Highly ordered mesoporous magnesium niobate high-$\kappa$ dielectric ceramic: synthesis, structural/mechanical characterization and thermal stability†

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The synthesis of a highly ordered mesoporous ternary Mg–Nb oxide by the Evaporation Induced Self-Assembly (EISA) method is presented for the first time. The as-prepared material shows 2D-hexagonal pore periodicity, with unimodal pore size distribution centered at 5.5 nm, and a large surface area (169 m$^2$ g$^{-1}$). The mechanical properties, determined by means of nanoindentation, are consistent with the presence of ordered domains of honeycomb-like hexagonal pore arrangements, in agreement with electron microscopy observations and N$_2$ sorption isotherm analyses. The dielectric constant of the mesoporous sample, measured at room temperature in the frequency range 1 kHz to 1 MHz, is rather high ($\kappa \sim 25$ at 1 MHz) and correlates well with the $\kappa$ value of the bulk and the porosity level of this material. Moreover, the thermal stability of the mesoporous magnesium niobate is investigated after air-annealing treatments at different temperatures. While a significant decrease of the surface area is observed for $T_{\text{ANN}} = 650$ °C, the mesostructure fully collapses after annealing at 800 °C.

Introduction

In recent years, the unprecedented growth of advanced mobile and wireless communication technologies has prompted the demand for new types of high-performance, low-cost dielectric ceramic materials. In particular, the so-called “high-$\kappa$ dielectrics” (oxide ceramics with a dielectric constant higher than that of SiO$_2$, $\kappa > 3.8$) have revolutionized the wireless and microwave communication industry by rendering an enhanced gate capacitance while circumventing the detrimental tunneling current leakage arising from the use of increasingly thinner oxide barrier layers in miniaturized electronic devices (e.g., transistors, filters or oscillators). By analogy, generation of porosity could be also a strategy to tailor the dielectric constant in high-$\kappa$ dielectrics. This would be desirable for certain applications, such as high-density computer storage using ferroelectrics or microwave-based devices. However, although the influence of porosity on the mechanical stability and dielectric properties of low-$\kappa$ ceramics has been extensively reported, studies on porous high-$\kappa$ dielectrics are rather scarce.

Among different classes of high-$\kappa$ ceramic materials, Mg and Nb based oxides have attracted much attention due to their high dielectric constants, low cost, high efficiency and ease of availability, as compared to conventional Ta$_2$O$_5$, SrTiO$_3$ and related complex perovskites. Columbite niobate MgNb$_2$O$_6$, for example, exhibits excellent dielectric properties ($\kappa \sim 19$–23 with quality factor $Q_f \sim 94$ 000 GHz, at frequencies in the GHz range$^{[6]}$ and it has been widely used as a precursor of relaxor Pb[(Mg$_{1/3}$Nb$_{2/3}$)]O$_3$ (PMN) perovskites.$^{[10]}$ Hitherto, the synthesis of magnesium niobate phases at high temperatures (>900 °C) has been carried out from MgO and Nb$_2$O$_5$, an approach that is neither easy nor totally efficient. Namely, such high-$T$ thermal annealing leads, in most cases, to a heterogeneous composition with irregular shapes of the grains, large crystallite sizes and the presence of impurities.$^{[11]}$ In addition, the materials obtained by
thermal treatments at high temperatures are characterized by having very small values of specific surface area. Furthermore, the working parameters used in the synthesis (>900 °C) drastically increase the cost of the production process. For these reasons, there is a growing interest in new synthetic routes that can reduce the manufacturing costs while improving the characteristics of magnesium niobate ceramics. With this aim, mechanochemical treatment of the reagent powders by high-energy ball milling has been attempted as an alternative synthetic approach.\textsuperscript{13,14} Kong et al.\textsuperscript{14} synthesized single phase MgNb\textsubscript{2}O\textsubscript{6} in the amorphous state upon milling together MgO and Nb\textsubscript{2}O\textsubscript{5} powders. Yet, the mechanochemical process does not guarantee improvements in terms of surface area. On the other hand, wet chemistry procedures have emerged as excellent candidates for the synthesis of highly pure and homogeneous magnesium niobate materials. In particular the sol–gel technique offers several advantages over the conventional solid state reaction method, such as better compositional control, lower processing temperature, higher surface reactivity and the opportunity to modulate the size and morphology of the particles.\textsuperscript{15} In such a process, the reactants, in the form of salts, are typically hydrolyzed in suitable solvents and pH conditions. Colloids or precipitate products are formed upon removal of the solvent from the “gel” phase. The sol–gel routes are widely exploited for the synthesis of ceramic materials, typically metal oxides, at low temperatures. Camargo et al.\textsuperscript{16} were able to obtain single phase crystalline MgNb\textsubscript{2}O\textsubscript{6} by a sol–gel process referred to as “Polymerized-Complex method”. Nevertheless, a modest surface area of 12.22 m\textsuperscript{2} g\textsuperscript{-1} was reported for this material. More recently, Zang et al. prepared nanocrystalline MgNb\textsubscript{2}O\textsubscript{6} (particle size between 20 and 50 nm) at temperatures below 700 °C.\textsuperscript{17} Further reduction of the particle dimension down to 20 nm was achieved by Fang et al.\textsuperscript{18} Despite the progress on the synthesis of magnesium niobate, there is still much room to explore. Seeking alternative synthetic routes to prepare magnesium niobate materials with nanoscale morphology control, high surface area and, certainly not least, mechanical stability is highly desirable. In fact, insulating materials require a sufficient rigidity to overcome the stress imposed by the mechanical compression during the assembly of the capacitor device.

One of the most direct and appealing methods to synthesize high surface area porous oxide materials is the so-called evaporation induced self-assembly (EISA).\textsuperscript{19,20} This synthetic approach allows obtaining materials with well-organized porosity at the mesoscale. Mesoporous materials are characterized by high surface areas, pore diameters between 2 nm and 50 nm, good corrosion resistance and high temperature stability. While the EISA approach has been demonstrated for mesoporous silicates, the preparation of non-siliceous based mesoporous materials by EISA is still far from being fully satisfactory as it requires a stringent control of the hydrolysis rate, condensation and mesostructure formation.\textsuperscript{21} This precludes the synthesis of most metal oxide frameworks by EISA. Instead, the hard-templating pathway has been commonly adopted to produce them.\textsuperscript{22} Nevertheless, this last approach suffers from several drawbacks: it is a two-step pathway (hence, more costly) and replication of the silica or carbon molds usually implies a certain loss of surface area and/or long-range order of the target products. Hence, EISA emerges as a very convenient and cost-effective method towards ordered mesoporous metal oxides with large surface areas. The successful syntheses of Nb–Ta\textsuperscript{23} and Y–Zr\textsuperscript{24} mesoporous double oxides by EISA have been recently reported in the literature.

This work represents the first successful attempt toward the synthesis of highly ordered mesoporous magnesium niobate (Mg : Nb = 1 : 2 molar ratio) via the EISA method. Remarkably, a pure magnesium niobate phase with a well-defined mesoporous structure is achieved in a reproducible manner after 3 days of gelation time. The material exhibits a high specific surface area and a hexagonal arrangement of pores characterized by a unimodal distribution. The mechanical properties of the mesoporous material are investigated in detail and correlated with the degree of porosity. Moreover, the relationship between the dielectric constant recorded at 1 MHz of porous and non-porous magnesium niobate materials is reported. Finally, the effect of the calcination temperature on the morphological properties of the oxide is also discussed.

Method section

Materials

The triblock copolymer surfactant, \textit{HO(CH\textsubscript{2}CH(CH\textsubscript{3})O\textsubscript{70}}(CH\textsubscript{2}CH\textsubscript{2}O\textsubscript{20})H, P-123 (AMW = 5800), was purchased from Sigma-Aldrich. Anhydrous metal chlorides, NbCl\textsubscript{5} (99.995% purity) and MgCl\textsubscript{2} (98% purity) were also purchased from Sigma-Aldrich.

Synthesis details

Typically, 1 g of surfactant (P-123) was dissolved in 0.212 moles of anhydrous ethanol by stirring under room temperature. MgCl\textsubscript{2} (0.0025 moles) and NbCl\textsubscript{5} (0.005 moles) were then added to the solution under constant stirring. To this solution, 0.017–0.061 moles of water were added with vigorous stirring for further 15 min. The resulting solution was transferred to an open Petri dish and gelled at 40 °C for 3 days in air. During the aging time, the relative humidity (RH) was kept constant at 40–60% by a saturated solution of Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O. The as-prepared samples were then calcined in air at 500 °C for 5 h to remove the templating agent.

Characterization

To investigate the crystallographic structure of the material, wide-angle X-ray diffraction (XRD) analysis was carried out using a Rigaku D/Max diffractometer equipped with a Cu radiation tube ($\lambda_{\text{Cu}} = 1.540598$ nm) and a graphite monochromator in the diffracted beam. A low-angle XRD pattern, which gives information on the periodicity of the mesoporous framework, was acquired using a Panalytical X’Pert Pro diffractometer in the 0.8–5° 2θ angular range operating in transmission mode using Cu Kα radiation. Rietveld refinement (full-pattern fitting procedure) of the wide-angle XRD patterns corresponding to the air-annealed powders was performed using the “Material Analysis Using Diffraction” (MAUD) software.
Morphological and microstructural characterization was performed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a Zeiss Merlin (operated at 1.2 kV) and a Jeol-JEM 2011 (operated at 200 kV) microscope, respectively. For SEM imaging, a small amount of powder was spread onto carbon tapes mounted on aluminum supports. For TEM measurements, the powder was dispersed in ethanol followed by sonication, and then one or two drops were deposited dropwise onto carbon-coated Cu TEM support grids. Elemental analysis was performed by energy-dispersive X-ray (EDX) spectroscopy.

\( \text{N}_2 \) sorption isotherms were measured using a Sorptomatic 1990 and the data were analyzed according to BET and BJH methods.\(^{25}\) 150 mg of sample was charged into a quartz tube and degassed under high vacuum \((1 \times 10^{-3} \text{ bar})\) at 300 °C for 48 hours. The empty volume in the quartz tube was evaluated using helium sorption isotherms.

Thermal stability was evaluated using a thermogravimetric apparatus (TGA) coupled with a differential scanning calorimeter (DSC) using a Labsys Setaram. The experiment was carried out on 50 mg of sample pre-calcinized under an Ar flow of 120 ml min\(^{-1}\) between 25 °C and 800 °C with heating and cooling rates of 5 °C min\(^{-1}\). A ceramic crucible was used for the analysis in order to avoid undesired reaction with the powders during the annealing.

To measure the mechanical properties, a layer of magnesium niobate material, with a thickness of about 10 \(\mu\)m, was deposited onto the surface of a Si substrate by drop casting a suspension of the mesoporous powder in polyethylene glycol. The hardness \((H)\) and reduced Young’s modulus \((E_r)\) were evaluated by nanoindentation, using an UMIS system from Fischer-Cripps Laboratories equipped with a Berkovich pyramidal-shaped diamond tip. The experiments were performed in the load control mode and the value of maximum applied force was 1 mN, sufficiently small to ensure that the maximum penetration depth during the tests was below one tenth of the overall layer thickness. The thermal drift during nanoindentation was kept below 0.05 nm s\(^{-1}\). Proper corrections for the contact area (calibrated with a fused quartz specimen), instrument compliance, and initial penetration depth were applied. The values of \(H\) and \(E_r\) were determined from the load–displacement curves at the beginning of the unloading segment using the method of Oliver and Pharr.\(^{26}\) The elastic recovery was evaluated as the ratio between the elastic and the total \((\text{elastic} + \text{plastic})\) indentation energies, \(W_{el}/W_{tot}\). These energies were calculated from the nanoindentation curves as the areas between the unloading segment and the displacement axis \((W_{el})\) and between the loading segment and displacement axis \((W_{tot})\). The presented results correspond to an average of 50 indentations.

The relative dielectric constant has been estimated by performing a capacitive investigation on different Metal–Insulator–Metal (MIM) devices in the frequency range 1 kHz to 1 MHz. Highly ordered Mg–Nb oxide thick films (300 and 900 \(\mu\)m) were prepared, and two gold electrodes were deposited on both sides of the samples, as depicted in Fig. 6b, in order to obtain the MIM structure. The electrodes were deposited by thermal evaporation in high vacuum, at a nominal pressure around 5 \(\times\) 10\(^{-6}\) Torr and patterned by means of a shadow mask interposed between the sample and the crucible during the evaporation process. Capacitance measurements were performed at room temperature on both pellets using an Agilent 4284A LCR Meter. To obtain homogenous disk-shape pellets, the calcined powders were subjected to high-pressure (150 bar) for 15 min each one.

**Results and discussion**

**Structural and morphological characterization**

The ordered mesoporous structure of the composite before its calcination \(\text{(i.e., after the gelation step)}\) is provided in the TEM micrograph displayed in Fig. 1a. The Selected Area Electron Diffraction (SAED) pattern shown as the inset in Fig. 1a reveals the amorphous character of the sample. Fig. 1b shows the TG–DSC curves of the composite after the gelation step. The TG profile (blue line) reveals an important weight loss in the range

![TEM image of the composite obtained after 3 days of aging time](image_url)

![TG and DSC signals against the temperature](image_url)
of 30–150 °C due to the evaporation of volatile solvents: namely, ethanol and water. This process is associated with a large endothermic peak indicated by the symbol A in the DSC curve (dark line) displayed in Fig. 1b. Around 150 °C, a slight weight loss related to the decomposition of the templating agent P-123 is detected. The DSC signal also reveals an exothermic peak (B) located at 600 °C, which likely results from the crystallization of Mg–Nb oxide.

In order to determine whether the mesostructural arrangement was preserved after removal of the templating agent via annealing at 500 °C, the calcined powder was characterized by low-angle X-ray powder diffraction. The pattern is consistent with a 2D-hexagonally ordered mesoporous structure (Fig. 2a). One can distinguish one main reflection indexed as (100) and two weak reflections located at higher angles corresponding to (110) and (200), produced from the periodicity of the mesopore arrays. The (100) peak reflects a $d$ spacing of 90 Å, corresponding to a unit cell parameter of 104 Å, as reported in Table 1. The relatively large peak broadening of (110) and (200) planes can be ascribed to both diffuse scattering originated from structural hierarchy and slight differences between particles and pore sizes.

The $N_2$ adsorption–desorption isotherm of the Mg–Nb oxide powder calcined at 500 °C and the corresponding pore size distribution are depicted in Fig. 2b. The material shows a type IV isotherm characteristic of mesoporous materials. The adsorption branch exhibits three distinct regions corresponding to monolayer-multilayer adsorption, capillary condensation at relative pressures in the range from 0.5 to 0.8, and multilayer adsorption on the outer particle surfaces. Moreover, an H1-type hysteresis loop is observed, typical of capillary condensation and evaporation processes in cylindrical and regular pore openings at both ends. The sample is characterized by a BET surface area of $169 \pm 2 \text{ m}^2 \text{ g}^{-1}$ (much larger than for ternary oxides synthesized by Camargo et al. and of the same order of magnitude as that reported by Domen et al. for the NbTa oxide prepared by the EISA method) and a unimodal pore size distribution (the inset of Fig. 2b) with a maximum pore width, $\rho_{\text{BjH}}$, of 5.5 ± 0.5 nm (see Table 1). The pore wall thickness, $b_{\text{BjH}}$, was estimated by subtracting the experimental pore size, $\rho_{\text{BjH}}$, from the distance between the centers of adjacent pores, $a$. The value of $b_{\text{BjH}}$, reported in Table 1, corresponds to 4.9 ± 0.5 nm.

Representative TEM images of the powder are shown in Fig. 3. At high magnification (HRTEM, Fig. 3a) the mesopore walls look rather diffuse (not well defined) due to the lack of crystallinity. The pore diameter (indicated by a red line in Fig. 3a) is around 5 nm, in agreement with BET observations. At lower magnification (Fig. 3b) the 2D hexagonally ordered mesoporous structure is observed.

Complementary SEM investigations were carried out in order to obtain more information about the morphology and size of the Mg–Nb–O particles. The material consists of rather thick particles (>500 nm) featuring an impressively regular hexagonal pore arrangement (Fig. 4).

These results indicate that the highly ordered mesoporous Mg–Nb oxide phase can be synthesized at temperature around 500 °C by the EISA method.

A typical EDX spectrum is presented in Fig. 5, while the relative amount of elements detected in the sample is shown in Table S1 in the ESI. The calcined sample basically consists of magnesium, niobium and oxygen atoms in 13%, 30% and 57% atomic percentages, respectively. The analysis proves that the Mg/Nb ratio is similar to that of the starting reagents and hence it is very close to the stoichiometric MgNb$_2$O$_6$.

![Figure 2](image-url) (a) Low-angle XRD patterns corresponding to Mg–Nb oxide powders calcined at 500 °C. (b) $N_2$ adsorption–desorption isotherms for the ternary oxide sample obtained after P-123 removal at 500 °C.

Table 1  | BET surface area, BJH pore size, wall thickness, $d$ spacing and cell parameter values of the Mg–Nb oxide sample
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<td>$\rho_{\text{BjH}}$ [±0.5 nm]</td>
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Mechanical characterization

The mechanical properties of the as-synthesized Mg–Nb oxide material were determined by nanoindentation and the obtained results were correlated with previous BET data. A representative load–displacement nanoindentation curve of the mesoporous Mg–Nb oxide material is shown in Fig. 6a. The obtained values of hardness and the reduced Young’s modulus are $H = 340 \pm 20$ MPa and $E_r = 12.5 \pm 1.0$ GPa, respectively.
The reduced Young’s modulus takes into account the elastic displacements that occur in both the specimen, with Young’s modulus $E$ and Poisson’s ratio $\nu$, and the diamond indenter, with elastic constants $E_i = 1140$ GPa and $\nu_i = 0.07$. The relationship between $E_i$ and $E$ can be expressed as:

$$\frac{1}{E} = \frac{1 - \nu^2}{E_i} + \frac{1 - \nu_i^2}{E_i}$$ (1)

For most ferroelectric ceramics and metal oxides analogous to Mg–Nb, such as MgO or Nb$_2$O$_5$, the Poisson’s ratio is around 0.2. This value would be slightly lower if one takes into consideration the existence of porosity. Assuming that $\nu = 0.2$, the Young’s modulus of the mesoporous Mg–Nb oxide would be $E \approx 12$ GPa, hence in practice very similar to $E_i$.

The porosity level is known to have a strong influence on the elastic constants of metallic and ceramic materials. In a first approximation, it has been shown that:

$$\frac{E_{\text{porous}}}{E_{\text{bulk}}} = \left(\frac{\rho_{\text{porous}}}{\rho_{\text{bulk}}}\right)^n$$ (2)

where $\rho_{\text{porous}}/\rho_{\text{bulk}}$ is the relative density; $n = 2$ for open-celled foams or sponge-like structures, whereas $n = 3$ for materials exhibiting an array of pores arranged forming a honeycomb hexagonal array normal to the surface.

The relative density is related to the porosity volume fraction:

$$\frac{\rho_{\text{porous}}}{\rho_{\text{bulk}}} = 1 - P$$ (3)

where:

$$P = \frac{C_{\text{pv}}}{C_{\text{pv}} + \frac{1}{\rho_{\text{bulk}}}}$$ (4)

Here $C_{\text{pv}}$ denotes the cumulative pore volume, as determined by BET analyses, which for the investigated material is $C_{\text{pv}} = 0.399$ cm$^3$ g$^{-1}$. Taking into account that the bulk density of MgNb$_2$O$_6$ is 5 g cm$^{-3}$, the relative density of the mesoporous magnesium niobate particles is $\rho_{\text{porous}}/\rho_{\text{bulk}} = 0.334$.

The Young’s modulus of bulk MgNb$_2$O$_6$ ceramics is approximately 150 GPa. Using eqn (2), a value $n = 2.3$ is obtained. Interestingly, this exponent is similar to the values reported for templated mesoporous silica thin films with ordered domains of honeycomb-like hexagonal pore arrangements exhibiting orientational disorder, a microstructure similar to our case.

Concerning the hardness, the value obtained in the mesoporous niobium oxide ($H = 340$ MPa) is also significantly lower than the Vickers hardness reported for the bulk ($H = 7.1$ GPa). The decrease of hardness (or compressive yield stress) with porosity is also a well-documented effect and has been modeled using finite element simulations of nanoindentation curves. It should be noted that an equation analogous to eqn (2) may be used to correlate the yield stress of the porous structure with that of the bulk solid material:

$$\sigma_{\text{porous}} = C_2\sigma_{\text{bulk}}\left(\frac{\rho_{\text{porous}}}{\rho_{\text{bulk}}}\right)^m$$ (5)

where $C_2 = 0.3$ and $m = 1.5$ for an open-cell foam. Although the relationship between hardness and yield stress in bulk oxide ceramic is often taken as $H_{\text{bulk}} = 1.66\sigma_{\text{bulk}}$, a quantitative relationship between hardness and yield stress in porous materials has yet to be established. Some authors consider that the indenter in porous structures is not constrained by the surrounding material regardless of eventual densification. Then, the nanoindentation would be equivalent to a uniaxial compression test and $H_{\text{porous}} = \sigma_{\text{porous}}$. In our case and using the aforementioned assumptions, eqn (5) would give $m = 1.3$, which is a quite reasonable value.

Finally, the elastic and total indentation energies are $0.030 \pm 0.005$ nJ and $0.120 \pm 0.005$ nJ, respectively, leading to an elastic recovery $W_{\text{el}}/W_{\text{tot}} = 0.25$. This parameter indicates how much energy is released from the material after being loaded and it could be of particular interest in applications subject to impact loading. Remarkably, this value is of the same order of magnitude as the elastic recovery measured in electrodeposited fully dense CuNi films.

**Capacitance characterization**

The dependence of the dielectric constant as a function of frequency is shown in Fig. 6b. The value of $\kappa$ progressively decreases with frequency, as expected from different types of polarization effects. The dielectric constant for the mesoporous Mg–Nb oxide is found to be $\sim 25$ at 1 MHz, about half the value reported by Singh and Bajpai for the completely dense MgNb$_2$O$_6$. This difference can be ascribed to the porosity level of the mesoporous magnesium niobate. In fact, for ceramic materials the dielectric constant can be related to porosity as follows:

$$\kappa_{\text{bulk}} = \kappa_{\text{porous}}(1 + 1.5P)$$ (6)

where $P$ is the porosity of the ceramic material calculated from eqn (4).

Since $P = 0.666$, our capacitance measurements ($\kappa_{\text{porous}} = 25$) would lead to $\kappa_{\text{bulk}} = 50$, thus in good agreement with the results of Singh and Bajpai.

**Microstructure characterization as a function of temperature**

In order to investigate the occurrence of crystallization events and the thermal stability of the mesoporous magnesium niobate material, the as-synthesized powder was air-annealed at different temperatures. The amorphous character of the starting material (i.e., the as-synthesized ternary oxide obtained at 500 °C) is corroborated by the absence of Bragg peaks in the XRD pattern shown in Fig. 7a. After air-annealing at 650 °C, just after the crystallization event observed in the DSC-TG analysis (Fig. 1b), the XRD pattern shows crystalline peaks. These peaks can be indexed in accord with the MgNb$_2$O$_6$ columbite phase. The average crystallite size determined for the columbite phase corresponds to $9 \pm 2$ nm, demonstrating the nanostructured character of the sample. As the annealing temperature increases, the intensity of diffraction peaks increases, and simultaneously the width of the peaks becomes narrower (see the pattern taken after annealing at 800 °C, for which the crystallite size is around 300 ± 2 nm). The
BET surface area (Fig. S1 in the ESI†), related to the powders thermally treated at 650 °C, decreases down to 99 ± 2 m² g⁻¹. Furthermore the pore size distribution is characterized by an enlarged bi-modal peak with a significant increase of the maximum pore width (12.9 ± 0.5 nm). In view of this experimental evidence, morphological properties are also expected to change during the crystallization process. In fact, SEM images (Fig. S2 in the ESI†) ensure that, despite the pores still being present on the surface of the columbite powders, their order is completely lost. Moreover, at 800 °C the mesostructure collapses into an inhomogeneous dispersion of nanoparticles (Fig. 7b). The specific surface area of this sample is estimated below 20 m² g⁻¹. This demonstrates that the mesostructure, on this sample, is strictly correlated with the increase of the specific surface area.

Conclusions

In this work, the formation of highly ordered mesoporous magnesium niobate via the EISA method is demonstrated for the first time. TEM, SEM and SAXS characterization proves that a 2D hexagonal mesophase is formed using MgCl₂, NbCl₅ (in a molar ratio of 1 : 2), ethanol and P-123 as metallic precursors, solvent and the templating agent, respectively. The EDX analysis corroborates that the stoichiometry of the starting material is very close to MgNb₂O₆, N₂ sorption isotherm experiments reveal a unimodal pore size distribution with a maximum pore width, \( R_{50}\), of 5.5 ± 0.5 nm and a pore wall thickness, \( b_{w}\), corresponding to 4.9 ± 0.5 nm. Interestingly, the as-prepared mesoporous ternary oxide exhibits a large surface area of 169 ± 2 m² g⁻¹, which represents the highest value reported so far for the columbite phase.

Nanoindentation measurements indicate a hardness value of 340 ± 20 MPa and a Young's modulus of 12.5 ± 1.0 GPa. The \( H\) value is significantly lower than the Vickers hardness reported for bulk MgNb₂O₆ (\( H = 7.1\) GPa), as expected from the high porosity degree of this material. The correlation between Young's modulus and relative density is consistent with the honeycomb-like hexagonal pore arrangements as revealed by TEM characterization. The dielectric constant of the mesoporous sample, measured in the frequency range 1 kHz to 1 MHz, is rather high (\( \varepsilon \approx 25\) at 1 MHz) and is in agreement with the \( \varepsilon \) value expected from the porosity level of this material. Regarding the thermal stability, the amorphous powders crystallize to the columbite phase (MgNb₂O₆) at around 600 °C, with an average crystallite size of 9 ± 2 nm. The mesostructure is preserved up to 650 °C, but at this calcination temperature a partial loss of periodicity takes place and the surface area decreases to 99 ± 2 m² g⁻¹. At higher temperature (800 °C), the periodic order of the mesostructure is completely lost, while the surface area becomes much lower, i.e. <20 m² g⁻¹.

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Notes and references


