Journal of the European Ceramic Society xxx (2016) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

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

Nanocrystalline multicomponent entropy stabilised transition metal oxides

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ARTICLE INFO

Article history:
Received 3 August 2016
Received in revised form
14 September 2016
Accepted 19 September 2016
Available online xxx

Keywords:
Spray pyrolysis
Reverse co-precipitation
Structural properties
Entropy stabilisation
Nanocrystalline

ABSTRACT

Multicomponent entropy stabilised oxides containing four and five metal elements in equiatomic amounts were successfully synthesised in nanocrystalline form by nebulised spray pyrolysis (NSP), flame spray pyrolysis (FSP) and reverse co-precipitation (RCP) techniques, demonstrating that entropy stabilisation of these recently discovered materials is independent of the synthesis method. Both 4- and 5-cationic systems, (Co,Mg,Ni,Zn)O and (Co,Cu,Mg,Ni,Zn)O, can be stabilised into a single rocksalt structure directly only using NSP, while in FSP and RCP, stabilisation can be achieved after thermal treatment. This result indicates, that in 5-cationic NSP system configurational entropy is high enough to directly stabilise single rocksalt phase at lower temperature, while higher synthesis temperature is required to compensate the lower configurational entropy in 4-cationic system. Retention of single-phase at room temperature indicates sluggish diffusion kinetics, making entropy stabilised phases quenchable.

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1. Introduction

In the era of material development, there is a constant and interminable quest for new materials. Several doped oxides and binary/ternary oxide ceramic compounds have been thoroughly studied, and as a result, a large potential for applications in the field of electronics as transistors, transparent conductors and sensors has been identified [1–5]. However, till date only a few studies have been reported on oxide ceramics having multiple transition metal (TM) elements in equimolar or near-equimolar ratios [6–8], the so called entropy stabilised oxides (ESOs). On the other hand, the near-equimolar metallic alloy systems commonly called high entropy alloys (HEAs) [9], are well-known, where the primary basis is the stabilisation of the crystalline phase by high configurational entropy. The HEAs have been a sought-after topic for research in the recent years owing to their augmented properties [10,11] when compared to conventional alloys with one or two principal elements. These systems also open the prospects not only for improved properties but also for studying the mid-range of the multicomponent phase diagrams [9], which in the earlier cases were limited to the apex of the diagrams as only one or two principal elemental alloys were studied. While high entropy carbide and nitride systems have been investigated [12–14], high-entropy oxide (HEO) based ceramic systems were not synthesised until recently. Rost et al. [6] successfully synthesised a multicomponent oxide system consisting of five elements (Co, Cu, Mg, Ni, and Zn). The authors demonstrated that an oxide system can be entropy stabilised into a single-phase structure (rocksalt, in this case). High entropy oxides can be very well considered to be equivalent to HEAs in terms of the configurational entropy calculations [9]. An oxide phase has two different kinds of sublattices: the oxygen sublattice and the cation sublattice(s). In case of HEO it is anticipated that only the cation

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http://dx.doi.org/10.1016/j.jeurceramsoc.2016.09.018
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Please cite this article in press as: A. Sarkar, et al., Nanocrystalline multicomponent entropy stabilised transition metal oxides, *J Eur Ceram Soc* (2016), http://dx.doi.org/10.1016/j.jeurceramsoc.2016.09.018

sublattice is altered and the oxygen sublattice is still only occupied by oxygen. Hence, the configurational entropy contribution of oxygen sublattice would remain zero and the entire configurational entropy of the system can be considered to be solely dependent on the cation sublattice. If a large number of cation species are randomly distributed in the cation sublattice, the configuration entropy would be significant. Due to the similarities with HEA, it is anticipated that HEOs would be enriched with novel properties like their metallic analogues owing to the synergising effect of the multiple elements present in equivalent amounts. Two recent studies by Bérardan et al. [7,8] showed that these new group of materials have interesting properties which can make them a strong contender in the field of energy. Besides “colossal dielectric constant” found in the (Co,Cu,Mg,Ni,Zn)O system [7], the study [8] also showed that the room temperature Li ion conductivity in Li-doped (Co,Cu,Mg,Ni,Zn)O is several orders of magnitude higher than the contemporary solid electrolyte (LiPON [15]) and are comparable to those attained in liquid electrolytes [16].

The present study deals with the possibility to synthesise the transition metal high entropy oxides (TM-HEOs) in the nanocrystalline form by several methods other than solid state techniques reported earlier [6,7]. The effects of different synthesis techniques on the crystal structure, elemental composition and particle morphology are analysed. Emphasis was placed on obtaining nanocrystalline transition metal HEOs as it is well-known that nanocrystalline materials can exhibit novel properties considerably different from their micron-sized counterparts. Based on the premise of wide range of functional properties (like magnetic, electronic, catalytic and mechanical) [4] related to the *d*-electron effect, two multicomponent oxide combinations containing transition metal ions were chosen for this study: (Co,Mg,Ni,Zn)O and (Co,Cu,Mg,Ni,Zn)O. The TM-HEO nanopowders were synthesised by two spray pyrolysis techniques – flame spray pyrolysis (FSP) and nebulised spray pyrolysis (NSP), and a wet-chemical technique – reverse co-precipitation (RCP). The approaches used here are known for their potential in the successful production of homogenous nanocrystalline oxides [17–19]. The techniques were selected such that FSP and NSP are rapid processes with short precursor/particle residence times, while RCP is a slower process with enough time for diffusion, which would additionally help in understanding the effect of reaction time on the phase composition, structure and morphology of the synthesised powders. Further, FSP and NSP being relatively faster processes not only reduce the synthesis time significantly but also enable stabilisation of metastable phases [20,21] due to their rapid quenching effect (fast cooling rates). Additionally, these processes have higher potential for industrial application compared to solid-state reaction technique in terms of production rate [6]. Reverse co-precipitation, on the other hand, was chosen over classical co-precipitation [22,23] because it has a greater potential in the production of homogeneous single-phase multicomponent systems as the pH is maintained constant throughout the process, and all the cations can be precipitated simultaneously into a mixed hydroxide.

Certain criteria were applied for the choice of the cations following Rost et al. [6]: (i) similar cationic radii at a specific oxidation state and co-ordination number; this approach is complementary to the Hume-Rothery rules [24,25] for metallic systems, which was followed in order to minimise distortion and strain effects that ensure complete miscibility in a single-phase, (ii) all the selected oxide systems should not have the same crystal structure; if all the oxides would have similar crystal structures then there would be a high probability that the multicomponent system will end up in a single-phase structure same as that of the individual oxides, and (iii) at least one binary oxide pair should not be miscible at 0.5 mol fraction. This information was obtained from available oxide pseudo-binary phase diagrams [26,27]. The last criterion uses the same analogy as the second mentioned earlier as otherwise it is quite natural for systems with complete miscibility in their binary phase diagrams to end-up as single-phase structures in multicomponent combinations. Table 1 gives an overview of the crystal structures, space groups, oxidation states, co-ordination numbers and corresponding cationic radii of the individual oxides used in this study.

Table 1
Crystal structures, space group (SG) [28], oxidation state, co-ordination number (CN) and corresponding cationic radii (r_c) [29].

Oxide	Structure	Space group (number)	Oxidation	CN	r_c [nm]
CoO	Rocksalt	$Fm\bar{3}m$ (225)	2+	VI	0.65[a]
CuO	Tenorite	$C12/c1$ (15)	2+	VI	0.73
MgO	Rocksalt	$Fm\bar{3}m$ (225)	2+	VI	0.72
NiO	Rocksalt	$Fm\bar{3}m$ (225)	2+	VI	0.69
ZnO	Wurtzite	$P6_3mc$ (186)	2+	IV	0.60
ZnO[b]	Rocksalt	$Fm\bar{3}m$ (225)	2+	VI	0.74

[a] Low spin.
[b] The rocksalt structure is only observed at high pressures (>9 GPa, [30]).

2. Experimental

2.1. Material synthesis

Two HEO systems (Co,Cu,Mg,Ni,Zn)O and (Co,Mg,Ni,Zn)O, where the elements are listed alphabetically for easy nomenclature, were synthesised using nitrates of the individual metals ($Co(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich, 99.9%), $Cu(NO_3)_2{\cdot}2.5H_2O$ (Sigma Aldrich, 99.9%), $Mg(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich, 99.9%), $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich, 99.9%), and $Zn(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar, 99.9%)) in the stoichiometric amounts in all three synthesis methods due to their high aqueous solubility. The total concentration of the aqueous solution was a synthesis/process dependent parameter used to enhance the rate of powder production. It will be specified in each synthesis procedure that was adopted.

2.1.1. Flame spray pyrolysis process

The total concentration of the precursor solution was 1 mol l^{-1} and was higher compared to NSP and RCP owing to its lower production rate (80–100 mg h^{-1} in the laboratory type reactor used). The FSP experimental setup is described in detail elsewhere [18,31]. The precursor solution was nebulised within a compressed air nebuliser and the mist formed was carried to the flame by oxygen as the carrier gas (5 standard l min^{-1}). Liquefied petroleum gas (0.04 standard l min^{-1}) and oxygen (20 standard l min^{-1}) were used as fuel and oxidiser for the flame, respectively. The gas flow rates were controlled by means of mass flow controllers. Thermal decomposition/pyrolysis reactions took place in the flame. The residence time of the particles formed in the flame was very short (typically, around 0.01 s [32]), leading to rapid heating as well as quenching. As a result, powders with very fine crystallite sizes were obtained. The formed particles were collected in a filter-based collection unit connected to a vacuum pump.

2.1.2. Nebulised spray pyrolysis process

The total concentration of the aqueous precursor solutions for NSP synthesis was 0.1 mol l^{-1}. The experimental setup is described in detail elsewhere [33]. The precursor solution was continuously delivered into the nebuliser at a rate of ~120 ml h^{-1}. The mist containing fine droplets of the precursor solution was formed by an ultrasonic nebuliser, which was transported by flowing oxygen (5 standard l min^{-1}) into the hot-wall reactor, where nanoparticles were formed at a temperature of 1150 °C and a total pressure of 900 mbar. One of the systems, (Co,Mg,Ni,Zn)O, was also synthesised at 1250 °C in order to study influence of temperature on phase com-

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