Incorporation of dysprosium ions into PbTiO_3 ferroelectric ceramic system

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A structural analysis concerning the incorporation of dysprosium into A- and/or B-sites of the lead titanate is shown. The two “boundary” refinements are presented, i.e., Dy^{2+} substitutes for Pb^{2+} (Dy^{3+} substitutes for Ti^{4+}) and Dy^{3+} substitutes for Pb^{2+} (Dy^{3+} substitutes for Ti^{4+}). The results offer quantitative information about the incorporation into both crystallographic sites. The increase of Dy^{3+} fraction into B-site provides the increase of the Ti^{4+} atomic displacement along the [001] direction and the tetragonal distortion.

Keywords: Lead titanate; lanthanides; perovskites; crystalline structure.

1. Introduction

Lead titanate (PbTiO_3) ferroelectric system has been studied for many years due to its high intrinsic polarization and relatively high ferroelectric–paraelectric transition temperature (T_C), which is very useful for the development of piezoelectric and ferroelectric devices.^{1–3} However, its porosity and high tetragonality (c/a) promotes microstructural tensions when the temperature changes around T_C , which prevents the sintering of high density ceramic materials. From this point of view, the study of lanthanide (Ln^{3+}) modified PbTiO_3 (PT) has attracted increasing attention.^{4–6} The Ln^{3+} addition in general favors low tetragonality, while good piezoelectric and ferroelectric properties are retained.

The incorporation of additional ions in the perovskite structure normally occurs at either cation site, the 12-coordinated A-site or the octahedral coordinated B-site. The lanthanides usually provides donor-doped materials, i.e., Ln^{3+} ions occupy the A-site. However, by using experimental and theoretical analysis, it has been showed that the lanthanides could occupy the A- and/or B-sites of the BaTiO_3 depending of its ionic radii.^{7–10} Other studies on the effect of Ln^{3+} on the properties and structural features of PT perovskite have been also reported. Structural studies have shown partial or total selectivity of the lanthanide ions at A- and B-sites of the perovskite structure.^{4–6}

Previous studies in $(\text{Pb}_{1-3x/2}\text{Ln}_x)\text{TiO}_3$ ceramic system ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$; $x = 2$ and 8 at.%) have shown an increase of the c/a ratio, cell volume, and a concomitant increase in the ferroelectric to paraelectric transition

temperature when one goes from La^{3+} to Dy^{3+} , recovering the values of the undoped PT being consistent with both A- and B-site substitution.¹¹ On the other hand, positron annihilation lifetime spectroscopy experiments have given evidence for a change in the A-site to B-site cation vacancy ratio with reducing ion size.¹² The results are consistent with the incorporation of the higher Ln^{3+} ions (La^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+}) into the A-site. The partial occupancy of the B-site occurs for Gd^{3+} and Dy^{3+} ions as was expected. X-ray diffraction and extended X-ray absorption fine structure experiments in the $(\text{Pb}_{0.88}\text{Eu}_{0.08})\text{TiO}_3$ ceramic have also showed that Eu^{3+} ions substitute to Pb^{2+} and Ti^{4+} ions at A- and B-sites of the ABO_3 structure, respectively.¹³

The present study will provide more insight concerning the incorporation of dysprosium into A- and/or B-sites of the PT perovskite structure. The dysprosium-doped PT system will be studied considering two nominal equations: (i) $(\text{Pb}_{0.88}\text{Dy}_{0.08})\text{TiO}_3$, dysprosium substitutes for Pb^{2+} (labeled as PT8Dy); (ii) $\text{Pb}(\text{Ti}_{0.92}\text{Dy}_{0.08})\text{O}_{2.96}$, dysprosium substitutes for Ti^{4+} (labeled as PTDy8). X-ray diffraction experiments will be used to refine the crystalline structure in order to obtain quantitative information about the possible incorporation of dysprosium ions at both crystallographic sites.

2. Experimental Procedure

The ceramics samples were prepared by the standard solid-state method from oxide precursors (PbO , TiO_2 , Dy_2O_3). The mixture of powders was prefired at 900°C in air atmosphere

for 2 h, and sintering was carried out at 1220°C for 2 h in a covered platinum crucible in air atmosphere. Both compositions were prepared without any lead excess. The total loss of mass for all the process of samples preparation was lower than 3% for both compositions. A detailed analysis for the loss of mass during the sintering process (where the lead can volatilize), i.e., it has been evaluated the mass before and after the sintering process, has showed only a 0.3% for the loss of mass, which is very low. This result has suggested low lead loss for the obtained samples. On the other hand, the densities were above 98% of the corresponding theoretical values.

The X-ray powder diffraction patterns were obtained at room temperature by using a Bruker D8 Advance diffractometer (CuK α radiation). The data were registered in the angular range 20° to 60° in 2 θ . The structure of the samples was refined by using the Rietveld method, which is available in the FullProf_Suit software.¹⁴ The initial structural model corresponds to the PT perovskite structure with the non-centrosymmetric space group P4mm (No. 99).¹⁵ The refinement was performed considering the incorporation of dysprosium ions into both sites of the PT perovskite structure, which was proposed considering previous analysis of the tolerance values.¹¹ The atoms coordinates in the asymmetric unit cell were assumed as Pb/Dy at the origin (0,0,0), Ti/Dy at (1/2, 1/2, $z_{\text{Ti/Dy}}$), and the O(I) and O(II) positions at (1/2, 1/2, $z_{\text{O(I)}}$) and (1/2, 0, $z_{\text{O(II)}}$), respectively. The initial occupation factors were assumed considering the amphoteric characteristic of the dysprosium ions (Dy²⁺/Dy³⁺), since they can be either acceptors or donors, according to their site.¹⁰ The A-site (B-site) occupancy was shared between lead and dysprosium ions (titanium and dysprosium ions). The A- and B-sites drive the lanthanide ions towards lower and higher valence, respectively, due to both columbic and strain energy contributions. It has been previously reported¹⁰ that dysprosium ions on the A-site can be 2+ and/or 3+ (with an ionic radii of 1.228 Å), and 3+ (with an ionic radii of 0.912 Å) on the B-site, for perovskite structures. There is not any report concerning the ionic radii for Dy²⁺ in A-site. The refinement cannot resolve the question of what would be the partition between those two possible oxidation states on the A-site. Therefore, the present study includes the two “boundary” refinements, i.e., Dy²⁺ substitutes for Pb²⁺ (Dy³⁺ substitutes for Ti⁴⁺) and Dy³⁺ substitutes for Pb²⁺ (Dy³⁺ substitutes for Ti⁴⁺).

3. Results and Discussion

Figures 1 and 2 show the Rietveld refinements of the X-ray powder diffraction patterns for PT8Dy and PTDy8 systems, respectively, considering Dy²⁺ into the A-site and Dy³⁺ into the B-site. The experimental data are represented by open circles and the calculated profiles by continuous line, respectively. The short lines below the diffraction patterns correspond to the calculated Bragg reflections. The difference

Fig. 1. Rietveld refinement for PT8Dy system at room temperature, considering Dy²⁺ into the A-site and Dy³⁺ into the B-site. The experimental data are represented by open circles and the calculated profiles by continuous line, respectively. The short lines below the diffraction pattern correspond to the calculated Bragg reflections. The difference between the experimental and the theoretical patterns are presented below.

Fig. 2. Rietveld refinement for PTDy8 system at room temperature, considering Dy²⁺ into the A-site and Dy³⁺ into the B-site. The experimental data are represented by open circles and the calculated profiles by continuous line, respectively. The short lines below the diffraction pattern correspond to the calculated Bragg reflections. The difference between the experimental and the theoretical patterns are presented below.

between the experimental and the theoretical patterns are presented at the bottom of the figures.

The unit cell parameters (a , c), the refined atomic coordinates, the occupation fraction are showed in Tables 1 and 2 for the studied samples. The goodness of fit parameters is also showed.

After the refinement process, the nominal compositions for PT8Dy and PTDy8 were, respectively, (Pb_{0.936}Dy_{0.064})(Ti_{0.967}Dy_{0.033})O_{2.984} and (Pb_{0.948}Dy_{0.052})(Ti_{0.957}Dy_{0.043})O_{2.978}. The

Table 1. Refined atomic data for PT8Dy system, considering Dy²⁺ into the A-site and Dy³⁺ into the B-site.

P4 mm		$a = 3.902(8) \text{ \AA}$		$c = 4.123(3) \text{ \AA}$	
Atom	Site	Fraction	x	y	z
Pb ²⁺	A	0.93(6)	0	0	0.003(5)
Dy ²⁺	A	0.06(4)	0	0	0.003(5)
Ti ⁴⁺	B	0.96(7)	0.5	0.5	0.537(5)
Dy ³⁺	B	0.03(3)	0.5	0.5	0.537(5)
O	O1	1	0.5	0.5	0.139(9)
O	O2	1	0.5	0	0.599(1)
$R_p = 12.8\%$		$R_{wp} = 13.5\%$			

Table 2. Refined atomic data for PT8Dy system, considering Dy²⁺ into the A-site and Dy³⁺ into the B-site.

P4 mm		$a = 3.897(3) \text{ \AA}$		$c = 4.155(8) \text{ \AA}$	
Atom	Site	Fraction	x	y	z
Pb ²⁺	A	0.94(8)	0	0	0.001(6)
Dy ²⁺	A	0.05(2)	0	0	0.001(6)
Ti ⁴⁺	B	0.95(7)	0.5	0.5	0.562(9)
Dy ³⁺	B	0.04(3)	0.5	0.5	0.562(9)
O	O1	1	0.5	0.5	0.075(9)
O	O2	1	0.5	0	0.618(6)
$R_p = 7.31\%$		$R_{wp} = 9.87\%$			

occupation factor values for the oxygen atoms could not be refined directly. The oxygen is a lighter atom whose atomic number is lower than that of the other elements in the structure, which provides a lower atomic scattering factor. Then, it is not very sensitive to the X-ray diffraction and it is very difficult to refine its occupancy.¹⁶ The corresponding occupation factor values were calculated considering the refined occupation factors for the dysprosium ions at B-sites $[(\text{Pb}_{1-x}\text{Dy}_x)(\text{Ti}_{1-y}\text{Dy}_y)(\text{O}_{3-y/2})]$ where $x + y = 0.08$. The results show that the dysprosium ions can be incorporated into both A- and B-sites of PT perovskite structure, which are in agreement with the positron annihilation lifetime spectroscopy experiments.¹²

Figures 3 and 4 show the Rietveld refinements of the X-ray powder diffraction patterns for PT8Dy and PT8Dy systems, respectively, considering Dy³⁺ into the A- and B-sites. The experimental data are represented by open circles and the calculated profiles by continuous line, respectively. The short lines below the diffraction patterns correspond to the calculated Bragg reflections. The difference between the experimental and the theoretical patterns are presented at the bottom of the figures. The unit cell parameters (a, c), the refined atomic coordinates, the occupation fraction are showed in Tables 3 and 4 for the studied samples. The goodness of fit parameters is also showed.

After the refined process, the nominal compositions for PT8Dy and PT8Dy were, respectively, $(\text{Pb}_{0.921}\text{Dy}_{0.049})$

Fig. 3. Rietveld refinement for PT8Dy system at room temperature, considering Dy³⁺ into the A- and B-sites. The experimental data are represented by open circles and the calculated profiles by continuous line, respectively. The short lines below the diffraction pattern correspond to the calculated Bragg reflections. The difference between the experimental and the theoretical patterns are presented below.

Fig. 4. Rietveld refinement for PT8Dy system at room temperature, considering Dy³⁺ into the A- and B-sites. The experimental data are represented by open circles and the calculated profiles by continuous line, respectively. The short lines below the diffraction pattern correspond to the calculated Bragg reflections. The difference between the experimental and the theoretical patterns are presented below.

$(\text{Ti}_{0.969}\text{Dy}_{0.031})\text{O}_{2.984}$ and $(\text{Pb}_{0.941}\text{Dy}_{0.041})(\text{Ti}_{0.951}\text{Dy}_{0.049})\text{O}_{2.976}$. The occupation factor values for the oxygen atoms were again calculated considering the refined occupation factors for the dysprosium ions at B-sites $[(\text{Pb}_{1-3x/2}\text{Dy}_x)(\text{Ti}_{1-y}\text{Dy}_y)(\text{O}_{3-y/2})]$ where $x + y = 0.08$. The results show that the Dy³⁺ ions can be incorporated into both A- and B-sites of PT perovskite structure.

On the other hand, for PT8Dy sample it can be seen that the results for the occupation of Dy³⁺ into B-sites are similar

Table 3. Refined atomic data for PT8Dy system, considering Dy³⁺ into the A- and B-sites.

P4 mm		$a = 3.902(9) \text{ \AA}$		$c = 4.123(1) \text{ \AA}$	
Atom	Site	Fraction	x	y	Z
Pb ²⁺	A	0.92(1)	0	0	0.003(5)
Dy ³⁺	A	0.04(9)	0	0	0.003(5)
Ti ⁴⁺	B	0.96(9)	0.5	0.5	0.537(5)
Dy ³⁺	B	0.03(1)	0.5	0.5	0.537(5)
O	O1	1	0.5	0.5	0.139(9)
O	O2	1	0.5	0	0.599(1)
$R_p = 12.5\%$		$R_{wp} = 13.3\%$			

Table 4. Refined atomic data for PT8Dy8 system, considering Dy³⁺ into the A- and B-sites.

P4 mm		$a = 3.897(3) \text{ \AA}$		$c = 4.155(5) \text{ \AA}$	
Atom	Site	Fraction	x	y	z
Pb ²⁺	A	0.94(1)	0	0	0.001(6)
Dy ³⁺	A	0.04(1)	0	0	0.001(6)
Ti ⁴⁺	B	0.95(1)	0.5	0.5	0.562(9)
Dy ³⁺	B	0.04(9)	0.5	0.5	0.562(9)
O	O1	1	0.5	0.5	0.075(9)
O	O2	1	0.5	0	0.618(6)
$R_p = 7.41\%$		$R_{wp} = 9.97\%$			

for both refinements. However, there is an important difference in the occupation of Dy²⁺ and Dy³⁺ into A-sites, i.e., the fraction of Dy²⁺ is higher. For PT8Dy8 sample, the analysis of the results is similar even when there is a higher difference between the fractions of Dy³⁺ into B-sites for both refinements.

Table 5 shows the tetragonal distortion $[(c/a) - 1]$, the angle between the polarization directions in adjacent 90° domains $[2\arctan(a/c)]$ and the Ti⁴⁺ atomic displacement $[\Delta z(\text{Ti}^{4+}) \times c]$ along the [001] crystallographic direction concerning the inversion center for the cubic cell, for the studied samples and both “boundary” refinements. The behavior of these parameters is similar for both “boundary” refinements. The tetragonal distortion increases with the

Table 5. The tetragonal distortion $[(c/a) - 1]$, the angle between the polarization directions in adjacent 90° domains $[2\arctan(a/c)]$ and the Ti⁴⁺ atomic displacement $[\Delta z(\text{Ti}^{4+}) \times c]$ along the [001] crystallographic direction concerning the inversion center for the cubic cell, for the studied samples and both “boundary” refinements.

Sample	$[(c/a) - 1]$	$[2\arctan(a/c)]$ (°)	$[\Delta z(\text{Ti}^{4+}) \times c]$ (Å)
For the refinement considering Dy ²⁺ into the A-site and Dy ³⁺ into the B-site			
PT8Dy	0.056(5)	86.9	0.154(6)
PT8Dy8	0.066(3)	86.3	0.261(4)
For the refinement considering Dy ³⁺ into the A- and B-sites			
PT8Dy	0.056(4)	86.8	0.154(6)
PT8Dy8	0.066(2)	86.3	0.261(4)

increase of Dy³⁺ fraction into B-sites as should be expected. The $[2\arctan(a/c)]$ values are closer to the PT value¹⁷ and decreases with the increase of the tetragonal distortion. The decrease of the $[2\arctan(a/c)]$ value is associated to a higher decoupling of the lattices to both sides of the domains wall, i.e., the distortion of the structure is higher in the adjacent 90° ferroelectric domains, which corresponds with the increase of the tetragonal distortion. On the other hand, a higher $[\Delta z(\text{Ti}^{4+}) \times c]$ value was obtained for PT8Dy8, which is in agreement with the higher tetragonal distortion value. The increase of the Ti⁴⁺ atomic displacement along the [001] crystallographic direction from PT8Dy to PT8Dy8 suggests a higher distortion in the structure along that crystallographic direction (the oxygen octahedron, TiO₆, is distorted in the z-axis) and then the tetragonal distortion increases as has been showed.

4. Summary

A detailed structural analysis by using Rietveld refinement has been carried out in dysprosium-doped PT ferroelectric ceramics. The refinement was performed considering the incorporation of dysprosium ions into both sites of the structure and their amphoteric characteristic. The study has included the two “boundary” refinements, i.e., Dy²⁺ substitutes for Pb²⁺ (Dy³⁺ substitutes for Ti⁴⁺) and Dy³⁺ substitutes for Pb²⁺ (Dy³⁺ substitutes for Ti⁴⁺). The results have showed that dysprosium ions occupy both A- and B-sites into the PT perovskite structure. The tetragonal distortion and the Ti⁴⁺ atomic displacement along the [001] crystallographic direction increase with the increase of Dy³⁺ fraction into B-site meanwhile the angle between the polarization directions in adjacent 90° domains decreases. These results offer an approach for a better understanding of the incorporation of lanthanide ions into the ferroelectric perovskite structure.

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