Structural and morphological characterization of rare earth modified lead titanate

(Caracterização estrutural e morfológica de titanatos de chumbo modificados por terras raras)

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Abstract

Rare earth modified lead titanate powders $Pb_{1-x}RE_xTiO_3$ (REPT), x = 0.01, 0.05, 0.07 and RE = Yb, Y, were prepared by the Pechini method. The materials were calcined under flowing oxygen at different temperatures from 300 to 700 ºC. Nanostructured REPT were investigated using X-ray diffraction, scanning electron microscopy and surface area analysis (BET). The results suggest that the modifier cation incorporated into the system has notable influence in the microstructure and a notable decrease in the crystallite sizes.
Keywords: $PbTiO_3$, rare earth, perovskite, Pechini method.

Resumo

Pós de titanatos de chumbo modificados por terras raras, $Pb_{1-x}RE_xTiO_3$ (REPT), x = 0,01, 0,05, 0.07 e RE = Yb, Y, foram preparados pelo método Pechini. Os materiais foram calcinados sob fluxo de oxigênio a diferentes temperatures de 300 a 700 ºC. Os REPT nanoestruturados obtidos foram investigados utilizando as técnicas de difração de raios X (DRX), microscopia eletrônica de varredura (MEV) e análise de area superficial (BET). Os resultados sugerem que o cátion dopante incorporado ao sistema tem notável influência na microestrutura e na diminuição dos tamanhos dos cristalitos
Palavras-chave: *$PbTiO_3$, terra rara, perovsquita, método Pechini.*

INTRODUCTION

Amongst the many ferroelectric oxides lead titanate (PT) is an important member of the family of perovskite-structured materials that exhibits useful dielectric, piezoelectric and electromechanical properties. The properties such as ferroelectric and piezoelectric can be improved by use of additives, especially the trivalent rare earth ions [1-3]. The incorporation of rare earth into PT ceramics is reported to decrease the Curie temperature [4, 5], affect the density and the band gap energy [6]. It is a high potential material for applications in photonic devices [7-9]. On the other hand, the substitution of these aliovalent ions results in the reduction of lattice anisotropy leading to hard and dense ceramics with high mechanical strength [10-12], influence the grain boundary mobility [13], stabilize particle growth at high temperatures [14, 15], promote a decrease in the average grain size [16]. It can then be used to control particle size.

In this work, a series of REPT (with 1, 5 and 7 at.% substitution of lead atoms and RE = Yb, Y) powder samples was prepared by the Pechini method [17]. We have studied the characterization of pure and Yb-doped PT (5 at.%) [18] and the results revealed that the obtained materials are formed by nanometric particles and the effect of Yb-doping concentration was also investigated; in particular, it was shown that the perovskite single phase formation was observed at 400 and 700 ºC for pure PT and Yb-doped PT, respectively. The aim of the present work is study the morphological properties of the obtained REPT powders at the above mentioned concentrations.

EXPERIMENTAL

The powder samples obtained by Pechini method, detailed elsewhere [8, 9, 18], was evaluated by X-ray diffraction using Cuk_α radiation in a Shimadzu 600 apparatus

with 2θ ranging between 5 and 75º. Grain size study was carried out by SEM and micrographs were recorded in a Zeiss DSM940A microscope. For the adsorption/desorption analysis the surface area was determined by means of the BET multi-point method in an ASAP 2000 equipment.

RESULTS AND DISCUSSION

The XRD patterns of ytterbium and yttrium REPT powders heat treated in air at various temperatures for 2 h are depicted in Figs. 1 and 2, respectively. The XRD results clearly display

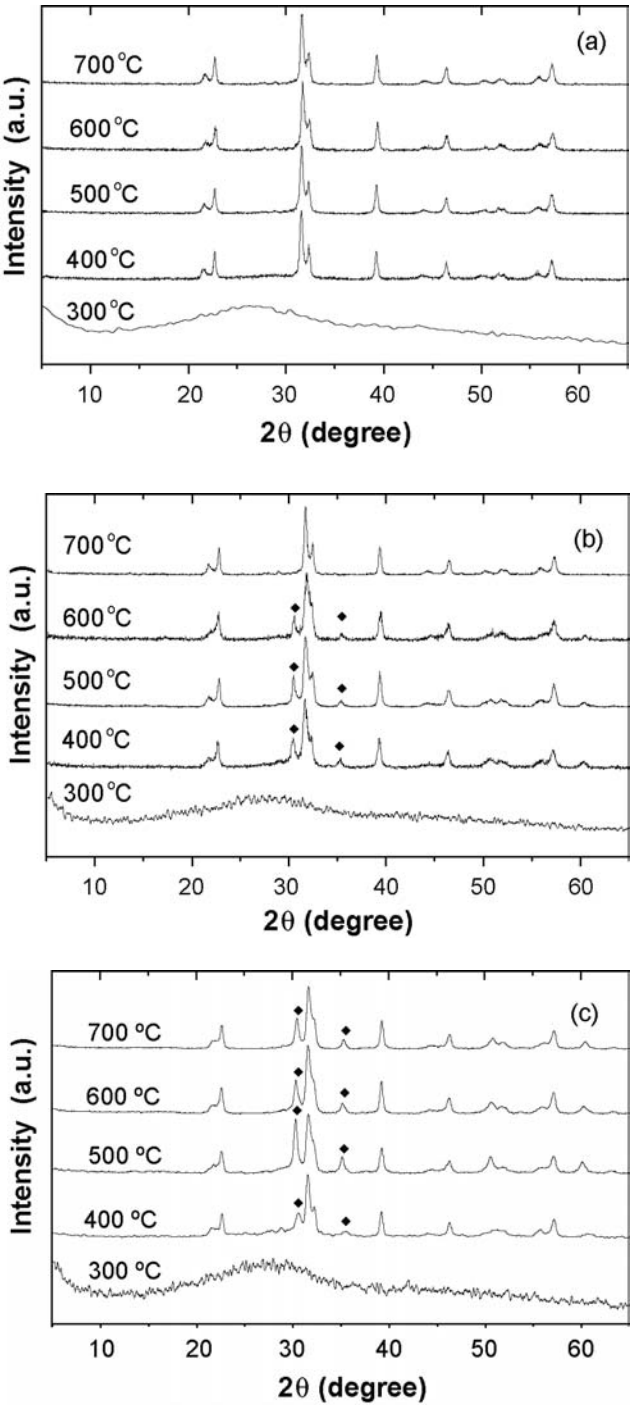

Figure 1: XRD patterns of Yb–REPT treated in air at various temperatures for 2 h : (a) 1%, (b) 5% and (c) 7%.
[Figura 1: Padrão de DRX dos Yb-REPT tratados em ar a várias temperatures por 2h: (a) 1%, (b) 5% e (c) 7%.]

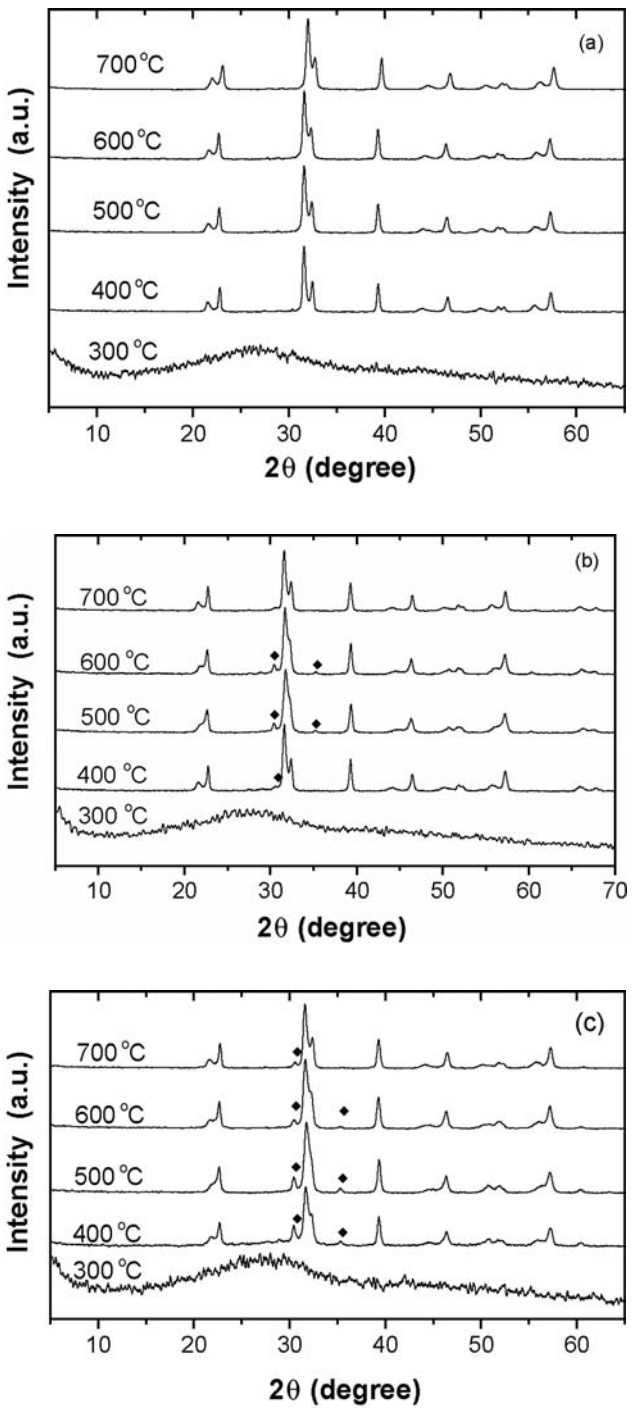

Figure 2: XRD patterns of Y–REPT treated in air at various temperatures for 2 h : (a) 1%, (b) 5% and (c) 7%.
[Figura 2: Padrão de DRX dos Y-REPT tratados em ar a várias temperaturas por 2h: (a) 1%, (b) 5% e (c) 7%.]

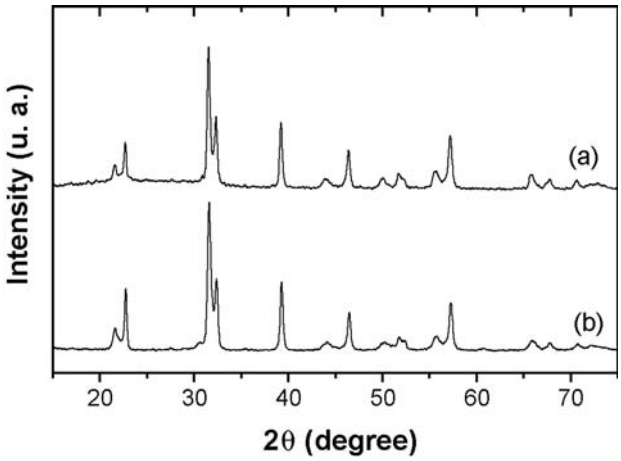

Figure 3: XRD patterns of 7 at.% doped REPT treated in air at 800 ºC for 2 h : (a) Yb-REPT and (b) Y- REPT.
[Figura 3: Padrão de DRX dos REPT dopados a 7 % tratados em ar a 800 ºC por 2h: (a) Yb-REPT e (b) Y- REPT.]

that all materials annealed at 300 ºC are amorphous and at 400 ºC the perovskite phase is obtained for the 1 at.% RE doped materials, while a mixture of phases for 5 and 7 at.% was observed in the same temperature. For the 5 at.% Yb and Y REPT doped, two peaks around 30.5 º and 35.2 º which were ascribed to TiO_2 (JCPDS-ICDD card number 35-0088) and TiO (JCPDS-ICDD card number 12-0754), respectively. Increasing the calcination temperature up to 700 ºC resulted in a further development of the tetragonal phase and most of the intermediate phases were eliminated. The same behavior with increasing temperature were observed to related peaks in 7 at.% Yb and Y REPT, however the tetragonal phase is obtained only at 800 ºC (Fig. 3).

Figs. 4 and 5 show the surface morphology of Yb (Fig. 4) and Y-REPT (Fig. 5) at 700 ºC by SEM. These micrographs reveal a porous structure with maxim grain sizes around 80 nm for Yb-REPT and 200 nm for Y-REPT. Also, an increase in agglomeration of grains, which increase with increase RE content, has been observed. For the 5 and 7 at.% doped REPT, in addition to porosity, the presence of small crystallites, agglomerates and the densification of grains, attributed to the effect of replacing lead atoms by Yb and Y atoms, were noticed (for a clear view, see micrographs in Figs. 4 and 5b-c) as well as a sort of heterogeneous morphology, which supports the existence of mixed of phases as also envisaged by XRD analysis.

The characterization of particle morphology normally involves the measurement of specific surface area, pore and particle size distribution by using the technique of isothermal gas adsorption and desorption. The use of this technique provides the analysis of pore morphology, from sub-nanometric dimensions (< 0.5 nm) up to approximately 180 nm, being especially indicated for the study of catalysts and ceramic materials prepared from ultrafine powders [19]. Several theoretical treatments exist for the calculation of the superficial area through gaseous adsorption. In this present

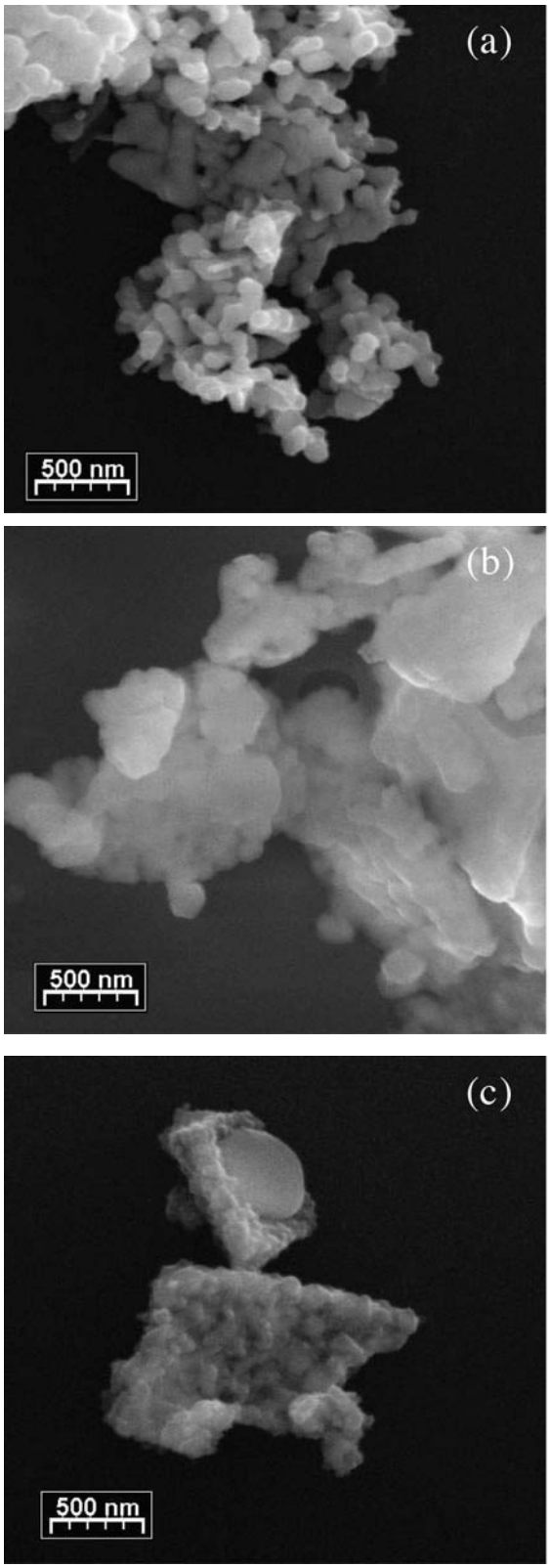

Figure 4: Scanning electron micrographs of powders Yb-REPT calcinated under flowing oxygen at 700 ºC for two hours: (a) 1%, (b) 5% and (c) 7%.
[Figura 4: Micrografias de varredura eletrônica dos pós de Yb-REPT calcinados sob fluxo de oxigênio a 700 ºC por duas horas: (a) 1%, (b) 5% e (c) 7%.]

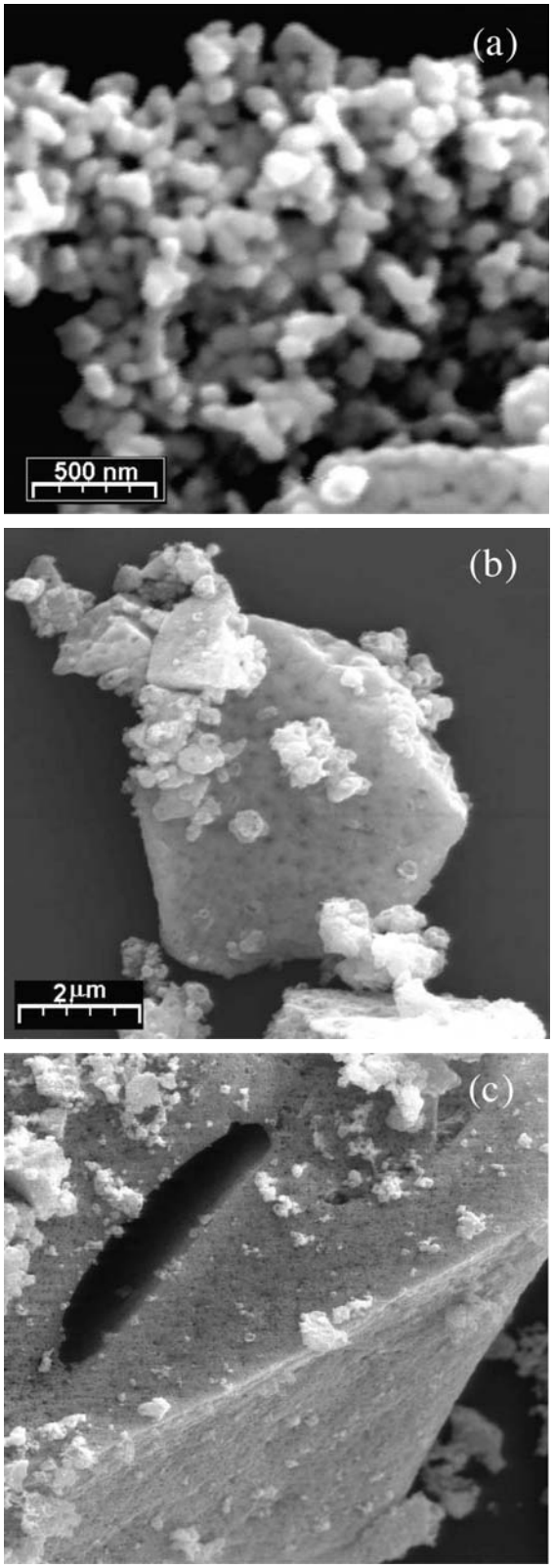

Figure 5: Scanning electron micrographs of Y-REPT powders calcinated under flowing oxygen at 700 ºC for two hours: (a) 1%, (b) 5% and (c) 7%.
[Figura 5: Micrografias de varredura eletrônica dos pós de Y-REPT calcinados sob fluxo de oxigênio a 700 ºC por duas horas: (a) 1%, (b) 5% e (c) 7%.]

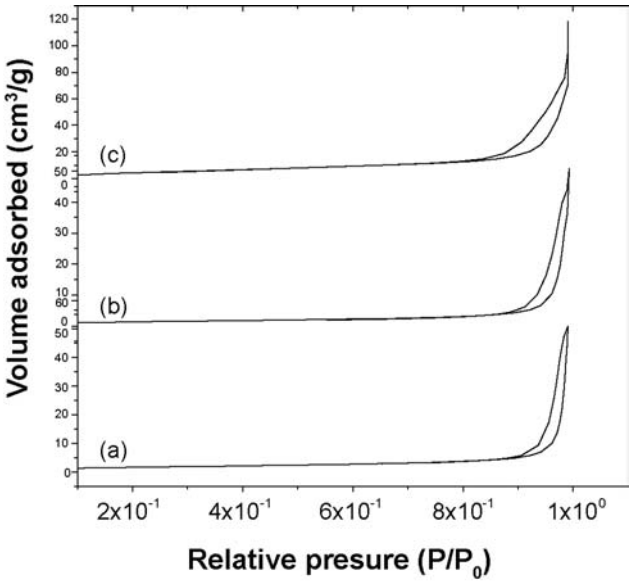

Figure 6: Nitrogen adsorption/desorption isotherms for Yb-REPT powders: (a) 1%, (b) 5% and (c) 7%.
[Figura 6: Isotermas de absorção/desorção de nitrogênio para os pós de Yb-REPT: (a) 1%, (b) 5% e (c) 7%.]

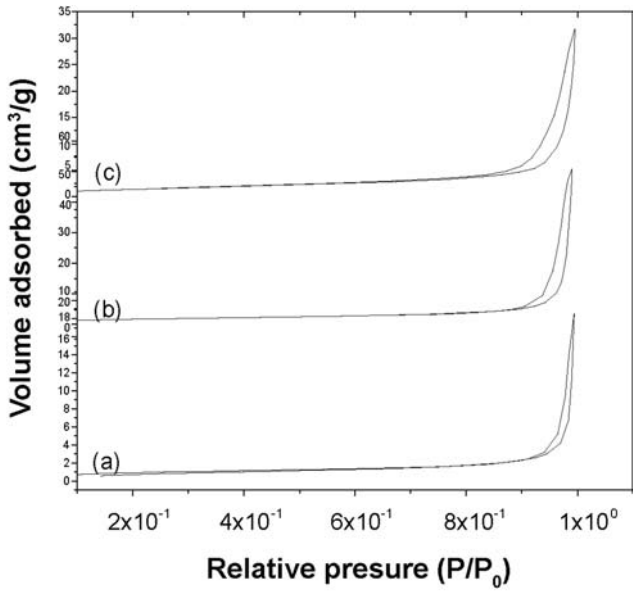

Figure 7: Nitrogen adsorption/desorption isotherms for Y-REPT powders: (a) 1%, (b) 5% and (c) 7%.
[Figura 7: Isotermas de absorção/desorção de nitrogênio para os pós de Y-REPT: (a) 1%, (b) 5% e (c) 7%.]

work we used the Brunauer-Emmett-Teller (BET) treatment. The ultrafine REPT powders submitted to the BET analysis are shown in Figs. 6 (Yb-REPT) and 7 (Y-REPT). The analysis of the plots in the Figs. 6 and 7 shows a type II isotherm [20] indicating the presence of mesopores (pores with a diameter of 2-100 nm) and an H-1 hysteresis [21]. The H-1 hysteresis suggests the presence of agglomerates with cylindrical pores for the powders. Table I shows results of surface areas (S_{BET}), particle size obtained by surface area (D_{BET}).

Table I - Morphologic characteristics of the REPT particles obtained at 700 º for 2 h.
[Tabela I - Características morfológicas das partículas de REPT a 700 º por 2 h.]

	REPT	S_{BET} (m^2/g)	D_{BET} (nm)
Yb	1%	14.94	50.4
	5%	18.84	40.0
	7%	21.17	35.6
Y	1%	3.71	202.8
	5%	5.30	123.9
	7%	6.85	109.9

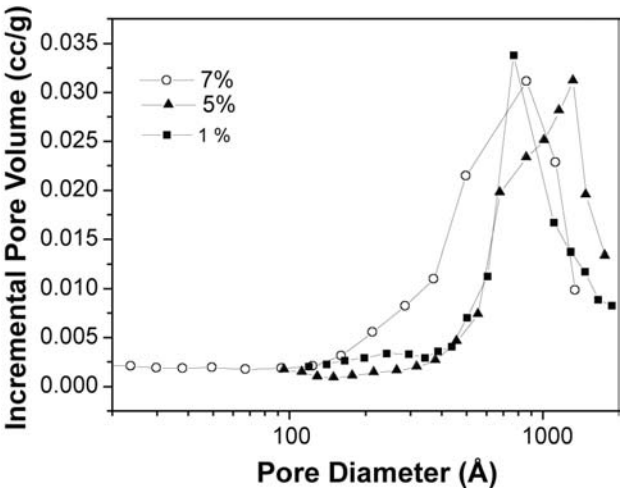

Figure 8: Pore size distribution of Yb-REPT at 700 ºC for two hours with different TR concentration.
[Figura 8: Distribuição de tamanhos de poros do Yb-REPT a 700 ºC por duas horas com concentrações diferentes de TR.]

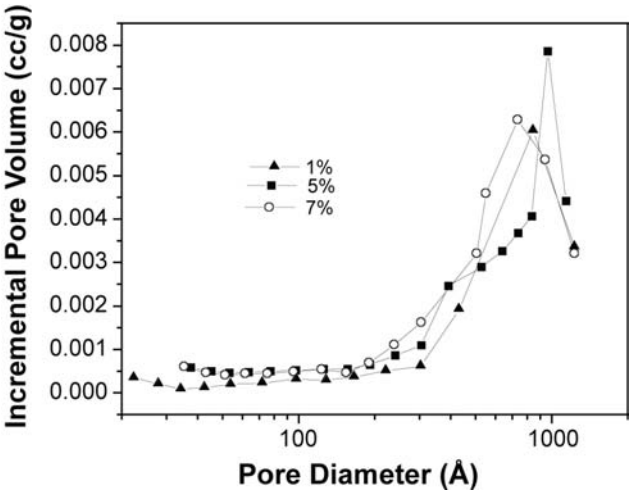

Figure 9: Pore size distribution of Y-REPT at 700 ºC for two hours with different TR concentration.
[Figura 9: Distribuição de tamanhos de poros do Y-REPT a 700 ºC por duas horas com concentrações diferentes de TR.]

Pore size distribution curves, obtained by Barret-Joyner-Halenda (BJH) [22] method, by considering desorption curves are shown in Figs. 8 (Yb-REPT) and 9 (Y-REPT). We can notice that the TR concentration influences the pore size distribution and the adsorption/desorption isotherm plots.

The effect in the reduction of the REPT crystallite sizes is attributed to the dopant incorporated within the system, which is affected by grain growth caused by heat treatments. In other words, the grain growth of doped materials caused by heat treatments could be prevented by using a metastable solid solution [15]. On the other hand, the densification observed with the increase of RE content may be attributed to replacing of lead ions by trivalents Yb and Y cations leading to the formation of oxygen vacancies, which is believed to increase oxygen diffusion at grain boundaries, promoting densification [16].

CONCLUSIONS

The influence of RE cations on the morphological and structural properties of PT is described. The results suggest that the modifier RE cations incorporated into the system are effective in crystallite size reduction, conferring its influence on the microstructure (that was qualitatively confirmed by nitrogen adsorption/desorption results) and improve the densification of grains, attributed to the possible effect of oxygen diffusion at grain boundaries by replacing Pb^{2+} for trivalent Yb and Y cations.

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