Materials Letters 126 (2014) 39–42

Contents lists available at ScienceDirect

Materials Letters

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

Fabrication, magnetic anisotropy and tunable fluorescence of amorphous $La_xCu_yO_z$ nanowire arrays

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ARTICLE INFO

Article history:
Received 7 January 2014
Accepted 25 March 2014
Available online 1 April 2014

Keywords:
Amorphous materials
Magnetic materials
Rare earth doping
Fluorescence

ABSTRACT

The amorphous $La_xCu_yO_z$ nanowire arrays (NWAs) with average diameter 90 nm and lengths 5 μm have been prepared by chemical co-precipitation assisted by subatmospheric pressure suction filtration (SPSF) in porous anodic aluminum oxide (AAO) template. There is obvious magnetic anisotropy in $La_xCu_yO_z$ NWAs, and unusual easily magnetized direction is perpendicular to the axis of nanowire. The tunable fluorescence of rare earth (Re=Tb, Eu, Sm) doped $La_xCu_yO_z$ NWAs and the respective contribution of La and Cu to the fluorescence of NWAs were investigated, the results show that the fluorescent intensity of Eu, Tb, Sm-doped $La_xCu_yO_z$ NWAs increased with accession of dopant contain different mole percents. The intensity of emission peaks gradually increased with Eu from 2 to 50 mol% at 591 nm, Sm from 2 to 50 mol% at 610 nm or achieved to maximum at 542 nm when doping content of Tb is 5 mol%. Furthermore, La exhibit facilitation or Cu present inhibition to fluorescent intensity of NWAs.

1. Introduction

CuO nanowires (NWs) have attracted extensive attention from chemists and material scientists owing to their intriguing properties such as photocatalysis, sensor, electrochemistry, magnetism [1–4]. La doping Cu-contained oxide followed by calcinations at high temperature led to a considerable increase in catalytic activity [5]. Magnetic and luminescent properties of $LaCuO_x$ were investigated in previous reports [6,7]. The fluorescent intensity can be significantly tuned by suitable selection of host material and doping concentration. The Eu, Gd-doped Sr_2CeO_4 show sharp emission peak with high intensity [8]. The luminescent spectra exhibited strong emission signals in Tb, Eu, Sm doped PbF_2 nanocrystals [9]. Furthermore, the effects of doping content in $Y_3Al_5O_{12}$:Tb, $YP_xV_{1-x}O_4$:Eu, La_2O_3:Sm nanoparticles, Y_2O_3:Eu hollow spheres, ZnO:Sm nanorod on the fluorescent intensity were detailed investigated, and their emission intensities were definitely depended on Tb, Eu or Sm doping content [10–14]. However, to our best knowledge, systematic study on the influence of doping content to the fluorescence of nanowire arrays has seldom been reported until now. Here, the amorphous $La_xCu_yO_z$ NWAs was prepared by chemical co-precipitation in the AAO template. The magnetic anisotropy and tunable fluorescence of NWAs were investigated.

2. Experimental methods

Lanthanum nitrate ($La(NO_3)_3$), Copper nitrate ($Cu(NO_3)_2$), Terbium nitrate ($Tb(NO_3)_3$), Europium nitrate ($Eu(NO_3)_3$) and Samarium nitrate ($Sm(NO_3)_3$) of high purity (99.9%) chemicals were used as starting materials. The AAO template with average aperture 100 nm was fixed on the subatmospheric pressure suction filtration (SPSF) device and the gas tightness was checked, then, the 1 M $NH_3 \cdot H_2O$ and the mixed solution of 0.01 M $La(NO_3)_3$ and 0.01 M $Cu(NO_3)_2$ would alternately pass through nanopores of AAO template under SPSF (about 0.01 MPa). Thus, the $La_xCu_y(OH)_n$ nanowire precursor was fabricated by the successive co-precipitation reaction between $NH_3 \cdot H_2O$ and mixed nitrate solution, then the precursors were calcined at 500 °C for 2 h [15]. The Tb, Eu, Sm-(2, 5, 10, 30 and 50 mol%)-doped $La_xCu_yO_z$ nanowire arrays were similarly prepared as described above. Rare earth ions were doped keeping the concentration of La^{3+} (0.01 M) and Cu^{2+} (0.01 M), then changed the molar ratio of Tb^{3+}, Eu^{3+}, Sm^{3+} to the sum of La^{3+} and Cu^{2+} were 2, 5, 10, 30 and 50 mol%, respectively. La_xO_y, Cu_xO_y, Tb_xO_y, $Cu_xTb_yO_z$, $La_xTb_yO_z$ NWAs were also similarly fabricated by nitrate solution of 0.01 M La^{3+}, 0.01 M Cu^{2+}, 0.01 M Tb^{3+} and mixed nitrate solution 0.01 M La^{3+} and 0.01 M Tb^{3+}, 0.01 M

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http://dx.doi.org/10.1016/j.matlet.2014.03.150
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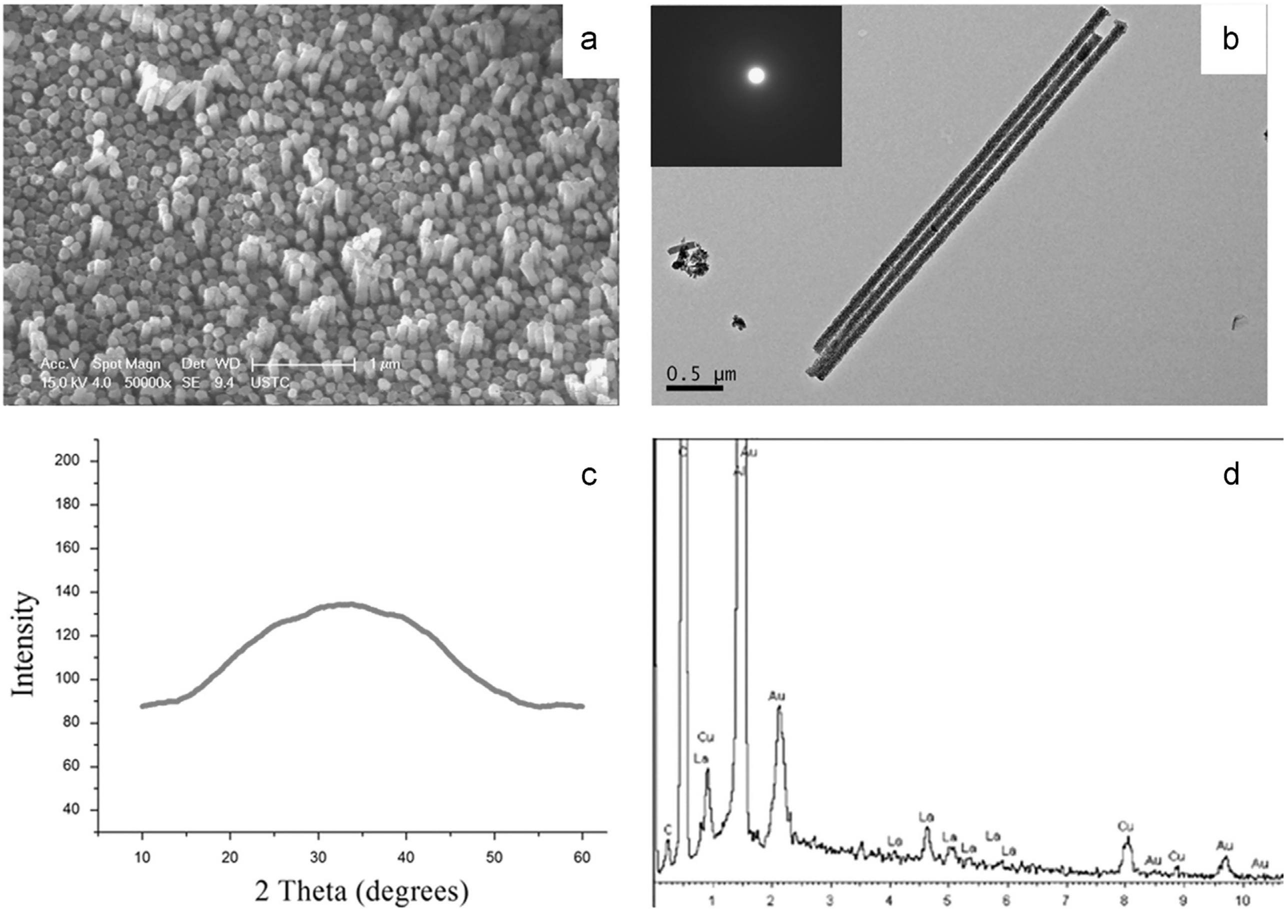

Fig. 1. (a) SEM image from top view of $La_xCu_yO_z$ NWAs; (b) TEM image of dispersive $La_xCu_yO_z$ nanowires, the inset is a SAED pattern; (c) XRD pattern, and (d) EDS of $La_xCu_yO_z$ NWAs.

Cu^{2+} and 0.01 M Tb^{3+}. The effective doping content in products is denoted by the ratio of raw materials.

The SEM (JSM-6700F) affixed with EDS, TEM (H-800) affixed with SAED and XRD (MXP18AHF) with Cu *K*α was used for study the morphology, structure and chemical composition of the $La_xCu_yO_z$ NWAs. The magnetic performance was characterized by VSM (BHV-55). The fluorescent spectra of as-prepared NWAs were measured by a PL spectrometer (F-4500) using a Xenon discharge lamp as the excitation light source.

3. Results and discussion

The morphology of the $La_xCu_yO_z$ NWAs was observed by SEM and TEM. Fig. 1a clearly indicates that the large scale of well-aligned $La_xCu_yO_z$ NWAs was obtained and their average diameters 90 nm is consistent with the aperture of AAO template. The products retain perfect arrays even though top of AAO templates was eliminated by etching of 1 M NaOH solution about 1 min. Their lengths usually achieve to 5 µm shown in the TEM image (Fig. 1b). The monodisperse $La_xCu_yO_z$ nanowires were obtained by complete elimination of AAO template, and their aspect ratio generally achieved to 50. The inset is the SAED pattern shows as-prepared nanowire is noncrystalline structure. No specific characteristic peak is found in the XRD pattern of $La_xCu_yO_z$ NWAs (Fig. 1c). Fig. 1d shows the EDS pattern exhibit the nanowire composing of La, Cu and O elements. The peak of Al is from the AAO template.

The hysteresis loops of $La_xCu_yO_z$ NWAs was measured by VSM at room temperature (Fig. 2), the applied magnetic field is parallel

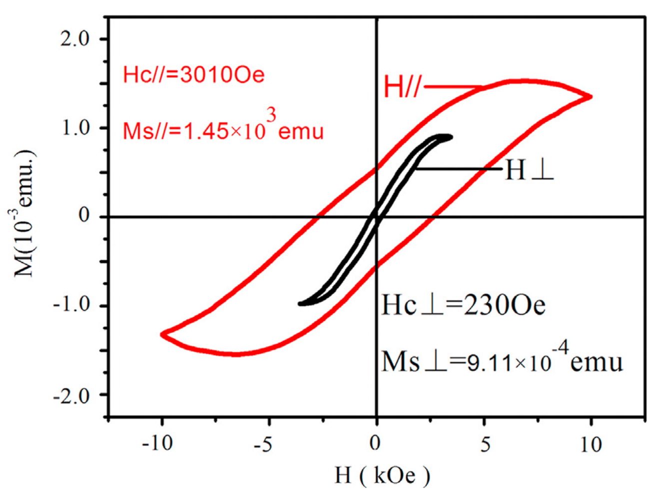

Fig. 2. M–H hysteresis loops of $La_xCu_yO_z$ NWAs.

(H//) or perpendicular (H⊥) to the axis of NWAs, respectively. The coercive force Hc(//) is 3010 Oe and Hc(⊥) is 230 Oe. Hc(//)/Hc(⊥) is achieved to 13. The saturation magnetization Ms(//) is 1.45×10^{-3} emu and remanence ratio Mr/Ms(//) is 0.33. Ms(⊥) is 9.11×10^{-4} emu and Mr/Ms(⊥) is 0.11. The hysteresis loops shows the easily magnetized direction of $La_xCu_yO_z$ NWAs is unusually perpendicular to the axis of nanowire, and the significant difference of coercive force and remanence ratio in parallel (//) or perpendicular (⊥) to the axis of NWAs lead to obvious magnetic anisotropy in $La_xCu_yO_z$ NWAs owing to the reduced dimension and