Effect of Site Locations on the Ferroelectricity of Lithium Niobate

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There are two kinds of cation locations in the lithium niobate crystallographic frame, i.e., the Li^+- and Nb^{5+}-sublattices, the difference between both cation locations is quantitatively studied by putting a +5 valence cation at both sublattices (i.e., by substituting Nb^{5+} for Li^+, and by substituting Ta^{5+} for Nb^{5+}), respectively. The different ferroelectric properties of both kinds of substituted lithium niobate crystals (i.e., both Li^+- and Nb^{5+}-site substituted single crystals) are comparatively studied, starting from the crystallographic characteristics of these crystals. The substituted lithium niobate crystals with the crystal formulae $[Li_{1-5x}Nb_x\square_{4x}]NbO_3$ and $Li[Nb_{1-y}Ta_y]O_3$ are quantitatively studied in this work. The effect of cation locations on the ferroelectricity of lithium niobate crystals is finally summarized, which shows that the Li^+-site is a sensitive sublattice in the lithium niobate crystallographic frame, and possesses the much stronger effect on the ferroelectricity of lithium niobate crystals. Comparing with the Li^+-site, the Nb^{5+}-site only has a relatively weak effect on the crystal ferroelectricity. The current conclusion agrees well with our previous studies on optical properties of lithium niobate crystals, which clearly shows how such a difference may be employed to modify the ferroelectricity of lithium niobate crystals.

Key words: Lithium niobate, Site locations, Ferroelectricity, Chemical bond

1. INTRODUCTION

Ferroelectric materials are of great interest for various applications with regards to their high permittivities and their large pyroelectric, piezoelectric, electro-optic and nonlinear optical coefficients. The fast development of optoelectronics, acoustoelectronics and photonics demands new materials with improved characteristics. In many cases, the required quality or parameters may be successfully achieved from those well-known materials with respective changes to the cation-site location (by employing the defect control to realize some variations on the defect system of the material) [1]. However, mainly the lack of knowledge on the complicated relationship between the site location (intrinsic and extrinsic defects and their mutual influence and correlation) and physical properties of the material obviously limits our abilities to overcome some drawbacks of the material characteristics in order to make them fit entirely to the specific industrial requirements.

Among ferroelectric materials, lithium niobate with the general crystal formula $LiNbO_3$ (abbreviated as LN) is well known for the unusual richness of its physical properties. Conventional LN crystals, grown from a congruent melt with the Li-deficiency constitution ($C^{Li}_{melt} = C^{Li}_{crystal} \approx 48.4\%$, where the Li-concentration is defined as a mole ratio $C^{Li} = [Li]/([Li]+[Nb])$), contain several percent of intrinsic defects. Many attempts to obtain crystals with low concentrations of intrinsic defects have got some exciting results, which attract many researchers' attention to produce such crystals by different growth techniques and to study their properties [2]. Many new interesting features have been discovered, initiating the booming interest in these materials [2].

Previous work on the effect of the site location on the dielectric properties of LN crystals shows that the Li-site is an active lattice site in the LN crystallographic frame, which plays an important role in improving dielectric properties of LN crystals [3-10]. In this work, we study the effect of the site location on the ferroelectric properties of LN crystals, with the aim to effectively improve their ferroelectric and ferroelectric-related properties.

2. BASIC RELATIONS

The Curie temperature T_c or the spontaneous polarization P_s may generally characterize the degree of the ferroelectricity of materials, due to the fact that both parameters are strongly correlated to the noncentrosymmetricity of the crystallographic structure of materials (which is the basic requirement of ferroelectric structures). Therefore, the values of both T_c and P_s of various LN crystals with the crystal formulae $[Li_{1-5x}Nb_x\square_{4x}]NbO_3$ and $Li[Nb_{1-y}Ta_y]O_3$, will be quantitatively calculated in this work.

The magnitude of P_s in a single crystal is directly related to the atomic displacement Δz that occurs in the ferroelectric reversal and may be calculated from the atomic positions within the unit cell if known. Δz is defined as the displacement of the homopolar cation, i.e. the ion associated with the driving mechanism of the phase transition. An empirical relationship between T_c, P_s and Δz of the displacive ferroelectric materials, was formulated by Abrahams *et al.* [11], which has been widely used and improved for a quantitative calculation or a theoretical prediction of both T_c and P_s of various ferroelectric materials [12,13]. Generally, both T_c and P_s can be universally expressed in terms of Δz by the following two equations [11],

$$T_c = (2.00 \pm 0.09) \times 10^4 (\Delta z)^2 \text{ K}, \qquad (1)$$

$$P_s = (258 \pm 9)\Delta z \times 10^{-2} \text{ Cm}^{-2}, \qquad (2)$$

by which the relationship between the specific substitution at both Li^+- and Nb^{5+}-sites in the LN crystallographic frame and the magnitude of both T_c and P_s can be explicitly stated.

3. RESULTS AND DISCUSSION

At low temperatures (below T_c), the crystallographic structure of LN crystals has been determined to be the space group $R3c$, while above T_c, it changes into the space group $R\bar{3}c$. As shown in Figs. 1 and 2, the crystal structure of LN crystals consists of distorted oxygen octahedra by sharing their common faces or edges, thus forming a trigonal (c-axial) lattice in its crystallographic frame. As shown in Fig. 1, the ideal cation stacking sequence along the trigonal axis of the crystal is ···-Li-Nb-□-Li-Nb-□-···, where □ represents a structural vacancy (an empty octahedron is $\square O_6$). Along the c-axis each octahedron shares its common oxygen planes with the neighboring ones (up and down), however, in the ab plane each octahedron shares its common oxygen edges with six neighboring ones (e.g., one LiO_6 octahedron is surrounded by three NbO_6 octahedra and three $\square O_6$ octahedra, and each NbO_6 octahedron is surrounded by three LiO_6 octahedra and three $\square O_6$ octahedra).
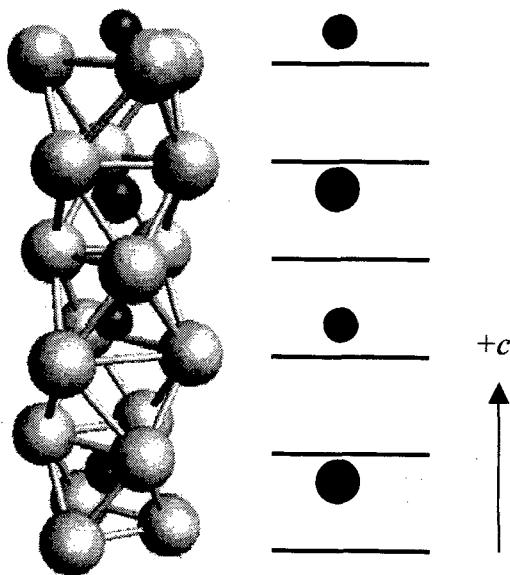

Fig. 1 The schematic drawing of the arrangement of constituent atoms (the details of the atomic stacking and the octahedral linking) in the ideal crystallographic frame of ferroelectric lithium niobate crystals, along the trigonal c-axis. The relative position of constituent atoms (oxygen, niobium and lithium atoms) is schematically described. The horizontal line shows the oxygen layer; the large gray ball represents the oxygen atom; the large black ball represents the niobium atom, and the small black ball represents the lithium atom.
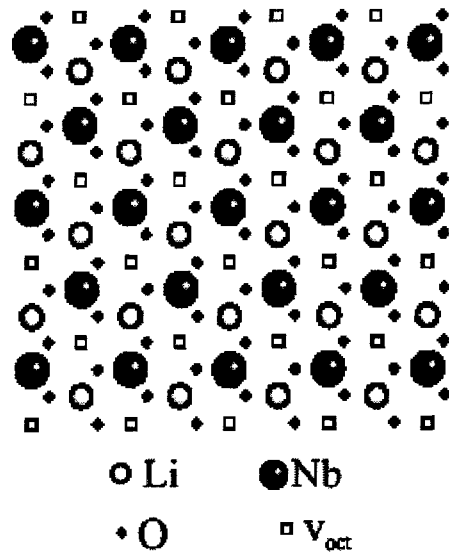

Fig. 2 The ideal lithium niobate lattice at the ab crystallographic plane.

Starting from the measured crystallographic data of lithium niobate crystals at different temperatures [14], we calculate the value of the displacement Δz of the niobium-site in the LN crystallographic frame, which can be expressed as a function of temperature. As shown in Fig. 3, we can see that with increasing temperature, the niobium-site slowly moves down, when the temperature is much lower than its T_c. However, the niobium-site approaches its octahedral center very fast, when the temperature is near its T_c.
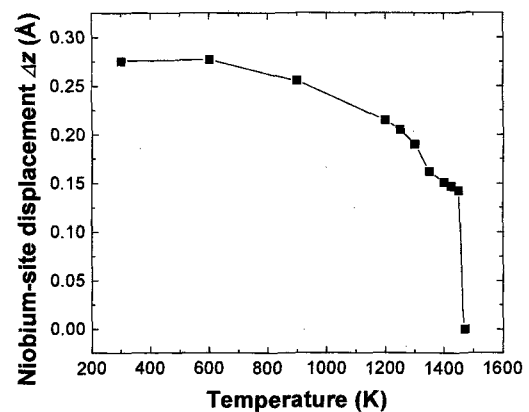

Fig. 3 The displacement Δz of the niobium-site in the lithium niobate crystallographic frame is a function of temperature.

By using Eq. 2, we calculate the value of P_s of LN crystals, at different temperatures. Similarly, the calculated value of P_s can also be expressed as a function of temperature. As shown in Fig. 4, we can find that with increasing temperature, the magnitude of P_s slowly decreases, when the temperature is much lower than its T_c. However, its magnitude very rapidly approaches zero, when the temperature is approaching its T_c. From Fig. 4, we can understand why LN crystals

are always regarded as a type of displacive ferroelectric materials (since people often pay much more attention to the niobium-site in the LN crystallographic frame).
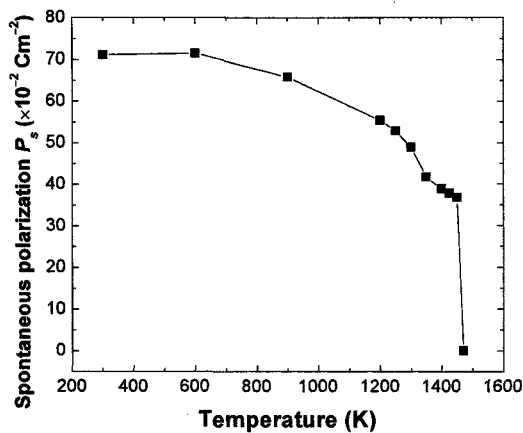

Fig. 4 The spontaneous polarization P_s of the lithium niobate crystal is a function of temperature.

Changes of the magnitude of T_c of crystal materials are very interesting to the crystal growers, due to the important effect on the crystal growth. Therefore, the experimental data of T_c of both [Li$_{1-5x}$Nb$_x\Box_{4x}$]NbO$_3$- and Li[Nb$_{1-y}$Ta$_y$]O$_3$-type crystals are easily available. By using the experimental data of T_c of [Li$_{1-5x}$Nb$_x\Box_{4x}$]NbO$_3$-type crystals [15], we plot Fig. 5 and find a very good linear relationship between T_c and the excess Nb content x. Fortunately, such a linear relationship has been widely used in determining the real crystal composition, when LN single crystals are obtained (by the crystal growers) [2].
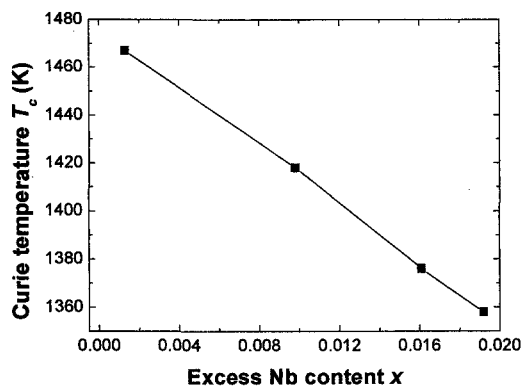

Fig. 5 The Curie temperature T_c of the lithium niobate crystal is a function of the excess Nb content x.

In order to compare the different effect of both kinds of substitutions at the Li$^+$ and Nb^{5+}-sublattices in the LN crystallographic frame (respectively), we plot Fig. 6. In Fig. 6, we can find that the niobium-site substitution leads to a relatively slow change on the magnitude of T_c of Li[Nb$_{1-y}$Ta$_y$]O$_3$-type crystals, while the lithium-site substitution produces a very fast change on the magnitude of T_c of [Li$_{1-5x}$Nb$_x\Box_{4x}$]NbO$_3$-crystals (i.e., leading to a sharpe decrease of the magnitude of T_c).
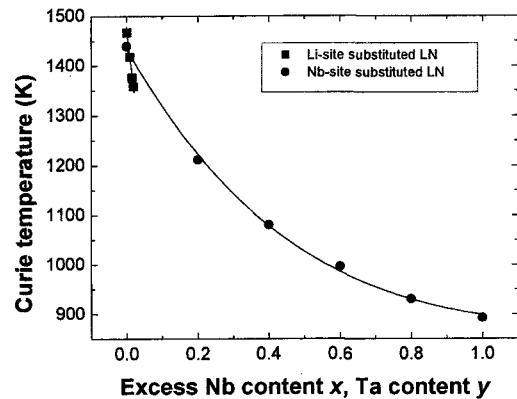

Fig. 6 The Curie temperature T_c of the lithium niobate crystal is a function of the excess Nb content x and the Ta content y.

By using Eq. 1, we can calculate the magnitude of the displacement Δz of the niobium-site in the LN crystallographic frame, if the measured data of T_c of [Li$_{1-5x}$Nb$_x\Box_{4x}$]NbO$_3$-type crystals are used. In Fig. 7, we can find that the magnitude of Δz of the niobium-site in the LN crystallographic frame may be expressed as a linear function of the excess Nb content x. From Fig. 7, we can see that with the increasing excess Nb content x in the LN crystallographic frame, the magnitude of Δz linearly decreases (which means that the niobium-site gradually approaches its octahedral center).
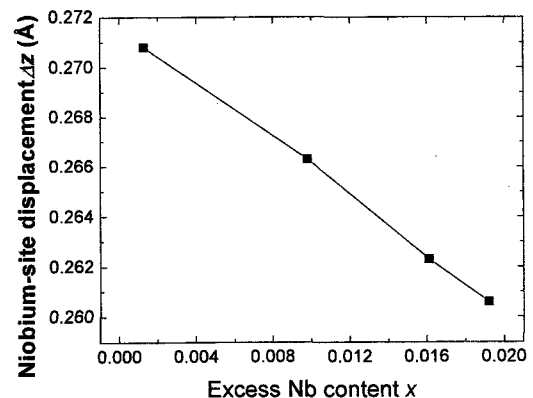

Fig. 7 The displacement Δz of the niobium-site in the lithium niobate crystallographic frame is a function of the excess Nb content x.

Similarly, by using Eq. 1, we can calculate the magnitude of Δz, if the measured data of T_c of Li[Nb$_{1-y}$Ta$_y$]O$_3$-type crystals [16] are used. In Fig. 8, we can find that the magnitude of Δz may be expressed as a non-linear function of the Ta content y. From Fig. 8, we can find that with increasing Ta content y in the LN crystallographic frame, the magnitude of Δz slowly decreases. From Fig. 8, we can see that the lithium-site substitution may give a strong effect on the niobium-site, which makes the niobium-site approach its octahedral center more rapidly.
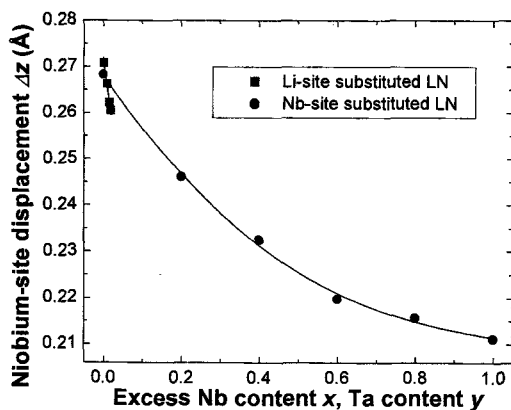
Fig. 8 The displacement Δz of the niobium-site in the lithium niobate crystallographic frame is a function of the excess Nb content x and the Ta content y.

By using Eq. 2, we can calculate the magnitude of P_s of both $[Li_{1-5x}Nb_x\square_{4x}]NbO_3$- and $Li[Nb_{1-y}Ta_y]O_3$-type crystals by using the calculated data of Δz. From Figs. 9 and 10, we can find that the lithium-site can give a much stronger effect on the magnitude of P_s of LN crystals.
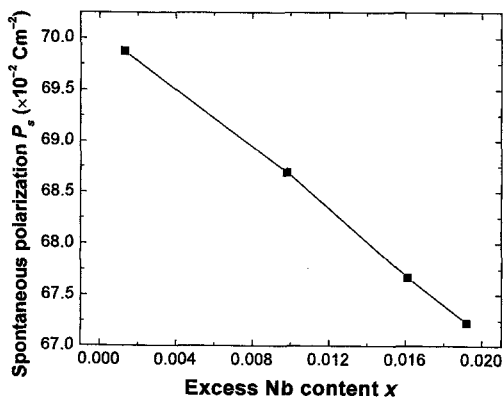

Fig. 9 The spontaneous polarization P_s of the lithium niobate crystal is a function of the excess Nb content x.
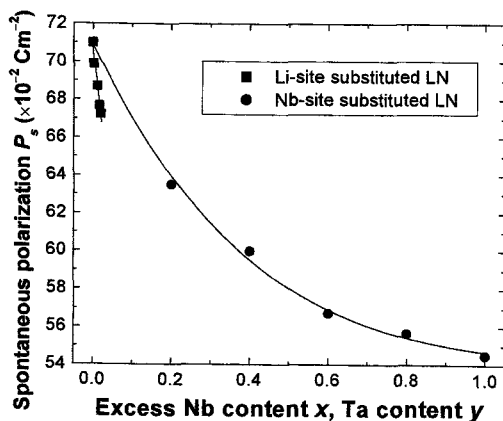

Fig. 10 The P_s of the lithium niobate crystal is a function of the excess Nb content x and the Ta content y.

4. CONCLUSION

Starting from the crystallographic characteristics of ferroelectric LN crystals, the relationship between the cation site location and the ferroelectricity is quantitatively studied. The ferroelectric or ferroelectric-related properties are strongly related to the niobium-site in the LN crystallographic frame, which can be modified by the cation site-substitution at both lithium- and niobium-sites. Since both Li^+ and Nb^{5+} cations have a large displacement away from the centers of their own octahedra, the magnitude of the spontaneous polarization P_s of lithium niobate crystals is thus quite large, about 0.71 Cm^{-2}. Our present work shows that the lithium-site can produce very strong effect on the ferroelectricity of LN crystals, while the niobium-site only has a relative weak effect. The present conclusion is in good agreement with our previous studies on dielectric properties of LN crystals. Therefore, the lithium-site is a suitable location to engineer the ferroelectricity of LN crystals.

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