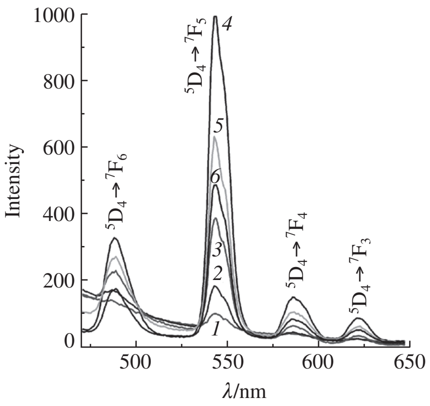

Figure 3 Emission spectra of $Al_{2-2x}Tb_{2x}O_3$, x is (*1*) 0.01, (*2*) 0.025, (*3*) 0.05, (*4*) 0.075, (*5*) 0.1 and (*6*) 0.125.

produced by the thermolysis of $Al_{1-x}Tb_x(HCOO)_3$ at 750 °C is shown in Figure 1. As the concentration of terbium in the solid solutions was increased, the surface of aggregates loosened. The reflectance spectra of all of the solid solutions $Al_{1-x}Tb_x(HCOO)_3$ are characterized by a sole broad line at 285 nm corresponding to the transition $^7F_6 \to {}^7D_5$ of the Tb^{3+} ion, which was chosen as an excitation wavelength for studying their luminescent properties. The emission spectra of $Al_{1-x}Tb_x(HCOO)_3$ (Figure 2) exhibit a very intense luminescence spectrum of terbium(III). The main radiative transitions at 425–700 nm belong to the local centers of Tb^{3+} from the $^5D_4$ level into $^7F_3$, $^7F_4$, $^7F_5$ and $^7F_6$ levels. The most intense line in the green region with a maximum at 545 nm is responsible for the transition $^5D_4 \to {}^7F_5$, which provides the basic contribution to the bright green luminescence of Tb^{3+} ions.[8] A maximum at 492 nm with weaker emission refers to the $^5D_4 \to {}^7F_6$ transition. The other transitions from the excited $^5D_4$ levels to the basic ^7F_J levels have much weaker intensities: a line at 584 nm ($^5D_4 \to {}^7F_4$ transition) and small-intensity line at 619 nm ($^5D_4 \to {}^7F_3$ transition). The spectra of pure $Al(HCOO)_3$ and the solid solutions $Al_{1-x}Tb_x(HCOO)_3$ with Tb concentrations <5 at% contain a very intense broad emission line with a maximum at ~460 nm. As the concentration of terbium increased ($x > 0.05$), the intensity of this line lowered, while the intensity of Tb^{3+} luminescence lines grew. This line is probably caused by the intrinsic luminescence of pure aluminum formate, which is due to an intra-ligand π–π* transition in the $HCOO^-$ ion during excitation by phonons with $\lambda = 285$ nm. A similar effect with intra-ligand π–π* transition is typical of some organometallic complexes of d^{10} metals, in particular, zinc.[9–11] To measure the luminescence spectra of $Al_{2-2x}Tb_{2x}O_3$ (x = 0.01. 0.025, 0.05, 0.075, 0.1, 0.125), we used the same wavelength of 285 nm ($^7F_6 \to {}^7D_5$). The emission spectra of $Al_{2-2x}Tb_{2x}O_3$ (Figure 3) were characterized by the concentration quenching of luminescence (green emission line at 545 nm responsible for the $^5D_4 \to {}^7F_5$ transition). When the concentration of terbium was raised, the line intensity initially increased to reach a maximum at $x = 0.075$ and then drastically decreased.

Thus, we were the first to synthesize $Al_{1-x}Tb_x(HCOO)_3$ ($0 \leqslant x \leqslant 0.125$) which was used as a precursor for producing nanodimensional samples of $Al_{2-2x}Tb_{2x}O_3$ with a large degree of terbium substitution for aluminum. The spectroscopic studies revealed that terbium-ion-doped aluminum sesquioxide with up to 7.5 at% Tb is a promising luminescent material with green emission. Containing no Tb^{3+} impurity cations, aluminum formate $Al(HCOO)_3$ possesses intrinsic luminescence with intense blue emission.

This work was supported by the Russian Foundation for Basic Research (grant no. 15-03-02908-a).

References

1 P. Mohanty and S. Ram, *J. Mater. Chem.*, 2003, **13**, 3021.
2 Z. Zhu, D. Liu, H. Liu, G. Li, J. Du and Z. He, *J. Lumin.*, 2012, **132**, 261.
3 E. H. Penilla, Y. Kodera and J. E. Garay, *Adv. Funct. Mater.*, 2013, **23**, 6036.
4 C. Feldmann and J. Merikhi, *J. Mater. Sci.*, 2003, **38**, 1731.
5 V. Lupei, A. Lupei, C. Gheorghe, A. Ikesue and E. Osiac, *J. Lumin.*, 2009, **129**, 1862.
6 I. V. Baklanova, V. N. Krasil'nikov, L. A. Perelyaeva and O. I. Gyrdasova, *Russ. J. Inorg. Chem.*, 2012, **57**, 1529 (*Zh. Neorg. Khim.*, 2012, **57**, 1627).
7 Q. I. Yang, *Bull. Mater. Sci.*, 2011, **34**, 239.
8 N. N. Solodukhin, V. V. Utochnikova, L. S. Lepnev and N. P. Kuzmina, *Mendeleev Commun.*, 2014, **24**, 91.
9 B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137.
10 Y. Zhou, *J. Inorg. Organomet. Polym.*, 2013, **23**, 458.
11 J. Heine and K. Muller-Buschbaum, *Chem. Soc. Rev.*, 2013, **42**, 9232.

Received: 14th November 2014; Com. 14/4502