Transactions of the Materials Research Society of Japan 28 [4] 1191-1194 (2003)

Crystallographic Structure and Ferroelectric Lithium Niobate

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The origin of the ferroelectricity in lithium niobate crystals is studied using the viewpoint of crystal chemistry. On the basis of the crystallographic characteristics of lithium niobate crystals, Pauling's third rule (i.e., Polyhedral Sharing Rule) and the bond-valence sum model are employed with the aim to find the relationship between the crystal structure and the ferroelectricity of lithium niobate crystals. The origin of the ferroelectricity in such ferroelectric crystals as lithium niobate can be ascribed to the face sharing octahedra along the *c*-axis of the crystal. In the lithium niobate crystal, both Li^+ and Nb^{5+} cations in the neighboring and face sharing octahedra repel each other rather strongly, which leads to a large displacement of Li^+ and Nb^{5+} cations away from the centers of their own octahedra towards the neighboring empty octahedra. Since Li–O bonds have a lower bond strength than Nb–O bonds, a net dipole moment results. This work presents us a new sight on the ferroelectric materials designing.

Key words: Lithium niobate, Crystallographic structure, Ferroelectricity, Chemical bond

1. INTRODUCTION

Lithium niobate (normally its crystal formula can be expressed as $LiNbO_3$, even if lithium niobate may include different single crystals with various Li/Nb ratios) is an important ferroelectric crystal, owing to its many applications in optical, electro-optical, and piezoelectric devices [1]. Although some efforts have been made to understand its ferroelectric behavior from fundamental physics [2], the origin of the ferroelectricity in the lithium niobate crystal is still an open and interesting subject for materials scientists. In this work, the viewpoint from crystal chemistry, i.e., some basic ideas starting from macroscopic crystallographic characteristics and microscopic properties of constituent chemical bonds of the lithium niobate single crystal, is employed to understand the origin of the ferroelectricity in lithium niobate crystals.

Generally speaking, crystals are built up of regular arrangements of atoms in three dimensions, these arrangements can be represented by a repeat unit of constituent atoms or ions, which can be understood in terms of *packing*, *linking*, or both. In a certain case, constituent atoms or ions can be approximately regarded as different kinds of spheres; different kinds of *packing* of spheres form different polyhedra, the *linking* of these different polyhedra forms a real crystallographic structure. In the lithium niobate crystallographic frame [3], there are three kinds of constituent octahedra, LiO_6, NbO_6, and $\square O_6$, where $\square$ represents a vacant site. As shown in Figs. 1 and 2 (for the ferroelectric phase of lithium niobate crystals), octahedra sharing faces along the *c*-axis form a helix, while octahedra at the *ab* plane share their common edges. In the present work, we analyze structural characteristics of lithium niobate single crystals with the aim to explain some interesting aspects of their lattice site locations, the ferroelectric origin, etc., which are helpful for us to improve physical properties of such crystals.

In the 1920's and 30's, Linus Pauling investigated the structures of a variety of inorganic compounds and found that an ionic compound always adopts a structure that minimizes the total electrostatic energy. With this in mind, Pauling developed a set of rules, now known as Pauling's Rules [4], which allow us to understand and predict the most stable structures adopted by ionic compounds. On the basis of Pauling's Rules [4], Brown *et al.* developed a useful bond-valence sum (BVS) model [5] that has very wide and successful applications in solid state sciences. In this work, Pauling's Rules and BVS model are applied on the current analysis of the ferroelectric origin in lithium niobate single crystals.

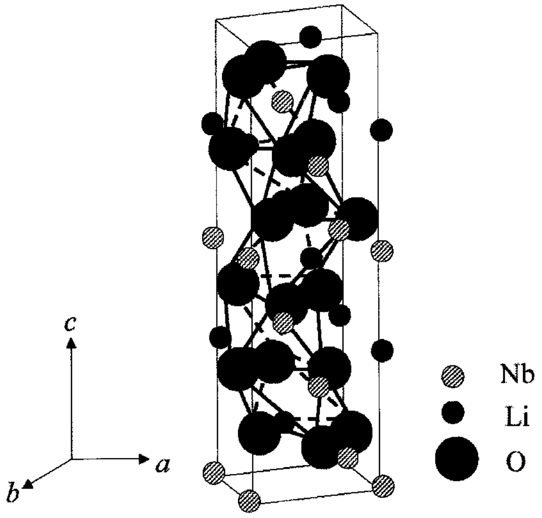

Fig. 1 Crystallographic structure of the lithium niobate single crystal in one hexagonal unit cell.

As well known, the octahedron and tetrahedron are the two dominant cation coordination polyhedra in solid state chemistry. Here we will look at lithium niobate structures as though they are constructed from those octahedral building blocks, which share corners, edges and faces from extended structures. As shown in Fig. 2, the detailed octahedral linking of constituent units in the lithium niobate crystallographic frame is schematically described in three dimensions. Along the *c*-axis direction, the constituent octahedra stack each other by sharing their common faces, the stacking sequence is ... –LiO$_6$–NbO$_6$–□O$_6$–LiO$_6$–.... At the *ab* plane, the constituent octahedra link each other by sharing their common edges, each LiO$_6$ octahedron is surrounded by three NbO$_6$ octahedra and three □O$_6$ octahedra; each NbO$_6$ octahedron is surrounded by three LiO$_6$ octahedra and three □O$_6$ octahedra, each □O$_6$ octahedron is surrounded by three NbO$_6$ octahedra and three LiO$_6$ octahedra. From Fig. 2 we can find that in the three dimensional frame, LiO$_6$ octahedra link each other by sharing their common corners and similarly, NbO$_6$ octahedra link each other by sharing their common corners. Therefore, the lithium niobate structure is an interesting subject to study by Pauling's rules, due to the coexistence of three kinds of octahedral linking in its crystallographic frame.

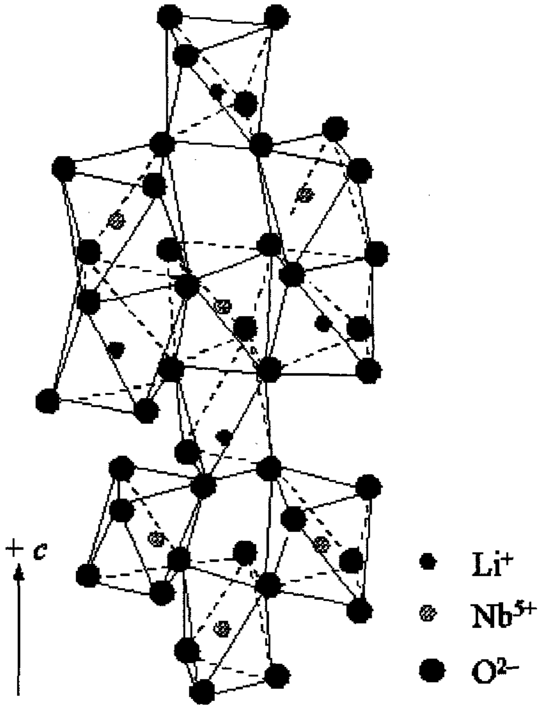

Fig. 2 Schematic drawing of octahedral linking conditions in the lithium niobate crystallographic frame.

Considering the energetic implications of these three sharing cases, we find the cation-cation distance, *M–M*, can be expressed in terms of the cation-anion distances, *M–X*, as shown in Table I. From Table I we can find that sharing faces leads to the shortest *M–M* value, which is the main reason why there is a helix along the *c*-axis as shown in Figs. 1 and 2. In order to decrease the system energy of LiNbO$_3$ (the high system energy comes from the strong interaction between two *M* cations, which locate at two neighboring octahedra with the face-sharing), such a helix including many cationic and anionic displacements plays a tremendous role in this regard, that is, in this helix the distances among Li$^+$, Nb^{5+}, and O^{2-} ions reach a reasonable value (after the lattice relaxation) that keeps the linking of LiO$_6$, NbO$_6$, and □O$_6$ octahedra in a stable way.

According to Coulomb's point of view, two ions with the charges q_i and q_j are separated by a distance, r_{ij}, the corresponding Coulomb potential (electrostatic) energy between both ions can be simply calculated as $E = q_i q_j / 4\pi\varepsilon_0 r_{ij}$, where ε_0 is the permittivity of free space with the value $8.854\times10^{-12}\,C^2/N\cdot m^2$. It can be seen that, sharing edges and faces is less favorable than sharing corners, therefore, in cases of edge and face sharing, it is common for cations to shift away from each other if possible. If all the ions have moved in the same direction, there is a net displacement of electric charge in the crystal, manifested by the crystal having a permanent electrical dipole moment. Such materials are known as *ferroelectrics*. In the case of lithium niobate, both Li$^+$ and Nb^{5+} cations move away from their positions in the paraelectric phase, i.e., from the oxygen planes below them.

2. BASIC RULES AND MODELS

Pauling's third rule (i.e., Polyhedral Sharing Rule – *The existence of edges and particular of faces, common to two anion polyhedra in a coordinated structure decreases its stability; this effect is large for cations with high valency and small coordination number, and is especially large when the radius ratio approaches the lower limit of stability of the polyhedra.*) [4] is helpful for us to understand the octahedral linking of LiO$_6$ and NbO$_6$, the site locations of constituent atoms in lithium niobate crystals. The reason for Pauling's third rule is that sharing of only corners of polyhedra places the positively charged cations at the greatest distance from each other, which can be clearly explained from the viewpoint of Coulomb repulsion, e.g., comparisons of r_{ij} values in Table I.

Table I Comparison of the cation-cation distance, *M–M*, in various types of linking of octahedra, which are expressed in terms of the cation-anion distances, *M–X*. Here *M* = Li and Nb, and *X* = O. These typical data listed are the maximum possible. Reduced distances occur if the octahedra are rotated in various ways [6].

Octahedra linking	Corner sharing	Edge sharing	Face sharing
M–M	2.00 *M–X*	1.41 *M–X*	1.16 *M–X*

In the BVS model [5], all atoms are considered to be cations or anions according to the sign of the oxidation state. All neighboring cation-anion distances (i.e., bond lengths) are considered to be chemical bonds although not all of equal strength. Each bond between atoms *i* and *j* is associated with the bond valence (or bond strength), s_{ij}, which may be related to the length d_{ij} of a given chemical bond (over the limited distance ranges observed for most bonds) by the function form of an inverse exponential or negative power,

$$s_{ij} = \exp[(d_0 - d_{ij})/B], \quad (1)$$

where the parameters d_0 and B are constants fitted empirically, B has frequently been taken as a fixed constant 0.37 [5]. Based on the above expression, the oxidation state contributions are quantitatively apportioned between the metal centers according to the BVS values. The sum of the nearest integers to each BVS value for a structure is equal to the total of the metal oxidation states, V_i, i.e.,

$$V_i = \sum_j s_{ij}. \quad (2)$$

The oxidation state or ionic charge, and the bond valence are measured in the valence unit (abbreviated as v.u.), which formally correspond to units of electronic charge, though the actual charges may be smaller. Expression (2) necessarily holds for sums around both the anions and the cations.

3. RESULTS AND DISCUSSION

By employing the BVS model on the lithium niobate crystal, we find that the bond strength $s_{\text{Li-O}} \approx 1/6$ v.u. for those Li–O bonds in the LiO_6 octahedron, and $s_{\text{Nb-O}} \approx 5/6$ v.u. for those Nb–O bonds in the NbO_6 octahedron. Further, the valence or the oxidation state of constituent atoms in the lithium niobate crystal can be calculated as, $V_{\text{Li}} \approx 1.0$ v.u., $V_{\text{Nb}} \approx 5.0$ v.u., and $V_{\text{O}} \approx 2.0$ v.u.. As shown in Figs. 2 and 3, the basic structure unit of lithium niobate crystals may be regarded as the perfect octahedra without any distortion, the distortion is formed by their different linkages when they stack each other in the crystallographic frame. The chemical bonding structure and the corresponding bond strength of the perfect LiO_6 and NbO_6 octahedra are schematically described in Fig. 3.

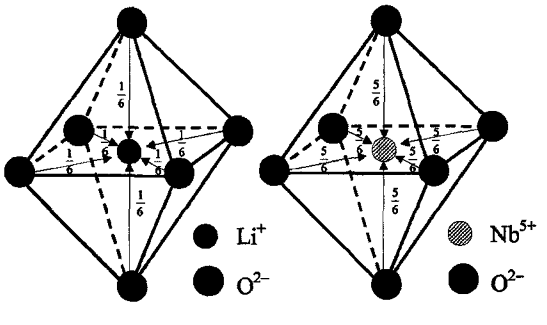

Fig. 3 Basic structure units (perfect MO_6 octahedra, LiO_6 and NbO_6), for constructing the crystallographic frame of lithium niobate crystals. The numbers labeled on the M–O (M = Li and Nb) bonds are theoretical data for the bond strength s (in a valence unit, v.u.), which shows how strong the interaction between two constituent ions (M and O) in the corresponding chemical bond M–O. The arrow shows an attractive interaction between two bonded ions M and O.

In Fig. 4 a real structure unit is schematically taken from the lithium niobate crystallographic frame, the BVS model is also employed on this unit. From Fig. 4 we can find that both Li and Nb atoms are bonded weakly to the common oxygen face, while they are bonded strongly to both end oxygen faces. The bond length data also show that both Li and Nb atoms leave each other towards both end oxygen faces, at the same time, they also leave their own octahedral centers, respectively.

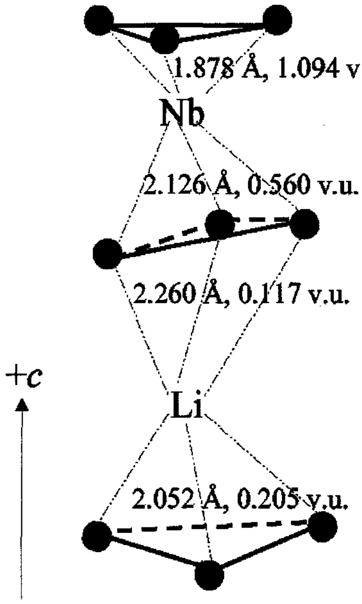

Fig. 4 A NbO_6-LiO_6 periodical part is schematically taken from the lithium niobate crystallographic frame, at room temperature, there is a $\square O_6$ octahedron above and below it, respectively. Chemical bonding behaviors of both Nb and Li atoms in the LiO_6 and NbO_6 octahedra are described using their respective bond length and bond strength data. There are two types of constituent M–O bonds in each MO_6 octahedron (M = Li and Nb), three longer M–O bonds and three shorter M–O bonds. The bond length is in the unit of Å, the bond strength is in the unit of valence.

In Fig. 5 we can see that both Li^+ and Nb^{5+} move away each other along the c-axis, Li^+ and Nb^{5+} cations are all moving toward the adjacent vacant octahedra, therefore, this vacant site is a useful buffer for Li^+ and Nb^{5+} cations to balance their strong interaction. The strong interaction is due to the face sharing octahedra along this direction. All numbers labeled in Fig. 5 are derived from corresponding crystallographic data measured at room temperature [7]. Owing to the weak bond strength of Li–O bonds compared with Nb–O bonds, Li^+ cations move much farther (away from the octahedral center) than Nb^{5+} cations. Fig. 5 also gives us a useful clue that this vacant site (the so called structural vacancy) is not available for any dopant (the impurity cation), therefore, which is not available for the structure modification of physical properties of lithium niobate crystals by occupying this vacant site. For the materials engineering of lithium niobate crystals, the available lattice site that may be used to dope guest cations in the lithium niobate crystallographic frame is both Li and Nb sites. The creation of a spontaneous ferroelectric polarization P_s in lithium niobate crystals is a direct consequence of the lattice relaxation, i.e., the relative movement of oxygen anions and cations in the crystal lattice.

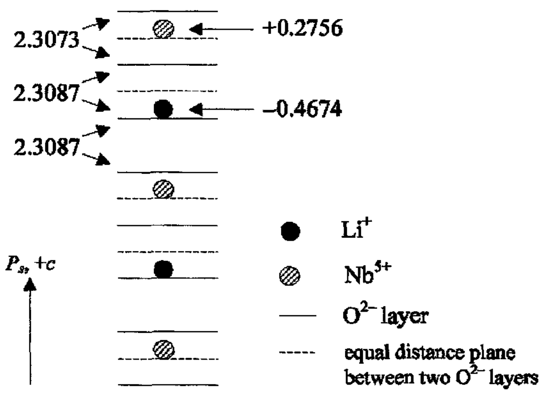

Fig. 5 Relative positions of constituent ions: Li$^+$, Nb^{5+}, and O^{2-} in the lithium niobate crystallographic frame, at room temperature. The numbers on the left side represent distances between two adjacent O^{2-} layers, the numbers on the right side represent distances above (with + sign) or below (with − sign) the equal distance plane between two adjacent O^{2-} layers (i.e., the plane across the octahedral center). Since all cations are moving along the *c*-axis, the spontaneous polarization P_s is thus along the *c*-axis.

In our newly finished work [8], we proposed a theoretical model to describe the crystallographic structure and the crystal growth of lithium niobate crystals, which can be validated by the available experimental study in this regard [9]. From this model we can find that high quality single crystals should be grown from the melt along the *c*-axis, since the growth speed is the lowest one among all possible directions. The low growth speed is directly due to the face sharing of constituent octahedra along the *c*-axis, which thus leads to the strongest interaction in this direction. The stacking of constituent octahedra along this direction is therefore much more difficult than others.

In the recent structural study of liquid lithium niobate by neutron diffraction [9], the presence of clusters (the grouping of NbO_6 octahedra) is confirmed. Both regular and irregular NbO_6 octahedra are observed in the liquid near solidification. With its high mobility in the melt (owing to the relatively weak bond strength between Li$^+$ and O^{2-} ions, as shown in Fig. 3), the Li atom plays an important role in the clustering. In fact, it is quite hard to form a stable crystallographic frame for constituent polyhedra by sharing faces, according to Pauling's third rule. However, owing to a serious relaxation of crystal lattices, which finally balances lattice sites of constituent ions, thus produces the spontaneous ferroelectric polarization P_s of lithium niobate crystals and those with similar crystal structures as $LiNbO_3$, such as $LiTaO_3$.

4. CONCLUSION

Macroscopic characteristics of the lithium niobate crystallographic structure below T_c and microscopic properties of the chemical bonding of constituent atoms of the lithium niobate crystal, are qualitatively and quantitatively studied, respectively. Pauling's rules and the BVS model of solids are employed in this work, by which the octahedral linking and the chemical bonding in the lithium niobate crystallographic frame are studied. The origin of the ferroelectricity of lithium niobate family crystals is from the common face sharing along the *c*-axis, the direction of the P_s is thus along the *c*-axis. The present work shows that the vacant site is not available for any cation due to its buffer function in the lithium niobate crystallographic frame, which greatly reduces the strong interaction (mainly the repulsion) between Li$^+$ and Nb^{5+}. Due to the weaker bond strength of Li–O bonds compared with that of Nb–O bonds, the Li-site may be easily used to modify physical properties of lithium niobate crystals by doping guest cations. The present work gives a further analysis on the structure-property relationship study of lithium niobate family crystals, which is definitely useful for the materials engineering of such crystals.

Acknowledgement: The Japan Society for the Promotion of Science (JSPS) is thanked for all financial support.

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(Received December 20, 2002; Accepted January 31, 2003)