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Study of the lithium insertion and de-insertion in perovskite praseodymium bismuth lithium titanate

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Abstract

The stoichiometry and lithium-insertion reactions with *n*BuLi in solid solutions $Pr_{0.5+x-y}Li_{0.5-3x}Bi_yTiO_3$ have been studied. The results indicate that bismuth affects these processes. Two joins with bismuth and lithium constant, respectively, are studied in the phase diagram. The amount of lithium inserted depends on the number of vacancies and the amount of bismuth in the original sample. The amount of lithium de-inserted depends only on the amount of bismuth. The cell volume increases when the amount of the lithium inserted increases, but anomalous dependence is observed in de-insertion. The presence of bismuth decreases the amount of lithium inserted in the sample, but favors the reversibility of the insertion.

Keywords: Perovskites; Insertion reactions; (Pr,Li,Bi)TiO_3; Intercalation

1. Introduction

The studies of solid electrolytes with lithium ionic conductivity have been of much interest because of their potential applications in batteries.[1] Attention has recently been paid to perovskite-type oxides (ABO_3). In these compounds a transition metal element (B cation) occupies the center of an octahedron of six oxygen ions, and cation A occupies a site in the middle of the net formed by these octahedra. Since the A-B-sites in this structure can tolerate different ions with different valence states, several studies have been reported in various systems.[2–9] Up to now, the best lithium-ion conducting electrolytes among these oxides are the lanthanum lithium titanates $La_{2/3-x}Li_{3x}TiO_3$ (LLTO), with a room temperature conductivity of $10^{-3}\,S\,cm^{-1}$ for $La_{0.51}Li_{0.35}TiO_{2.94}$.[4,5] The compounds in this system are ionic conductors but show negligible electronic conduction. Lanthanum has been substituted by other rare-earth elements (Pr, Nd and Sm), but the resulting conductivity is lower.[6–10] Substitutions in the B-site in $RE_{0.5+x+y}Li_{0.5-3x}Ti_{1-3y}Cr_{3y}O_3$ (RE $=$ Pr, La and M $=$ Mn, Cr, Sn, Zn and Ge) have been reported to increase electronic conduction without affecting ionic conduction.[11–14]

Recently, the rare-earth cations were partially substituted by bismuth.[15,16] In the system $Pr_{0.5+x-y}Li_{0.5-3x}Bi_yTiO_3$ a pure phase solid solution exists only in the domain $0.033 < x < 0.133$ and $y \leq 0.10$.[16] The presence of A-site vacancies favors high mobility of lithium ions. A maximum ionic conductivity of $7 \times 10^{-6}\,S\,cm^{-1}$ has been found at room temperature for $x = 0.067$. Substitution of praseodymium by bismuth decreases the temperature and time of thermal treatment.[16] Intercalation of Li^+ ions in the structure is possible by lowering the valence state of transition metal ions (Ti^{4+}) according to the process:

$$xLi^0 + Ti^{4+} \leftrightarrow xLi^+ + (1-x)Ti^{4+} + xTi^{3+} \qquad (1)$$

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Intercalation (also referred to as insertion) has been previously reported in the LLTO system.[17,20–23] In some cases more lithium is inserted than the number of vacancies in A-sites.[21,23] There are conflicting reports about the reversibility of the insertion and de-insertion of lithium ions.[17,20] Variations in the lattice parameters have been reported in the LLTO system during insertion[21] while no differences were found in the system with chromium.[23] To examine the behavior of these materials in more depth, it is very important to understand the nature of this process. Such understanding may lead to the development of new materials with better properties.

Here we examine the chemical insertion and de-insertion of lithium in the $Pr_{0.5+x-y}Li_{0.5-3x}Bi_yTiO_3$ system.

2. Experimental

2.1. Synthesis

Polycrystalline samples were prepared by conventional solid-state reaction. Pr_6O_{11} (99.9%, Fluka), TiO_2 (99.9%, Aldrich), Bi_2O_3 (>99%, J.T. Baker) and Li_2CO_3 (>99%, Merck) were used as starting materials. Details of the sample preparation are given in reference 16.

2.2. X-ray diffraction

Crystalline phase identification and lattice parameters were obtained by powder X-ray diffraction with a Siemens D-500 diffractometer in reflection mode with a detector and graphite monochromator, using Cu-K_α radiation. Lattice parameters were obtained using a silicon internal standard.

2.3. ICP

Chemical analysis was performed by inductively coupled plasma (ICP) spectroscopy (Thermo Jarrel ASH Corporation, Model Spectrometer Polyscan TM 61E) in order to determine Li, Bi and Ti contents in the sample.

2.4. Chemical lithium intercalation

Chemical lithium intercalation was carried out by reacting the ground sample with *n*BuLi (1.6 M) in N_2 atmosphere at 60 °C for 3 days with stirring. The X-ray diffraction pattern of the intercalated products was recorded after washing in hexane.

2.5. Chemical lithium de-intercalation

The de-intercalation was carried out by reacting the inserted samples with I_2 at 60 °C in an acetonitrile solution in a N_2 atmosphere for 3 days with stirring. The resulting powders were washed in acetonitrile.

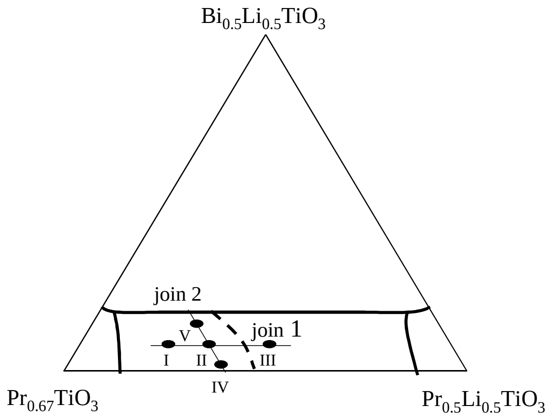

Fig. 1. Composition triangle and joins of chemical lithium intercalation. The five compositions are pointed out with Roman numbers.

3. Results and discussion

Chemical lithium intercalation was carried out on a range of compositions within the region of perovskite-like solid solutions in the phase diagram, shown above in equation 1.[16] Along join 1 [$Pr_{0.46+x}Bi_{0.05}Li_{0.5-3x}TiO_3$] the lithium and praseodymium composition and the number of vacancies changed while the composition of bismuth was constant. Along join 2 [$Pr_{0.6-y}Bi_yLi_{0.325}TiO_3$] the number of vacancies and the amount of lithium were constant (Fig. 1). This is the most conducting zone of the phase diagram in this system.[16] The phase diagram in Fig. 1 shows the solid solution range of the system.[16]

Insertion is accompanied by a color change from green to black, which indicates the presence of one element in two oxidation states. In this case it is associated with the change from Ti^{4+} to Ti^{3+} as shown in Fig. 1. This change occurs in the first hours of the experiment, but the samples were maintained in these conditions for 3 days to make sure insertion was complete. Incorporation of lithium in this kind of system is more rapid than in almost any other oxide.[17] The amount of *n*BuLi is three-fold greater than the number of lithium vacancies in the material.

ICP analyses were carried out (Table 1), with the Ti amount set to unity and the remaining values re-normalized in the formula $Pr_{0.5+x-y}Li_{0.5-3x}Bi_yTiO_3$. The relation between the amount of lithium inserted (δ) and the number of vacancies is discussed below. For all the compositions Pr:Bi:Li:Ti ratios were in consistent with the values expected from starting compositions. In the case of bismuth the amount of bismuth obtained was slightly lower than expected, and although this value was within the error of measurement, there was a tendency to be lost at higher bismuth concentrations. The melting point of $Bi_4Ti_3O_4$ is lower than the synthesis temperature,[24] which enhance the rate of the reaction and decreases the final treatment time.[16] At the same time it facilitates the loss of bismuth. In samples with lower bismuth concentration this loss was not observed.

Table 1
Sample composition and number of vacancies before and after the insertion of lithium

	Starting composition $Pr_{0.5+x-y}Li_{0.5-3x}Bi_yTiO_3$	Experimental composition	Inserted lithium $Pr_{0.5+x-y}Li_{0.5-3x+\delta}Bi_yTiO_3$	A-site vacancy	δ
I	$Pr_{0.577}Bi_{0.04}Li_{0.150}TiO_3$	$Pr_{0.577}Bi_{0.038}Li_{0.159}TiO_3$	$Pr_{0.570}Bi_{0.038}Li_{0.398}TiO_3$	0.233	0.240
II	$Pr_{0.56}Bi_{0.04}Li_{0.200}TiO_3$	$Pr_{0.557}Bi_{0.037}Li_{0.203}TiO_3$	$Pr_{0.540}Bi_{0.036}Li_{0.352}TiO_3$	0.200	0.150
III	$Pr_{0.535}Bi_{0.04}Li_{0.275}TiO_3$	$Pr_{0.533}Bi_{0.038}Li_{0.274}TiO_3$	$Pr_{0.530}Bi_{0.038}Li_{0.372}TiO_3$	0.150	0.990
IV	$Pr_{0.59}Bi_{0.01}Li_{0.200}TiO_3$	$Pr_{0.579}Bi_{0.011}Li_{0.224}TiO_3$	$Pr_{0.583}Bi_{0.012}Li_{0.456}TiO_3$	0.200	0.232
V	$Pr_{0.53}Bi_{0.07}Li_{0.200}TiO_3$	$Pr_{0.516}Bi_{0.066}Li_{0.214}TiO_3$	$Pr_{0.534}Bi_{0.068}Li_{0.329}TiO_3$	0.200	0.115

The amount of lithium inserted (δ) is also shown.

Figs. 2 and 3 show the amount of lithium inserted versus amount of praseodymium for joins 1 and 2, respectively.

The number of vacancies is represented in each case to facilitate the analysis. In join 1 (where the bismuth composition is constant and the number of vacancies changes) the amount of lithium inserted increases while the number of vacancies also increases (Fig. 2). In the $Pr_{0.577}Bi_{0.038}Li_{0.159}TiO_3$ composition (I) all vacancies are occupied, while in the other compositions they are not. This difference may be attributable to the increasing of the cell volume[16] and the increase in mobility for higher numbers of vacancies.[19] There is a high correlation between conductivity and diffusion in these materials,[18] but maximum conductivity is reached composition II[16] while the insertion is higher in composition I. The conductivity depends on the mobility (which in turn depends on the number of vacancies) and lithium concentration, and they are inversely proportional. This dependence is consistent with the parabolic relationship between conductivity and lithium concentration.[19] In the insertion, lithium is incorporated to the sample and the diffusion is enhanced with the increase in the number of vacancies and percolation sites.[2,3] Along join 2 the inserted lithium decreases with the increase of bismuth concentration, although the number of vacancies is constant (Fig. 3). Conductivity decreases in this line.[16] The presence of ions in A-sites stabilizes the crystalline electric field. While praseodymium ions have a rigid structure, bismuth has a lone-electron pair, which makes this ion highly polarizable. This polarizability affects the crystalline field and the environment of the ions, decreasing the mobility of lithium in the material. Composition IV, with a lower bismuth concentration, inserts more lithium than the number of vacancies as in the LLTO system.[21,23] In this system lithium ions are inserted into the 3c-site when the A-site positions are fully occupied.[21]

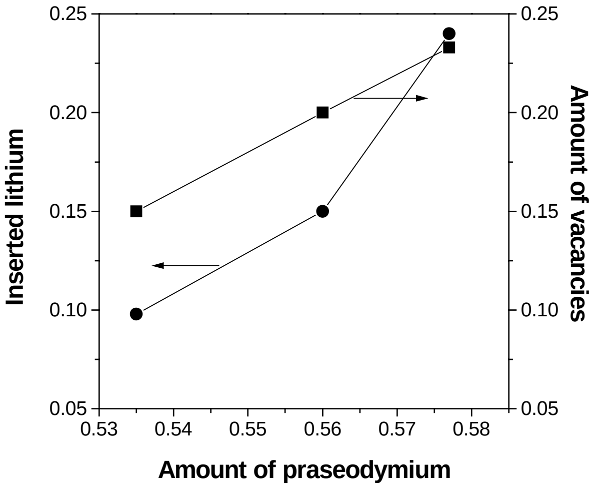

Fig. 2. Plot of amount of lithium inserted and vacancies vs. amount of praseodymium in join 1.

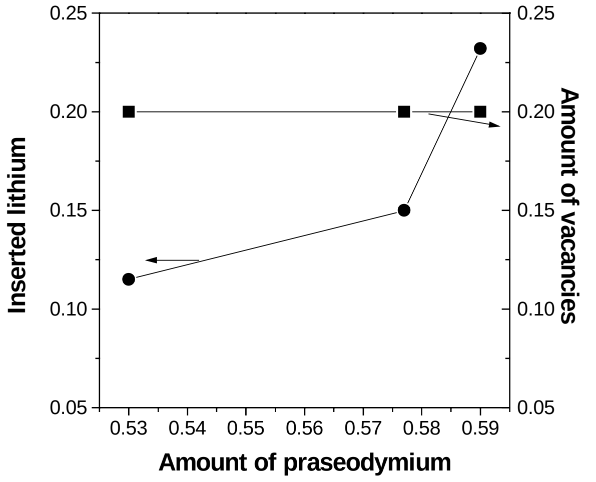

Fig. 3. Plot of amount of lithium inserted and vacancies vs. amount of praseodymium in join 2.

Compositions with more bismuth insert less lithium than the number of vacancies, which confirms the decrease of lithium mobility in the material in the presence of bismuth.

When inserted samples were left in open atmosphere for several days, the color turned to green-gray. This change indicates of the oxidation of Ti^{3+} and could be caused by the absorption of oxygen on the surface of the sample or by the formation of Li_2O, as the lithium can not be lost in these conditions. This change was irreversible when the samples were re-exposed to reduction with *n*BuLi. For this reason the de-lithiation reaction was performed immediately after the samples were extracted from lithiation. The results of the de-lithiation reactions and the cell parameters of the starting, inserted and de-inserted composition are shown in Table 2.

Fig. 4 shows the relation between the amount of lithium in the starting sample and the inserted and de-inserted samples

Table 2
Cell parameters of the samples before and after the insertion and removal of lithium

Experimental composition	Inserted composition	De-inserted composition	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
$Pr_{0.577}Bi_{0.038}Li_{0.159}TiO_3$			3.8388		7.7275	113.88
	$Pr_{0.570}Bi_{0.038}Li_{0.398}TiO_3$		3.8444		7.7322	114.28
		$Pr_{0.563}Bi_{0.037}Li_{0.167}TiO_3$	3.8421		7.7330	114.15
$Pr_{0.557}Bi_{0.037}Li_{0.203}TiO_3$			3.8406		7.6989	113.56
	$Pr_{0.540}Bi_{0.036}Li_{0.352}TiO_3$		3.8465		7.7036	113.98
		$Pr_{0.550}Bi_{0.037}Li_{0.215}TiO_3$	3.8402		7.7023	113.59
$Pr_{0.533}Bi_{0.038}Li_{0.274}TiO_3$			5.4324	7.6887	5.4340	226.97
	$Pr_{0.530}Bi_{0.038}Li_{0.372}TiO_3$		5.4324	7.6910	5.4352	227.08
		$Pr_{0.530}Bi_{0.038}Li_{0.285}TiO_3$	5.4358	7.6819	5.4208	226.36
$Pr_{0.579}Bi_{0.011}Li_{0.224}TiO_3$			3.8377		7.7146	113.62
	$Pr_{0.583}Bi_{0.012}Li_{0.456}TiO_3$		3.8435		7.7290	114.18
		$Pr_{0.567}Bi_{0.012}Li_{0.276}TiO_3$	3.8372		7.7124	113.56
$Pr_{0.516}Bi_{0.066}Li_{0.214}TiO_3$			3.8415		7.6966	113.58
	$Pr_{0.534}Bi_{0.068}Li_{0.329}TiO_3$		3.8505		7.6963	114.11
		$Pr_{0.520}Bi_{0.069}Li_{0.209}TiO_3$	3.8461		7.7099	114.05

in both joins. Composition IV with less bismuth ($y = 0.01$) retained part of the inserted lithium (Fig. 4b). This is consistent with reports on similar materials without bismuth.[11,21] In join 1, where bismuth content was constant, $y = 0.04$ (Fig. 4a), part of the lithium was also retained, although this quantity was at the limit of detection. All along this join the lithium retained is approximately constant in spite of variations in the amount of lithium inserted. This indicates that, at this level of lithium inserted, the lithium retained does not depend upon the amount of lithium previously inserted for the same amount of bismuth. In the sample (V) with most bismuth ($y = 0.07$) the insertion and de-insertion was totally reversible (Fig. 4b). This behavior may be attributable to the amount of intercalated lithium, but the lack of such behavior in join 1 indicates that the presence of bismuth is essential to the lithium de-intercalation properties of the material.

The cell parameters of the starting compositions, lithium inserted and de-inserted phases are presented in Fig. 5. As an orthorhombic cell is described as the double of a tetragonal cell, in composition III, which is orthorhombic, the half the cell volume is represented to facilitate comparison with the other compositions. The cell volume of inserted samples is different from that of the starting composition. This result conflicts with previous reports on the system without bismuth. While Martínez-Sarrión et al.[23] found no differences, Shan et al.[21] shows significant differences only for high degrees of insertion. In join 1 the cell volume increased when the amount of inserted lithium increased (Fig. 5a). The presence of a lithium ion occupying an empty site may be responsible for this increase as it shows direct dependence on the amount of lithium inserted. However, volume decreased according to the amount of lithium in the starting composition (inversely to insertion) when the lithium was extracted (Fig. 5a). The phase change from orthorhombic to tetragonal may be responsible for this difference. In join 2, cell volume increased with the lithium insertion, as in join 1. In compositions IV and II the volume in the de-inserted samples was the same as the starting composition, but composition V showed anomalous behavior, Fig. 5b. A phase transition in the system without bismuth is assumed to take place during the first lithium insertion step[21] and although it is not observed in the XRD diagrams, the presence and

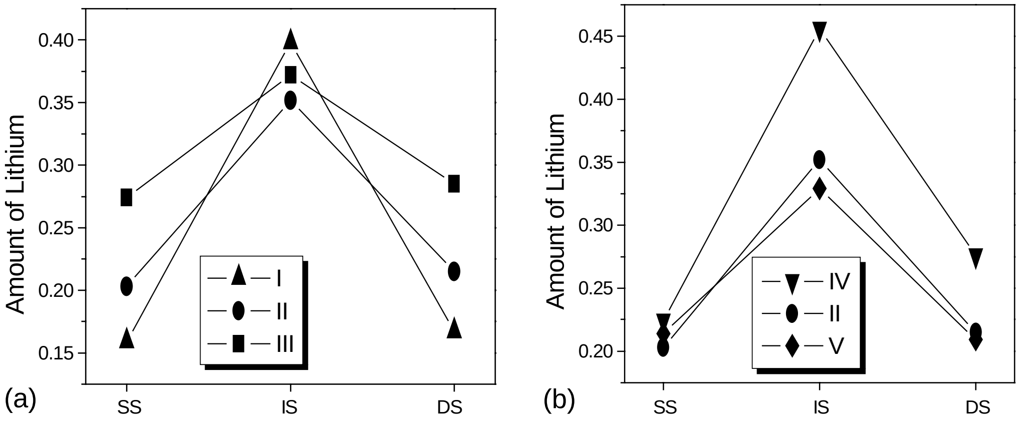

Fig. 4. Amount of lithium in the starting (SS), inserted (IS) and de-inserted (DS) compositions in (a) join 1 and (b) join 2.

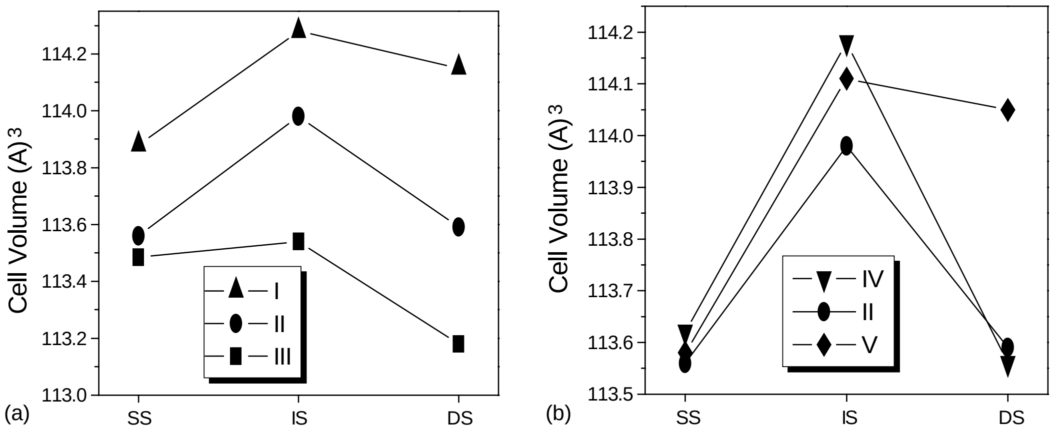

Fig. 5. Cell volume in the starting (SS), inserted (IS), and de-inserted (DS) compositions in (a) join 1 and (b) join 2.

non-reversibility of this transition may explain this behavior. Further studies are needed to establish the effect of bismuth on cell volume. A study of the distribution of ions in the A-site in this system is in preparation.

4. Conclusions

Lithium ions can be inserted and de-inserted from perovskite-type oxides $Pr_{0.5+x-y}Li_{0.5-3x}Bi_yTiO_3$. The presence of bismuth affects in these processes. Lithium insertion reduces transition metal ions (Ti) and increases the lattice parameter. The cell volume is proportional to the amount of lithium inserted. This relation is not observed in the de-insertion. Bismuth decreases the amount of lithium inserted, but favors the reversibility of the insertion.

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