



# Effect of europium concentration on its distribution in the host sites of lithium tantalite



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## ABSTRACT

Europium ion incorporation, and the effect of its concentration in the relative population of  $\text{Eu}^{3+}$  ions for each host site, was investigated using atomistic simulations based on the Mott–Littleton and Mean Field approaches. We predicted the most favorable sites occupied by the europium ion and the related charge-compensation mechanisms involved in these substitutions. It was found that Eu ions are the most energetically favorable for incorporation at both Li and Ta sites. A series of the occupation fraction, which was set as the relative population of Eu ions for each site, for different Eu concentrations in  $\text{LiTaO}_3$ , also was considered. Several schemes for the distribution of the Eu dopant were also calculated and compared with experimental results.

## 1. Introduction

Lithium tantalate ( $\text{LiTaO}_3$ ) is a material with many applications due to its electro-optical, electro-acoustic, and nonlinear optical properties besides having good mechanical and chemical stability [1,2]. Due to these properties,  $\text{LiTaO}_3$  has great potential for applications in optical fiber communications, range finding, military counter measures, optical data storage, remote sensing, reproduction graphics [3], and quantum memory [4,5].

$\text{LiTaO}_3$  is a ferroelectric material belonging to the family of the  $\text{A}^{1+}\text{B}^{5+}\text{O}_3$  type perovskite with a  $R3c$  space group. The crystal structure is a  $\alpha\text{-Al}_2\text{O}_3$  corundum structure with an ordered arrangement of  $\text{Li}^+$  and  $\text{Ta}^{5+}$  cations occupying two thirds of the octahedral sites, while one third remain empty and are likely to host ions [6,7].

Intrinsic (structure) and extrinsic defects (dopants) strongly influence the properties of  $\text{LiTaO}_3$ . In such materials, for example, the spectroscopic properties of rare earth ions as dopants have a strong dependence on the environment that surrounds them [8–11]. Many of the issues related to spectroscopic properties raise questions in relation to the dopant preferred sites, the charge-compensating defects, and how to determine the most energetically favorable doping process. The influence of other factors such as dopant concentration and stoichiometry on the spectroscopic properties has also been investigated. Muñoz Santisteban et al. [12], for example, studied the influence of the deviation from stoichiometry on the substitution of  $\text{Eu}^{3+}$  at host sites through the

spectroscopic profile analysis of the  $\text{Eu}^{3+} \ ^5D_0 \rightarrow \ ^7F_1$  intra-configurational transition. Gasparoto et al. [13] observed the evolution of  $\text{Eu}^{3+}$  in each site with dopant concentration.

In this paper, an atomistic simulation method is applied to investigate the process of  $\text{Eu}^{3+}$  doping into the  $\text{LiTaO}_3$  host. Correlation between the dopant concentrations and the occupation of Eu ions in the host sites of Eu-doped  $\text{LiTaO}_3$  was also investigated. From calculated solution energies, the most probable charge compensation mechanisms and the host site preference for Eu doping was identified. The solution energies for different schemes of distribution of Eu dopant was also calculated and compared related with experimental results.

## 2. Computational methods

In our calculations, the interaction between ions are described by interatomic potentials formed by a long-range Coulombic term and a short-range term of the Buckingham form based on the Born model. The energy minimization criterion, in which the ion positions are systematically adjusted to obtain a minimum energy configuration, is adopted. The ionic polarizability was incorporated using the Shell Model [14]. In this model, the anion ion is treated in terms of a core connected by a harmonic spring. The defect calculation was performed using the Mott–Littleton methods [15], in which relaxations close to the defect are treated explicitly and the remainder of the lattice is treated using quasi-continuum methods. All calculations were performed using the

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**Table 1**  
– Potentials parameters for the LiTaO<sub>3</sub> structure.

Buckingham	$A_{ij}$ (eV)	$\rho_{ij}$ (Å)	$C_{ij}$ (eV Å <sup>6</sup> )
Li <sup>+</sup> core – O <sup>2-</sup> shell	950.0	0.2610	0.0
Ta <sup>5+</sup> core – O <sup>2-</sup> shell	970.0	0.3960	0.0
O <sup>2-</sup> shell – O <sup>2-</sup> shell	22764.0	0.1490	27.88
Eu <sup>3+</sup> core – O <sup>2-</sup> shell	1.924.71	0.3403	20.59
Shell parameters	Shell charge	Spring Constant k (eV Å <sup>-2</sup> )	
O <sup>2-</sup>	-2.9	70.0	
Three-boby parameters	Force Constant, k <sub>θ</sub> (eV rad-2)	Equilibrium angle, θ <sub>0</sub> (deg)	
O <sup>2-</sup> shell- Ta <sup>5+</sup> core- O <sup>2-</sup> shell	0.5776	90	

GULP code [16]. The calculations for the Eu-doped LiTaO<sub>3</sub> (Li<sub>1-x</sub>Eu<sub>x</sub>Ta<sub>1-y</sub>Eu<sub>y</sub>O<sub>3</sub>) were realized using a “mean field method”. In this method, point defects are treated via a correction to the potential energy terms of particular atoms, to generate a hybrid species. In the hybrid atom, the interaction energies are scaled by the product for the fractional site occupancies. A hybrid atom consisting of (1-x)Li and xEu occupying the Li site, and another one with (1-y)Ta and yEu occupying the Ta site, was defined. The interaction between the hybrid atom and oxygen ions can be given by the following equations:

$$V_{\text{hybrid}} = (1-x)V_{\text{Li-O}} + xV_{\text{Eu-O}} \quad (1)$$

$$V_{\text{hybrid}} = (1-y)V_{\text{Ta-O}} + yV_{\text{Eu-O}} \quad (2)$$

This method allows for simulation of the homogenous distribution of the dopant ions.

### 3. Results

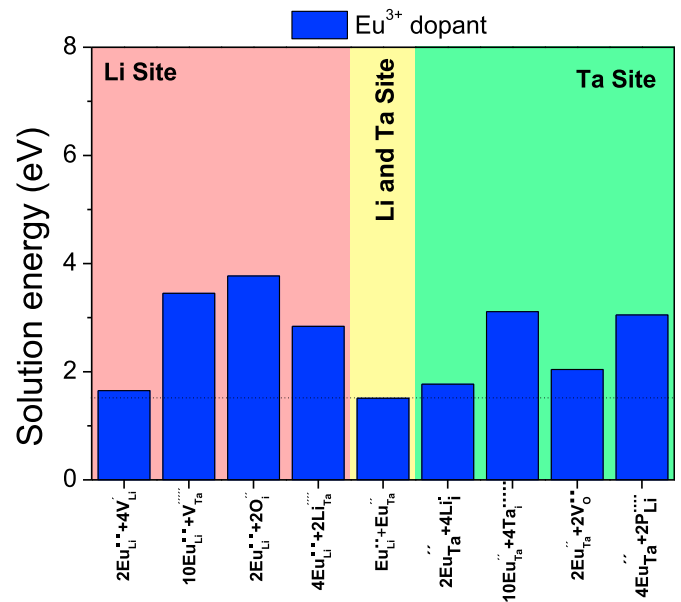
The changes in the spectroscopic and structural characteristics of the LiTaO<sub>3</sub> structure caused by an extrinsic dopant have been investigated in several experimental studies [9,17–21]. But before carrying out a defect calculation, the LiTaO<sub>3</sub> structure was optimized. For this, a set of potential parameters was obtained from an empirical fitting procedure. The

**Table 2**  
– Comparison of experimental and calculated lattice properties of LiTaO<sub>3</sub>.

Parameters	Present work	Exp.
a(Å)	5.16	5.15 [7]
c(Å)	13.67	13.78 [7]
C <sub>11</sub> (10 <sup>9</sup> N/m <sup>2</sup> )	243.64	233.1 [23]
C <sub>12</sub> (10 <sup>9</sup> N/m <sup>2</sup> )	81.94	46.4 [23]
C <sub>13</sub> (10 <sup>9</sup> N/m <sup>2</sup> )	91.15	83.5 [23]
C <sub>14</sub> (10 <sup>9</sup> N/m <sup>2</sup> )	-20.99	-10.8 [23]
C <sub>33</sub> (10 <sup>9</sup> N/m <sup>2</sup> )	304.93	275.2 [23]
C <sub>44</sub> (10 <sup>9</sup> N/m <sup>2</sup> )	102.89	95.3 [23]
C <sub>66</sub> (×10 <sup>9</sup> N/m <sup>2</sup> )	80.84	93.3 [23]
??(10 <sup>3</sup> kg/m <sup>3</sup> )	7.45	7.46 [23]

**Table 3**  
– Reaction schemes of defects due to the Eu<sup>3+</sup> incorporation in the LiTaO<sub>3</sub> structure.

Site	Charge compensation	Reaction
Li <sup>+</sup>	Lithium vacancies	$\text{Eu}_2\text{O}_3 + 6\text{Li}_{\text{Li}} \rightarrow 2\text{Eu}_{\text{Li}}^{3+} + 4\text{V}_{\text{Li}} + 3\text{Li}_2\text{O}$
	Tantalum vacancies	$5\text{Eu}_2\text{O}_3 + 5\text{Li}_{\text{Li}} + 4\text{Ta}_{\text{Ta}} \rightarrow 10\text{Eu}_{\text{Li}}^{3+} + 4\text{V}_{\text{Ta}}^{5+} + 5\text{Li}_2\text{O} + 2\text{Ta}_2\text{O}_5$
	Oxygen interstitial	$\text{Eu}_2\text{O}_3 + 2\text{Li}_{\text{Li}} \rightarrow 2\text{Eu}_{\text{Li}}^{3+} + 2\text{O}_i^{2-} + \text{Li}_2\text{O}$
Ta <sup>5+</sup>	Anti-site (LiTa <sup>5+</sup> )	$2\text{Eu}_2\text{O}_3 + 4\text{Li}_{\text{Li}} + 2\text{Ta}_{\text{Ta}} \rightarrow 4\text{Eu}_{\text{Li}}^{3+} + 2\text{Li}_{\text{Ta}}^{5+} + \text{Li}_2\text{O} + \text{Ta}_2\text{O}_5$
	Lithium interstitial	$\text{Eu}_2\text{O}_3 + 2\text{Ta}_{\text{Ta}} + 2\text{Li}_2\text{O} \rightarrow 2\text{Eu}_{\text{Li}}^{3+} + 4\text{Li}_i^{+} + \text{Ta}_2\text{O}_5$
	Tantalum interstitial	$5\text{Eu}_2\text{O}_3 + 10\text{Ta}_{\text{Ta}} \rightarrow 10\text{Eu}_{\text{Ta}}^{3+} + 4\text{Ta}_i^{5+} + 3\text{Ta}_2\text{O}_5$
	Oxygen vacancies	$\text{Eu}_2\text{O}_3 + 2\text{Ta}_{\text{Ta}} + 2\text{O}_o \rightarrow 2\text{Eu}_{\text{Ta}}^{3+} + 2\text{V}_o^{2-} + \text{Ta}_2\text{O}_5$
Li <sup>+</sup> and Ta <sup>5+</sup>	Anti-site (TaLi ... •)	$2\text{Eu}_2\text{O}_3 + 2\text{Li}_{\text{Li}} + 4\text{Ta}_{\text{Ta}} \rightarrow 4\text{Eu}_{\text{Li}}^{3+} + 2\text{Ta}_{\text{Li}}^{5+} + \text{Li}_2\text{O} + \text{Ta}_2\text{O}_5$
	Self-Compensation	$\text{Eu}_2\text{O}_3 + \text{Li}_{\text{Li}} + \text{Ta}_{\text{Ta}} \rightarrow \text{Eu}_{\text{Li}}^{3+} + \text{Eu}_{\text{Ta}}^{3+} + \text{LiTaO}_3$



**Fig. 1.** Histogram of solution energies for the incorporation of Eu ions in the LiTaO<sub>3</sub> structure.

potential parameters assigned to Li<sup>+</sup>–O<sup>2-</sup> and O<sup>2-</sup>–O<sup>2-</sup> interaction were derived from Araujo et al. [22], and for the Ta<sup>5+</sup>–O<sup>2-</sup> interaction, a new parameter was obtained empirically by fitting to the observed structures of LiTaO<sub>3</sub>. The potentials for the Eu<sup>3+</sup>–O<sup>2-</sup> interactions were obtained from the literature [22]; the empirically derived potential parameters are reported in Table 1.

The validation of potential parameters was achieved by comparing the calculated structural and physical properties with available experimental ones. Using the potential parameters showed in Table 1, it was possible to reproduce the LiTaO<sub>3</sub> structure and the lattice parameters to within 0.8%. These potential parameters also it was possible to reproduce simultaneously the start oxides (Li<sub>2</sub>O and Ta<sub>2</sub>O<sub>5</sub>) commonly used to synthesize LiTaO<sub>3</sub> structure to within 2%. Table 2 compares some calculated and experimental elastic constants and densities of the LiTaO<sub>3</sub> structure calculated on the basis of the interatomic potentials presented in Table 1. Note that the potential gives a good agreement between calculated and experimental values, and reproduces the trends in their relative values correctly. Thus, we can conclude that the interatomic potential parameters obtained in this work reproduce the main structural characteristics of the LiTaO<sub>3</sub> structure.

Many of the issues associated with photoluminescence properties are related to the Eu preferred sites, local symmetry, and dopant concentration; also important are the charge-compensating defects and the most energetically favorable doping process, and that, in general, is intractable in experimental work. Therefore, our calculation was used to investigate the quantitative estimate of the relative energies of Eu incorporation, and the distribution of Eu<sup>3+</sup> ions at Li<sup>+</sup> and Ta<sup>5+</sup> sites of LiTaO<sub>3</sub> for different concentrations of Eu using a mean field method. For this, we first

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