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Studies on the structural, quantitative and semi-quantitative analyses of NiO–GDC nanocomposites

Miguel Ángel Niño Galeano,^{*a} Ramalinga Viswanathan Mangalaraja,^{*a}
José Antonio Jiménez Rodríguez,^b Marta López,^c Ricardo E. Ávila^d
and Felipe Sanhueza^e

A simultaneous analysis of the crystallite size and strain of $x\text{NiO} \cdot (1 - x)\text{GDC}$ nanopowders prepared in stoichiometric proportions of $x = 0, 0.1, 0.2 \dots$ to 1 was performed by a self-sustained combustion (SC) process and calcination of the thus-synthesized nanopowders at 600 °C. The nanopowders were examined by powder X-ray diffraction (XRD) pattern using two approaches: integral breadth of multiple peaks (multi-line) with Pearson VII (PVII), and pattern analysis of powders through total adjustment of the diffraction peaks with the double-Voigt (V–V) method. The synthesis route and stoichiometric variation allowed a quantitative study using the global setting profile with Rietveld refinement and semi-quantitative analysis by X-ray fluorescence (XRF) of nickel oxide (NiO) and gadolinium doped ceria (GDC) phases in the as-prepared and the calcined samples. The investigation of the microstructures of the nanopowders was further supported by high-resolution transmission electron microscopy (HR-TEM) and scanning electronic microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS).

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Introduction

The development of X-rays in the twentieth century is a cornerstone of evolution in the field of solid-state sciences and also in understanding chemical bonds. Although Roentgen discovered X-rays (1898), several other pioneers, such as Moseley (1912) and Bragg (1913), have paved the way for improvement in many essential techniques for the characterization of metals, ceramics, semiconductors, glasses, minerals and biological materials. Diffraction studies, along with fluorescence and absorption studies, provide qualitative and quantitative information on the structure and composition, which are indispensable elements to understanding the nature of materials.¹

Recently, nanostructured ceramic materials have received significant attention because they demonstrate better returns or possess unique properties compared to conventional ceramic materials. Cerium based materials such as cerium doped gadolinium (GDC) and compounds of nickel oxide (NiO) with GDC are considered to be promising candidates as electrolytes and anodes, respectively, in the design of intermediate-temperature solid oxide fuel cells. GDC, a mixed conductor,

possesses higher ionic conductivity than yttrium stabilized zirconia (YSZ) at intermediate temperatures (between 400 °C and 700 °C); therefore, the difficulties arising from degradation of the materials can be minimized by using high temperatures (≈ 1000 °C). In addition, the usage of GDC reduces manufacturing costs and increases production.²

NiO–GDC powder can be synthesized by a self-sustaining citrate–nitrate combustion technique (SC), which has emerged as a facile and inexpensive method to facilitate the formation of nanoceramics with homogeneous microstructures at low temperature and with short reaction times. This SC technique is based on the principles of chemical propellants,³ which involve a redox reaction between a thermal-induced oxidant and a fuel.⁴

Theoretical and experimental procedure

Stoichiometric quantities of cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, $\geq 99.5\%$), gadolinium nitrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, $\geq 99.5\%$), and nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich, $\geq 99.5\%$) were mixed with a calculated amount of citric acid (Sigma Aldrich, ACS reagent, $\geq 99.5\%$). This mixture was dissolved in the amount of distilled water required to achieve a clear homogeneous solution and was then stirred for three hours using a magnetic stirrer. The amount of citric acid was calculated by the chemical propellant principle, *i.e.* the ratio of the oxidizing and reducing valences must be equal to 1. The resulting solution obtained after stirring was poured into an alumina crucible, and the crucible was maintained for 10

^aAdvanced Ceramics and Nanotechnology, Department of Materials Engineering, University of Concepción, Chile. E-mail: miguelnino@udec.cl; mangal@udec.cl; Fax: +56 41 2203391; Tel: +56 41 2207389

^bNational Center for Metallurgical Investigations, Spanish National Research Council (CENIM-CSIC), X-ray Manager Laboratory, Madrid, Spain

^cDepartment of Materials Engineering, University of Concepción, Chile

^dChilean Commission of Nuclear Energy, Santiago, Chile

^eTechnological Development Unit, University of Concepción, Chile

minutes in an oven preheated to 500 °C while the self-sustained combustion process occurred. The high exothermic energy generated during the combustion process releases many gases, such as N₂, CO₂ and water vapor, to form a foam with a fragile, porous and irregular nature; this was powdered using an agate mortar.⁵ To remove the organic residues, the thus-obtained fine powder was finally calcined at 600 °C for 2 hours.⁶ The chemical reaction that leads to SC is given by

where $x = 0, 0.1, 0.2, \dots, 0.9, 1$ (in mol%), and y is obtained from the chemical propellant; z_1, z_2 and z_3 are constants arising from the combustion process.^{7,8} The total sum of the products of the cation and anion valences by the stoichiometric coefficients should be zero:

$$\Sigma(\text{oxidant element coefficients} \times \text{valences}) + \Sigma(\text{reductor element coefficients} \times \text{valences}) = 0 \quad (2)$$

These valences must be balanced by the total valence of the fuel; therefore, the composition requires the determination of the y value for each case in order to release the maximum energy of the reaction.⁹

XRD analysis was used to characterize the phases of the as-prepared and calcined samples. These measurements were carried out using a Bruker AXS D8 diffractometer equipped with an X-ray tube with a copper target (CuK_α wavelength $\lambda = 1.54 \text{ \AA}$), a nickel filter and a point detector. The operating conditions of current = 30 mA and voltage = 40 kV in the tube were selected for high quality XRD profiles as well as for good statistical analysis, narrow peaks and detection of small peaks. The XRD data was collected over the 2θ range from 10° to 70°, with a step size of 0.02° and a counting time of 1 second per step, which was sufficient for the intensity obtained (usually, if the peaks are weak, more time is required to acquire data¹⁰).

In this work, Rietveld analysis using TOPAS version 4.2 (Bruker AXS) and XRD refinement were used. The Rietveld method of nonlinear least-squares fit is the best fit between the experimental profile and the profile calculated based on the peak intensities after an entire refinement of the parameters given by the method.¹¹ For the application of the Rietveld method, the instrumental function was empirically parameterized from the profile shape of a corundum standard sample (NIST 676^a) and measured under the same conditions. The refinement protocol also included major parameters such as background, zero displacement, scale factors, peak breadth and unit cell parameters. On the other hand, line broadening effects that arose due to crystallite size and lattice strain were analyzed in this refinement with the double-Voigt approach, in which both comprise a convolution of Lorentzian and Gaussian with varying 2θ as a function of $1/\cos \theta$ and $\tan \theta$, respectively.^{12–14} The quality and reliability of the Rietveld analysis was

quantified by the corresponding figures of merit: adjusting the weighted sum of least squares (R_w), adjusting the statistically expected sum of least squares, (R_{exp}), the residual profile (R_p), and the goodness of fit (GoF, often referred to as chi-square).¹⁵ Since $\text{GoF} = R_w/R_{\text{exp}}$, a value of one GoF equal to 1 indicates a perfect fitting.

The XRF dispersion wavelength to quantify the phases of the synthesized and calcined samples was carried out with a ZSX Primus II Rigaku spectrometer. The semi-quantitative analysis was performed with SQX software. This program is based on spectral series sweeps which are optimized for spectral resolution (choice of collimator glass) rather than sensitivity. The peaks of the elements are identified by automatically subtracting the background rate accounts. The program applies theoretical approaches of “basic parameters” using information from the physics of the X-rays to calculate matrices (correction) individually for each element detected in the sample. This procedure is an iterative process which ultimately provides the concentrations of the elements.

The XPHS program, which allows the peak of each line in position to be distinguished, was used. The phases of the powders were identified with the software database. The information processed by XPHS was resolved with Origin 8.0 software to mathematically adjust each peak at a PVII distribution within the multi-line approach.¹⁶

For the β width, the value w (or Full Width at Half Maximum = FWHM), is corrected to the mathematical profile adjustment of a Lorentz [L] or Gauss [G] instrument. This FWHM, which computes PVII, is included in the relationship described in terms of β , w and gamma function (Γ), i.e., the shape coefficient for a PVII.

$$\left(\frac{w}{\beta}\right)^{\text{PVII}} = \frac{2(2^{1/m} - 1)^{1/2} \Gamma[m]}{\pi^{1/2} \Gamma\left[m - \frac{1}{2}\right]} \quad (3)$$

The peak shape is subjected to adjustment of the parameter m , which effectively combines functions [L] and [G] to describe the profile.¹⁷ Individual contributions to the broadening occurring due to crystallite size and deformation can be determined only after subtracting the effect of peak broadening due to the instrument.¹⁸ The peak width and shape vary with respect to 2θ . It is fundamental to examine the variation in 2θ FWHM regarding the instrument.¹⁹ Polynomials describing the instrumental resolution function (IRF) were proposed by Cagliotti *et al.*²⁰ in the Rietveld refinement to explain the broadening behavior [G] or [L] due to the instrument.

$$(\text{FWHM}_{\text{ins}})^2 = U \tan^2 \theta + V \tan \theta + W \quad (4)$$

$$\text{FWHM}_{\text{ins}} = X \tan \theta + Y/\cos \theta \quad (5)$$

U, V, W and/or X , and Y are refinable parameters.

For multi-line analysis, the change in $\text{FWHM}_{\text{ins}}(w_{\text{ins}})$ for the sweep interval is smooth and does not change significantly. Therefore, it can be considered to be a linear model for the IRF with three measuring points: 35.16°, 43.36° and 57.51°. The

effects of the instrument are described by the mathematical relationship $w_{\text{ins}} = 6.532 \times 10^{-5}(2\theta) + 8.457 \times 10^{-4}$.

The FWHM correction (w_{obs}) due to the instrument was conducted with three mathematical approaches: [L], [G] and parabolic [P]. If the peak has a [L] or [G] profile, the instrumental influence is removed in eqn (3) to obtain the β value. Accordingly,

$$[\text{L}]: w = w_{\text{obs}} - w_{\text{ins}} \quad (6)$$

or

$$[\text{G}]: (w)^2 = (w_{\text{obs}})^2 - (w_{\text{ins}})^2 \quad (7)$$

Wagner and Aqua²¹ suggested the parabolic relationship of integral breadths given by

$$[\text{P}]: \beta_{\text{T}} = \beta(1 - (\beta_{\text{ins}}/\beta)^2) \quad (8)$$

In eqn (8), all the instrumental effects on the Gaussian profile are calculated in accordance with the assumption of $\beta_{\text{ins}} = [\sqrt{(\pi/2 \ln(2))}] \times w_{\text{ins}}/2$.¹⁷

The microstructural features of the 0.5NiO–0.5GDC nanocomposite were examined for both the as-prepared and calcined nanopowders. High-resolution transmission electron (HR-TEM) micrographs and selected area of electron diffraction patterns (SAED) were obtained with a FEI TITAN G2 80-300 microscope and were examined with GATAN software. Also, scanning electron micrographs (SEM) were acquired with QUANTA QEMSCAN 650 equipment, and elemental chemical identification was conducted using energy dispersive X-ray spectroscopy (EDS).

Results and discussion

In broadening line analysis, the generalization of the approximation in adjustments to Lorentz and Gaussian has been experimentally justified.²² Therefore, if it is not assumed with the conviction of a mathematical adjustment to the diffraction peak profile, a convolution of functions [L] and [G] is the best way to describe the structural peak.^{13,23,24} The mathematical

structure of β enables approximation of the pattern diffraction profile in the analytic functions [L] and [G].

The PVII distribution is a function ranging from [G] (broadens towards the tip and narrows at the base) to [L] (opposite to Gaussian) with the selection of an adjustable parameter m to accommodate the shape of the diffraction profile of each peak.^{16,19} It should be noted that Voigt (V), pseudo-Voigt (p-V) and PVII provide descriptions of the shape of the peaks with the same approximate degree of accuracy.^{25,26} However, PVII does not confer the ability to solve (analytically) the convolution of functions [L] and [G]. In addition, while providing high reliability in the setting, there is no function V that enables extraction of the microstructural physical information.

Fig. 1 shows the clear differences between the adjustments V, p-V and PVII. It is clear that both V and p-V lose precision throughout the profile; however, the presence of disagreement is evident from the magnified image of the inflection zone where the queues originate. PVII fits properly at the top, agrees with the contour and even stands out for the queues. The proximity between the precision values of the adjustment profiles did not limit the categorical decision that PVII gives the best mathematical representation of the peaks.

Crystallite size and microdeformation

Imperfections modify the intensity distribution of the Bragg reflection and the peak shape of polycrystalline materials. This modification of peak shape, which defines the microstructure, in turn strongly indicates the physical, mechanical and chemical properties of materials.¹⁹

Among the major existing methods for extracting the sizes of coherent domains from the diffraction peak, the Scherrer equation is the most widely used. Thus, for incident monochromatic radiation on a mono-dispersed powder of cube-formed crystallites,²⁷ the expression derived by Scherrer (except for a constant that arises from the Gaussian representation of the peak) for the crystallite size²⁸ is

Fig. 1 Comparative graph of the adjustments V, p-V and PVII for the NiO (200) (left) and GDC (111) (right) peaks of the calcined sample.

$$t_{hkl} = \frac{\lambda}{\beta_{hkl}^f \times \cos \theta_{hkl}} \quad (9)$$

In other words, t_{hkl} is the “apparent” crystallite size in the perpendicular direction to the network planes, hkl are the Miller indices of the planes under consideration, β_{hkl}^f is the integral width of the peak at 2θ radians of adjustment f , θ_{hkl} is the Bragg angle and λ is the wavelength of the X-rays used.

Crystal lattice deformations are represented by multiple displacements of atoms from their positions into an idealized structure due to dislocations, vacancies, interstitial and substitutional defects. It should be noted that the distances between planes are continually changing according to $d_0 - \Delta d$ and $d_0 + \Delta d$ (where d_0 and Δd are the interplanar distances of an ideal crystal and the average change in the distance between hkl planes in the crystal volume, respectively). The derivation of ε from the Bragg equation is

$$\eta = 4\varepsilon = \beta_{hkl}^f / \tan \theta_{hkl} \quad (10)$$

If all values are assumed with equal likely stress values between 0 and a maximum value, then 4ε corresponds to the maximum deformation limit.²⁹

If the crystallite size and deformation are simultaneously present, microstructure analysis naturally involves a competition between the contributions of the crystallite size and the deformation to the width of the diffraction peak.

Schoenin suggested that size-broadening is represented by the [L] profile and deformation-broadening by the [G] profile and proposed a graphical method for the separation of each contribution to the broadening of each peak.³⁰ However, much earlier, Williamson and Hall assumed that the width originates from a relationship of type [L]. Based on the above, the following equations are used in the analysis of multiple lines:¹³

For Hall,³¹ both profiles are described by [L] functions:

$$[L] - [L]: \beta_T^f = \beta_C^f + \beta_S^f \Rightarrow \beta_T^f = \frac{K \times \lambda}{t \times \cos \theta} + 4\varepsilon \tan \theta \quad (11)$$

Meanwhile, Kurdyumov *et al.*³² proposed that both profiles are described by [G] functions:

$$\begin{aligned} [G] - [G]: (\beta_T^f)^2 &= (\beta_C^f)^2 + (\beta_S^f)^2 \Rightarrow (\beta_T^f)^2 \\ &= \left(\frac{K \times \lambda}{t \times \cos \theta} \right)^2 + (4\varepsilon \tan \theta)^2 \end{aligned} \quad (12)$$

However, Schoenin³⁰ and Halder and Wagner³³ showed that the profile describing the crystallite size is given by the [L] function and the deformation is represented by the [G] function. Thus, Halder and Wagner³³ developed the equation

$$[L] - [G]: \frac{\beta_C^f}{\beta_T^f} = 1 - \left(\frac{\beta_S^f}{\beta_T^f} \right)^2 \Rightarrow \beta_T^f = \frac{K \times \lambda}{t \times \cos \theta} + \frac{(4\varepsilon \tan \theta)^2}{\beta_T^f} \quad (13)$$

where β_T^f is the width of the profile, β_C^f is the contribution to the profile width due to crystallite size and β_S^f is the contribution to the profile width due to deformation.

Eqn (11) is called the Williamson–Hall equation. Eqn (13) is similar to the approach of Halder and Wagner²⁴ for the integral width of a function V , and expression (12) is valid for a Gaussian presumption.

Corrections to the observed width using eqn (6)–(8) are applied in their order of relations with eqn (11)–(13) under the assumption of the mathematical profiles that represent the crystallite size and the microstrain, respectively.

Microstructure analysis of crystallite size and the micro-strain multi-line comes from an extensive study supported by propagation error theory.

Identification of phases of NiO–GDC composites

XPHS is a first step to confirm the polycrystalline nature as well as the nanosize of both the as-prepared and calcined powders. With regard to the synthesis route and the calcination temperature, the powders showed imperceptible amounts of carbon, nitrogen and hydrogen. In short, during the calcination process, all the waste obtained from combustion was eliminated. Also, this thermal treatment promoted the complete oxidation of nickel.³⁴

The XRD patterns of the $x\text{NiO} \cdot (1-x)\text{GDC}$ nanopowders (Fig. 2) were identified with JCPDS (Joint Committee on Powder Diffraction Standards) standards. The cubic phases of nickel oxide (78-0423), gadolinium doped ceria (75-0161) and metallic nickel (87-0712) belong to the space group $Fm\bar{3}m$. The crystal-line phases of NiO and GDC (which indicates that there was no solid solution between them) remained unchanged even after calcination, without the appearance of new diffraction peaks.

An increase in peak intensity accompanied by a decrease in peak width is indicative of crystallite growth by the calcination process. Changes in the conditions of thermal treatment, an important step in structural formation, not only determine the final shape but also ensure the formation of high-dispersion material.³⁵

XRF

The intensity of the energy associated with each electron transition is proportional to the concentration of the elements present. Based on this principle, XRF analysis can be defined as a spectrum, showing the radiation intensity as a wavelength function. The results obtained from the XRF analysis (Fig. 3) of the as-prepared and calcined samples suggest that the amounts of NiO and GDC are not consistent with the theoretically predicted results obtained using the starting stoichiometry.

The fitted impurities percentage, obtained using the software, remained in the range of 0 to 0.67; this can be attributed to semi-quantification error because the metallic nickel has been assumed to be nickel oxide in the fluorescence analysis.

The exothermic reaction of the SC can generate an intense amount of heat because the critical temperature produced during the reaction is between 2000 K and 3000 K.^{36,37} This

Fig. 2 Experimental XRD profiles of the as-prepared (left) and calcined samples (right).

intense amount of heat manifests the ability to melt or volatilize the reagents as well as the products; sometimes, both melting and volatilizing will occur. Therefore, the adiabatic flame temperatures of combustion were calculated as a possible cause of divergence between the theoretical expected values and the outcomes obtained from both Rietveld and XRF.

The thermodynamic data of reagents and products include the enthalpies of reaction for combustion,^{38–41} while the amounts of gases generated were calculated based on eqn (1). It is assumed that $\text{GDC} \approx \text{CeO}_2 = -260 \text{ kcal mol}^{-1}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} \approx -700 \text{ kcal mol}^{-1}$. Therefore, the flame temperatures as a function of the fuel/oxidant ratio were estimated:

$$\Delta H = \sum n\Delta H_{\text{prod}} - \sum n\Delta H_{\text{reac}} = - \int_{298}^{T_c} \left(\sum nC_p \right) dT \quad (14)$$

where ΔH_{prod} and ΔH_{reac} are the enthalpies of formation of the products and reagents, respectively, T_c is the critical

temperature of the theoretical adiabatic flame and C_p is the molar heat capacity at constant pressure.^{39,41}

Despite the complexity of the combustion thermal behavior, eqn (14) assumes an ideal thermodynamic process in which there will be no heat exchange with the environment. The adiabatic argument is under the first law of thermodynamics, which allows a maximum temperature that can be generated during the combustion process. Thus, for the as-prepared samples, the maximum range of temperatures calculated according to the nickel content was $1189.5 \text{ K} \leq T_c \leq 1301.8 \text{ K}$. These temperatures are consistent with the measurements made in image analysis by Chinarro *et al.*⁴² to study the synthesis of ceramic and ceramic-metal materials using combustion. However, it can be suggested that the temperatures during the synthesis were not solely responsible for the differences found between the expected results and the results obtained by Rietveld and XRF. The deviation from linearity shows that SC is rarely a complete reaction, and as a result, the products are highly heterogeneous in nature.

Fig. 3 Nominal weight fractions (stoichiometric) with XRF of NiO in the as-prepared and calcined samples.

Fig. 4 Nominal weight fractions (stoichiometric) with Rietveld refinement of NiO in the as-prepared and calcined samples.

Fig. 5 GDC and NiO crystallite sizes obtained with Rietveld refinement and the [L]–[L], [G]–[G] and [L]–[G] graphical methods for the as-prepared samples.

Rietveld refinement

Within modern X-ray diffraction analysis, the TOPAS program is distinguished by the definition of new standard sets for profile and structural analysis by an efficient method where all the profiles use convergence and apply it to fitting techniques. In fact, among the most important applications, it excels at the incorporation of a modified Rietveld refinement that increases precision and avoids the deconvolution of overlapping peaks. As shown in Fig. 4, even after applying the Rietveld method, the amounts of NiO and GDC do not match the theoretically predicted amounts.

The amounts of NiO and GDC found in the calcined sample are the same as those found in the starting sample. The areas of the diffraction peaks of the two phases coincide with each other, which indicates that during calcination, crystallization of the

amorphous phase has not occurred in the starting material. During calcination, the nickel in the starting material is only oxidized, without any crystallization of the amorphous phase; this is evident from the identical baselines of the diffractograms and the doubled peak areas of the calcined sample compared with those of the starting material. The goodness interval of the as-prepared samples was $1.06 \leq \text{GoF} \leq 1.33$ and that of the calcined samples was $1.05 \leq \text{GoF} \leq 1.10$. The lattice parameter of the phases was independent of x and had a marginal error of 0.0002 (lattice parameter JCPDS $a_{\text{NiO}} = 4.1790 \text{ \AA}$, $a_{\text{GDC}} = 5.4180 \text{ \AA}$, and $a_{\text{Ni}} = 3.5238 \text{ \AA}$) due to the absence of nickel in the as-prepared sample ($x = 0.1$).

Size-microdeformation analysis with V-V

A precise description of powder pattern shape profiles is critical to the success of any adjustment application. The V-V approach

Fig. 6 GDC and NiO crystallite sizes obtained with Rietveld refinement and the [L]–[L], [G]–[G] and [L]–[G] graphical methods for the calcined samples.

Table 1 Microstrain values of as-prepared and calcined samples calculated using Rietveld refinement and the [L]–[L], [G]–[G] and [L]–[G] graphical methods

As prepared										Calcined									
Rietveld					Lorentz–Lorentz					Gauss–Gauss					Rietveld				
η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)	η ($\times 10^{-3}$)	Error ($\times 10^{-3}$)
GDC																			
1GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.1NiO–0.9GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.2NiO–0.8GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.3NiO–0.7GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.4NiO–0.6GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.5NiO–0.5GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.6NiO–0.4GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.7NiO–0.3GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.8NiO–0.2GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.9NiO–0.1GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
NiO																			
0.1NiO–0.9GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.2NiO–0.8GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.3NiO–0.7GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.4NiO–0.6GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.5NiO–0.5GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.6NiO–0.4GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.7NiO–0.3GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.8NiO–0.2GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.9NiO–0.1GDC	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ni																			
0.8NiO–0.2GDC	1.7	0.17	No medible	—	—	No medible	—	No medible	—	—	—	No medible	—	—	—	—	—	—	—
0.9NiO–0.1GDC	1.9	0.17	0.47	—	—	3.0	—	—	—	—	—	42	—	—	—	—	—	—	—
1NiO	1.9	0.34	—3.5	—	—	3.3	—	—	—	—	—	2.8	—	—	—	—	—	—	—

employed by TOPAS⁴³ allows the calculation of L_{Vol} according to eqn (9) for an intermediate crystallite size and according to eqn (10) for deformation, which are modeled by a function V. The approach with the TOPAS fundamental parameters assumes the calculation of η with distortion $\Delta d/d$ and a network with 50% probability of being related to the distortion.⁴⁴

The obtained crystallite sizes confirmed their nanosized natures. The crystallite growth obeys the thermo-chemical events involved in their synthesis and subsequent calcination. As shown in Fig. 5 and 6, GDC has a tendency toward crystallite growth (both in preparation and calcination of the samples) irrespective of the nickel concentration. Furthermore, NiO growth was intrinsically linked to the increase in nickel concentration during both the preparation and the calcination process.

Although the XRD patterns did not show significant peak shifting, the lines are broadened slightly with respect to the diffraction angle, which indicates the minimal presence of microstrain (see Table 1). In many cases, the difference between the coefficients of thermal expansion is responsible for the deformation.⁴⁵ Consequently, the physical meaning of the results can be related to the proximity between the thermal expansion coefficients of GDC ($12 \times 10^{-6} \text{ K}^{-1}$) and NiO ($14 \times 10^{-6} \text{ K}^{-1}$).

Size-microdeformation multi-line analysis

Usually, the crystallites in a sample have the same shape and dimensions; therefore, the apparent size is influenced by variations in the crystallite shape and size, and it is thus difficult to evaluate the apparent size. These restrictions are also implicitly

Fig. 7 (a) Graphical method [L]-[L], (b) graphical method [G]-[G] and (c) graphical method [L]-[G] for GDC with 5 peaks for $x = 0.3$.

included in the graphical method, which essentially combines eqn (9) with an apparent strain relation derived from Bragg's law, *i.e.*, eqn (10).⁴⁶

Single-line analysis requires adjustment profiles that allow deconvolution into analytic functions, whereas multi-line analysis requires any distribution that is used as an adjustment which will allow separation of the contributions to the broadening of the peak, crystallite size and microstrain, without deconvolution by means of interpreting the specific parameters for the linear fit.

The graphical method [L]–[L] shows the importance of the sign of the microstrain value. GDC shows compressive strain and NiO shows tensile strain for both the as-prepared and calcined samples. The Gaussian shape assumption for the deformation results in a positive elongation for the nanocomposites. An atom such as gadolinium within cerium oxide is seen as a substitutional defect which can induce microstrain by compression of the neighboring crystals, while nickel oxide can cause microstrain due to stress.⁴⁵ There is no possibility of resolving the overlap between the background diffractogram baseline and the low intensity NiO peaks ($x = 0.1, 0.2, 0.3$ for the as-prepared and $x = 0.1, 0.2$ for the calcined samples) in accordance with the results of Chavan *et al.*⁴⁵

The standard error adjustment parameter (m) presented at GDC peaks (222) and (400) and the three NiO peaks for $x = 0.4$ and 0.5 for the as-prepared and $x = 0.2, 0.5$ for the calcined samples was high. The magnitude of the plastic deformation was very small, on the order of 10^{-3} , 10^{-4} and 10^{-5} .⁴⁷

Table 1 shows that the [G]–[G] method describes the deformation much better for the as-prepared samples, whereas for the calcined samples, [L]–[L] and [G]–[G] fit better to the GDC peaks and NiO peaks, respectively.

Multi-line analysis considers the intrinsic contribution of the deformation to the broadening of the diffraction peak; therefore, it indicates a strain significantly larger than or less than zero, and also confers an increase of the average

crystallite size for all the crystallographic directions,⁴⁸ as shown in Fig. 7. However, the microstrain resulting from multi-line analysis allows dismissal of the microstrain effect in both the as-prepared and calcined samples. Indeed, these results are comparable with the microstrain value of silicon powder (considering the microstrain value of silicon, which is almost free of dust, 0.01%).⁴⁹

SEM and HR-TEM analyses

Particle size is a critical parameter in processing materials and fine crystallites from nanopowders, and this parameter generally improves the mechanical, thermal, electrical and magnetic properties of ceramics, sintered metals and composites.⁵⁰ The SEM images of the calcined nanocomposites (Fig. 8) showed homogeneity and less agglomeration compared to the as-prepared nanopowders. The spectrograms (inset) of the elemental chemical analysis confirmed the presence of nickel, oxygen, cerium and gadolinium along with the chemical composition of the as-prepared and calcined samples, respectively.

The nanocrystalline nature and the arrangement of the network of planes with atomic resolution is shown in Fig. 9. Also, the SAED images confirmed the electron diffraction from the network planes of the respective phases of the nanocomposites. The crystallographic planes of GDC (yellow) and the crystallographic planes of NiO (green) were identified. Unfortunately, the measurement accuracy has limited the identification (red) of nickel (220), GDC (331) and NiO (311), due to their measurements of 8.03 nm^{-1} and 8.08 nm^{-1} ; these match the measurements of GDC (420) and NiO (222), which are 8.25 nm^{-1} and 8.35 nm^{-1} , respectively.

Fig. 9 AP1 and CA1 clearly show the appearance of aggregates of nanoparticles with internal crystalline structures. A size distribution of nanoparticles between 5 and 10 nm is observed in AP1, whereas in the case of CA1, a size distribution of nanoparticles between 10 nm and 20 nm is observed due to their crystallite growth during the heat treatment. Both the as-

Fig. 8 SEM micrographs at 200 $\times$ for the as-prepared and calcined samples of 0.5NiO–0.5GDC. The top and bottom insets are their corresponding EDS spectra and SEM micrographs at 4000 $\times$.

Fig. 9 HR-TEM micrographs at two different magnifications (1 and 2) and SAED patterns of the as-prepared (AP) and calcined (CA) 0.5NiO–0.5GDC samples.

synthesized and calcined samples show a mixture of spherical and irregular, non-spherical morphologies.

Conclusions

The self-sustained combustion (SC) route is an effective and low-cost method for the production of materials on an industrial scale. This synthesis technique ensures the preparation of $x\text{NiO} \cdot (1 - x)\text{GDC}$ nanomaterials. However, the reaction rarely goes to completion, and the end product is highly heterogeneous.

Heat treatment by calcination is a versatile technique that promotes the complete oxidation of nickel, removes organic residues, reduces heterogeneity, releases stress within the composites and also increases the crystallite size.

PVII is a simple and convenient mathematical function to represent XRD patterns with the highest precision, even without physical justification for the choice of an adjustment profile.

The behavioral inspection of the XRD patterns with respect to x showed a strange tendency regarding the peak intensities. In fact, the quantitative analysis by Rietveld refinement and XRF confirmed that the amounts of NiO and GDC phases in the as-prepared samples do not match those of the subsequently calcinated samples.

The maximum theoretical adiabatic flame temperatures calculated for the combustion process were not as high as those for melting and/or volatilizing reagents or products of the synthesis.

To apply the appropriate correction for instrumental broadening, the peak shape is mandatory, since the Gaussian

form appropriately demonstrated the effects arising due to the instrument.

The crystallite size behavior with respect to the concentration of nickel in both the preparation as well as the calcination is similar in both the approaches proposed in this study. The V–V analysis resulted in a minimum margin of error with a maximum of 5% only.

It is possible to correct the difference in the results obtained from the crystallite size between the V–V and graphical methods by subtracting the “noise” background baseline with the XPHS software tool and the application of the basic parameters of TOPAS software.

The non-zero values of microstrain obtained from the graphical methods are due to the deformation effects in the diffraction line and, hence, to the highest crystallite size. The V–V method did not detect the deformation; thus, a smaller crystallite size was observed.

Graphical methods differ in the expansion or compression of the network, giving a positive or negative sign for the linear fit parameter which interprets the microdeformation. In general, the results obtained from $[G] - [G]$ and $[L] - [G]$ indicate an expansion in the network of GDC and NiO, which gives a Gaussian character to the microstrain. The $[L] - [G]$ method definitely represents the best linear fit.

The quasi-imperceptible values of the microdeformation allow us to infer them to be the cause of the proximity of the thermal expansion coefficients of NiO and GDC. The results obtained for the crystallite size with XRD are in agreement with the HR-TEM results.

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