CHARACTERISATION OF PRASEODYMIUM OXIDES USED IN CERAMIC PIGMENT SYNTHESIS

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1. INTRODUCTION

Praseodymium is a lanthanide that, thanks to its numerous oxidation states, can form different oxides, such as PrO_2, Pr_2O_3, Pr_6O_{11}, Pr_7O_{12}, and Pr_9O_{16}. This property makes praseodymium oxide an interesting and versatile material for industries such as ceramics or optics [1].

Praseodymium oxide is used, particularly, as a raw material in yellow ceramic praseodymium pigment synthesis, it therefore being important to know the exact praseodymium concentration in these materials [2].

Although studies are available on praseodymium oxide behaviour, the information found in the literature is sometimes contradictory. Different experimental conditions have led to opposite results owing to praseodymium oxide's rapid transformations. Many authors have pointed out the high mobility of the oxygen atoms, which gives rise to phase transformations during the heating and cooling processes.

A study was therefore undertaken to perform a complete characterisation of the different oxide species by X-ray fluorescence spectrometry (WD-XRF), X-ray diffraction (XRD), differential thermal and thermogravimetric analysis (DTA-TG), and determination of the oxygen content by an elemental analyser.

2. EXPERIMENTAL

A method was established, first, to fully characterise a praseodymium oxide, including the minor elements and traces present, praseodymium content being determined by WD-XRF, phase identification by XRD, weight losses and gains by DTA-TG, and oxygen content by an elemental analyser. In addition, praseodymium oxide behaviour relative to temperature was studied under different cooling conditions.

Various praseodymium oxides, involving three materials used in yellow ceramic praseodymium pigment synthesis and one reference material, were analysed.

3. RESULTS AND CONCLUSIONS

The results obtained are set out in Table 1. Different praseodymium oxidation states and, therefore, different praseodymium concentrations were observed, entailing different concentrations of the chromophore element.

As may be observed, the experimental oxygen values matched the theoretical values calculated from the crystalline phase concentrations obtained from the Rietveld refinement, validating the developed methodology.

	PR (%)	Cryst. phases (Rietveld)(%)	O_{calc}(%)	O_{exp}(%)
Sample A	79.9	$Pr(OH)_3$ – 20.3	19.8	20.0 ± 0.4
		PrO_2 – 79.7		
Sample B	82.5	$Pr(OH)_3$ – 17.9	17.2	17.2 ± 0.4
		PrO_2 – 20.0		
		Pr_2O_3 – 62.0		
Sample C	80	$Pr(OH)_3$ – 19.5	19.7	19.9 ± 0.4
		PrO_2 – 75.5		
		Pr_6O_{11} – 5.0		
Pr_6O_{11} Strem Chemicals	81.5	PrO_2 – 100.0	18.5	18.6 ± 0.4

Table 1. *Characterisation of the studied praseodymium oxides*

In addition, praseodymium oxide behaviour was studied when these oxides were subjected to different thermal treatments, as the DTA-TGs performed exhibited up to 5 phase transformations, as shown by way of example in sample C in Figure 1.

Thermal treatments were performed at the temperatures at which variations in weight were observed, cooling by two different processes (slow cooling and quenching) to determine the different oxide species that formed. The results obtained in the treatment at 980ºC are shown in Figure 2, which indicate that, on slow cooling, the most stable praseodymium oxide phase at room temperature was the binary oxide Pr_6O_{11}.

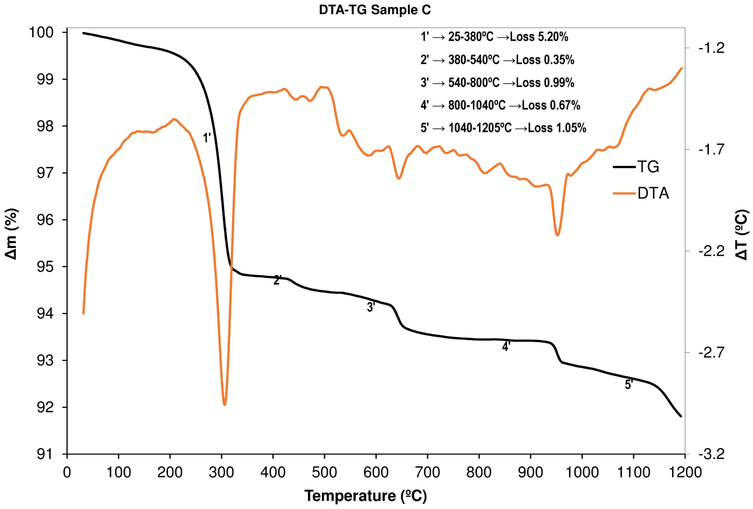

Figure 1. *DTA-TG of sample C*

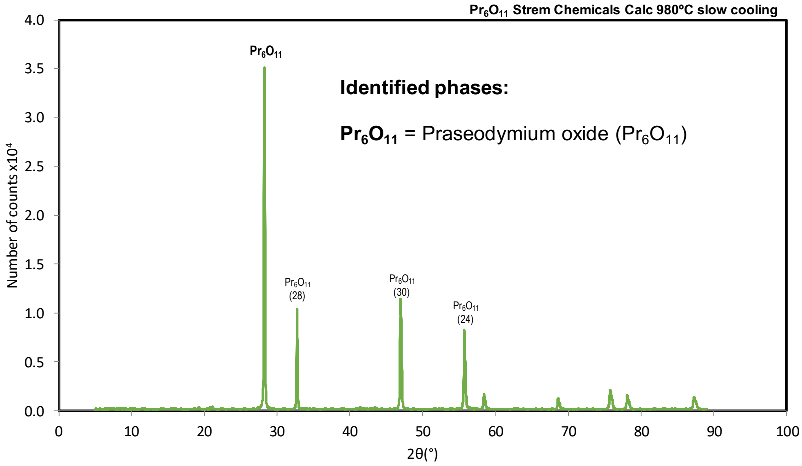

Figure 2. *Diffractogram of reference material Pr_6O_{11} Strem Chemicals at 980 ºC, on slow cooling*

Temp (ºC)	O_{exp}(%)	O_{calc}(%)	Crystalline phases
500	17.7 ± 0.5	17.8	PrO_2, Pr_6O_{11}
650	16.9 ± 0.5	16.8	Pr_9O_{16}
760	16.5 ± 0.5	16.3	Pr_7O_{12}
980	16.6 ± 0.5	16.3	Pr_7O_{12}
1040	16.5 ± 0.5	16.3	Pr_7O_{12}

Table 2. *Determination of oxygen concentration in the material treated at different temperatures*

On the other hand, the phases observed in the different fractions cooled by quenching were PrO_2 and Pr_6O_{11} at 500ºC, Pr_9O_{16} at 650ºC, and Pr_7O_{12} at 760, 980, and 1040ºC, coinciding with the phases mentioned in the literature surveyed, which was corroborated by determination of the oxygen content. The results obtained are detailed in Table 2.

In short, a method was developed to fully characterise a praseodymium oxide. In addition, praseodymium oxide transformations at different temperatures were studied. It was concluded that, as praseodymium can exhibit different oxidation states, this needs to be taken into account in the complete characterisation of praseodymium oxide by complementary analysis of the oxygen content.

4. AKNOWLEGEMENTS

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5. REFERENCES

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