

Li K-Edge XANES Spectra of Lithium Niobate and Lithium Tantalite

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Abstract. The x-ray emission with the single crystal of lithium niobate (LiNbO_3) or lithium tantalite (LiTaO_3) by thermal changes in a vacuum system is closely concerned with the electronic state of each crystal. Therefore, lithium K-edge x-ray absorption near edge structures (XANES) spectra of these materials were measured in the region from 50 eV to 90 eV by means of total electron yield method (T.E.Y.), using the extremely soft x-ray. Samples were powder of lithium carbonate (Li_2CO_3) and single crystal of lithium fluoride (LiF), LiNbO_3 and LiTaO_3 in order to compare the shapes of these XANES spectra. Various peak structures appear in these spectra in the range from 55 eV to 80 eV and each spectrum has different shapes as a result of the difference of bond length and bond angles for the atoms which are in less than 60 nm from the absorbing atom. The relationship between these spectra and the electronic states was discussed by FEFF 8.

Keywords: LiTaO_3 , Li K-edge, XANES, total electron yield, FEFF

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INTRODUCTION

LiNbO_3 and LiTaO_3 are famous ferroelectric materials and have been used in industrial applications such devices as modulators, SAW filters and sensors. In recent years, the x-ray emission from pyroelectric crystal induced by thermal changes in a vacuum system was first reported and has been investigated by Brownridge [1-3]. The Amptek corporation developed portable x-ray source such as Cool-X [4]. Our groups have also systematically investigated the x-ray emission with ferroelectrics. In our experiments [5-8], not stoichiometric lithium tantalite (SLT) and lithium niobate (SLN), but congruent lithium tantalate (CLT) and lithium niobate (CLN) were used in consideration of their electrical characteristics. It was found that the main factor of x-ray emission at high vacuum pressure is closely related to the phenomenon generally called electron emission from ferroelectrics (FEE) [9]. Comparing SLT and CLT for the amount of the x-ray emission at high vacuum pressure, i.e., the amount of FEE, the x-ray emission with CLT will be much generated unlike that with SLT. It seems that FEE is concerned with the electronic state closely. And then, detailed single-crystal x-ray structure analysis of CLT was carried out from 269 K to 473 K far below the

phase transition (~ 930 K) for elucidating the mechanism of the x-ray emission and theoretical calculations of electronic states of CLT. As a result, the lattice parameter 'a' and the unit cell volume 'V' show a linear increase with temperature, however, the lattice parameter 'c' is almost constant with slight changes except for 269 K [5].

It is generally recognized that XANES is very sensitive to unoccupied levels in many cases. So, first of all, we try to measure Li K-edge XANES spectra of congruent LiNbO_3 , congruent LiTaO_3 and the other compounds to evaluate the electronic state of Li ions in the region from 50 eV to 90 eV by T.E.Y method in the present work. Though Sonntag, Tsuji et al. and others have reported Li K-edge XANES spectra of various lithium compounds [10,11], the Li K-edge XANES spectra of LiNbO_3 and LiTaO_3 have not been reported in the past papers. And the experimental XANES spectrum of LiTaO_3 was compared with the theoretical spectrum which was obtained by the FEFF 8 self-consistent potential full multiple scattering calculations.

EXPERIMENTAL

The Li K-edge XANES spectra were measured at the beam line 2 (BL2) at SR Center of Ritsumeikan University. Each XANES spectra were corrected by T.E.Y. method. The beam current was about 300mA at the maximum.

Samples were the powder of Li_2CO_3 and the single crystals of LiF , LiNbO_3 and LiTaO_3 in order to compare the shapes of these Li K-edge XANES spectra. The powder sample was mounted on the first dynode of the photomultiplier detector with the carbon adhesive tape and the crystal samples were mounted on the aluminum plate with the carbon adhesive tape. The emitted photoelectrons were captured by the photomultiplier detector, which was set at the position to each sample (Figure 1).

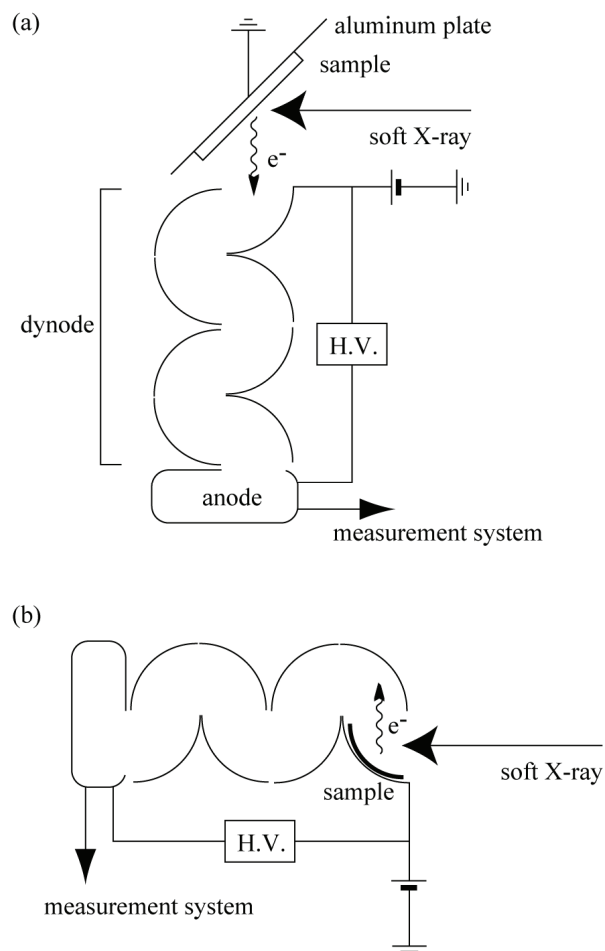


FIGURE 1. The position of the sample and the photomultiplier detector; (a) crystal (b) powder.

RESULTS AND DISCUSSION

The Li K-edge XANES spectra of LiF , Li_2CO_3 , LiTaO_3 and LiNbO_3 were measured. In these experiments of LiNbO_3 and LiTaO_3 , it was very difficult to obtain the XANES signal because of the absorption of heavy elements. Especially in LiNbO_3 , the background was not able to be removed well because of the noise around 60eV. It is necessary to remeasure the spectrum of LiNbO_3 . Figure 2 shows the lithium K-edge XANES spectra of LiF , Li_2CO_3 , LiTaO_3 and LiNbO_3 . The spectral intensity was normalized by the peak of each spectrum. Various peak structures appear in these spectra in the range from 55 eV to 80 eV and each spectrum has different shapes as a result of the difference of bond length and bond angles for the atoms which are in less than 60 nm from the absorbing atom. The energy shifts of the Li K-edge of each lithium compounds were seen.

The lithium K-edge XANES spectrum of LiTaO_3 was compared with the theoretical spectra by FEFF8 package. The details about FEFF 8 were described in previous report [12]. The following data was used on the FEFF calculation: the space group of LiTaO_3 crystal was R3c below the Curie temperature ($T_c \sim 900$ K), the lattice parameters at 303 K were $a = 0.5151$ (nm) $c = 1.3774$ (nm) and atomic positional parameters were listed in Table 1.

TABLE 1. Atomic positional parameters of LiTaO_3 at 303 K	
	(<i>x</i> , <i>y</i> , <i>z</i>)
Li	(0.0000, 0.0000, 0.2883)
O	(0.0497, 0.3447, 0.0695)
Ta	(0.0000, 0.0000, 0.0000)

The spectra obtained by the experiment and the calculation were well in agreement, although there were some different points (FIGURE 3). This showed that FEFF 8 was useful method in evaluating XANES spectrum of LiTaO_3 in future. And about each component, it is under consideration now.

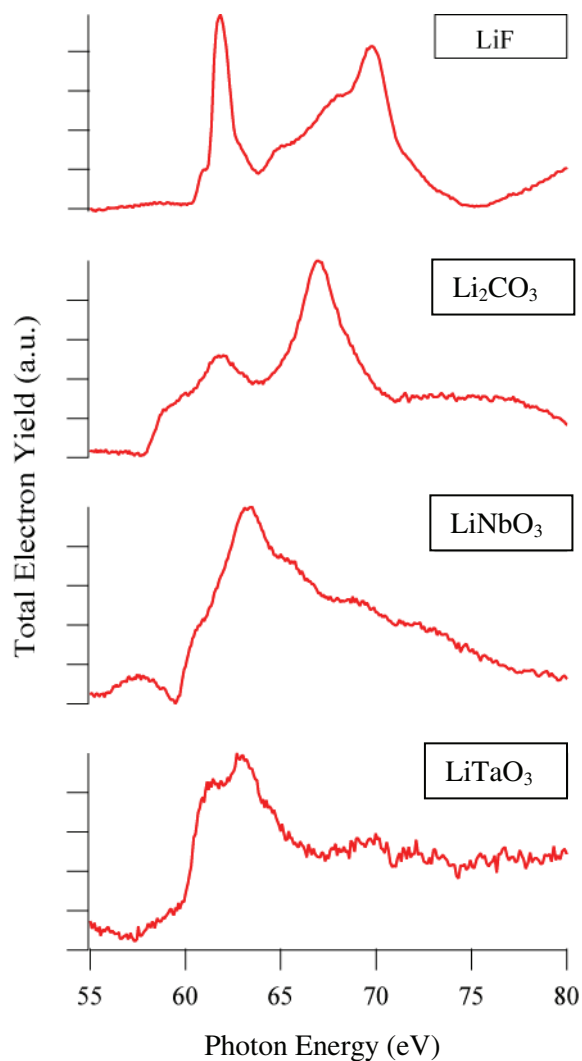


FIGURE 2. Li K-edge XANES spectra of LiF, Li_2CO_3 , LiTaO_3 and LiNbO_3 .

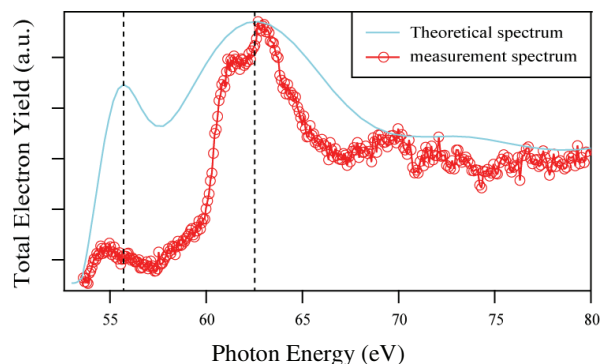


FIGURE 3. Comparison between the experimental and theoretical K-edge XANES spectrum of LiTaO_3 .

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