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Chlorination of Pr₂O₃ and Pr₆O₁₁. Crystal Structure, magnetic and

spectroscopic properties of Praseodymium Oxychloride

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ABSTRACT

The reactions of Pr_2O_3 and Pr_6O_{11} with $Cl_2(g)$ were studied thermodynamically and experimentally, and proposed in the systems $Pr_2O_3/Cl_2(g)$ and $Pr_6O_{11}/Cl_2(g)$. A kinetic analysis was performed on Pr_6O_{11} chlorination, which differs from with other light rare earth oxide chlorinations. The praseodymium oxychlorides obtained by full chlorination of Pr_6O_{11} at 425 °C and 800 °C are different, being well charact erized by X-ray diffraction, scanning electron microscopy, magnetic susceptibility measurements and X-ray photoelectron spectroscopy. The crystal structures of the oxychlorides were refined with the Rietveld method. The comparison between the theoretical magnetic moment of Pr^{3+} and the estimated magnetic moment in the praseodymium oxychloride obtained at 425 °C revealed the presence of Pr^{3+} and Pr^{4+} , whereas no significant difference was observed between the theoretical and the experimental values of Pr^{3+} obtained for the praseodymium oxychloride prepared at 800 °C. These observations are consistent with the analyses in the X-ray photoelectron spectra for both oxychlorides. Finally, a general formula of $PrO_{1+x}Cl$ is proposed for the oxychlorides synthesized at T<800 °C.

KEYWORDS: Praseodymium; oxychloride; chlorination; kinetics; light rare earth.

1. INTRODUCTION

Lanthanides are the elements spanning atomic number 57 to 71. They all occur in nature, although promethium, the rarest, only occurs in trace quantities in natural materials, as it is not long-lived and has no stable isotopes. Rare earths are usually divided into lower atomic weight elements, lanthanum to europium, referred to as the light rare earth elements (LREE), and heavy rare earth elements (HREE) gadolinium to lutetium and yttrium. The division is sometimes arbitrary and the term middle REE (MREE) is sometimes used to refer to those elements between europium to dysprosium. Lanthanum, cerium, praseodymium and neodymium are the most abundant rare earths [1]. It is known that Pr can be consumed in

Nd-Fe-B magnet alloys and in other alloys such as magnesium and aluminum alloys, improving some mechanical properties and even increasing resistance to the corrosion. Pr is used as a bright yellow pigment in praseodymium-doped zirconia and is added as a green colorant for decorative glass ($ZrSiO_4$:Pr⁴⁺). Several studies have been conducted on its optical properties for use in amplification of telecommunication systems, including its use as a doping agent in fluoride fibers. It is also used in scintillator for medical CAT scans [1,2]. One of the methods for obtaining these REEs is the high-temperature chlorination process, which enables anhydrous rare earth chlorides or oxychlorides to be obtain directly. This method has been widely explored as a way of extracting no just REEs but also other metals from different ores [3]. Dry chlorination of several LREE oxides using $Cl_2(g)$ as chlorinating agent have been studied [4-9]. Praseodymium oxide behaves differently from these oxides in that it has two oxidation states (3+ and 4+), enabling praseodymium oxide with Pr^{3+} to be oxidized during the chlorination reaction. The Pr-O system shows a number of discrete phases, with all the REE oxides being the most complex system [10,11].

Few papers have been published on the chlorination of Pr oxides. Mendil et. al. [12] studied the reaction between Pr_6O_{11} and NH_4CI in the temperature range of 250-450 °C under Ar atmosphere, obtaining $PrCI_3$ as a product. They report the influence of various synthesis parameters (temperature, contact time and chemical composition) on the reaction yield. Holsa et. al. [13] analyzed the paramagnetic susceptibility of some rare earth oxychlorides. They synthesized oxychlorides through the reaction between the REE_2O_3 and NH_4CI at temperatures between 900 and 1050 °C under $N_2(g)$ atmosphere.

The present paper analyzes Pr_2O_3 and Pr_6O_{11} chlorination reactions by means of thermodynamic studies and characterized the products formed at different temperatures. A kinetic study was performed for the chlorination of Pr_6O_{11} . The results will contribute to the understanding of the chemistry of praseodymium oxides under different condition and the products obtained in the Pr-O-Cl system.

2. EXPERIMENTAL SECTION

2.1 Materials and sample preparation

The starting praseodymium oxide is composed of a mixture of Pr oxides, $Pr(OH)_3$ and $Pr_2O_2SO_4$ (oxysulphate content is lower than 1%). Three samples were prepared with this starting oxide to perform the different studies, as follows:

a) Chlorination of Pr_2O_3 : the starting oxide was treated in Ar-5 % H₂(g) atmosphere at 970 °C for 4 h to transform it into the form Pr_2O_3 . Powder X-ray diffraction (PXRD) showed the typical profile of Pr_2O_3 (>97%) and minor impurities of the phases Pr_7O_{12} (<1%) and praseodymium oxysulphite (<1%).

b) Chlorination of Pr_6O_{11} : the starting oxide was treated in $O_2(g)$ at 900 °C for 4 h to convert the $Pr(OH)_3$ and obtain the crystalline phase Pr_6O_{11} , which was confirmed by PXRD. The praseodymium oxysulphate is still present in the sample, but does not undergo any change during the chlorinations.

c) Characterization of Praseodymium Oxychloride: in order to obtain Pr_6O_{11} and eliminate the praseodymium oxysulphate in the initial samples, the starting praseodymium oxide was treated in a furnace in simulated air (20 % $O_2(g)$ and 80 % $N_2(g)$) at 1400 °C. The PXRD pattern of the product shows high crystallinity and high purity of Pr_6O_{11} without trace phases.

2.2 Equipment and procedure

A silica glass fixed-bed reactor was used in chlorination reactions. It consisted of a horizontally mounted tube 30 mm in diameter located inside an electric furnace where the sample was introduced using a silica glass crucible (area = 1 cm², height = 0.5 cm). The reactant gas was introduced when the system reached the working temperature. The experimental conditions in non-isothermal reactions were: $PCI_2(g) = 1$ atm; $CI_2(g)$ flow = 3 l h⁻¹; m₀ ≈ 5 mg; $\Delta T \Delta t^{-1} = 4 \ C min^{-1}$. To end each run, the reactant gas was cut off and a nitrogen stream was introduced to purge the reactor.

Samples were characterized by X-ray diffraction, Scanning Electron Microscopy (FEI Inspect S50). PXRD were collected using a D8 Advance diffractometer (Bruker AXS, Germany) with Bragg-Brentano θ/θ geometry and Cu K α radiation (40 kV, 30 mA). The diffraction angles

were measured from 10 to 100° of 2 θ in 0.02° steps with a counting time of 2.5 s per s tep. The X-ray diagrams were refined and the phases present were quantified by the Rietveld method using DIFFRACplus TOPAS 4.2 software [14]. The following parameters were refined: scale factor, background coefficients (Chebychev polynomial of 7 order), crystallite size, zero-shift and sample displacement, peak shape parameters (using Fundamental Parameters FP), atomic positions and unit-cell parameters.

The magnetic measurements were performed using a Quantum Design SQUID magnetometer model MPMS2 on powdered samples, between 2 and 200 K with an external magnetic field of 1000 Oe.

Surface compositions were analyzed by means of X-ray photoelectron spectroscopy (XPS) using a standard Al/Mg twin-anode X-ray gun and a hemispherical electrostatic electron energy analyzer. The measurements were carried out in high vacuum conditions (HV), with a base pressure of $\sim 10^{-9}$ Torr. For the analysis, the powdered samples were spread on adhesive graphitic carbon tape.

3. RESULTS AND DISCUSSION

3.1 Thermodynamic study

Figure 1 shows the Kellogg stability field diagrams of the system Pr-O-Cl at 300 and 500 °C. These diagrams were made with HSC 6.0 software [15]. The proposed condensed phases in the calculations were Pr, PrCl₃, PrOCl, Pr₂O₃, Pr₇O₁₂, Pr₆O₁₁ and PrO₂. It can be seen that all of the proposed species are thermodynamically feasible to be formed in the ranges selected of Cl₂(g) and O₂(g) pressures, except Pr₆O₁₁. The diagrams also show a feature of the Pr oxides: the most stable oxide is PrO₂ in the diagram at 300 °C under oxygen pressure of 1 bar, whereas Pr₇O₁₂ is the most stable oxide at 500 °C (not the most oxidized oxide).

The phase stability diagrams show that there is not thermodynamic equilibrium between praseodymium oxides and $PrCl_3$ phases except in the PrO_2 chlorination. Therefore, PrOCl has to be formed prior to the formation of $PrCl_3$. This behavior is typical in the chlorination of REE_2O_3 oxides [4-9, 16].

The following experimental conditions were used: $PCI_2 \sim 1$ atm and PO_2 : 10⁻⁴ atm (indicated with an asterisk in Figure 1). According to the stability diagrams, $PrCI_3$ is the most stable species under these conditions, being very close to the stability field of PrOCI.

Ellingham diagrams (Standard Gibbs free energy vs. temperature) were also prepared. The following chlorination reactions of the praseodymium oxides were considered for this analysis (the Δ Gs^o were fitted with linear functions between 250 and 700 °C):

$$Pr_2O_3 + Cl_2(g) = 2PrOCl + 1/2O_2(g) \qquad \Delta G^{\circ}(kJ/mol) = 0.577 T(^{\circ}C)-517.8$$
(1)

$2/7 \Pr_7 O_{12} + Cl_2(g) = 2 \Pr OCI + 5/7 O_2(g) \qquad \Delta G^{\circ}(kJ/moI) = 0.227 I (^{\circ}C) - 138.6$	$\Delta G^{0}(kJ/mol) = 0.227 T(^{\circ}C) - 138.6 $ (2)
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 $1/3Pr_6O_{11} + Cl_2(g) = 2PrOCl + 5/6O_2(g)$ $\Delta G^{\circ}(kJ/mol) = 0.187 T(^{\circ}C)-169.6$ (3)

 $2PrO_2 + Cl_2(g) = 2PrOCI + O_2(g)$ $\Delta G^{\circ}(kJ/mol) = 0.184 T(^{\circ}C)-117.7$ (4)

Praseodymium oxychloride can be chlorinated according to reaction 5:

$$PrOCI + CI_{2}(g) = PrCI_{3} + 1/2 O_{2}(g) \qquad \Delta G^{0}(kJ/mol) = -0.039 T(^{\circ}C) - 7.6$$
(5)

The Ellingham diagrams of the reactions 1 a 5 are shown in the Figure 2. It can be seen that all of the reactions with PrOCI formation are feasible thermodynamically in the temperature range of 250 to 600 °C. The Pr_2O_3 chlorination has the lowest ΔG° , and Pr_7O_{12} and PrO_2 chlorinations have $\Delta G^\circ > 0$ at temperatures higher than 600 °C. The PrO_2 chlorination reaction has $\Delta G^\circ = 0$ at 640 °C and $\Delta G^\circ = 19$ kJ molCl₂⁻¹ at 700 °C.

The PrOCI chlorination (reaction 5) has ΔG° close to zero in the temperature range analyzed (-21.7 and -35.9 kJ molCl₂⁻¹ at 250 and 700 °C, respectively).

Calculations were also made for the oxidation reactions of the following type:

$$PrO_x + (y-x)/2 O_2(g) = PrO_y \quad (y > x)$$
 (6)

All oxidation reactions of Pr oxides to produce a more oxidized Pr oxide have $\Delta G^{\circ} < 0$ except Pr₇O₁₂ oxidation with formation of Pr₆O₁₁ ($\Delta G^{\circ}(kJ/mol) = 0.02 \text{ T}(^{\circ}\text{C})+15.9$), whereas if the product is PrO₂, $\Delta G^{\circ} < 0$ at temperatures lower than 500 °C ($\Delta G^{\circ}(kJ/mol) = 0.022 \text{ T}(^{\circ}\text{C})-10.9$), being -5.5 and 4.4 kJ molCl₂⁻¹ at 250 and 700 °C, respectively. Pr₆O₁₁ oxidation with formation of PrO₂ has $\Delta G^{\circ} < 0$ in the temperature range analyzed ($\Delta G^{\circ}(kJ/mol) = 0.003 \text{ T}(^{\circ}\text{C})-26.7$).

3.2 Non-isothermal chlorinations

Figure 3 shows the percentage ratio between the mass change and initial sample mass as a function of temperature for Pr_2O_3 and Pr_6O_{11} chlorinations (and its error bar). Rietveld analyses were performed on the final products to quantify the crystalline phases, and were consistent with the mass changes measured. The chlorination of Pr_2O_3 begins at approximately 260 °C, whereas the chlorination of Pr_6O_{11} begins at 320 °C, showing a final mass increase of 14.3 % and 18.7 % in the Pr_6O_{11} and Pr_2O_3 chlorinations, respectively.

The Pr_2O_3 chlorination begins with formation of praseodymium oxychloride and Pr_6O_{11} , and the PrO_2 phase is observed in addition to these phases at 330 °C. When the temperature is higher than 340 °C, the only praseodymium oxide determinate by PXRD is PrO_2 . Finally, the only product of the chlorination is PrOCI. Therefore, the following reactions may occur during the non-isothermal chlorinations:

$$Pr_2O_3 + Cl_2(g) = 2PrOCl + 1/2O_2(g)$$
(1)

$$Pr_2O_3 + 1/3O_2(g) = 1/3Pr_6O_{11}$$
(7)

$$Pr_6O_{11} + 1/2CI_2(g) = 5PrO_2 + PrOCI$$
(8)

$$1/3Pr_6O_{11} + CI_2(g) = 2PrOCI + 5/6O_2(g)$$
(3)

$$2PrO_2 + Cl_2(g) = 2PrOCl + O_2(g)$$
 (4)

Initially, Pr₂O₃ is chlorinated, producing PrOCI and oxygen. Then, oxygen can form Pr₆O₁₁ by

reacting with Pr_2O_3 (this reaction has been verified experimentally at the same temperature range and reported in other works) [11]. Subsequently, Pr_6O_{11} can be chlorinated, producing PrOCI, PrO_2 and oxygen through reactions 8 and 3 (both reactions have $\Delta G^\circ < 0$ at reaction temperature). The last reaction of the overall process is the chlorination of the recently formed PrO_2 , shown by a change in the slope in the non-isothermal curve. The oxidation of Pr_6O_{11} to produce PrO_2 is not proposed because calcinations of Pr_6O_{11} were carried out and no change was observed. During the chlorination reactions, oxysulphite transforms into oxysulphate, a reaction which is negligible with respect to the other reactions involved. The reactions involved in the system $Pr_2O_3/Cl_2(g)$ can be expressed by the following general

equation:

$$(x+y+z)/2\Pr_2O_3 + x/2Cl_2(g) = x\Pr OCl + y\Pr O_2 + z/6\Pr_6O_{11} + (1/4x-1/4y-1/6z)O_2(g)$$
(9)

The global reaction in the full (complete) Pr_2O_3 chlorination has the stoichiometry of reaction (1), however the final % Δ M/mi observed (18.7 %) is higher than the expected value for this reaction (16.65 %).

 Pr_6O_{11} chlorination begins at about 320 °C with formation of the praseodymium oxychloride. Pr_6O_{11} is not observed in the initial phase at temperature higher than 375 °C, so equation 4 can be considered the only reaction to occur above this temperature. The reactions involved in Pr_6O_{11} chlorination could thus be 8, 3 and 4. The global reaction can be expressed as reaction 3, in which $\Delta M/m_i = 12.99$ %. However, a higher value (14.1 %) is observed. This behavior is analogous to that observed in the Pr_2O_3 chlorination which will be explained later. The reactions involved in the system $Pr_6O_{11}/Cl_2(g)$ can be expressed by the following general equation:

$$(x+y)/6Pr_6O_{11} + x/2Cl_2(g) = xPrOCl + yPrO_2 + (5/12x-1/12y)O_2(g)$$
 (10)

3.3 Kinetics of Pr₆O₁₁ chlorination

The experimental conditions under which mass-transfer resistance is absent were evaluated by performing chlorinations at 425 $\$ and 1 atm of Cl₂(g) for 400 s. No difference in the % Δ M/mi of reaction was observed for gaseous flow rates from 2 to 8 l h⁻¹ and 12 mg of sample mass (Figure 4). This suggests that the reaction does not occur under conditions of gas reactant starvation. When the sample mass is 5 to 15 mg, there is no effect on the rate of reaction obtained (inset in Figure 4). Consequently, it can be concluded that temperatures below 425 $\$, gas flow rate of 2 l h⁻¹ (or higher) and sample mass of 12 mg (or lower) is enough to eliminate mass-transfer resistance.

A chlorine diffusion rate through crucible top of 10^{-2} mol Cl₂ s⁻¹ for PCl₂ = 1 atm, Cl₂(g) flow = 6 l h⁻¹, m_o = 12 mg was calculated at 425 °C according to the R anz & Marshall correlation [17,18], using the procedure described in the paper "Kinetic Study of Europium Oxide Chlorination" [8]. The experimental rate at 425 °C calculated using the mass change and Rietveld data was 4.0 x 10^{-5} mol Cl₂ s⁻¹. Thus, the value of the experimental rate is two or more orders of magnitude smaller than the calculated rate and it can be assumed that at 425 °C the convective mass transfer through the boundary layer does not affect the kinetic regime.

3.3.1 Effect of Temperature. Activation Energy calculation

Figure 5 outlines the effect of reaction time on Pr_6O_{11} conversion degree (α) for chlorination at 425 °C and the Rietveld results in the products obtained. Alpha was determined from the weight change after long chlorination times when no further increase in sample weight was detected, $\alpha = \frac{m(t)-m(t=0)}{m(t\to\infty)-m(t=0)}$. With increasing reaction time, the PXRD analyses indicate that the beginning of the reaction promoted the chlorination of Pr_6O_{11} with formation of PrO_2 and PrOCI. For times longer than 500 seconds, the chlorination of intermediate PrO_2 to form PrOCI is observed according to reaction 4. Based on this observation, the overall chlorination Pr_6O_{11} is further divided into two parts. In other LREE oxides chlorinations, the isothermal curves exhibit a sigmoidal (S-shaped) response upon increase in time, indicating that the

reaction proceeds according to a nucleation and growth model (JMA model) [4,9]. However, this shape is not observed in the Pr_6O_{11} chlorination due to the presence of different reactions in the overall reaction.

The effect of temperature in the kinetic parameters of Pr_6O_{11} chlorination was determinate through experiments performed at different temperatures between 300 and 425 °C, with 1 atm of $Cl_2(g)$, 12 mg samples and a flow rate of 6 l h⁻¹. Activation energy (Ea) can be calculated by applying a "model-free" method [19-20] from the slope of the plot In Time_i vs T⁻¹, where Time_i is the time necessary to reach a given degree of conversion value. Apparent activation energies of 105 ± 3 kJ mol⁻¹ and 123 ± 2 kJ mol⁻¹ were determined for α 0.42 and 0.90, respectively. The graphical representations of these results are shown in the Figure 6. The nonconstant value of Ea with α suggests that the rate controlling step changes during the total reaction. This can be understood by considering the formation of PrO₂ and its subsequent chlorination such as was explained in the non-isothermal reaction. Reactions 8 and 4 can occur at the beginning of the reaction, whereas the main reaction is 4 to higher conversion degrees, so the mechanism changes with the conversion degree. Consequently, the apparent activation energy also changes.

3.4 Characterization of Praseodymium oxychloride

Chlorination reactions using high purity Pr_6O_{11} as reactant were done between 425 °C and 800 °C with 6 I h⁻¹ and $PCl_2 = 1$ atm, during 2 (425 °C) and 1 h. The products o btained in these reactions are named PrOCI-T, where T is the reaction temperature. The first difference observed was color, PrOCI-425 is *light grayish orange* and the oxychlorides turn *light green* when the temperature increases. The colors of some praseodymium compounds have been reported. Many Pr^{3+} compounds such as $Pr(NO_3)_3$, $PrBr_3$, PrF_3 and $PrCl_3$ are green, the same color observed in PrOCI-800, whereas if traces of Pr^{4+} are presents in solids, the color will be darker [21,22].

The percentage ratio between the mass change and initial sample mass was determined in the reactions by using a more sensible balance (Sartorius Cubis Ultra Micro Balance). The

%ΔM/mi = 13.000 ± 0.002 was calculated for the reaction at 800 ℃, which agrees with the change expected in reaction 3. However, %ΔM/mi = 14.004 ± 0.002 was observed in the reaction at 425 ℃, which suggests that the product obtained is not PrOCI. Percentage mass changes between these values were calculated for reactions at 500, 600 and 700 ℃ (13.95, 13.64 and 13.09, respectively). Moreover, PrOCI-425 was heated at 800 ℃ in N₂(g) atmosphere. This sample suffered a loss of mass, achieving %ΔM/mi ≈ 13 (referred to the initial mass of the starting Pr_6O_{11}) and the color of the final product is light green. This observation agrees with the formation of PrOCI after this treatment (PXRD is similar to PrOCI-800).

Calcinations reactions of praseodymium oxychlorides were performed at 950 $^{\circ}$ in air for 4 h. Pr_6O_{11} was formed in both PrOCI-425 and PrOCI-800 calcinations (confirmed by PXRD). This result disagrees with Yang et. al. [23], who proposed the conversion of PrOCI into PrO_2 under various oxygen partial pressures at temperatures higher than 827 $^{\circ}$ C.

The PXRD patterns for praseodymium oxychlorides are shown in Figure 7. As it can be seen in these patterns, there are notable changes in the peak's shape in the samples. The material presents a more amorphous state (with wide peaks) in the reaction at 425 ℃ and starts crystallizing at higher temperatures observing the intensities increases. It can be considered that the PrOCI has high crystallinity when was prepared at 800 ℃, while the oxychloride prepared at 425 ℃ has wide peaks and t herefore smaller crystallite sizes. The structures were refined with tetragonal symmetry and P4/nmm (#129) space group. The crystallites sizes (between 21.8 and 423.9 nm) calculated by Rietveld method increase when the reaction temperature increases (between 425 and 800 ℃).

Figure 8 shows SEM images of the Pr_6O_{11} and the product after full chlorinations at 425 °C and 800 °C. Figure 8 a) shows that the starting reactant, which is formed for particles with average sizes of 10 µm, these particles are formed for agglomerates of smaller particles with non-uniform plate shape of around 2 µm. Figure 8 b) and c) shows that the praseodymium oxychlorides are formed by particles with microstructures more heterogeneous than microstructures of Pr_6O_{11} . No significant morphological difference between the oxychlorides

is observed. EDS analysis performed of the oxychlorides (prepared between 425 $^{\circ}$ C and 800 $^{\circ}$ C) indicated that they present 1:1 Pr:Cl molar relation.

The magnetic susceptibility of praseodymium oxychlorides was measured for PrOCI-425 and PrOCI-800. The experimental data were fitted with a function described by Curie-Weiss law: $\chi = C/(T-\theta)$, where χ is the magnetic susceptibility, C is the Curie constant, T is the absolute temperature, and θ is the Curie temperature measured in Kelvin. Figure 9 shows the measured data and fits of the χ^{-1} vs. T curves with Curie-Weiss law between 50 and 200 K. The parameters obtained in the oxychlorides were: $\theta = -20.2 \pm 0.1$ K, C = 1.4641 ± 10⁻⁴ emu K mol⁻¹, and estimated effective magnetic moment $\mu_{eff} = 3.42 \ \mu$ B for the PrOCI-425 and $\theta = -24.2 \pm 0.1$ K, C = 1.5719 ± 10⁻⁴ emu K mol⁻¹, and estimated effective magnetic moment $\mu_{eff} = 3.42 \ \mu$ B for the PrOCI-425 and $\theta = -24.2 \pm 0.1$ K, C = 1.5719 ± 10⁻⁴ emu K mol⁻¹, and estimated effective magnetic moment $\mu_{eff} = 3.55 \ \mu$ B for the PrOCI-800. The theoretical values of magnetic moment for Pr³⁺ in Pr₂O₃ and Pr⁴⁺ in PrO₂ are 3.59 and 2.51 \ \muB, respectively [25,26]. The difference between the theoretical magnetic moment of Pr³⁺ and the estimated magnetic moment in the PrOCI-425 agrees with the presence of Pr³⁺ and Pr⁴⁺. However, no significant difference is observed between the Pr³⁺ theoretical value and the experimental value obtained for PrOCI-800.

Figure 10 shows the XPS spectrum of samples of PrOCI-425 and PrOCI-800. Peaks of Pr3d, O1s, Pr4s, C1s, Cl2s, Pr4p, Cl2p, Pr4d, Pr5s and Pr5p can be distinguished in both spectra. Charging effects are observed in the peaks of C1s and O1s (especially in PrOCI-800); however, the peaks of Pr3d have the proper form of the oxide type Pr^{3+} and Pr^{4+} . The spectra in detail of the Pr3d peaks are shown in Figure 11 a). The references of Pr^{3+} corresponding to the compound Pr_2O_3 in BE = 932.9 eV and of Pr^{4+} corresponding to the compound PrO_2 in BE = 935 eV are represented with vertical lines [27,28]. The main peak of PrOCI-425 is compatible with the presence of Pr^{3+} . Spin orbit splitting is 20.5 eV for the oxide with Pr^{3+} and 17.8 eV for the oxide with Pr^{4+} . The shapes of the two spectra are compared in Figure 11 b), for which the PrOCI-800 spectrum is corrected horizontally in 1.4 eV to the right. The shapes of the peaks are very similar in both spectra. When the spectra are superimposed, they have the same spin-orbit-splitting of 20.5 eV, compatible with the presence of Pr^{3+} and a small shift is observed to lower energies in PrOCI-425 which could correspond to the presence of Pr^{4+} .

The energy scale was calibrated taking references from the Fermi level.

According to the results and considering a formula of type $PrO_{1+x}CI$ for the PrOCI-425, the mass balance in the chlorination reaction agrees with a value of x = 0.108, whereas PrOCI formation was observed in the chlorination at 800 °C. The molecular formula $PrO_{1.108}CI$ agrees with the results obtained in magnetic susceptibility measurement. For the chlorinations between 425 °C and 800 °C, oxychlorid es of type $PrO_{1+x}CI$ are formed according to the mass balance, with values of 0<x<0.108. When the $PrO_{1+x}CI$ is treated at 800 °C in N₂(g) atmosphere, PrOCI is obtained according to reaction 11:

(11)

 $PrO_{1+x}Cl = PrOCl + x/2O_2(g)$

3.5 Comparison between RE₂O₃ chlorinations with Cl₂(g)

Dry chlorinations of LREE oxides using $Cl_2(g)$ as chlorinating agent were studied using similar methodology. In the present work, it was observed that the chlorination of praseodymium oxide has different behaviors due to the fact that it has two oxidation numbers, 3+ and 4+, so of all the REE oxides, this system is the most complex. The starting temperatures of LREE₂O₃ chlorinations are between 250 and 260 °C [4, 6-8], except Ce₂O₃ chlorination, which was not studied. This temperature change for REE≥Gd, where it was determined that the reaction between Gd₂O₃ and Cl₂(g) begins at 327 °C [9]. This observation agrees with the consideration that the gadolinium presents different characteristics from LREEs. It was also shown that LRE₂O₃ chlorinations, PrO₂ is observed as intermediate in the reaction and the oxychloride formed presents a general formula of PrO_{1+x}Cl with presence of Pr³⁺ and Pr⁴⁺. Similar behavior was observed in EuOCl, where the presence of Eu²⁺ impurity was determined [29].

4. CONCLUSION

The chlorination reactions between praseodymium oxides (Pr₆O₁₁ and Pr₂O₃) with Cl₂(g) as

chlorinating agent were studied. Thermodynamic analysis of praseodymium oxide chlorination was conducted and the results showed that the formation of PrOCI is feasible and that Pr oxides can undergo oxidation during the process.

The non-isothermal reactions were analyzed by mass change and Rietveld analysis of PXRD data. Pr_2O_3 chlorination begins at 260 °C and Pr_6O_{11} chlorination begins at 320 °C. In both reactions, it was observed that PrO_2 was formed as the intermediate product and praseodymium oxychloride as the final product. This behavior is also observed in the kinetic analysis carried out in the Pr_6O_{11} chlorination, where it was determined that the apparent activation energy changes during the reaction. It was established that the praseodymium oxychloride formed by full chlorination of Pr_6O_{11} at 425 °C has the general formula $PrO_{1+x}CI$ with presence of Pr^{3+} and Pr^{4+} , where x = 0.108 considering the mass balance in the chlorination reaction, Whereas the formation of PrOCI is observed in the full chlorination at 800 °C. Oxychlorides with values of 0 < x < 0.108 are formed at temperatures between 425 and 800 °C.

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FIGURE CAPTIONS

Figure 1. Phase stability diagrams of Pr-O-Cl system at 300 and 500 °C. Experimental conditions are indicated in the graphics.

Figure 2. Standard Gibbs free energy (per mole of chlorine) vs. temperature for reactions involved in the PrO_x - $Cl_2(g)$ system.

Figure 3. Non-isothermal curves of Pr_2O_3 and Pr_6O_{11} chlorinations.

Figure 4. Effect of the flow rate of $Cl_2(g)$ and (inset) effect of the initial mass on the chlorination of Pr_6O_{11} .

Figure 5. Isothermal chlorination of Pr_6O_{11} at 425 °C.

Figure 6. Fits of the In Time_i vs T⁻¹ at α = 0.42 and 0.90 to calculate the apparent activation energies.

Figure 7. PXRD of praseodymium oxychlorides formed by full chlorination at temperatures between 425 and 800 ℃.

Figure 8. SEM images of: a) Pr_6O_{11} , b) PrOCI-425 and c) PrOCI-800.

Figure 9. Fits of the χ^{-1} vs. T curves with Curie-Weiss law of PrOCI-425 and PrOCI-800. Scatter graphs: experimental curves; line graphs: calculated curves.

Figure 10. Spectra of PrOCI-425 and PrOCI-800. The AI-K α line was used as source of excitation. The dotted line boxes indicate the peaks that were subsequently measured in detail.

Figure 11. Experimental spectra of the Pr3d level (a) and modifying the horizontal scale of PrOCI-800 in 1.4 eV (b).

Table 1. Unit-cell parameters, crystallite size, and discrepancy factors obtained by theRietveld refinement from PXRD data of PrOCI-425 and PrOCI-800.

	Space group	Crystallite Size(nm)	Colour	a(Å)	b(Å)	GOF	Rwp(%)	Rp(%)	RBragg(%)
PrOCI-425	P4/nmm	20.8		4.0510	6.8077	2.1	6.2	4.9	2.1
PrOCI-800	P4/nmm	418.5		4.0514	6.8001	1.8	5.4	4.1	2.6





























Highlights

- The chlorinations of Pr_2O_3 and Pr_6O_{11} start at 260 °C and 320 °C, respectively.
- Kinetic analysis in the reaction between Pr₆O₁₁ and Cl₂(g).
- Existence of Pr^{3+}/Pr^{4+} in the praseodymium oxychloride synthesized at 425 °C.
- Praseodymium oxychloride was characterized by XRD, SEM, XPS and magnetic measurement.

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