Thin Solid Films 596 (2015) 18–23

Contents lists available at ScienceDirect

Thin Solid Films

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

Functionalization of SiC-based materials by a selective $YBa_2Cu_3O_{7-\delta}$ coating via sol–gel route in order to optimize their optical properties

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A R T I C L E I N F O

Article history:
Received 1 April 2015
Received in revised form 24 August 2015
Accepted 27 August 2015
Available online 28 September 2015

Keywords:
Functionalization
SiC
Sol–gel
Coating
Spectral selectivity

A B S T R A C T

SiC-based materials are good candidates for the application as solar receivers except concerning their optical properties. Indeed, considering the use at high temperature, materials used as solar receivers have to efficiently absorb the visible-near infrared waves (corresponding to solar spectral range) and simultaneously reflect the mid and far-infrared rays but SiC is absorbent in all the whole visible-infrared spectral domain. In this challenging work, a suitable $YBa_2Cu_3O_{7-\delta}$ oxide which can present appropriate optical properties is studied. It was synthesized following a sol–gel route and it was obtained with a high level of purity. $YBa_2Cu_3O_{7-\delta}$ pellets were realized and heat treated at different temperatures revealing that the higher the heat treatment is, the better the oxygen stoichiometry (7-δ) is and the smoothest the surface is. This directly acts on the $YBa_2Cu_3O_{7-\delta}$ optical properties. Considering these results, an $YBa_2Cu_3O_{7-\delta}$ coating was realized on SiC pellets by dip-coating. A homogenous and covering layer of about 10 μm was obtained presenting very promising optical properties which were predominant in the FIR-MIR range whereas absorptance was increased in NIR-visible range.

1. Introduction

Solar thermal energy processes are able to play an important role in providing both thermal energy and electrical energy for use in industry and in the residential sector. Among the different technologies, concentrated solar power plants appear promising for the conversion of solar radiation in hot air which drives a heat engine connected to an electrical power generator.

Between all the optical systems used to collect the incoming solar radiation, the solar receiver that must deliver hot air is one of the key components. To design it, porous ceramic foams appear very interesting in the range of 300–1200 °C because of their large specific surface which directly heats the air flowing through them. Generally, porous SiC-based materials are chosen as solar receivers because of their high temperature mechanical resistance [1]. Note that materials used as solar receivers have to efficiently absorb the visible-near infrared waves (corresponding to the solar spectral range). Simultaneously it has to reflect the mid and far-infrared rays (responsible for the thermal losses) and thus it has to present a low emittance in this spectral domain. This rule defines here the spectral selectivity. However, selected SiC compounds absorb all rays in the whole visible-infrared spectral domain making them less optimized for our purpose [2]. In order to enhance the spectral selectivity of volumetric absorbers, several works consisting of bilayer structures have been studied. [3] presents a two-slab structure: the first slab is composed of glass-beads transmitting the solar rays to the absorbent second slab made of silica honeycomb. Another way to make bilayer structure is to functionalize the absorber with a selective coating: [4], [5] or [6] present different spinel oxide coatings with a high temperature and oxidation stability and good selective efficiencies, showing that oxide coatings can be a suitable way to improve spectral selectivity of SiC absorbers.

To solve this challenging issue, a first step is to enhance the spectral selectivity of SiC receivers by depositing a suitable coating with appropriate optical properties on the whole solid network. $YBa_2Cu_3O_{7-\delta}$ coatings, when their thicknesses are higher than 400 nm and for $\delta \sim 0.2$–0.1, present a high reflectance in the mid-infrared spectral range and a high absorptance in the near infrared and visible spectral range at $T = 20$ °C [7] [8]. The understanding of the required experimental conditions to elaborate efficient $YBa_2Cu_3O_{7-\delta}$ coatings on 2D planar substrates will be used to foresee the passage towards the coating of 3D open-cell foams. To obtain the $YBa_2Cu_3O_{7-\delta}$ oxide, a lot of routes are available. It is thus possible to synthesize $YBa_2Cu_3O_{7-\delta}$ starting with metal acetate precursors, water, acetic acid and tri-ethanolamine followed by an adapted thermal treatment [9]. It is also possible to use metal alkoxides as starting materials but this route needs a lot of different solvents to dissolve the precursors [10]. These routes allow the coating of substrates by dip-coating but need several dips to obtain a thick layer. A different way to realize a thicker coating is by using vacuum coevaporation of Y, Cu and BaF_2 on the substrate [11] but this technique creates hydrofluoric acid vapor and is difficult to use on complex substrates as foams. We propose here a versatile way to synthesize the $YBa_2Cu_3O_{7-\delta}$

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http://dx.doi.org/10.1016/j.tsf.2015.08.063
0040-6090/

oxide by sol–gel route based on the Pechini's patent [12] allowing to easily control both the stoichiometry and the nanostructure of the synthesized oxide. Then, the crystallized powder obtained after a suitable thermal treatment is dispersed into an azeotropic solvent allowing to shape, after dipping the substrate into the suspension, a thick $YBa_2Cu_3O_{7-\delta}$ layer of about 10 μm.

However, the spectral selectivity of $YBa_2Cu_3O_{7-\delta}$ depends on the oxygen stoichiometry, which is governed by the thermal treatment used to synthesize it [13]. Many experimental methods have been used to evaluate the oxygen content in the $YBa_2Cu_3O_{7-\delta}$ samples: iodometric titration [14], thermogravimetric analysis [15], but all these measurements are destructive. [16] implemented a method to calculate oxygen stoichiometry based on the crystallographic cell parameters and the orthorhombicity degree. This non-destructive method seems to be the most suitable for this study. In this work, $YBa_2Cu_3O_{7-\delta}$ oxide is firstly synthesized and then SiC pellets with an $YBa_2Cu_3O_{7-\delta}$-type coating are studied, in particular its optical properties. The influence of the oxygen stoichiometry and the microstructure on the optical properties at room temperature are then evidenced.

2. Experimental

2.1. Materials

SiC pellets are first used as substrates, SiC powder synthesized by SICAT Company (Willstätt, Germany) is mixed with a binder (a solution of Rhodoviol 4/125, Prolabo) and pressed in a pelletizer with a pressure of 15 t. SiC pellets are sintered at 700 °C during 2 h with a heating rate of 100 °C/h which leads to pellets with a diameter of 20 mm and a thickness of 2 mm.

A route derived from the Pechini's patent [12] is used to prepare a precursor sol which leads to the formation of a metallic oxide ($YBa_2Cu_3O_{7-\delta}$ in this study) after a suitable heat treatment that we will discuss later. This process, followed by a suitable heat treatment, allows easily synthesizing various oxides with a totally controlled stoichiometry.

Two kinds of starting materials are used: inorganic compounds (metallic nitrates) providing cations and organic compounds such as acetylacetone (acac, Sigma-Aldrich 99%, chelating agent) and hexamethylenetetraamine (HMTA, Sigma-Aldrich 99%, polymeric precursor). A polymeric chain is formed by a hydrolysis reaction between HMTA and acac organic compounds. The cations are then homogeneously distributed through a complexation process in the structural network. The precursor sol is so prepared using acetic acid and water as solvents.

The nitrates $Y(NO_3)_3$, $6H_2O$ (Aldrich, 99.9%), $Ba(NO_3)$ (Acros Organics, 99%), and $Cu(NO_3)_2$, 3 H_2O (Sigma Aldrich 99.1%) are dissolved in distilled water (250 ml), with a respective molar ratio of 1:2:3 in cations (in order to obtain the convenient stoichiometry $YBa_2Cu_3O_{7-\delta}$ after a heat treatment) and a total concentration in cations of 1.2 M. Organic compounds (HMTA and acac) are dissolved into acetic acid with a molar ratio of 1:1. The nitrates and the organic compounds are then mixed with a ratio of 1:3.5 according to previous works [17] and the total volume is adjusted to 400 ml with acetic acid. The kinetics of the polymerization is increased by heating the mixture to 100 °C, until the total volume reaches 150 ml. A first step of calcination is carried out at 450 °C during 2 h with a heating rate of 100 °C/h according to previous work [18] in order to eliminate organic compounds then followed by a second treatment at 850 °C during 1 h with a heating rate of 100 °C/h under air flow in order to obtain crystallized $YBa_2Cu_3O_{7-\delta}$ without secondary phase as the green phase Y_2BaCuO_5. The black powder obtained is grounded in an agate ball mill at 400 rpm during 2 h in order to break the aggregates. The powder is used to prepare pellets (powder is melt with a binder and pressed in a pelletizer with a pressure of 15 t) in order to analyze their optical properties. 4 pellets are shaped and heat treated at 850 °C, 875 °C, 900 °C and 925 °C, under air flow, during 1 h, at a heating rate of 100 °C/h. The $YBa_2Cu_3O_{7-\delta}$ powder is also used to process suspensions in order to coat SiC pellets and analyze their optical properties too.

2.2. Processing of coatings on SiC pellets

$YBa_2Cu_3O_{7-\delta}$ thick films are prepared by dipping SiC pellets into the suspension. The $YBa_2Cu_3O_{7-\delta}$ powder is first dispersed in MEK–EtOH (60–40) azeotropic mixtures by using a commercial dispersant (Polyvinylpyrrolidone 3500 PVP K12, Acros Organics). In order to obtain a homogeneous suspension, 2.5% in weight of dispersant compared to $YBa_2Cu_3O_{7-\delta}$ powder is first dispersed in the azeotropic mixture and then powder (30% in weight) is added under constant magnetic stirring.

A withdrawal speed of 200 mm/min is used to prepare the films. After the dip-coating process, the $YBa_2Cu_3O_{7-\delta}$ film is dried at 90 °C and is finally heated to the convenient temperature (850 °C) under air flow by using a ramp of 100 °C/h, kept at this temperature for 1 h and then cooled to 500 °C during 10 h and finally allowed to cool to ambient temperature.

2.3. Characterization techniques

Powder structure is determined by X-ray diffraction using a BRUKER AXS D4 Endeavor diffractometer operating with a Cu-Kα radiation source.

$YBa_2Cu_3O_{7-\delta}$ pellets and coating microstructures are determined using a scanning electron microscope JEOL 6700F.

Optical properties of SiC and coated SiC are characterized with a BRUKER VERTEX 80v spectrometer in the spectral range of 500–25,000 cm^{-1} corresponding to the far, mid and near infrared ranges (FIR, MIR and NIR respectively) and the visible range. Measurements of diffuse reflection are realized with two integrating spheres, respectively a gold-coated sphere (∅ = 75 mm) associated with a liquid N_2 cooled HgCdTe detector to cover the range of 500–8500 cm^{-1} and a PTFE sphere (∅ = 75 mm) associated with a Silicon Diode detector to cover the range of 8500–25,000 cm^{-1}. Reference measurements are performed on caps respectively coated with gold and PTFE. Acquisitions are all made at room temperature under normal atmosphere.

3. Results and discussion

3.1. Synthesis of $YBa_2Cu_3O_{7-\delta}$

The black powder obtained after the heat treatment at 850 °C under air flow is analyzed by X-ray diffraction (Fig. 1). The powder is crystallized and the XRD pattern is indexed into the orthorhombic structure and a Pmmm space group (JCPDS n°00-050-1886). The $YBa_2Cu_3O_{7-\delta}$ powder obtained is pure according to these results. This powder is then used after gridding to realize pellets.

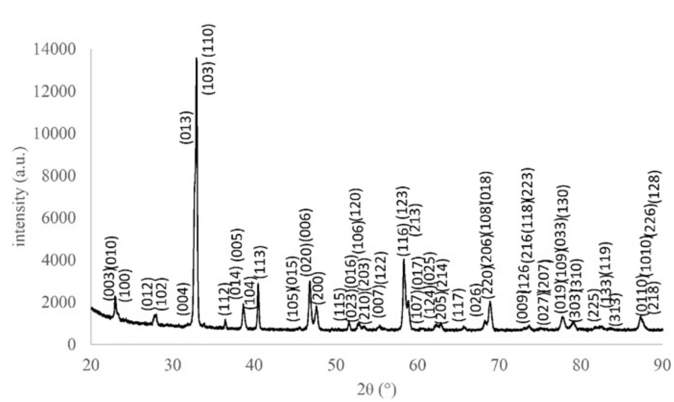

Fig. 1. XRD pattern of the $YBa_2Cu_3O_{7-\delta}$ powder obtained after a heat treatment at 850 °C under air flow.