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Preparation and microstructure characterization of novel $La_{2-x}Sr_{2-x}Nb_2O_{10-x}$ oxides

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ABSTRACT

The aim of the present work is to report the study of samples with the $La_{2-x}Sr_{2-x}Nb_2O_{10-x}$ stoichiometry obtained under different synthesis conditions. The materials were characterized and studied by means of Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM), X-ray diffraction analysis (XRD), and AC Susceptibility. A preliminary identification of the main peaks appearing in the diffraction patterns is shown for the synthesized phases. The $La_{2-x}Sr_{2-x}Nb_2O_{10-x}$ compound undergoes a structural change as a function sintering temperature, with three kinds of the stabilized structure, one is from $1173 < T \leq 1373$ K, another from $1423 < T \leq 1573$ K and the last one from $1623 < T \leq 1723$ K.

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1. Introduction

$LaM_xN_yO_z$ mixed oxides where M = Sr and N = Nb, Nd, Ce, in different oxidation states exhibit a broad spectrum of interesting physical properties, among them superconductivity, giant magneto resistance and catalysis. Mainly, attention is given to correlations between composition, structure, and physical properties. Analysis of the effect that chemical composition, preparation procedure and stoichiometry posses on their structure helps to optimize the search for new materials with desired properties. In the past, La–Sr–Nb mixed oxides were extensively studied looking for superconductivity [1–3], which was not fully demonstrated [4]. Now, perovskites are important materials due to its versatility in technological applications. By example membrane applications [5] or colossal magneto resistance in thin films [6]. In catalysis, Sr–Nb–Co compounds have been studied for oxidation of ethylacetate and other volatile organic compounds, VOC [7] also in the combustion of propylene under $La_{2-x}Sr_xNiC_4$ and $La_{1-x}Sr_xCoO_3$ compounds to produce CO_2, H_2O, acroleine and acetaldehyde acetone [8]. Also research has been conducted on these materials as oxygen sorbent doping La–Sr mixed oxides with Co, Ni, Ba [9], and more recently in solid oxide fuel cells [10–12]. Its versatility can be explained because of these compounds crystallize in various distorted perovskites were Nb and Sr can be found in different oxidation states. The result of this competition depends mainly on the

relationship between the ionic radii of the substituent and host. Accordingly to several reports in the $Sr_{1-x}La_xNb_2O_6$ solid solutions, the unit-cell volume varies no monotonically with composition, because of the interplay between the effects above mentioned.

The ionic radii of Sr $^{2+}$ and La $^{3+}$ differ not very much, $r_{sr}^{2+} = 1.25$ Å and $r_{La}^{3+} = 1.18$ Å; as a result, the lattice parameter varies in a complex manner across the solid-solution series [3]. La–Sr–Nb compounds have an extremely open structure that tolerates a high level of atomic disorder, which can be induced by doping. Partial substitution of La by Sr can lead to a defect-like structure, increasing oxygen mobility and possibly modification of the electronic states. From the results discussed above it is concluded that potentially La–Sr–Nb–O compounds have many applications that are associated with its chemical composition. Consequently the present work was addressed to report the preparation of compounds with the $La_{2-x}Sr_{2-x}Nb_2O_{10-x}$ stoichiometry, which were obtained under several heating and time conditions and performing characterization by means of SEM Microscopy, HRTEM microscopy and XRD analysis.

2. Experimental procedure

Samples were prepared starting from La_2O_3, $SrCO_3$ and Nb_2O_5 with 99.99% purity, by means of solid sate reaction accordingly to the proposed reaction:

$$(1-x)La_2O_3 + (2-x)SrCO_3 + Nb_2O_5 \rightarrow La_{2-x}Sr_{2-x}Nb_2O_{10-x} + 2CO_2$$
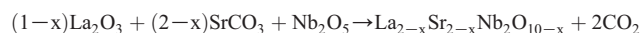
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The resulting mixture was placed in a high purity ceramic crucible and sintered in air according to a proposed heating/cooling route (see Table 1 for details) starting from room temperature. Our procedure was carried out in a simple way differently from complicated processes that involved quartz vials sealed off under vacuum [3]. In a second cycle, the samples obtained were grounded again in an Al_2O_3 mortar and pellets of 2.5 cm of diameter were produced using a pressure of 6 t/cm². The samples were sintered at temperatures, ranging from 1173 to 1673 K during 24 h and cooled inside the oven (C) or quenched (Q) in air, depending on the selected purpose. Samples obtained were of a typical beige color. Afterwards, samples were characterized by means of several techniques. The XRD analysis was performed in a Philips diffractometer using Cu K_α radiation at 40 KeV and 45 mA. The structural features were studied in a SEM JSM-6400 JEOL Noran Instrument, at 20 keV and 10^{-6} Torr. The TEM microscope used was a JEOL JEM-2010. Magnetic susceptibility was measured in an applied field of 1000 G using a variable temperature vibrating sample magnetometer Model MagLab 2000.

3. Results and discussion

Samples were prepared with the desired $La_{2-x}Sr_{2-x}Nb_2O_{(10-x)}$ stoichiometry under several sintering routes considering temperature and time. The temperature range was established from previous work [4] from 1173 to 1673 K. Initially through carefully XRD analysis it was detected that preferentially, some phases were stabilized while small amounts of minority phases remain mixed, probably due to precursors not fully processed. Then the work was addressed to increase the amount of those phases by sintering and heating again. Initially X-ray diffraction analysis demonstrates that starting from 1423 K (see Fig. 1) the material showed reflections between 25 and 35° (2θ) reminiscent of those attributable to perovskite-like materials. All the X-ray diffraction

Table 1
This table resumes calculated dimensions and main diffraction peaks found in the present work. Also data from the JCPDS-ICDD file. Stoichiometric composition was established through EDS analysis. In this table (C) means cooled inside the oven while (Q) means quenched.

Compound	JCPDS file no.	Experimental procedure	Main reflections observed 2θ	Intens	Reported structure	Ref. no.
$LaSr_3Nb_3O_{12}$	41-0148	1173 K for 10 days and 1523 K for 7 days	29.327	100	Hexagonal	JCPDS-ICDD
			31.624	100	a = 6.656Å	
			43.671	100	c = 27.19Å	
			54.901	90		
α-$La_2Sr_3Nb_{12}O_{36}$	39-1123	Non described	29.777	100	Tetragonal	JCPDS-ICDD
			32.533	100	a = 17.481Å	
			46.397	80	c = 3.866	
			46.969	80		
β-$La_2Sr_3Nb_{12}O_{36}$	41-0142	Non described	23.162	90	Monoclinic	JCPDS-ICDD
			28.028	100	a = 17.494Å	
			28.559	90	b = 7.738	
			29.716	100	c = 61.82	
			29.910	100		
β-$La_{1.5}Sr_{1.25}NbO_6$	37-0968	Non described	28.118	40	Tetragonal	JCPDS-ICDD
			30.645	100	a = 11.636Å	
			43.962	25	c = 16.513	
			54.544	30		
$LaSr_5Nb_{10}O_{30}$	46-0231	1523 K for 5 h in sealed silica tube	27.999	54	Tetragonal	JCPDS-ICDD
			29.802	53	a = 12.3491 Å	
			32.424	100	c = 3.8969	
$La_{0.4}Sr_{0.6}Nb_2O_6$	44-0564	1373 K for 50h with intermediate regrinding (annealed in sealed silica tube)	29.058	78	Orthorhombic	JCPDS-ICDD
			29.424	100	a = 11.0392Å	
			32.094	25	b = 7.6512	
			47.493	18	c = 5.5714	
L2-0502 $La_{2.3}Sr_{1.8}Nb_{1.8}O_{9.7}$		1273 K and 1423 K each one for 24 h with intermediate regrinding. (C) Heating and cooling rate was 15 K/min.	27.885	68.9	Hexagonal	This work
			28.210	37.2	a = 25.6 Å	
			29.205	100	c = 5.89	
			30.485	70.5		
			31.455	81.7		
L1-051397 $La_{2.2}Sr_2Nb_{1.8}O_{9.8}$		Heated two times 1573 K for 24h with intermediate regrinding. (C) Heating and cooling rate was 1 K/min.	27.970	34.6	a = 11.242Å	This work
			29.315	100	b = 4.951	
			30.580	49.5	c = 7.101	
			31.575	68.5	α = γ = 90, β = 98.2°	
			43.630	42.3		
L3-150597 $La_{2.2}Sr_{1.9}Nb_{1.8}O_{9.7}$		1573 K and 1623 K each one for 24h with intermediate regrinding. (C) Heating and cooling rate was 1 K/min.	29.085	52.8	a = 7.137Å	This work
			29.370	92.2	b = 8.138	
			29.485	100	c = 7.101	
			29.965	47.8	α = β = 112.6°,	
			31.630	51.6	γ = 94.4°	
			32.030	53.5		
L3-0502 $La_{1.1}Sr_{2.6}Nb_{2.7}O_{10.9}$		1273 K and 1573 K each one for 24h with intermediate regrinding. (C) Heating and cooling rate was 15 K/min.	27.905	49.0	Cubic	This work
			29.210	100	a = 16.511 Å	
			30.510	62	α = β = γ = 90°	
			31.480	70.3		
			43.535	46.8		
L1-1009 $La_{1.1}Sr_{2.6}Nb_{2.6}O_{10.9}$		1273 K and 1573 K each one for 24h with intermediate regrinding. (Q) Heating rate was 15 K/min.	29.385	61.4	a = 12.068 Å	This work
			31.660	61.9	b = 7.498	
			43.750	35.9	c = 6.675	
			44.635	100	α = γ = 90°, β = 105°	

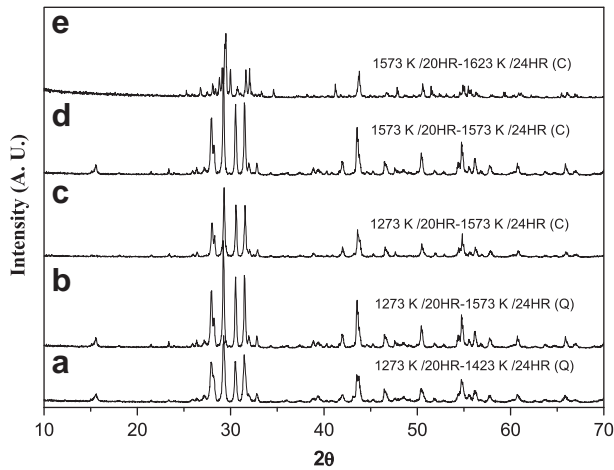**Fig. 1.** Diffraction patterns for sintered samples. For a and b heating and cooling rate was 2°/min while for c and d was 1°/min. Sample sintered at 1623 K shows the growing of a new different structure. Q means quenched. C means cooled inside the oven.

patterns of the prepared samples posses peaks within the 2θ range afore mentioned. Above 1623 K (Fig. 1e) the La–Sr–Nb–O material undergoes to a different structural change, promoted by the increase of temperature.

Fig. 1 shows XRD patterns for different samples prepared at temperatures ranging from 1573 K to 1623 K produced under several heating and cooling rates. It was performed a detailed analysis of the X-ray diffraction patterns in order to monitor the changes of structure

promoted thermal process and sintering time. As shown on Fig. 1, sample 1 (a) was sintered, initially, two times at 1273 K and afterwards sintered again at 1423 K using heating and cooling ramps of 2°/min. Sample 1 (b) was quenched from 1573 K. Sample 1 (c) was cooled inside the oven from 1573 K at 2°/min. Diffraction pattern on Fig. 1d belongs to the sample sintered two times at 1573 K and cooled inside the oven. Finally on Fig. 1e, it is appreciated the growing of a different phase promoted by the temperature increase (1623 K). Both samples Fig. 1d and e were cooled inside the oven at cooling rates of 1°/min. Characteristics peaks of each processed material were carefully established and summarized on Table 1. In order to establish a comparison with previous reported patterns, we present observed high reflections for existent patterns from La–Sr–Nb–O system as reported on JCPDS data-file. For determination of lattice parameters and for structural studies, the scanned range was only performed from 2θ = 10 to 80°, where the main peaks of those materials are presented. The step size was 0.01°, with 20 s/step. Structural refinements, from XRD powder diffraction data, were performed using the FullProf-Suite program as Rietveld software [13].

From XRD analysis (see Table 1) it is possible to ascertain that several structural changes occur within the range of temperature considered. The analysis shows that initially a hexagonal structure appears under 1423 K, which subsequently transforms into a cubic structure and finally at 1623 K a new structure takes place (still undetermined). From the above findings we establish that three different phases can be stabilized considering the adequate temperature range. The first is from 1173 K and until 1373 K, the next between 1423 K and 1573 K and the last one is from 1623 K.

The stoichiometry of the samples found through EDS shows that samples were very close to the desired formulation. However, samples
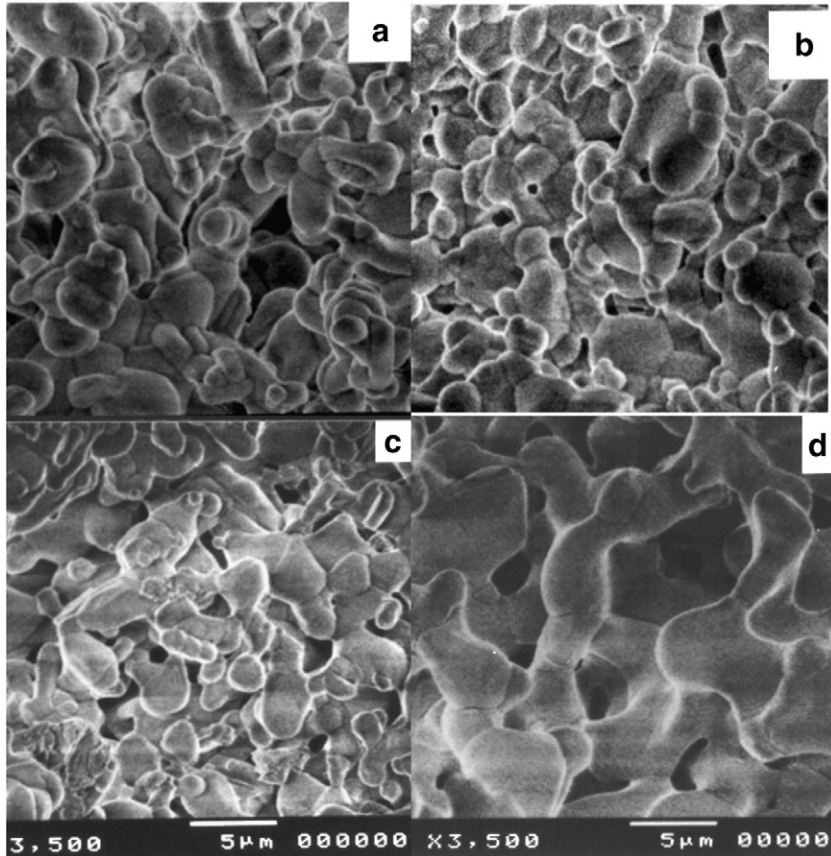

Fig. 2. SEM micrographs of freshly broken samples. (a) Annealed at 1273 and 1573 K and cooled inside the oven at 2°/min, (b) annealed at 1273 and 1573 K for 24 h and quenched, (c) sample sintered at 1573 K for 2 times and cooled at 1°/min and (d) sample sintered two times at 1623 K and cooled at 1°/min.

processed below 1473 K shown small quantities of minor phases, which can be partially attributable to precursors that still do not react (not shown in the X-ray diffraction patterns). The stoichiometry for every sample is also presented in Table 1.

Surface morphology of the $La_2Sr_2Nb_2O_{10-x}$ samples is presented in Fig. 2. Fig. 2a shows a SEM micrograph corresponding to the sample which was sintered in air at 1273 K during 24 h, and sintered again at 1573 K/24 h. Fig. 2b shows a SEM micrograph of the compound sintered at the same conditions of sample a, except that this material was quenched (Q) to room temperature in air. Both figures show rounded crystals of about 5 μm with the same crystalline shape. In Fig. 2c we present an image of the sample, which was prepared at 1573 K with small particles consisting of well-rounded grains. Regarding the Fig. 2d micrograph, which belongs to sample sintered at 1623 K, it is appreciated the growing of big welded crystals of 5×20 μm. Apparently, the structure is close to their melting point, however even at 1673 K it was not found direct evidence by observing the alumina crucibles.

HRTEM Microscopy provided further evidence of the crystalline structure in large domains. Periodicity of the order of 5.7 Å was visible, as shown on Fig. 3. On it, arrows followed by the proper values indicate distances between planes. The image was obtained from sample prepared at 1573 K by using cooling and heating rate of 2°/min.

The electrical resistance was measured at room temperature for all the samples. It is extremely high, in the order of several Mega-Ohms. Regarding the magnetic behavior, the magnetization as a function of temperature is shown in Fig. 4. There we show the measurements of $La_{1.1}Sr_{2.6}Nb_{2.7}O_{10.9}$ (C) and $La_{1.1}Sr_{2.6}Nb_{2.7}O_{10.9}$ (Q) samples prepared at 1573 K. As can be observed, the magnetic behavior is paramagnetic-like. There is not any signal of magnetic order or diamagnetism that can be associated to superconductivity.

4. Conclusions

From the results it was distinguished three different phases within the considered range of temperature. One from 1173 K to 1373 K, the other among 1423 and 1573 K and at 1623 K, it was observed the appearance of a different phase. No one of the synthesized samples matches with previous established patterns on JCPDS 2008 consequently the compounds shown here are truly new phases. Preparation of single crystals is in progress and will be presented in a next publication. Interesting physical properties and possible application of these materials by example in fuel cells, oxidation catalysis or VOC decomposition remain to be determined.
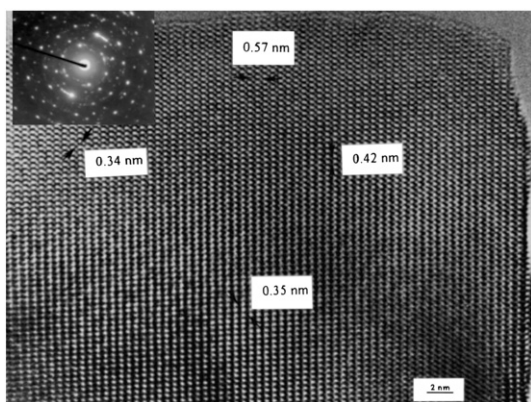
Fig. 4. Magnetic susceptibility χ (10^{-6} emu/G) vs. temperature (K) curves are shown for samples sintered at 1273 and 1573 K and cooled inside the oven (C) or quenched (Q). No diamagnetic response is shown in both samples.

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Fig. 3. High Resolution Transmission Electron Microscopy (HRTEM) micrographs of La2Sr2Nb2O$_{10-x}$ sample annealed at 1573 K with heating and cooling rate of 15 K. It is observed periodicity of order 5.7 Å. Arrows followed by their characterist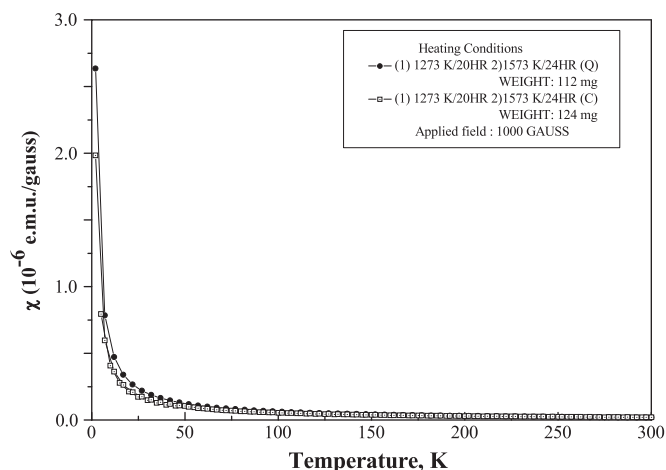ics values indicate the data on interplane distances.