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Studies on structural and optical properties of rare earth copper oxides synthesized by template free hydrothermal method

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ABSTRACT

The present work investigates the structural and optical properties of rare earth copper oxides (RE_2CuO_4; RE: Pr, Nd, Sm and Gd) and mixed metal oxides (CeO_2/CuO) synthesized by template free hydrothermal method. RE_2CuO_4 were obtained after calcination at 700 °C, temperature appreciably lower than that employed in the conventional ceramic technique. The phase composition, particle size, thermal stability, morphology, elemental distribution and optical properties of the products were elucidated by various analytical techniques. X-ray diffraction patterns revealed tetragonal phase of products except for Cerium. Oval shaped particles forming agglomerates, and homogenous distribution of elements in the sample was evidenced by electron microscopy and elemental mapping. The optical band gap of the rare earth copper oxides is observed to be in the range of 0.79–1.36 eV, while CeO_2/CuO shows absorption band in the UV region and a band gap of 3.24 eV. ESR analysis shows the paramagnetic behaviour of the samples.

1. Introduction

In the recent years, the preparation and characterization of nanoparticles of various chemical compositions, structures and morphologies has gained importance in inorganic material research due to their broad range of applications [1]. The rare earth copper oxides have attracted much attention in the field of optoelectronics, magneto-optics, superconductivity, fuel cells, sensor material, electrode, gas separation membrane and catalysis due to their novel properties [2–7]. The rare earth copper oxides (RE_2CuO_4; RE: rare earth metal) with Ruddlesden popper structure consist of alternate layer of RE_2O_2 and square-planar CuO_2 planes with the absence of apical oxygen.

The literature reveals that these materials are mainly synthesized by multistep or complex methods under specific reaction conditions, high temperature and prolonged calcination time, intermediate grinding, presence of particular gaseous atmosphere, etc [8–16]. Solid state combustion has been a commonly adopted method for synthesizing such type of materials which involve the conditions as mentioned above. The sample thus obtained using high temperature synthesis method shows large particle size and poor homogeneity. To overcome these problems, template free hydrothermal method has been adopted in the present work. The hydrothermal synthesis is an ecofriendly method in terms of energy conservation with low processing temperature. The lower reaction temperature avoids the problems such as control of stoichiometry and volatilization of precursors. Depending on the temperature of reaction the hydrothermally synthesized products are amorphous, crystalline and anhydrous. Temperature of reaction enables the control of size while the particle shape can be controlled by starting materials as well as use of templates and surface active agents [17]. The method of synthesis is seen to affect the performance of the materials in various applications.

The present work gives a first hand report on the template free hydrothermal synthesis of rare earth copper oxides and mixed metal oxides. Pure phase products have been obtained after calcining the hydrothermally obtained products at 700 °C for 6 h, a temperature significantly lower than 1000–1100 °C as reported in the literature [3,5,10–14,18–22]. The synthesis was done to obtain pure phase products in nanosize.

The products have been characterized for their structural and optical properties in terms of crystallite size, morphology, chemical composition and band gap. The optical band gap of the rare earth copper oxides is observed to decrease with increase in the ionic radii of the rare earth metal.

Abbreviations: Pr_2CuO_4, Praseodymium copper oxide; Nd_2CuO_4, Neodymium copper oxide; Sm_2CuO_4, Samarium copper oxide; Gd_2CuO_4, Gadolinium copper oxide; CeO_2, Cerium oxide; CuO, copper oxide

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2. Materials and methods

2.1. Chemicals

All the chemicals used for the experimental purpose were of A. R. grade and were used without further purification. The hexahydrate precursors of Praseodymium (III) nitrate ($Pr(NO_3)_3·6H_2O$, 99.9%), Neodymium (III) nitrate ($Nd(NO_3)_3·6H_2O$, 99.9%), Samarium (III) nitrate ($Sm(NO_3)_3·6H_2O$, 99.9%), Gadolinium (III) nitrate ($Gd(NO_3)_3·6H_2O$, 99.9%) and Cerium nitrate ($Ce(NO_3)_3·6H_2O$, 99.9%) were from Alfa Aesar. Copper (II) nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, 99.5%) and Methanol (CH_3OH, 99.5%) were from S.D. Fine Chemicals Ltd. (SDFCL). Potassium hydroxide (KOH) extrapure pellets were from Sisco Research Laboratory (SRL). Double distilled water was used wherever necessary.

2.2. Experimental

A series of rare earth cuprates (RE_2CuO_4, RE: Ce, Pr, Nd, Sm and Gd) were synthesized by template free hydrothermal method. The nitrate precursors of rare earth element and copper were mixed together in 2:1 M ratio followed by the addition of 5–10 mL of double distilled water. The mixture was then heated on a hot plate at 80 °C for few minutes to obtain a dry mass followed by the addition of KOH as a hydrolyzing agent (5 times in molar proportion). To this, appropriate volume of water was added and the mixture was transferred to a Teflon-lined stainless steel autoclave and subjected to hydrothermal activation at 140 °C under autogenous pressure for 6 h. The products thus obtained, were centrifuged and washed repeatedly with distilled water to remove water soluble impurities and then with methanol and dried at room temperature.

The synthesized products were calcined at 700 °C for 6 h and further characterized by Fourier transform infrared (FTIR) and Ultraviolet–visible (UV–vis) spectroscopy, X-ray diffraction (XRD), Thermogravimetry (TG), Field emission scanning electron microscopy (FESEM), Energy dispersive X-ray (EDS) spectroscopic analysis and Elemental mapping, Brunauer-Emmett-Teller (BET) surface area measurement, Electron spin resonance (ESR) spectroscopy and Inductively coupled plasma-atomic emission spectroscopic (ICP-AES) analysis.

2.3. Characterizations

Fourier transform infrared (FTIR) spectra of the samples were recorded on a Shimadzu 8400 infra-red spectrophotometer with a maximum resolution of 0.85 cm^{-1} using KBr as a reference material in the frequency range of 400–4000 cm^{-1}.

The crystal phase, crystallite size and phase purity of the products were determined by X-ray diffraction (XRD) analysis on a Bruker D8 Advance Diffractometer using Ni-filtered Cu-Kα radiation ($\lambda = 1.5406$ Å) with the acceleration voltage of 40 kV, current of 40 mA and step time: 1°/min in the 2θ range of 20–80° at room temperature, silicon was used as an external standard for correction due to instrumental broadening. The average crystallite size of the powder was estimated by Scherrer formula. Crystal phases were identified by comparing the XRD analysis data with JCPDS (Joint committee on Powder Diffraction Standards) database. The thermal analysis of the samples was carried out by thermogravimetric method. The TG curves of the samples were recorded between room temperature to 1000 °C in air atmosphere at a heating rate of 10 °C min^{-1} and flow rate of 50 mL min^{-1} using Shimadzu instrument (Model DTG-60H).

The particle size and morphological characteristics of the ceramic samples were determined with the help of Field emission scanning electron microscopy (FESEM) (JEOL, JSM-7600F, FESEM). Images of the samples were recorded by coating the samples with a thin film of Ag-Pd alloy by vapour deposition technique. Elemental mapping of the samples were carried out using FEI (model) Quanta FEG 450 with Bruker XFlash 6130 detector.

The specific surface areas of the samples were determined by N_2 adsorption/desorption at liquid nitrogen temperature, using Thermo Fischer Scientific surface area analyzer, Model-surfer working on Brunauer-Emmett-Teller (BET) equation. Before analysis, the samples were desorbed under a vacuum ($< 10^{-2}$ Pa) for 2 h at 200 °C to remove moisture and adsorbed impurities.

The Ultraviolet–visible spectra of the samples were recorded on Shimadzu UV-3600, UV–vis spectrophotometer in the wavelength range of 200–1500 nm and the maximum resolution was 0.1 nm with $BaSO_4$ as a standard.

The electron spin resonance (ESR) spectra of the samples were recorded at room temperature on JES-FA200 ESR Spectrometer with X band with standard frequency 8.75–9.65 GHz (Make: JEOL, Japan), sensitivity 7×10^9 spins/0.1 mT and resolution 2.35 µT or better.

The elemental composition of the samples was obtained by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using spectrometer (model: ARCOS from M/s. Spectro, Germany with Charge Coupled Device detector) with a wavelength range of 130–770 nm. For this, the samples were prepared by chemical dissolution in aqua regia ($3HCl:1HNO_3$) at 60 °C for few minutes, followed by evaporation to dryness. The dry mass was diluted to a known volume with double distilled water before elemental analysis.

3. Results and discussion

The results (X-ray diffraction analysis) of the products revealed the formation of pure phase products of layered perovskite phase of Pr (Pr_2CuO_4), Nd (Nd_2CuO_4) and Sm (Sm_2CuO_4). Gadolinium yielded product (Gd_2CuO_4) with small concentration of CuO as impurity while mixed oxide phases of Ce and Cu (CeO_2/CuO) were obtained in case of cerium. The formation of particles in the nanoscale could be observed from SEM analysis while, those reported are in micron size [3,12,13,23] except for the report by Khandale et al. [9] for Nd_2CuO_4 with the particles size ∼77 nm.

3.1. Fourier transform infrared analysis

The Fourier transform infrared (FTIR) spectra of the rare earth copper oxides and mixed metal oxides are shown in Fig. 1.

Fig. 1a–d shows the FTIR spectra of the samples with the presence of distinct absorption bands at around 510 cm^{-1} and 680 cm^{-1}. The bands observed at 510 cm^{-1} and 680 cm^{-1} correspond to the stretching vibrations of O—Cu—O and Cu—O in the basal plane of CuO_6 octahedra in the Ln_2CuO_4 structure (Ln: Nd, Pr, Gd, Sm) [8,24–26]. The broad absorption band in the range of 429–605 cm^{-1} can be attributed to characteristic stretching vibrations of RE—O bond [26–28]. The band observed at 608 cm^{-1} is related to the Cu—O stretching vibrations [29]. For CeO_2/CuO sample the bands appearing at 718, 1346 and 1541 cm^{-1} are attributable to the formation of CeO_2 (Fig. 1e, as shown in inset) while, the metal–oxygen stretching bands of Cu—O are observed in the range of 600–1000 cm^{-1} in agreement with those reported in the literature [30–32].

3.2. X-ray diffraction analysis

The X-ray diffraction (XRD) patterns of the samples are shown in Fig. 2. Fig. 2a–c shows the formation of pure tetragonal phase of praseodymium copper oxide (Pr_2CuO_4, PDF # 79-0958), neodymium copper oxide (Nd_2CuO_4, PDF # 82-1728) and samarium copper oxide (Sm_2CuO_4, PDF # 82-0878) with an average crystallite size of 205 nm, 83 nm and 138 nm respectively [33].

Fig. 2d depicts the formation of gadolinium copper oxide (Gd_2CuO_4, PDF # 79-0102) as a predominant phase with the monoclinic copper oxide (CuO; PDF # 80-1917) as a minor phase. The average crystallite size of Gd_2CuO_4 is observed to be around 68 nm. The peaks observed at