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Preparation and characterization of $LaNbO_4$ from amorphous precursors

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Amorphous precursors of $LaNbO_4$ have been prepared by coprecipitation and mechanical alloying. Powder characteristics before and after calcination were studied by thermogravimetric analysis, differential thermal analysis, Fourier transform–infrared spectroscopy and X-ray diffraction, and the crystallographic changes during thermal treatment were documented by high-temperature X-ray diffraction. The tetragonal structure was stabilized at room temperature for the mechanically alloyed product; cells dimensions were determined from the X-ray diffraction patterns and volume change between monoclinic and tetragonal phase was evaluated and is discussed.

1. Introduction

Much effort has been devoted to improve the properties of ceramics for structural as well as functional applications, so that polyfunctional materials can be obtained. In this context, lanthanum niobate is a solid solution able to emit ultraviolet radiation in the region 300–500 nm when it is excited by an ultraviolet or X-ray source [1]. It can be also used in solid solution with other oxides to produce material for dielectric resonators [2]. In addition, lanthanum niobate, as well as lanthanum tungstates and tantalates, is ferroelastic [3].

It has been demonstrated that lanthanum niobate undergoes a reversible polymorphic transformation at 550–600 °C, changing from the monoclinic to the tetragonal form, the former being stable at room temperature, the latter at high temperature [3–8]. This phase transformation, as in the case of the widely studied zirconia, might have advantages when lanthanum niobate is dispersed in a matrix by exploiting a transformation toughening effect. In fact, when $LaNbO_4$ particles are dispersed within a ceramic oxide matrix, if the matrix has a Young's modulus higher than that of the dispersed phase, they may be constrained in the metastable form at room temperature [9–13]. Then the tetragonal particles can be transformed to monoclinic by external factors such as an applied stress field or chemical agents.

A further factor that must be considered in the preparation of a composite is the thermal expansion coefficient: dispersed particles must have a value lower than that of the matrix so that on cooling after sintering they can be forced into the metastable form.

On these grounds lanthanum niobate is considered a top candidate in the substitution of zirconia for all applications where the matrix must have functional as well as structural properties, i.e. solid solutions mainly containing $ZrTiO_4$.

Only a few papers have been published on this material, and not sufficient to make a priori assumptions. Nevertheless, the possibility of $LaNbO_4$ giving toughening effects must be evaluated, i.e. the volume change in the tetragonal to monoclinic transformation must be positive at least at room temperature.

In this work, lanthanum niobate was produced by calcination of coprecipitated products and its crystallographic behaviour as been compared to that of mechanically alloyed and thermally treated commercial powders. Mechanical alloying was chosen for this comparison because it is a new method of powder preparation which induces chemical reactions, reduces the crystallite size and allows the formation of phases which are usually stable only at high temperature [14, 15]. On the other hand the traditional ceramic preparation by solid-state diffusion of La_2O_3 and Nb_2O_5 is not appropriate, because the long thermal treatment necessary to complete the process leads to excessive crystallite growth. This fact is incompatible with the existence of the tetragonal phase at room temperature because particles spontaneously transform to monoclinic on cooling after the thermal treatment, as they exceed a critical dimension.

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2. Experimental procedure

2.1. Coprecipitation route

Unfortunately, $LaNbO_4$ powders cannot be prepared by coprecipitation from aqueous solutions of lanthanum and niobium salts, because niobium salts decompose to hydroxide in aqueous environments at room temperature. Their solution must be obtained through another solvent, and we have chosen ethanol.

Two 0.5 M solutions of niobium chloride and lanthanum chloride were separately prepared by dissolving Aldrich reagents (99.9% purity) in the required quantity of alcohol and stirring for 2 h. The yellowish solutions were then mixed, stirred again and successively coprecipitated into a 0.5 M ammonia solution under continuous stirring for 6 h, and then filtered.

The material was washed following the ATA procedure [16], dried at 80 °C, and sieved through a 63 μm sieve. The dried product, after characterization by Fourier transformation–infrared spectroscopy (FT–IR), X-ray diffraction (XRD), high-temperature XRD, (HTXRD) and differential thermal analysis/thermogravimetric analysis (DTA/TGA), was crystallized by calcination at 800 °C for 2 h followed by slow cooling; the powders were then again characterized by FT–IR, XRD and HTXRD.

2.2. Mechanical alloying route

Mechanically alloyed powders were obtained by mixing in air adequate proportions of Aldrich La_2O_3 and Nb_2O_5 (99.99% in purity) powders and ball milling the mixture in a zirconia jar with Tosoh 1 cm diameter zirconia balls using a highly energetic Spex mill (series 8000); six balls and 1 g powder were used for each milling process so that the weight ratio between powders and milling media was 1/18.

The milling time has a strong influence on the crystallographic nature of the resulting powders. The X-ray spectra of the starting oxides are rapidly distorted, and after 1 h milling some of the original peaks disappear. After 3 h only the peaks having the highest intensity remain and a progressive amorphization takes place.

Longer milling times lower the crystallinity of the powders and after 6 h an amorphous powder can be detected. This modification is in agreement with the results obtained by other authors [17] who have studied the amorphization on niobium pentoxide by fine grinding. After 11 h milling, a new crystalline structure arises from the amorphous product, but it is still characterized by few, broad and not well-defined XRD peaks so that it is not possible to identify this structure with certainty. A longer milling time does not change this crystalline structure.

On this basis, the milling process was stopped after 10 h in order to reduce as much as possible the powders crystallite size and, at the same time, to avoid the development of a new crystalline phase. The FT–IR spectra of single products were performed on KBr pellets using a Nicolet Magna-IR 550 apparatus, controlled by the Omnic System.

XRD and HTXRD were made on a Philips diffractometer using the nickel-filtered CuK_α radiation and having a high-temperature cell. Cell parameters have been calculated using the program "Treor 90" which makes use of the Visser algorithm.

Simultaneous DTA/TGA were performed using a Netzsch instrument at a heating rate of 10 °C min^{-1} up to 1300 °C.

3. Results and discussion

3.1. Characterization of the amorphous powders

Fig. 1 reports FT–IR spectra of precursors obtained by coprecipitation and mechanical alloying. The very broad patterns suggest that the powders are substantially amorphous. Nevertheless, the bands split between 800 and 300 cm^{-1} in the mechanically alloyed product indicate incompletely homogeneous mixture. In addition, these spectra indicate that precursors powders have OH^- groups differently bonded (bands at 1630, 1400 and shoulders at 1070 and 850 cm^{-1}) and $CO_3^=$ (band at 1480 cm^{-1}) which are pollutants commonly found with these processes. This is supported by the XRD patterns which show the presence of very large peaks indicating a cryptocrystalline product in the case of mechanically alloyed powders (Fig. 2). The presence of OH^- and $CO_3^=$ groups is due to the interaction of powders with water and CO_2 in the atmospheric environment. In fact, chemiadsorption has been normally observed in ceramic powders: it is generally a weak phenomenon, but it can be exaggerated when powders are activated and therefore extremely reactive.

Fig. 3 shows DTA and TGA curves for the precursors. Both the DTA plots show an endothermic peak followed by an exothermic effect. The former begins at 80 °C and ends at about 400 °C for the coprecipitated powder, whereas it begins at 180 °C and ends at about 450 °C and is less evident for the mechanically alloyed powder.

Simultaneously to the endothermic effects, the TGA indicates a weight loss of 2.5% and 0.4% for the coprecipitated and mechanically alloyed powders, respectively.

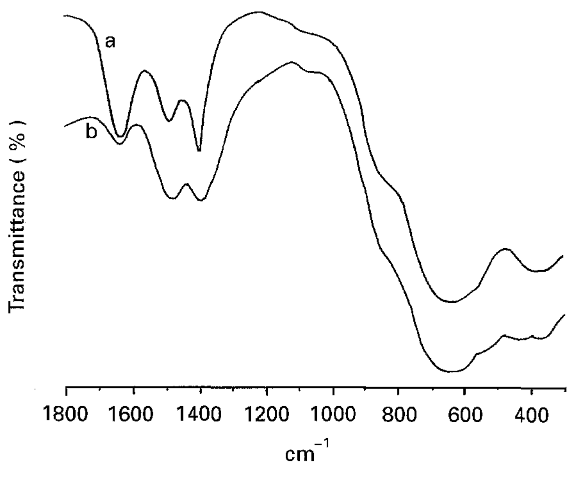

Figure 1 FT–IR spectra of precursors obtained by (a) coprecipitation and (b) mechanical alloying. X-ray diffraction patterns of (A) La_2O_3, (B) Nb_2O_5 and (C) a mixture of both oxides milled for 1 h are depicted.

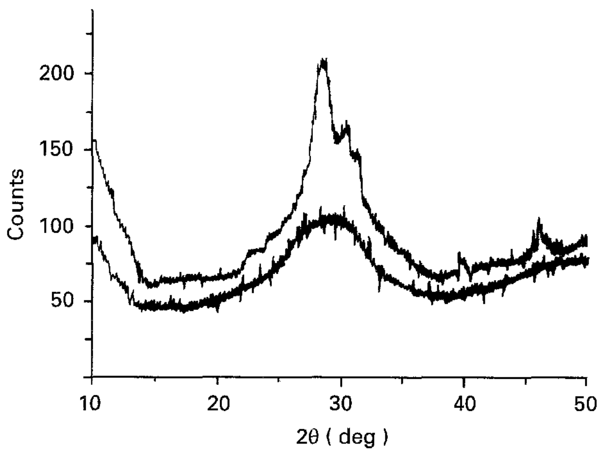

Figure 2 XRD of (a) the coprecipitated and (b) mechanically alloyed amorphous precursors.

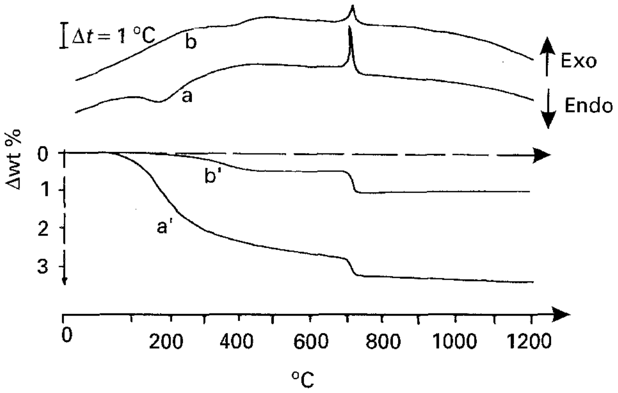

Figure 3 DTA and TGA curves of precursors obtained by coprecipitation (a, a') and by mechanical alloying (b, b').

The FT–IR spectra, not reported in this communication, of powders thermally treated at 500 °C, do not show peaks at 1600 and 1400 cm^{-1} and shoulders at 1070 and 850 cm^{-1}, which are representative of the oxydrilic groups. It follows that the weight loss is due to dehydroxylation of the mixture.

The exothermic peaks of the DTA curves have different intensities, but the same area, so that it can be supposed that the same energy is involved in the crystallization. This phenomenon begins at 695 °C and ends at 725 °C in the coprecipitated powders, while it beings at 675 °C and ends at 735 °C in the mechanically alloyed powder.

The crystallization peaks are associated with a further weight loss of 0.4% and 0.5%, respectively, as shown in the TGA curves. Weight loss during crystallization of amorphous powders, has been recently observed by other authors [18–20] and is due to the end of the dehydration process accompanied by CO_2 emission. This assumption is confirmed by the FT–IR spectra performed on powders at the end of the thermal analysis, which do not show the relative absorption bands.

By means of high-temperature XRD it has been pointed out that the amorphous precursors directly crystallize into the tetragonal $LaNbO_4$ phase [8] (Fig. 4), but on cooling, the lattice of the coprecipitated products tends to be more distorted than that of the mechanically alloyed product, giving less definite peaks and a higher background noise (Fig. 5). On the basis of these results the precursors were calcined for 2 h at 800 °C for producing a crystalline powders.

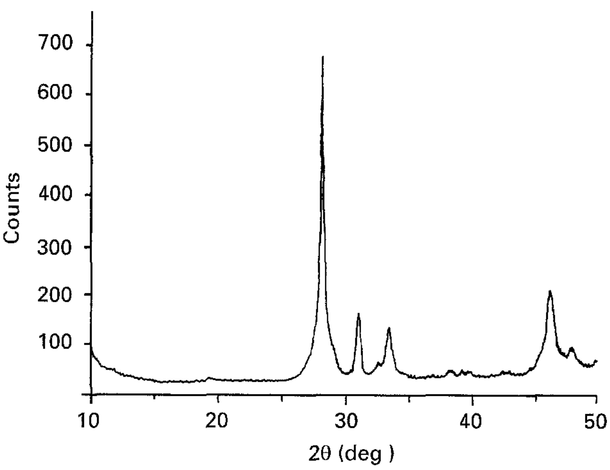

Figure 4 XRD pattern of the high-temperature tetragonal phase.

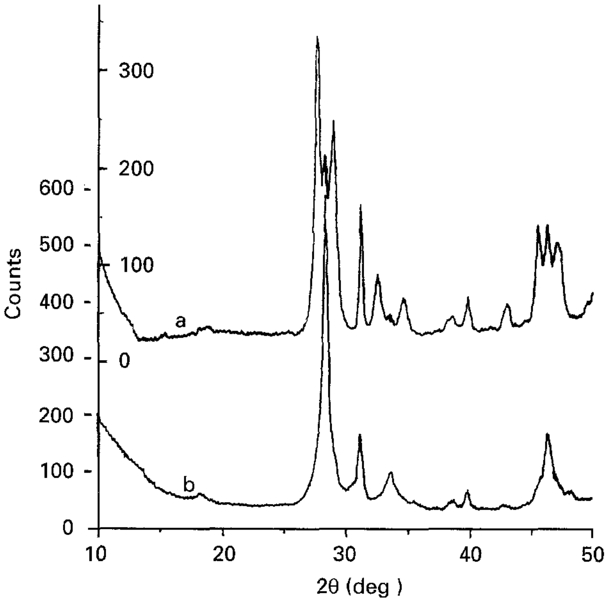

Figure 5 XRD patterns of (a) the room-temperature coprecipitated and calcined and (b) mechanically alloyed and calcined powders.

3.2. Characterization of calcined powders

Fig. 6 shows FT–IR spectra of the calcined powders. That of the coprecipitated and crystallized powder corresponds to the monoclinic phase, because the tetragonal structure of niobates should present, within the explored range, only three bands: the most important between 600 and 730 cm^{-1}, the second, more definite between 550 and 500 cm^{-1}, the third, with a double peak, between 415 and 275 cm^{-1} [21–23], that are not present here.

At the same time it can also be observed that the powder obtained by mechanical alloying, is slightly contaminated by a non-tetragonal phase (the presence of shoulders in the peaks at 800 °C and 495 cm^{-1}).

Both the powders were analysed after calcination by HTXRD during a re-heating up to 800 °C and it has been observed that:

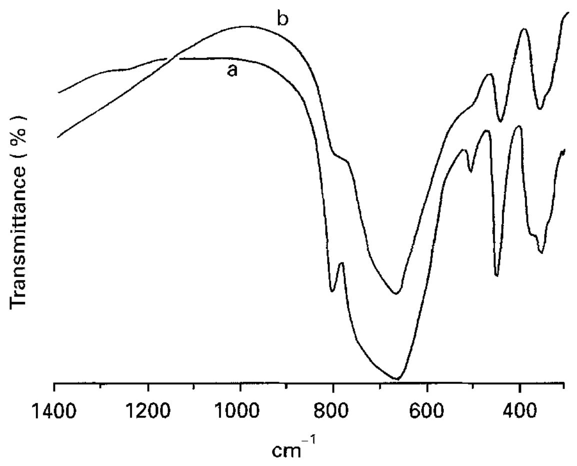

Figure 6 FT–IR spectra of $LaNbO_4$ obtained by calcination of (a) coprecipitated and (b) mechanically alloyed powders.

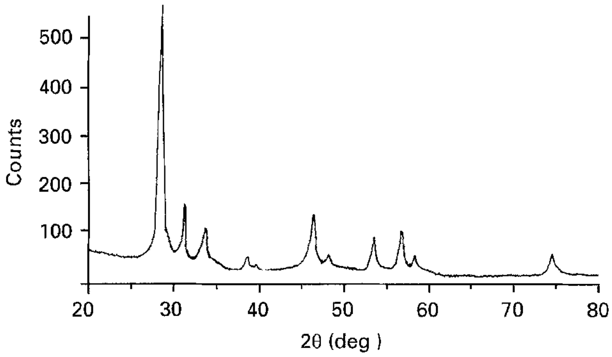

Figure 7 XRD pattern of the room-temperature tetragonal phase.

TABLE I Miller indices 2θ observed, measured *d*-spacing (nm) and relative intensity of the room-temperature tetragonal phase

h	*k*	*l*	2θ (deg)	*d* (nm)	Intensity
2	1	1	28.174	0.31648	100
0	0	2	30.980	0.28843	30
3	1	0	33.440	0.26775	18
3	2	0	38.400	0.23423	6
2	1	2	39.380	0.22862	3
3	1	2	46.220	0.19626	28
4	2	0	48.060	0.18916	6
2	1	3	53.420	0.17138	15
5	0	1	56.600	0.16248	20
4	2	2	58.260	0.15824	7

(i) Samples obtained by coprecipitation directly transform to tetragonal at 400 °C and maintain that structure on further heating, but change to monoclinic on cooling below 400 °C;

(ii) also samples obtained by mechanical alloying crystallize in the tetragonal structure before 400 °C and further heating improves the crystallization (sharper diffraction peaks and higher intensity), but, on cooling, even if a lattice distortion is observed, there is no transformation to the monoclinic phase.

The room-temperature tetragonal X-ray pattern is presented in Fig. 7. Table I shows the relative numerical data. Cell parameters have been calculated using the program "Treor 90" working on the Visser algorithm and the following data have been evaluated: $a = 0.535$ nm; $c = 1.153$ nm, cell volume $= 330.38 \times 10^{-3}$ nm^3 thus having a volume change of 1% with respect to the monoclinic phase [24, 25] which has a volume of 333.18×10^{-3} nm^3. This fact leads to a volume increase of about 1% in the tetragonal–monoclinic transformation. Unfortunately, in this procedure, a first error factor exists in the determination of the peak's position which is not so well defined as for a single crystal; a second error is related to the thermal treatment which is reduced to avoid crystallite growth and therefore the tetragonal–monoclinic phase transformation. As a consequence, peaks of the X-ray pattern are broad and their intensity is low, so that they are not sufficiently defined because of the high background noise. This effect can induce errors in the 2θ observation.

The different behaviour between coprecipitated and mechanically alloyed products is due to the different dimensions of the powder crystallites. In the former they can agglomerate to sufficiently coarse particles during thermal treatment, exceed a critical dimension and transform to monoclinic on cooling. In the latter, even if the composition is not uniform, very small crystallites are present which do not transform on cooling after thermal treatments.

Cell parameters and volume are sensibly lower than those reported by Rooksby and White [8] ($a = 0.54$ nm; $c = 1.166$ nm; cell volume $= 340 \times 10^{-3}$ nm^3) who made their X-ray aquisition above 500 °C, while we have done ours at room temperature. Different temperatures mean different cell dimensions so that at higher temperatures larger cell parameters can be determined and, consequently, a larger volume.

The conclusion that can now be drawn is that the volume change between tetragonal and monoclinic is not negative, but not sufficiently high for significant transformation toughening, as in the case of zirconia. The tetragonal–monoclinic transformation of zirconia is accompanied by a volume increase of 4.9% at room temperature. The shape change can be subdivided into the unit cell (angular) change and the macroscopic change associated with the tetragonal to monoclinic martensitic mechanism: both these changes contribute in the creation of a stress field within a matrix.

In the case of $LaNbO_4$ we can suppose that the angular change is the main one of these concomitant effects, the other being very small; therefore, a matrix is required with a thermal expansion coefficient much higher than that of the $LaNbO_4$ reinforcement to avoid spontaneous transformation on cooling after sintering.

4. Conclusion

The formation of $LaNbO_4$ by coprecipitation and mechanical alloying has been studied. Coprecipitated and calcined powders are present in monoclinic phase at room temperature, but a reversible transformation to the tetragonal at 400 °C has been established. The highly energetic ball milling of a mixture of La_2O_3 and Nb_2O_5 leads to the formation of amorphous powders which crystallize to tetragonal $LaNbO_4$ at 400 °C and remain in this structure on further heating and on subsequent cooling, permitting the stabilization of the metastable form at room temperature. By this procedure it is possible to obtain the XRD pattern of the room-temperature tetragonal phase which has a volume 1% lower than that of the monoclinic.

In conclusion, $LaNbO_4$ can be considered as a material able to give toughening effects if contained in a matrix with a higher thermal expansion coefficient.

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