

Praseodymium oxides. Complete characterization by determining oxygen content



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ABSTRACT

Praseodymium ions are available in many oxidation states, so they are capable to form a huge number of different oxides, which make them an interesting and versatile material in many industries, such as ceramics or optics.

Although praseodymium oxides behavior has been studied, the information found in the literature is sometimes contradictory. The different conditions of experimentation have led to opposite results due to rapid praseodymium oxide transformations. Many authors have pointed out the high oxygen mobility upon phase transformations during heating and cooling processes.

Four materials based on praseodymium oxide compounds were characterized by physicochemical analysis. Praseodymium concentration was determined by WD-XRF and oxygen content was determined by the elemental analyzer TC-436, while XRD gave crystalline phases information and thermal analysis was carried out to obtain information about phase transformations. The combination of these analytical techniques allowed to have the real and accurate praseodymium concentration of a determined product, as it was found out that, two products that intended to have the same praseodymium concentration, were actually different.

PrO_2 and Pr_2O_3 were the major phases identified in these materials by XRD, although $\text{Pr}(\text{OH})_3$, and Pr_6O_{11} were also found as minor phases in the original materials. From the results obtained by WD-XRF, XRD and simultaneous thermal analysis; crystalline phases concentration was calculated, but the determination of oxygen content by the elemental analyzer TC-436 was the key to validate the results obtained from WD-XRF, XRD and simultaneous thermal analysis. The oxygen determination method was optimized by increasing a 400% the sample weight introduced into the piece of equipment, which resulted in a precision improvement.

In addition, one sample underwent different thermal treatments at the temperatures of 500, 650, 760, 980 and 1040 °C and two different cooling processes (slow cooling and quenching), to study phase transformations at these temperatures by measuring the oxygen content and determine the crystalline phases by XRD. It was found that, when the sample was quenched, different phases were formed at different temperatures, such as Pr_9O_{16} and Pr_7O_{12} , while cooling slowly the calcined sample was always giving Pr_6O_{11} because the intermediate phases were not stable enough to be determined.

Thus, the aim of this work was to devise an adequately robust test method and use it to expand the present knowledge base concerning the praseodymium oxide physicochemical characterization and its behavior across different heating and cooling processes.

1. Introduction

Praseodymium oxides are used in ceramics as raw material for praseodymium yellow zircon synthesis. This type of pigment is one of the most frequently used in ceramics due to its great stability [1]. Sulcová et al. studied the synthesis of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ pigments, where Pr_6O_{11} ($4\text{PrO}_2\cdot\text{Pr}_2\text{O}_3$) is used as raw material. Praseodymium ions are

available in many oxidation states, so they are capable to form a huge number of different oxides, which make them an interesting and versatile material [2].

Praseodymium oxides are not only used as raw materials in ceramics, yet their optical properties make them precious materials in optical area. Gâcon et al. studied the optical properties of Pr^{3+} ions in concentrated phosphates [3].

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As many authors said, for the proper synthesis of optical materials, it is of substantial interest to know the thermal decomposition of the commercially available oxides, such as Pr_6O_{11} . In the range between room temperature and 1327°C it turns out that praseodymium oxide decomposes to many praseodymium oxides [4–6].

According to Ferro, Praseodymium oxides represent a variable system of phases, which composition and structure changes in a defined range. In addition to Pr_2O_3 and PrO_2 , which are commonly known, at least other five suboxides have been found, having the general composition $\text{Pr}_n\text{O}_{2n-2}$. Some authors wonder about the existence of PrO_x intermediate phases, where x would get different values among 1.585, 1.658, 1.703, 1.804 or 1.833. In addition, praseodymium can also be forming hydroxides ($\text{Pr}(\text{OH})_3$) or carbonates ($\text{Pr}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$) and their decomposition process has been studied by different authors [5,7,8,11].

According to Nezt et al., transitions between phases use to occur very rapidly when heating and cooling the sample in a high oxygen activity environment, which means an unusually high oxygen mobility. Some authors affirm that the equilibrium phase at room temperature in air is not PrO_2 , but Pr_6O_{11} [9], although not all the literature consulted agree. Some authors, such as Treu et al., emphasizes the need of keeping the materials in an inert atmosphere, precisely to avoid these phase modifications [10].

Sulcová and Trojan sustain that the crystal lattice of Pr_2O_3 is characterized by excess of oxygen. From Differential Thermal Analysis (DTA) curve, they assumed that the content of oxygen is decreased with increasing temperature. This loss of oxygen assumed is represented by several endothermal effects on DTA curve [12].

Treu et al. studied the thermal decomposition behavior of Pr_6O_{11} , Pr_2O_3 , $\text{Pr}(\text{OH})_3$, $\text{Pr}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$. They attributed the mass losses for each species to the removal of hydroxide and carbonate groups. X-Ray diffraction (XRD) analysis identified the final decomposition product at 1400°C for each species as Pr_6O_{11} regardless of the starting material [10]. Netz et al. affirm that Pr_6O_{11} can absorb significant amounts of water, even at ambient temperature. According to the high mobility of the oxygen in this structure, this water is irreversibly desorbed at relatively low temperatures [9].

As many authors sustain, there is certainly space for further research on the physicochemical and electrical properties of praseodymium oxides, even though there are some papers from 50 years ago that already showed some interest for the changes produced in the praseodymium oxidation state by the thermal treatment [5,6]. There is some contradiction about the results found by different studies so, some doubts appear about the praseodymium oxide phases formed at different temperatures. These contradictory results come from the different experiment conditions carried out by the different authors and so, they are not comparable.

Therefore, there is a need of experimental information about praseodymium oxides that could be found out by the quantitative determination of oxygen. No one scientific paper has been found about the determination of the amount of oxygen in a solid sample, which could give a complete information about the stoichiometric composition of certain material and clarify the changes that the praseodymium oxides undergo with a specific thermal treatment.

Summarizing, praseodymium oxide is one of the group of binary oxides that show a wide range of stoichiometry. So, the aim of this work is to carry out the complete characterization of different praseodymium oxides by WD-XRF, simultaneous thermal analysis, XRD and Oxygen determination by an elemental analyzer, to verify the different praseodymium species present in each material studied, and so, having a robust method to carry out the complete characterization of a praseodymium oxide.

2. Experimental

2.1. Instrumentation

A LECO model TC-436 Oxygen Elemental Analyzer was used to determine the Oxygen content. The technique consists on heating the sample in an inert atmosphere to turn it into gas, which passes by the carbon dioxide converter where oxygen reacts with carbon, forming CO_2 and is measured by infrared absorption.

A Mettler-Toledo model XS105 balance with a sensibility of 0.01 mg was used for preparing all the working standards and samples.

The preparation of the fused beads for Wavelength Dispersive X-Ray Fluorescence (WD-XRF) analysis was carried out in an EQUILAB model F2 Induction Fluxer instrument, using a Pt–Au crucible and dish from EQUILAB. WD-XRF analysis was conducted using a PANalytical model AXIOS spectrometer with a Rh target tube and 4-kW power.

The crystalline structures were identified by XRD using a Bruker Theta-Theta model D8 Advance diffractometer.

The simultaneous differential thermal analysis (DTA-TG) was performed in a Mettler-Toledo thermal analysis instrument model TGA/STDA851e. The measurements were performed at a maximum temperature of 1205°C with a heating rate of $10^\circ\text{C}/\text{min}$ and using a platinum vessel in a dynamic air atmosphere.

A vacuum device from JATA was used to store the samples and standards in vacuum atmosphere.

A N50 electric muffle furnace from Nabertherm capable to achieve a temperature of 1200°C was used to treat the samples at different temperatures.

2.2. Standards and samples

Standards:

A praseodymium oxide standard from Strem Chemicals was chosen to undergo the developed method. It was labelled as:

- Praseodymium Oxide Strem Chemicals

Pure chromium (Cr_2O_3) and iron oxides (Fe_2O_3) from Fluka and Merck respectively, were used as calibration and validation standards in the determination of oxygen by the elemental analyzer TC-436.

Samples:

Samples chosen were three praseodymium oxides used as raw materials for the synthesis of ceramic pigments. They were supposed to have the same composition. Samples were labelled as:

- Sample 1
- Sample 2
- Sample 3

An important point of the study was to control the storage conditions, as praseodymium oxide phases are quite unstable, and they change with temperature and moisture in the atmosphere. So, all the standards and samples were stored under vacuum atmosphere.

2.3. Experimental procedure

The complete characterization of the praseodymium oxides was carried out by combining different analytical techniques. The praseodymium content was determined quantitatively by WD-XRF. Weight

losses and gains experienced by the materials as increasing the temperature, mostly due to OH losses or phase transformations involving loss of oxygen, were given by simultaneous thermal analysis. On the other hand, the XRD analysis provided information about the different crystalline phases present in the sample. Rietveld-refinement was carried out to quantify the crystalline phases. Finally, the oxygen was quantitatively determined by the Oxygen Elemental Analyzer TC-436, to validate all the assumptions made about the praseodymium species present in each material, i.e., to compare the results obtained by Rietveld-refinement and to calculate the exact stoichiometry.

First, the materials were analyzed by all the analytical techniques cited before without having undergone any previous treatment, in order to establish a method to completely characterize a praseodymium oxide.

According to Netz et al., the equilibrium phase in air at room temperature is Pr_6O_{11} , instead of Pr_2O_3 [9] in spite of what other authors sustain. Thus, as the literature consulted was found to be contradictory, the studied materials were calcined at 980 °C and then, one fraction was let to cool slowly to room temperature and the other one was quenched by diving it into liquid nitrogen. After that, the samples were submitted to a physicochemical characterization by XRD, WD-XRF and an oxygen elemental analyzer.

Finally, another experiment was designed from the results obtained in the simultaneous thermal analysis that underwent the samples analyzed as-received. So, the materials were calcined at different temperatures (500, 650, 760, 980 and 1040 °C), and each fraction prepared at each temperature was quenched with liquid nitrogen to frost the praseodymium oxide phases formed at these temperatures. They were stored in vacuum atmosphere to preserve the current phases and then, they were characterized by determining the crystalline phases by XRD analysis, the praseodymium content by WD-XRF, and the oxygen content by an elemental analyzer.

In summary, experiments carried out in the materials were the following:

Samples after being dried at 110 °C for 2 h.

- Determination of Praseodymium content by WD-XRF
- Determination of Oxygen by elemental analyzer TC-436
- Determination of the crystalline phases by XRD
- Determination of phase transformations with the temperature by simultaneous thermal analysis

Samples after being calcined at 980 °C, cooled slowly at air atmosphere and quenched in liquid nitrogen

- Determination of Praseodymium content by WD-XRF
- Determination of Oxygen by elemental analyzer TC-436
- Determination of the crystalline phases by XRD

Samples after being calcined at 500, 650, 760, 980 and 1040 °C and quenching with liquid nitrogen

- Determination of Praseodymium content by WD-XRF
- Determination of Oxygen by elemental analyzer TC-436
- Determination of the crystalline phases by XRD

2.3.1. Chemical characterization by WD-XRF

Samples were analyzed by the program UNIQANT to determine the elements in their composition. The concentration of Si, Al, Fe, Ca, Mg, Na, K, Ti, Zn, P, Mn, Cr, Ni, Cu and Co was lower than 0.05% w/w. Thus, Praseodymium content was determined by preparing a calibration curve in the SuperQ program in WD-XRF; using LiF_2O as crystal analyzer, La line, a collimator of 150 μm and a Flow detector, then. For WD-XRF analysis, the sample was prepared in the form of beads. A 50:50 mixture of $\text{LiBO}_2\text{:Li}_2\text{B}_4\text{O}_7$ was used as flux and a 250 $\text{g}\cdot\text{L}^{-1}$ solution of LiI from Merck was used as bead-releasing agent.

2.3.2. Crystalline phase identification by XRD and phase quantification by Rietveld refinement

Praseodymium species were determined by XRD, giving information

about the oxides and hydroxides crystalline phases that might be in the sample. The mineralogical species present were identified using the ICDD files for pure crystalline phases [13–18].

A refinement Rietveld protocol was performed using the specific software DIFFRACplus TOPAS (version 4.2). The agreement indices, as defined in Topas, for the final least-squares cycles of all refinements were in the following ranges: $6.2 \leq \text{Rwp}$ (Weight profile R-factor) ≤ 9.2 and $1.06 \leq \text{GOF}$ (Goodness of fit) ≤ 1.77 .

2.3.3. Simultaneous differential thermal analysis (DTA-TG)

Simultaneous thermal analysis determined the transformations that the praseodymium oxides experienced by increasing the temperature. Samples were decomposed in air atmosphere using a heating rate of 10 °C/min from 25 to 1205 °C against a platinum crucible reference of 50 ml capacity.

2.3.4. Determination of oxygen by TC-436 Elemental Analyzer

Oxygen content was determined by the TC-436 Elemental Analyzer after preparing the corresponding calibration curves and optimizing the amount of sample introduced in the piece of equipment.

The aim of the Oxygen determination was to confirm all the theoretical assumptions made about the species present in each sample from the results obtained by the other techniques used, i.e. XRD and simultaneous thermal analysis.

2.3.4.1. Optimization of the measurement conditions.

Optimization of furnace constants

TC-436 furnace constants were optimized as the piece of equipment is able to operate with different conditions. After several trials changing power and analysis time, it was concluded that the optimum conditions were at 5 kW for 60 s.

Optimization of the amount of sample

Measurement conditions to carry out the determination of oxygen were optimized to find the maximum amount of sample that the instrument was able to measure without the cell saturation, in order to reach the lowest quantification limit possible. The amount of sample recommended by the instrument specialist was 4 mg, yet, as this was not a representative amount of sample and it supposed a high quantification limit, the aim was to find the maximum sample weight without collapsing the piece of equipment.

Calibration

The developed method was calibrated with different metal oxides. Chromium and iron oxides were used as calibration standards to check the influence of the sample matrix with the validation standards. The stability of their oxide compounds were the main reason why they were used to calibrate the instrument.

Validation

Chromium and iron oxides were measured to validate the developed method. The results obtained using both calibrations were almost identical, which means that the method is robust.

3. Results

3.1. Optimization of the measurement conditions

Table 1 and Fig. 1 show the results obtained in the sample weight optimization. As it can be seen, the highest sample weight that allowed the measurement of oxygen without collapsing the instrument was

Table 1
Optimization of the sample weight introduced in the instrument.

Weight (g)	Oxygen concentration (%)
0.00422	30.05 ± 0.66
0.00825	30.05 ± 0.78
0.01069	30.05 ± 0.53
0.01485	30.05 ± 0.45
0.02003	30.05 ± 0.12
0.02248	Saturated

0.02000 g. This 400% increment implied an important reduction of the standard deviation and therefore, to decrease the quantification limit and the uncertainty.

3.2. Complete characterization of the praseodymium oxide

Table 2 summarizes the results obtained in the phase analysis by XRD and the thermal analysis by simultaneous registration of the thermoanalytical curves TG and DTA.

Sample 1 to 3 and the Praseodymium Oxide Strem Chemicals were analyzed by different analytical techniques after being dried at 110 °C for 2 h. The Praseodymium concentration was analyzed on the four materials by WD-XRF and the results obtained are shown in Table 3. The rest of the elements analyzed were Si, Al, Fe, Ca, Mg, Na, K, Ti, Zn, P, Mn, Cr, Ni, Cu and Co, and all of them had a concentration lower than 0.05%.

It may be noted that Sample 1 show PrO₂ and Pr(OH)₃ crystalline phases, while Sample 2 presents Pr₂O₃ as major phase and PrO₂ and Pr(OH)₃ as minor phases. Sample 3 diffractogram shows PrO₂ as major phase, such as Sample 1, but being Pr(OH)₃ and Pr₆O₁₁ minor phases in this case. They were supposed to have the same composition but, it was found that each sample was having different crystalline phases. The only crystalline phase found in Praseodymium Oxide Strem Chemicals diffractogram was PrO₂, contrary to what it was expected from the certificate, that reports Pr₆O₁₁ as the only crystalline phase.

According to Sulcová et al., Pr₆O₁₁ is transformed to Pr₂O₃ at about 350 °C [2,12]. Treu et al. found that treating the praseodymium oxide at different temperatures was leading to Pr₆O₁₁ [10], which contradicts Sulcová affirmations, who decomposes Pr₆O₁₁ at 350 °C. Netz et al., who agree with Treu et al. about that all the PrO₂ was converted into Pr₆O₁₁, also sustained that they could not cool fast enough the samples to freeze in-equilibrium compositions above about 350 to 400 °C [9].

Thus, a series of experiments were carried out undergoing the sample different thermal treatments to know exactly the praseodymium oxide species formed during the treatments.

Regarding the thermal analysis, it is worth to point the appearance of a huge peak between 25 and 380 °C in all the materials that show Pr(OH)₃ in their composition. In addition, a series of losses was observed in all the materials at 540, 800 and 1040 °C, probably due to the phase transformations experienced by the materials by increasing the temperature. Regarding the results obtained in the DTA curve, all the peaks obtained were endothermal, which agreed with the literature consulted.

Crystalline phases concentration obtained in the XRD - Rietveld analysis, was compared with the calculations from the praseodymium and oxygen concentration. Theoretical oxygen concentration was calculated using the crystalline phases concentration obtained by Rietveld refinement, and it was compared to the oxygen concentration obtained by the elemental analyzer TC-436. The results achieved were coherent with the calculated values, which confirmed that the crystalline phases concentration calculated were correct.

Sample 1, 2 and 3 were supposed to have the same praseodymium oxide specie in their composition, but it was observed that they presented significant differences in their composition. In addition, while Sample 1 and 3 had similar amount of praseodymium, Sample 2 showed a different praseodymium concentration.

It was noticed that Sample 1 and 3 had the same praseodymium and oxygen content, but they had different crystalline phases in their composition. This fact points out the need of the XRD analysis to identify the crystalline phases.

In conclusion, the developed method to completely characterize a praseodymium oxide consists on the identification and quantification of the crystalline phases by XRD and Rietveld-refinement, which results are verified by calculating the crystalline phases concentration from the praseodymium content, determined by WD-XRF, and the oxygen concentration, determined by an elemental analyzer.

The oxygen determination allowed to validate the methodology used to carry out a complete characterization of a praseodymium material.

3.3. Study of the phase praseodymium transformations during different thermal treatments

Sample 1 was thermal treated and analyzed by XRD. Praseodymium and oxygen content were also determined by WD-XRF and an elemental analyzer.

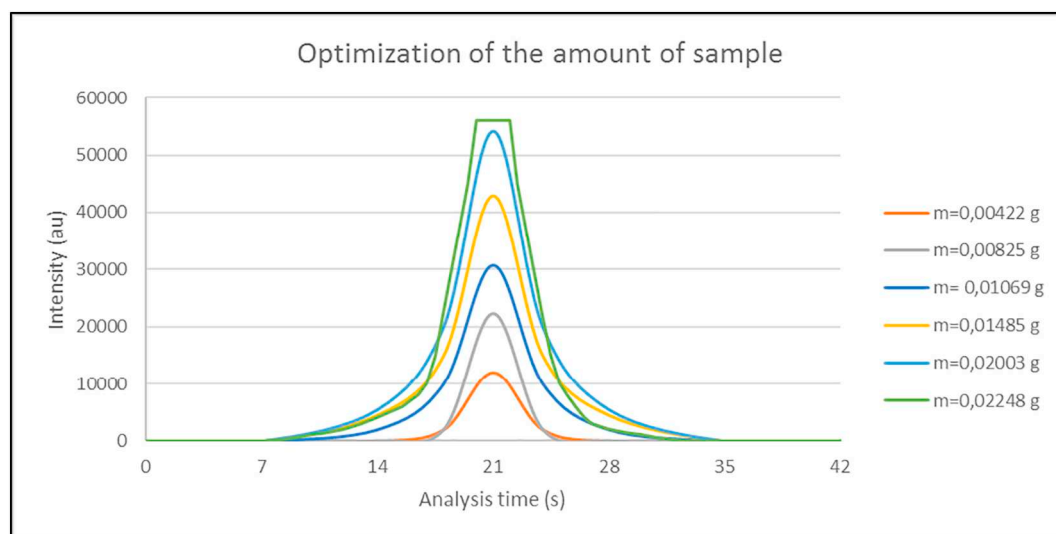


Fig. 1. Optimization of the amount of sample.

Table 2
Physicochemical characterization of Sample 1 to 3 and Praseodymium (III, IV) Oxide.

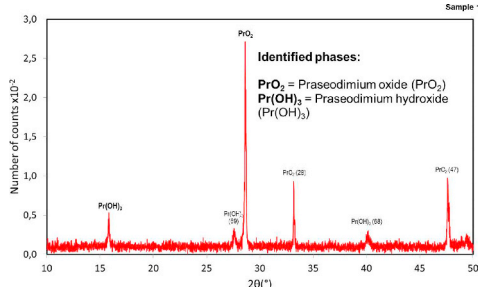
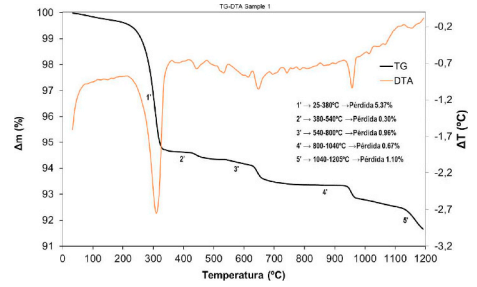
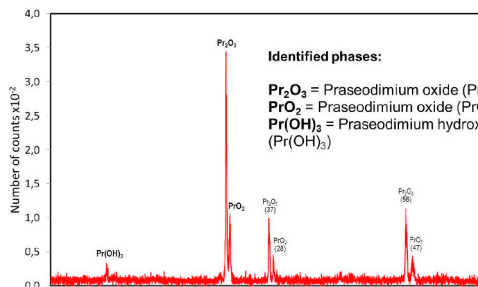
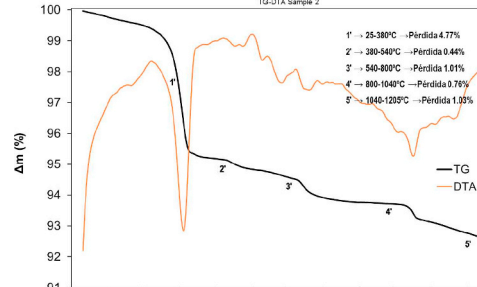
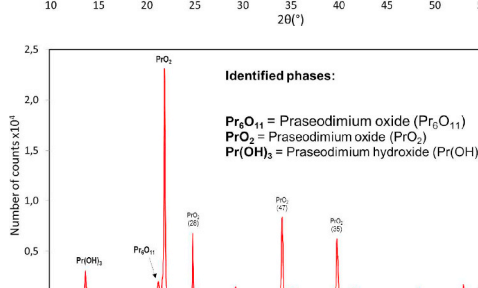
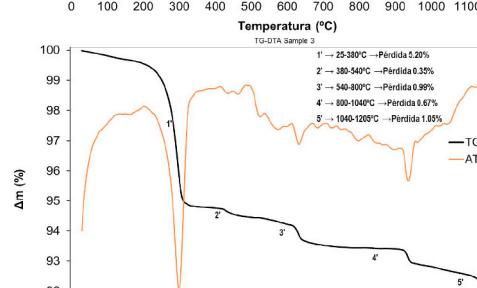
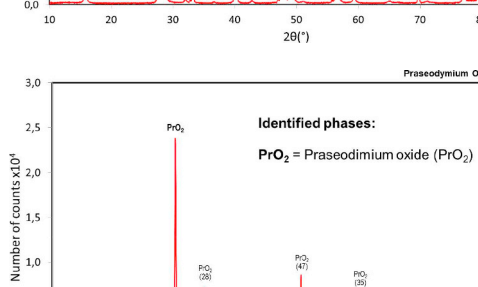
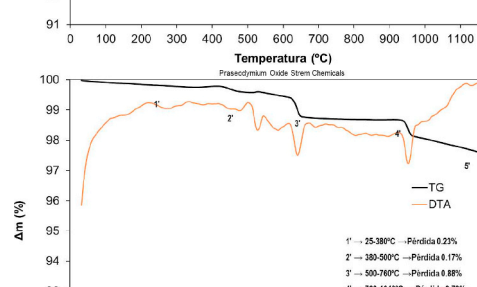
	Crystalline phases	Thermal analysis
Sample 1	 <p>Identified phases: PrO_2 = Praseodymium oxide (PrO_2) $\text{Pr}(\text{OH})_3$ = Praseodymium hydroxide ($\text{Pr}(\text{OH})_3$)</p>	 <p>1' → 25-380°C → Pérdida 5.57% 2' → 380-540°C → Pérdida 6.30% 3' → 540-800°C → Pérdida 6.86% 4' → 800-1040°C → Pérdida 6.67% 5' → 1040-1200°C → Pérdida 1.19%</p>
Sample 2	 <p>Identified phases: Pr_2O_3 = Praseodymium oxide (Pr_2O_3) PrO_2 = Praseodymium oxide (PrO_2) $\text{Pr}(\text{OH})_3$ = Praseodymium hydroxide ($\text{Pr}(\text{OH})_3$)</p>	 <p>1' → 25-380°C → Pérdida 4.77% 2' → 380-540°C → Pérdida 0.44% 3' → 540-800°C → Pérdida 1.01% 4' → 800-1040°C → Pérdida 0.76% 5' → 1040-1200°C → Pérdida 1.25%</p>
Sample 3	 <p>Identified phases: Pr_6O_{11} = Praseodymium oxide (Pr_6O_{11}) PrO_2 = Praseodymium oxide (PrO_2) $\text{Pr}(\text{OH})_3$ = Praseodymium hydroxide ($\text{Pr}(\text{OH})_3$)</p>	 <p>1' → 25-380°C → Pérdida 5.20% 2' → 380-540°C → Pérdida 0.35% 3' → 540-800°C → Pérdida 0.99% 4' → 800-1040°C → Pérdida 0.67% 5' → 1040-1200°C → Pérdida 1.65%</p>
Praseodymium Oxide Strem Chemicals	 <p>Identified phases: PrO_2 = Praseodymium oxide (PrO_2)</p>	 <p>1' → 25-380°C → Pérdida 0.23% 2' → 380-540°C → Pérdida 0.17% 3' → 500-760°C → Pérdida 0.88% 4' → 760-1040°C → Pérdida 0.73% 5' → 1040-1200°C → Pérdida 0.91%</p>

Table 3
Praseodymium oxides characterization.

	Praseodymium concentration	Crystalline phases concentration (Rietveld)	Calculated oxygen concentration	Experimental oxygen concentration
Sample 1	Pr – 79.9%	$\text{Pr}(\text{OH})_3$ – (20.3 ± 2.0) % PrO_2 – (79.7 ± 3.0) %	19.8%	20.0 ± 0.4%
Sample 2	Pr – 82.5%	$\text{Pr}(\text{OH})_3$ – (17.9 ± 2.0) % PrO_2 – (20.0 ± 2.0) % Pr_2O_3 – (62.0 ± 3.0) %	17.2%	17.3 ± 0.4%
Sample 3	Pr – 80.0%	$\text{Pr}(\text{OH})_3$ – (19.5 ± 2.0) % PrO_2 – (75.5 ± 3.0) % Pr_6O_{11} – (5.0 ± 1.0) %	19.7%	19.9 ± 0.4%
Praseodymium Oxide Strem Chemicals	Pr – 81.5%	PrO_2 – 100.0%	18.5%	18.6 ± 0.4%

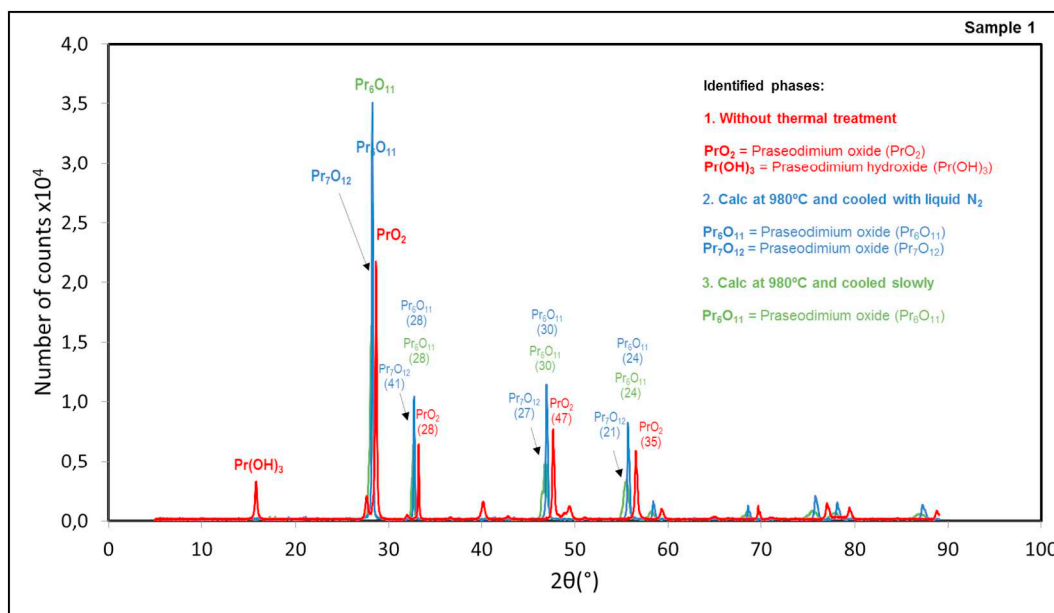


Fig. 2. XRD of Sample 1 without thermal treatment and after undergoing calcination at 980 °C with both cooling treatments.

3.3.1. Calcination of Sample 1 at 980 °C with different cooling treatments

The literature consulted was contradictory regarding to the phase transformations at the different temperatures which lead to the thought that these differences came from the cooling process. An experiment was designed where Sample 1 was calcined at 980 °C and then one fraction was quenched with liquid nitrogen and the other one was cooled slowly into the furnace. Crystalline phase diagrams of the original sample and both thermal treatments are overlaid in Fig. 2.

Sample 1 without a previous thermal treatment presented PrO_2 and Pr(OH)_3 crystalline phases. Diffractogram of sample 1 after being calcined at 980 °C and cooled slowly in air atmosphere showed exclusively Pr_6O_{11} , which result agrees with Netz et al., who also stated the concern about being the cooling process an issue to identify the correct phases formed [9]. Finally, the diffractogram of Sample 1 calcined at 980 °C and quenched with liquid nitrogen showed Pr_6O_{11} and Pr_7O_{12} , which agrees with the praseodymium-oxygen system proposed by Ferro and Netz et al. [5,9].

According to Treu et al., Pr_6O_{11} was the only phase present when heating over 800 °C [10]. But, according to our experience, these results could come from the evolution during cooling process, as they did not quench the sample.

It was noticed that Pr_6O_{11} crystalline phase was being formed in the cooling process, as Pr_7O_{12} was appearing in the diffractogram of the sample quenched with liquid nitrogen. The analysis of these fractions brought about the conclusion that, when the sample was cooling down, the crystalline phases formed at certain temperature were not stable so, they were changing to Pr_6O_{11} .

Table 4

Praseodymium, oxygen and crystalline phases concentration in Sample 1 without thermal treatment and after undergoing calcination at 980 °C with both cooling treatments.

	Experimental praseodymium	Crystalline phases concentration	Experimental oxygen
Sample 1	(79.9 ± 0.3) %	PrO_2 –79.7% Pr(OH)_3 –20.3%	(20.0 ± 0.4) %
Sample 1 calc. at 980 °C and cooled slowly	(82.8 ± 0.3) %	Pr_6O_{11} –100.0%	(17.2 ± 0.4) %
Sample 1 calc. at 980 °C and cooled with liquid N ₂	(83.2 ± 0.3) %	Pr_6O_{11} –60.0% Pr_7O_{12} –40.0%	(16.9 ± 0.4) %

3.3.2. Calcination of Sample 1 at different temperatures and quenching with liquid nitrogen

The thermal analysis carried out on the characterization of the fourth analyzed materials showed different peaks at temperatures of 500, 650, 760, 980 and 1040 °C, which should correspond to praseodymium oxide transformations. Plewa and Jüstel, mention the existence of different suboxides formed with the increasing temperature, finding until 5 suboxides, while other authors, such as Sastry et al., differed with this information and only obtained 3 or 4 different praseodymium oxides [10,19].

It was also observed in simultaneous thermal analysis from Table 2, that the different peaks obtained during the thermal analysis were very similar between them, regardless of the original crystalline phase. These facts and the contradictory information found in the consulted literature, led to the design of a new experiment that would characterize each praseodymium oxide at the same temperature that had shown a peak on the simultaneous thermal analysis, determining the crystalline phases by XRD and the oxygen concentration by the elemental analyzer TC-436 after calcining the sample and quenching the crystalline phase formed with liquid nitrogen. The results obtained are shown in Table 5.

The oxygen concentration of each crystalline phase obtained at each temperature was calculated. The results obtained by determining the oxygen content by an elemental analyzer coincide with the calculated values, which validated the formation of these species (Table 4).

As said by Ferro, the crystalline phase formed at 490 °C should be Pr_5O_9 , while at 520 °C should appear Pr_9O_{18} [5]. Those crystalline

Table 5

Experimental and calculated Oxygen determination and crystalline phases of Sample 1 calcined at different temperatures and quenched with liquid nitrogen.

Temperature	Experimental oxygen (%)	Calculated oxygen (%)	Crystalline phases
500 °C	17.7 ± 0.5	17.8	PrO ₂ Pr ₆ O ₁₁
650 °C	16.9 ± 0.5	16.8	Pr ₉ O ₁₆
760 °C	16.5 ± 0.5	16.3	Pr ₇ O ₁₂
980 °C	16.6 ± 0.5	16.3	Pr ₇ O ₁₂
1040 °C	16.5 ± 0.5	16.3	Pr ₇ O ₁₂

phases are different to the ones obtained in this work and it is believed that the reason is the cooling process. Quenching gave us the possibility to actually see the right crystalline phase, as it did not have the possibility to change.

Stubblefield et al. established the heat formation for each crystalline phase and defined the stoichiometry of the compounds based on the PrO_x formula, being *x* 1.500, 1.703, 1.717, 1.804, 1.833 and 2.000 [20]. Expressing the crystalline phases obtained in a PrO_x form, the *x* values obtained in this work would be 2.000, 1.833, 1.778 and 1.714; which are similar to those proposed by Stubblefield et al.

As it can be seen in Table 5, crystalline phases found at different temperatures quenching the samples with liquid nitrogen, agree with the praseodymium-oxygen system transformations proposed by Ferro and Netz et al. on their respective works [5,9]. As it was expected from literature, Pr₉O₁₆ was obtained at 650 °C and, finally, from 760 °C to 1040 °C, Pr₇O₁₂ was the major phase obtained.

Diffractograms obtained were compared to appreciate the differences among the different XRD peaks. In addition, it also agrees with the Sulcová and Trojan assumption that oxygen content decrease as the temperature increases [12].

Figs. 3 and 4 showed the comparison of the main XRD peaks. It could be seen that XRD from temperatures 760, 980 and 1040 °C were so similar because they were mostly the same phase. Peaks from the different four species identified by the XRD could be clearly differentiated, as well as the oxygen content obtained from the oxygen determination.

It can be noticed in Figs. 3 and 4, that peak 650 °C is not as high as the others identified in the XRD, which is an indicator that this specie

was not well crystallized. According to Ferro [5], this lack of crystallization might be produced from the short temperature interval. It is shown that, 760, 980 and 1040 °C spectra are equals because they present the same crystalline phase in its composition (Pr₇O₁₂).

In conclusion, praseodymium oxide transformations can be identified by quenching the sample after undergoing the corresponding thermal treatment and being stored under vacuum conditions. Otherwise, the praseodymium-oxygen will evolve to the stable phase Pr₆O₁₁.

In addition, the quantification of the phases has been validated by carrying out independent analytical techniques to characterize the samples. The quantification of the praseodymium oxide species obtained by the Rietveld-refinement were the same than those calculated with the results obtained by determining the praseodymium content by WD-XRF and the oxygen concentration determined by an elemental analyzer, which means that the method developed is validated.

4. Conclusions

1. After the thermal treatments applied, it was found that the cooling process rate was affecting on the crystalline phase obtained in XRD analysis, so that the materials quenched with liquid nitrogen were showing the real phases formed at each temperature (PrO₂, Pr₆O₁₁, Pr₉O₁₆ and Pr₇O₁₂). Otherwise, when the material was cooling slowly in air atmosphere, only the stable phase Pr₆O₁₁ was found, regardless the initial material.
2. A methodology for the complete characterization of praseodymium oxides has been set up using different analytical techniques, such as WD-XRF, XRD, simultaneous thermal analysis and determination of the oxygen content by combustion at IR detection.
3. A method to determine oxygen in high-oxygen content solid samples has been developed. The optimization of the amount of sample introduced in the piece of equipment has allowed to reduce the uncertainty, as higher amount of sample analyzed takes to more precise determination. The sample weight has been increased from 0.00400 g to 0.02200 g.
4. The oxygen determination in chemical compounds that usually have different oxidation states, such as praseodymium, provides valuable information that allows a complete characterization.
5. The loss on ignition (LOI) at 980 °C is the sum up of losses and gains, i.e. the loss of OH and the oxide transformations. For example, for

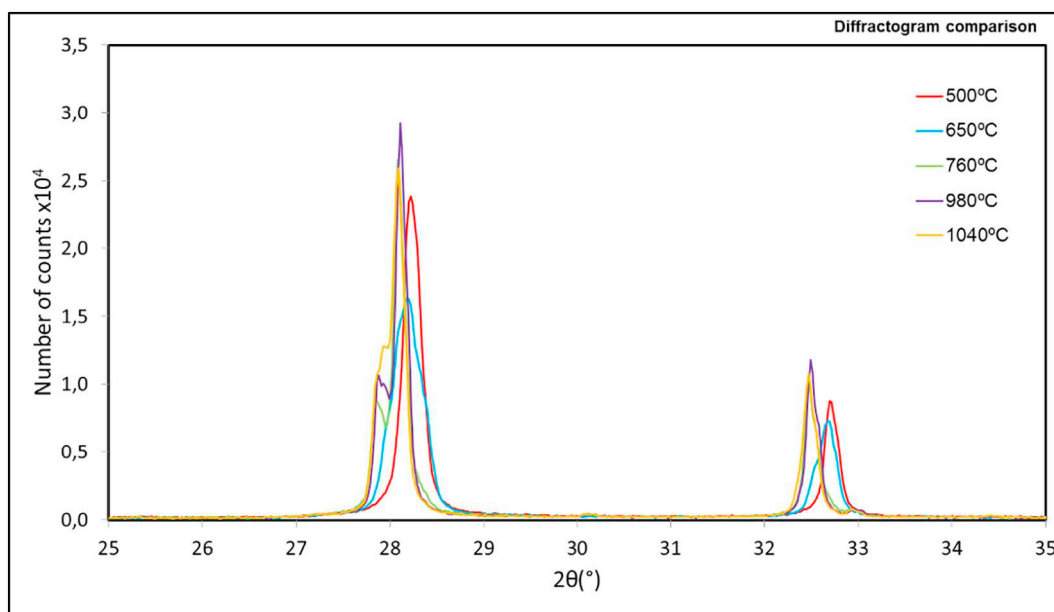


Fig. 3. XRD comparison at different temperatures of Sample 1 calcined at different temperatures and frozen with liquid nitrogen.

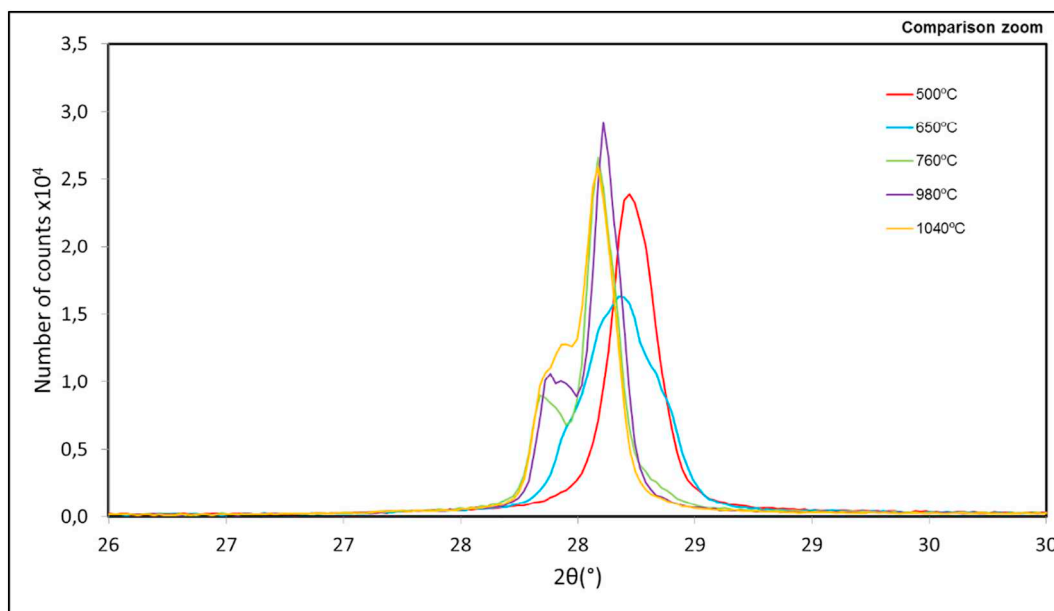


Fig. 4. Diffraction pattern comparison zoom of Sample 1.

Sample 1, $\text{Pr}(\text{OH})_3$ loses its OH but, in addition, PrO_2 changes to Pr_6O_{11} , passing by Pr_9O_{16} and Pr_7O_{12} , so it has no sense to do the LOI at a certain temperature as the final value does not give information about the losses of water or CO_2 that the sample contains.

6. Praseodymium oxide were treated at the temperatures where a peak was emerging in simultaneous thermal analysis (500, 650, 760, 980 and 1040 °C), and then they were analyzed by XRD and oxygen determination to show that the crystalline phases formed were: a mixture of PrO_2 and Pr_6O_{11} at 500 °C, Pr_9O_{16} at 650 °C and Pr_7O_{12} at 760, 980 and 1040 °C.

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