

CHAPTER 4

RESULTS AND DISCUSSIONS

In this chapter, the x-ray absorption spectra analysis results of perovskite oxide compounds are described in details i.e. x-ray absorption edge identification of atomic oxidation state of doping atom, x-ray absorption near edge structure (XANES) verification of local structure geometry around doping atom and extended x-ray absorption fine structure (EXAFS) extraction of local structure information around doping atom.

In the partial substitution of other atoms into oxide compounds, oxidation state, atomic position and local structure (coordination number and radial distribution of neighboring atoms) around the doping atoms are very important to understand and control the effect of the doping atom on the electric properties of materials. In this research, XANES and EXAFS analysis, i.e. the local structure distortion of Mn-doped $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) ceramics and Mn-doped $((\text{K}_{0.5}\text{Na}_{0.5})_{0.935}\text{Li}_{0.065})\text{NbO}_3$ (KNNL) ceramics, and the local structure configuration and the formation behavior of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ (PZN) ceramic, were carried out.

4.1 Mn-doped BLT

Lanthanum-doped bismuth titanate ($\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ or BLT) has been gain in attentions due to its excellent fatigue resistance behavior, with the possible application as ferroelectric random access memories (FeRAMs) [23-25]. However, its current ferroelectric properties are still insufficient for the application of high-density FeRAMs because BLT has low remnant polarization and large coercive field [26-28]. Recently, there was an attempt in substituting Mn in BLT to improve its ferroelectric properties [29, 30], but the underlying description of why ferroelectricity improves is still left opened. Therefore, the local structure of BLT especially around Mn atom is believed to be in fulfilling essential the gap. In this section, x-ray absorption spectroscopy (XAS) was used to investigate local structure around absorbing Mn atom. The information of microscopic local structure is expected to be useful to explain the role of Mn atom in

BLT, and tell how the ferroelectric properties improve. This knowledge can be used to improve the preparation method (e.g. information of doping atom, doping ratio and doping synthesis conditions) to obtain more efficient electronic devices.

4.1.1 Crystal structure of Mn-doped BLT

In this thesis, Mn-doped $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (MnO_2 content = 0, 0.01, 0.03, 0.05, 0.07, 0.09 and 0.10 mol) ceramics were synthesized by solid state reaction procedure. More details of the samples preparation are described in elsewhere [31]. To verify the global crystal structure, x-ray diffraction patterns were measured using Philips PW 1729 diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation at room temperature. The x-ray diffraction patterns (Figure 4.1) well match with ICDS No. 150091 database, which indicates orthorhombic phase in space group $Aba2$.

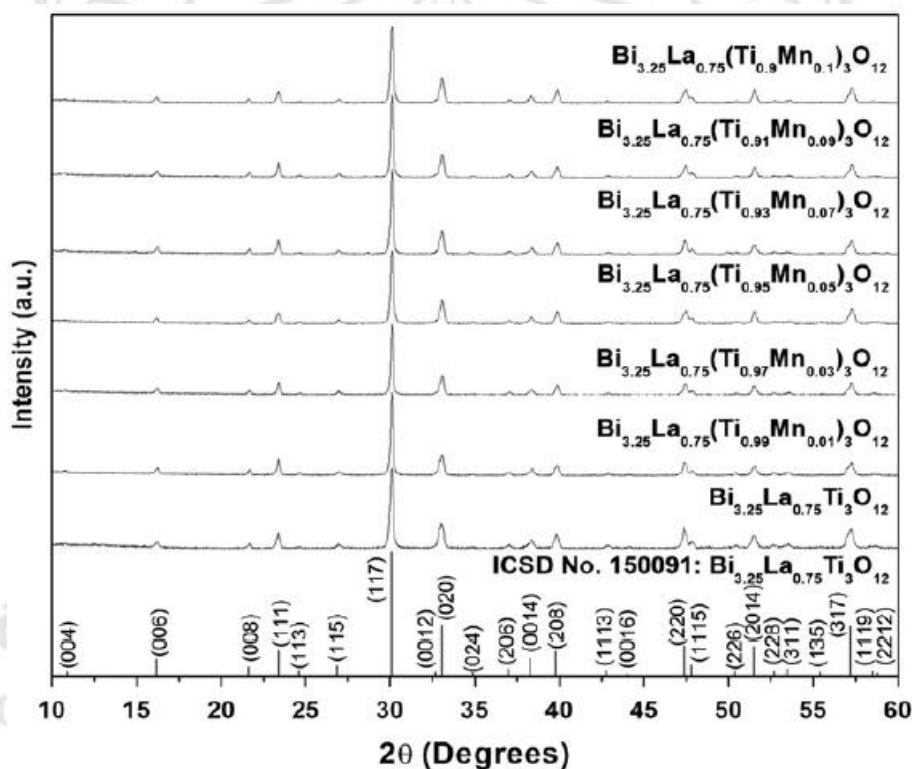


Figure 4.1 The x-ray diffraction pattern of Mn-doped $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramics with various MnO_2 dopants match with ICDS No. 150091 database, which indicates orthorhombic phase in space group $Aba2$ [31].

The orthorhombic structure of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramic is shown in Figure 4.2. Constituent atoms mostly deviate along the three axes of the tetragonal structure. The

Bi_2O_2 layers and TiO_6 octahedron in the perovskite units are distorted and the TiO_6 octahedron along the c -axis is buckled. These displacements are the main cause of the remnant polarization of BLT at room temperature [32].

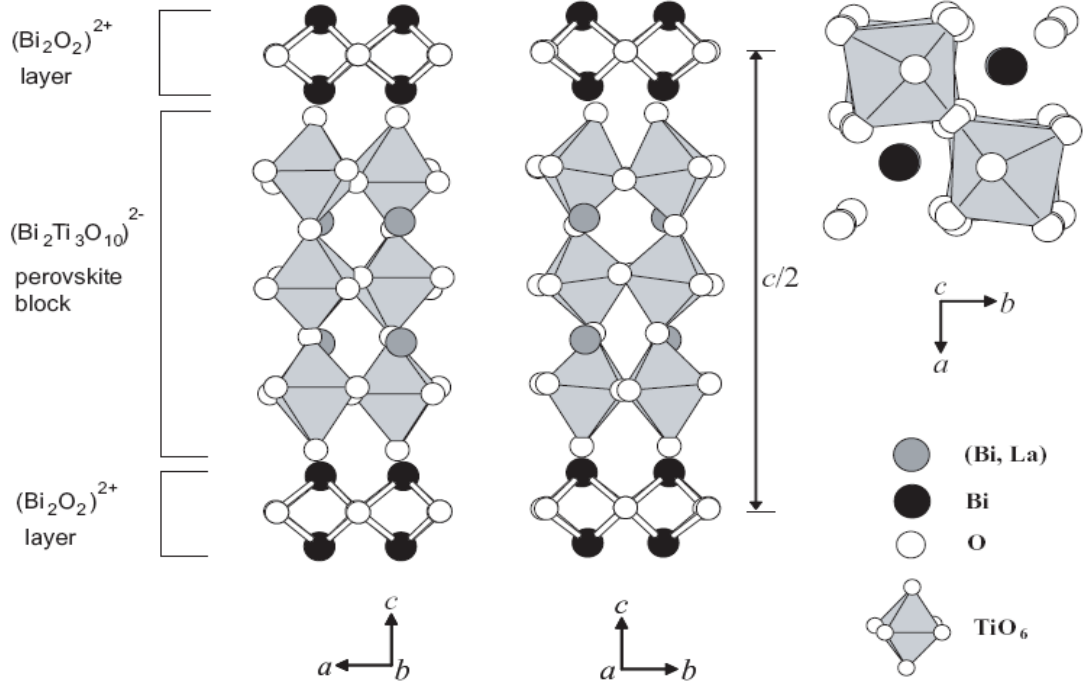


Figure 4.2 The orthorhombic structure of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ceramic [32].

In x-ray diffraction pattern, there is no evidence that Mn atom remains in MnO_2 or associated in BLT. Then, the atomic position of orthorhombic $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ host-structure (Table 4.1) was used to create the starting model for the microscopic local structure for the x-ray absorption spectroscopy analysis. The atomic position of Mn atom in the sample was verified by XANES analysis, and then the radial distribution around Mn atom was extracted from EXAFS analysis.

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Table 4.1 Atomic coordinates and Wyckoff positions of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ in space group *Aba2* [32], where the symbol *g* is occupation factor.

Atoms	Wyckoff position	Atomic coordinate			<i>g</i>
		<i>X</i>	<i>y</i>	<i>z</i>	
<i>Bi1</i>	<i>4a</i>	0.0559	0.5030	0.5667	0.87
<i>La1</i>	<i>4a</i>	0.0559	0.5030	0.5667	0.13
<i>Bi2</i>	<i>4a</i>	0.0530	0.4863	0.7104	1.0
<i>Ti1</i>	<i>4a</i>	0.0756	0.0073	0.5008	1.0
<i>Ti2</i>	<i>4a</i>	0.0880	0.0048	0.6261	1.0
<i>O1</i>	<i>4a</i>	0.3014	0.2908	0.5048	1.0
<i>O2</i>	<i>4a</i>	0.3222	0.2519	0.2500	1.0
<i>O3</i>	<i>4a</i>	0.1048	-0.0623	0.5584	1.0
<i>O4</i>	<i>4a</i>	0.0767	0.0586	0.6813	1.0
<i>O5</i>	<i>4a</i>	0.3269	0.2630	0.6093	1.0
<i>O6</i>	<i>4a</i>	0.3823	-0.2146	0.6226	1.0
<i>Bi3</i>	<i>4a</i>	0.0557	0.4913	0.4321	0.37
<i>La2</i>	<i>4a</i>	0.0557	0.4913	0.4321	0.63
<i>Bi4</i>	<i>4a</i>	0.0445	0.5180	0.2879	1.0
<i>Ti3</i>	<i>4a</i>	0.0793	0.0031	0.3691	1.0
<i>O7</i>	<i>4a</i>	0.3732	-0.2170	0.4924	1.0
<i>O8</i>	<i>4a</i>	0.3199	-0.2431	0.7503	1.0
<i>O9</i>	<i>4a</i>	0.1189	0.0423	0.4401	1.0
<i>O10</i>	<i>4a</i>	0.0822	-0.0329	0.3171	1.0
<i>O11</i>	<i>4a</i>	0.3282	-0.2653	0.3839	1.0
<i>O12</i>	<i>4a</i>	0.3650	0.2214	0.3768	1.0

4.1.2 Local structure of Mn-doped BLT

The Mn and Ti *K*-edge x-ray absorption spectra of the sample and its standards were measured at Beamline 8, Synchrotron Light Research Institute (SLRI), Thailand, with the storage ring running at energy of 1.2 GeV and current of 120-80 mA. These spectra were collected in the fluorescence mode with 13-element germanium detector at room temperature. These multiple scan spectra were recorded and merged after performing an absolute energy calibration. The normalized spectra were obtained by subtracting the background and set the pre-edge jump height as unity. More details of the normalization procedure can be found in elsewhere [33]. The Mn and Ti *K*-edge x-ray absorption spectra were analyzed using the IFEFFIT package [15, 16].

To identify the oxidation state of Mn atom, the absorption edge position of the samples were compared with their standards. Note that valence state is useful to predict the atomic environment around Mn atom. To further verify the predicted position of Mn atom in the structure, the program ATOMS was used to generate atomic position of model structure. After that, with the supplied structure information, the program FEFF was used to compute XANES spectra based on ab initio self-consistent multiple scattering calculations. The comparisons between the measured and calculated XANES spectra were then used to confirm the atomic position of Mn atom in model structure. After that, EXAFS Fourier transform of Mn *K*-edge in Mn-doped BLT was compared with that of Ti *K*-edge of BLT in *r*-space, to demonstrate the radial distributions of neighboring atoms around Mn atom.

4.1.2.1 Oxidation state of Mn in BLT

The absorption edge energies of Mn *K*-edge XANES spectra were used to verify oxidation state of Mn atom. The Mn *K*-edge XANES spectra of Mn-doped BLT ceramics were compared with MnO (Mn^{2+}), Mn_2O_3 (Mn^{3+}) and MnO_2 (Mn^{4+}) standards (Figure 4.3). The absorption edge energies (at the half of normalized edge height) of the higher oxidation states shift to the higher energies due to the lower density of states. From the same absorption edge energy shift, it can be implied that the doping Mn atom also has oxidation state equal to MnO_2 (Mn^{4+}) standard. The atomic environment of Mn^{4+} atom was then considered using the feature of XANES spectra, which were derived from backscattering of the emitted photoelectron. As can be seen in Figure 4.3, the feature of Mn-*K*-edge XANES spectra of Mn-doped BLT inconsistent with that of MnO_2 standard, indicate that Mn^{4+} vanishes from MnO_2 but being associated in BLT.

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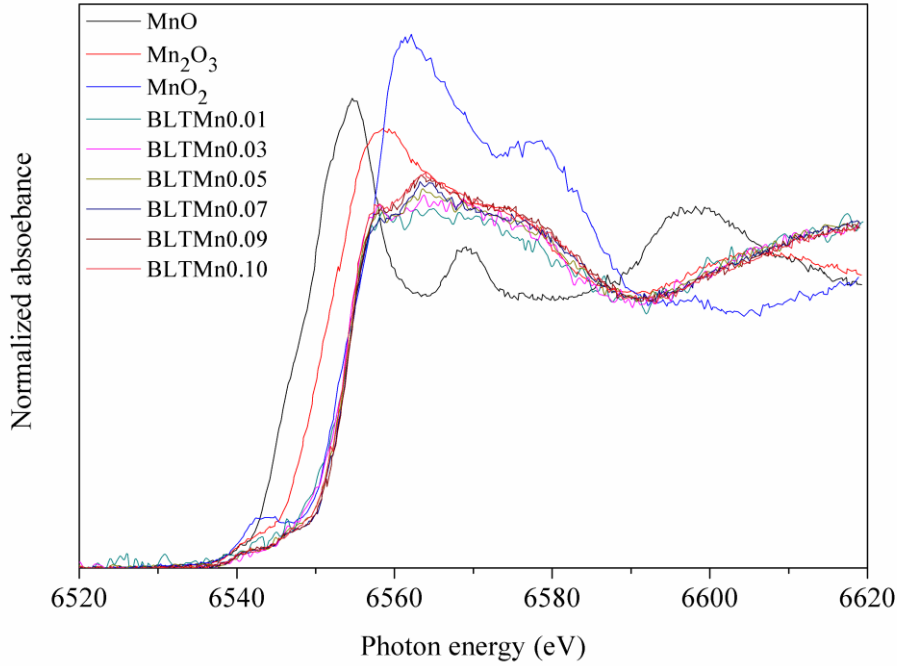


Figure 4.3 The Mn-K-edge XANES spectra of Mn-doped BLT ceramics compared with MnO, Mn₂O₃ and MnO₂ standards [34].

4.1.2.2 Atomic position of Mn in BLT

To further identify the atomic position of Mn⁴⁺ atom in BLT, Mn K-edge XANES spectra were simulated with Mn⁴⁺ atom at different locations based on the orthorhombic BLT [32]. The atomic position of Mn substituting on Bi/La site (Mn_{Bi/La}), Mn substituting on Ti site (Mn_{Ti}), and Mn substituting on interstitial (Mn_i) were generated using ATOMS code. With the supplied structure information, the program FEFF was used to compute XANES spectra based on ab initio self-consistent multiple-scattering calculations. The spherical cluster size of electron wave function was increased until the spectra converged. The self-consistent calculations were performed in a cluster radius of 5.2 Å (about 40 atoms) around the absorbing Mn atom. The full-multiple scattering calculations included all possible paths within a larger cluster radius of 7.5 Å (about 140 atoms) around the absorbing Mn atom. From the direct comparison with the measured Mn K-edge XANES features, the measured XANES is consistent with the calculation of Mn⁴⁺ on Ti⁴⁺ site (Figure 4.4), but inconsistent with Mn at other locations (not shown). This confirms that Mn⁴⁺ substituting on Ti⁴⁺ site in perovskite unit, due to the same oxidation state and the proximate ionic radius. Moreover, the consistent with slight

deform features between measured and calculated XANES of Mn^{4+} substituting on Ti^{4+} site indicates the slight distortion of sample structure.

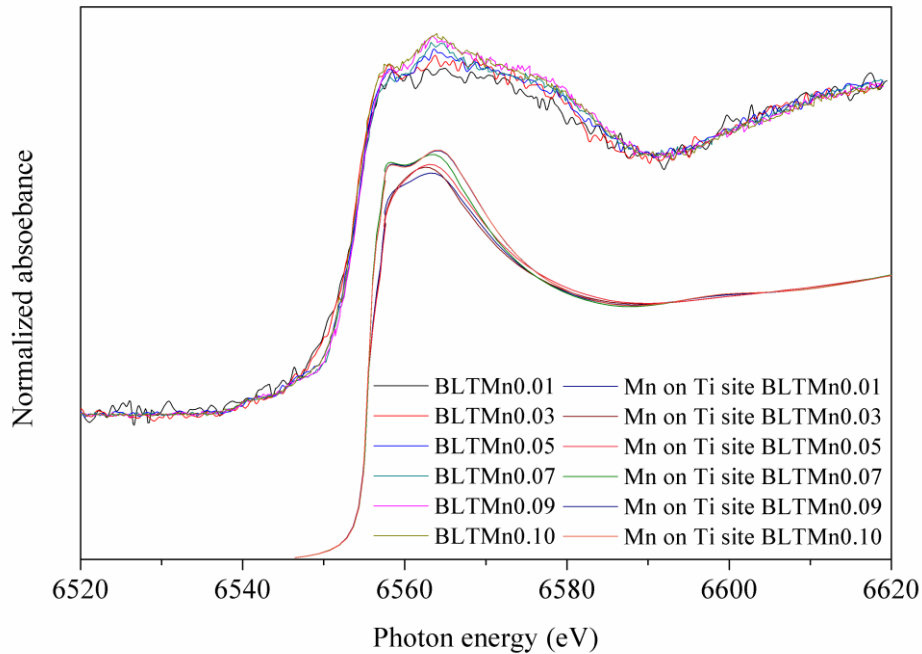


Figure 4.4 The measured and calculated Mn K-edge XANES spectra with Mn^{4+} substituted on Ti^{4+} site in BLT [34].

4.1.2.3 Atomic distortions around Mn in BLT

The radial distributions of the neighboring atoms around the absorbing Mn atom with the different Mn-doping contents were demonstrated by EXAFS analysis. From the substitution of Mn^{4+} on Ti^{4+} site, EXAFS Fourier transform of Mn K-edge in Mn-doped BLT and Ti K-edge in BLT were compared in r -space (Figure 4.5). For TiO_6 octahedral site in BLT, the average radial distances of Ti^{4+} and O^{2-} is about 1.49 and 1.89 Å in ab -axis, and about 2.22 Å in c -axis [32]. Therefore, for Ti K-edge EXAFS Fourier transform in BLT, the first and second shells are presented by the backscattering of emitted photoelectron between Ti^{4+} and O^{2-} in ab -axis, while the third shell is presented by the backscattering of emitted photoelectron between Ti^{4+} and O^{2-} in c -axis. Otherwise, for Mn K-edge EXAFS Fourier transform in Mn-doped BLT, the first and second shells combine and radial distances of Mn^{4+} and O^{2-} in ab -axis are shorter than those of BLT, and the third shell shifts and radial distances of Mn^{4+} and O^{2-} in c -axis are longer than those of BLT with increasing Mn-doping content. This means that the

average radial distances of Mn^{4+} and O^{2-} ions in ab -axis are almost the same and decrease with increasing Mn-doping content, due to that Mn^{4+} has ionic radius smaller than that of Ti^{4+} . From Mn^{4+} and O^{2-} radial distances decreasing in ab -axis, Mn^{4+} and O^{2-} radial distances in c -axis are then longer to decrease electric force. This is a strong evidence that Mn-doping atom plays an important role in reducing the orthorhombicity, which increases the polarization domains size and enhances remnant polarization, speeds up the polarization domains movement and lessens coercive field [35, 36]. This result is in good agreement with previous studies [37, 38]. However, when Mn-doping concentration exceeds 0.10 mol, the oxygen vacancies are generated by structural distortion, polarization domains separating and remnant polarization is decreased [39].

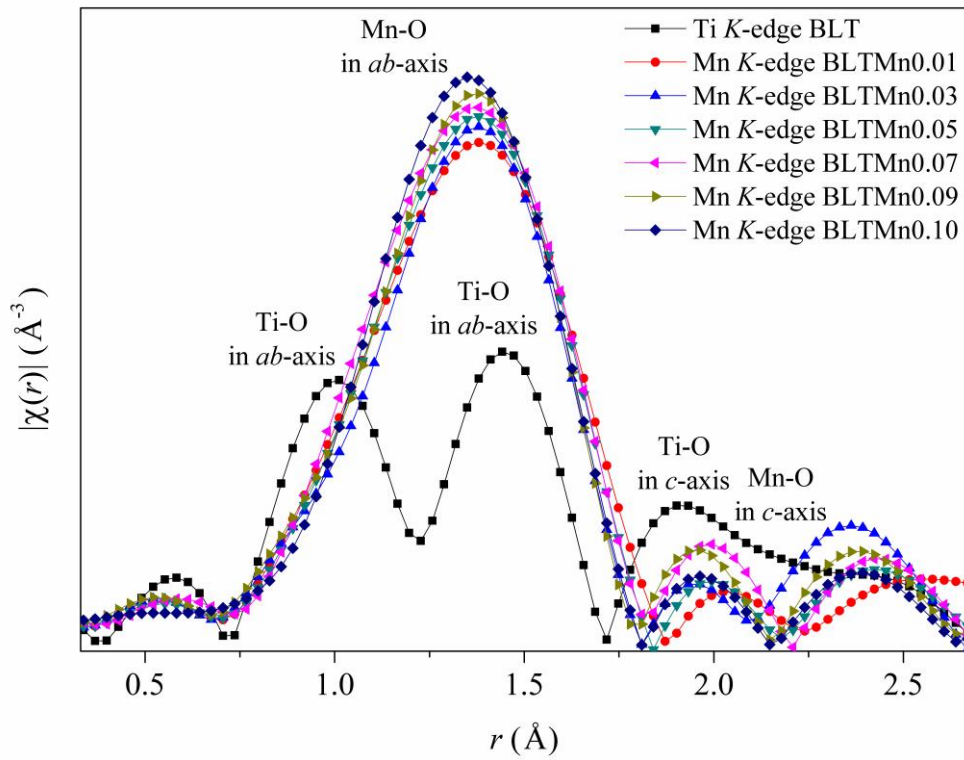


Figure 4.5 The comparison of Mn K-edge in Mn-doped BLT and Ti K-edge in BLT EXAFS Fourier transform in r -space [34].

4.2 Mn-doped KNNL

Potassium sodium niobate ((K,Na)NbO₃ or KNN) has been receiving great attentions in substituting the widely used lead zirconate titanate (Pb(Zr,Ti)O₃ or PZT) in high performance electronic applications [40, 41]. This is as lead and its associated compounds pollute the environment and are harmful to human. However, KNN still has

especially synthesis problem. Then, lithium-doped potassium sodium niobate ($((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$ or KNNL) has been synthesized to transform from an orthorhombic to a tetragonal phase [42]. Additionally, there was an attempt in substituting MnO_4 in KNNL to improve its ferroelectric properties, but the underlying description of why ferroelectricity improves is still left opened. Therefore, the local structure of KNNL especially around Mn atom is believed to be in fulfilling essential the gap. In this section, the x-ray absorption spectroscopy (XAS) was analyzed in combination with the density functional theory (DFT) calculation to demonstrate the local structure around Mn atom. The information of microscopic local structure will be useful to explain the role of Mn atom in KNNL on the ferroelectric properties improvement. This knowledge can be used to improve the preparation method (e.g. information of doping atom, doping ratio and doping synthesis conditions) to obtain more efficient electronic devices.

4.2.1 Crystal structure of Mn-doped KNNL

In this thesis, Mn-doped $((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$ (MnO_2 content = 0.25, 0.50, 1.00 and 1.50 mol%) ceramics were synthesized by conventional mixed-oxide method. More details of the samples preparation are described in elsewhere [43]. The phase formation was analyzed by x-ray diffraction patterns, using Philips PW 1729 diffractometer with Ni-filtered CuK_{α} radiation at room temperature. The x-ray diffraction patterns (Figure 4.6) indicate the formation of tetragonal phase in space group $P4mm$.

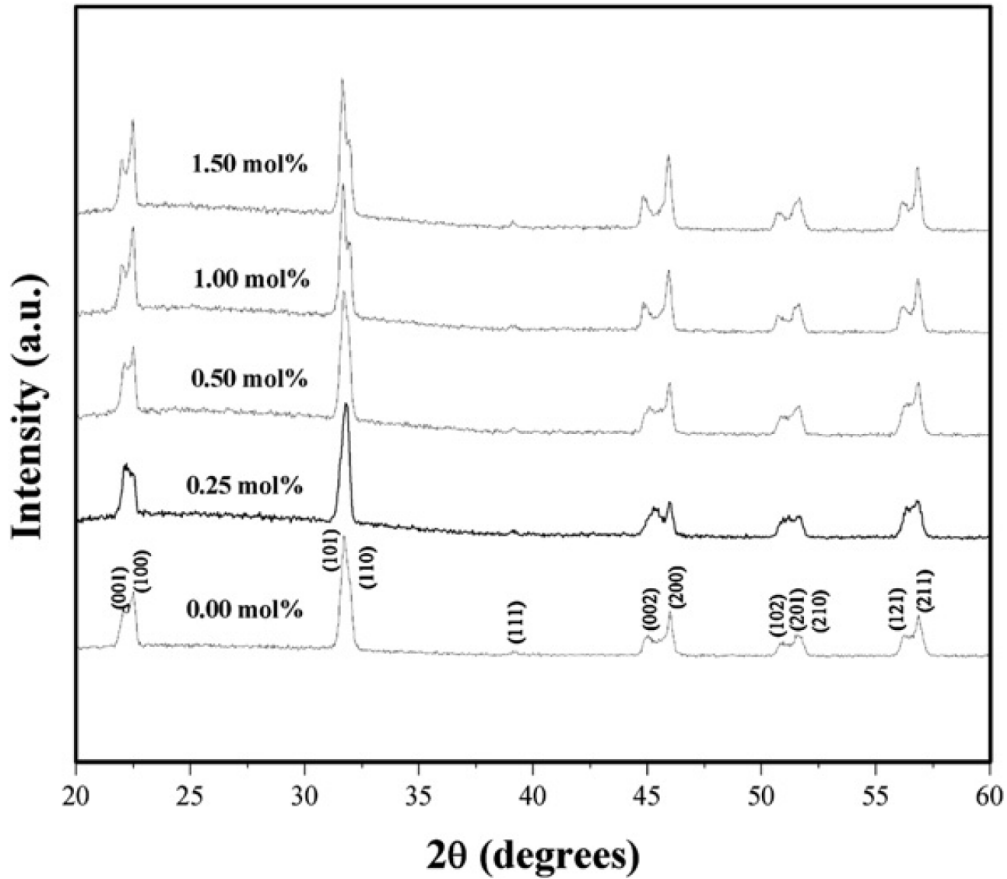


Figure 4.6 The x-ray diffraction patterns of Mn-doped $((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$ ceramics with various MnO_2 dopants indicate the formation of tetragonal phase in space group $P4mm$ [43].

The atomic position of tetragonal $(K_{0.3}Na_{0.7})NbO_3$ host-structure was used to create the starting model for the microscopic local structure for the x-ray absorption spectroscopy analysis. In x-ray diffraction pattern, there is no evidence that Mn atom remains in MnO_2 or associated in KNNL. Then, the atomic position of Mn atom in the sample was verified by XANES analysis, and the radial distribution around Mn atom was extracted from EXAFS analysis.

4.2.2 Local structure of Mn-doped KNNL

The Mn K -edge x-ray absorption spectra of the samples were measured at Beamline 8, Synchrotron Light Research Institute (SLRI), Thailand, with the storage ring running at energy of 1.2 GeV and current of 120-80 mA. These spectra were collected in the fluorescence mode with 13-element Ge detector at room temperature.

The spectra ranging for 6400 to 6900 eV were recorded in step-by-step mode. To increase the signal-to noise ratio, 10 spectra were recorded and merged after performing an absolute energy calibration. The normalized spectra were obtained by subtracting the background and set the pre-edge jump height as unity. More details of the normalization procedure can be found in elsewhere [33]. The Mn *K*-edge EXAFS were analyzed using the IFEFFIT package [15, 16].

To identify the oxidation state of Mn atom, the absorption edge position of the samples were compared with their standards. Note that this valence state is useful to predict the atomic environment around Mn atom. To further identify the predicted position of Mn atom in the structure, the program ATOMS was used to generate atomic position of model structure. After that, with the supplied structure information, the program FEFF8.2 was used to compute XANES spectra based on ab initio self-consistent multiple scattering calculations. The comparison between the measured and calculated XANES spectra used to identify the atomic position of Mn atom in model structure. After that the local structural distortion around the substituting Mn was extracted base on the density functional theory (DFT) using Quantum-Espresso package [44]. The structural model was taken from a tetragonal ($K_{0.3}Na_{0.7}$)NbO₃ host-structure [45]. After the structural relaxation, the extended x-ray absorption fine structure (EXAFS) was used to reveal local structure of these dilute doping structures using DFT calculation as a structural relaxation guideline.

4.2.2.1 Oxidation state of Mn in KNNL

The absorption edge energies of Mn *K*-edge XANES spectra were used to verify oxidation state of Mn atom. The Mn *K*-edge XANES spectra of Mn-doped BLT ceramics were compared with MnO (Mn²⁺), Mn₂O₃ (Mn³⁺) and MnO₂ (Mn⁴⁺) standards (Figure 4.7). The absorption edge energies (at the half of normalized edge height) of the higher oxidation states shift to the higher energies due to the lower density of states. From the same absorption edge energy shifts, it can be implied that Mn atom also has oxidation state equal to Mn₂O₃ (Mn³⁺) standard. The atomic environment of Mn³⁺ atom was then extracted using the feature of XANES spectrum, which was derived from backscattering of the emitted photoelectron. As can be seen in Figure 4.7, XANES

features of Mn-doped KNNL are inconsistent with that of MnO_2 standard, which indicates that Mn^{3+} vanishes from MnO_2 but instead being associated in KNNL.

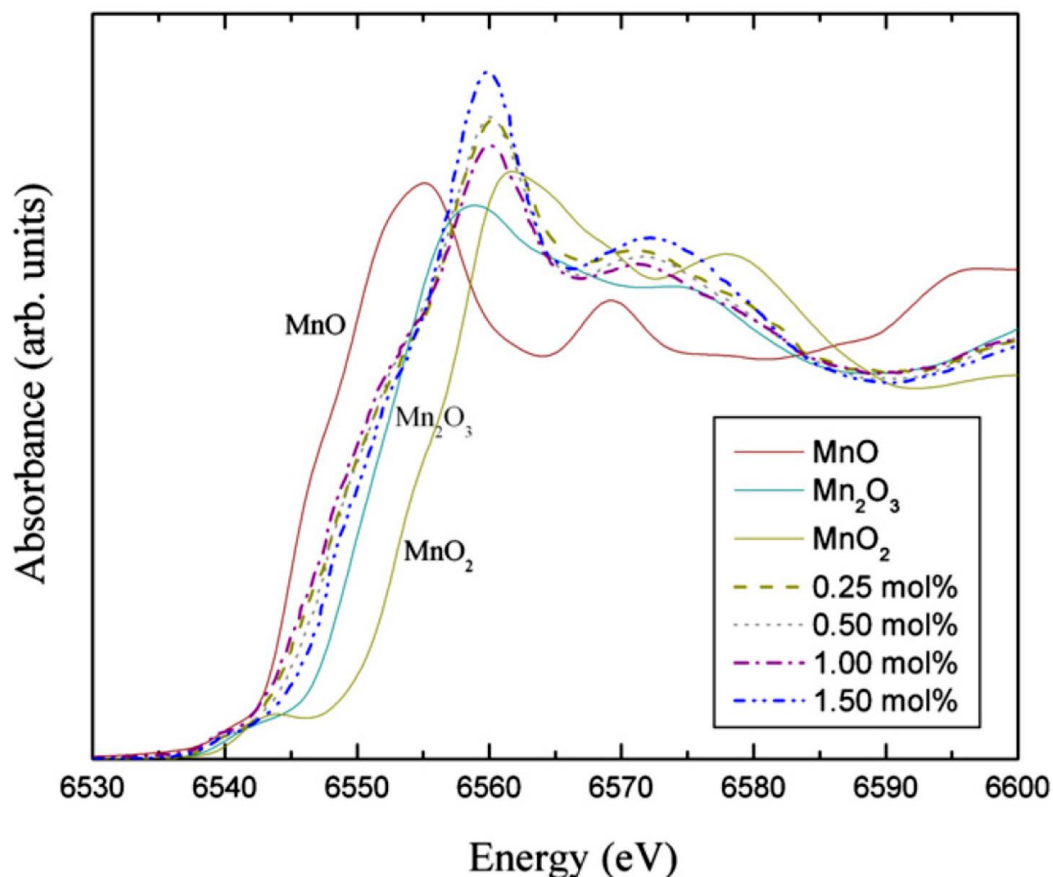


Figure 4.7 The Mn-K-edge XANES spectra of Mn-doped KNNL ceramics compared with MnO , Mn_2O_3 and MnO_2 standards [43].

4.2.2.2 Atomic position of Mn in KNNL

To further identify the atomic position of Mn^{3+} atom in KNNL, Mn K-edge XANES spectra were simulated with Mn at different locations based on the orthorhombic BLT. The atomic position with Mn substituting on K/Na/Li site ($\text{Mn}_{\text{K/Na/Li}}$), Mn substituting on Nb site (Mn_{Nb}), and Mn substituting on interstitial (Mn_i) were generated using ATOMS code. With the supplied structure information, the program FEFF was used to compute XANES spectra based on ab initio self-consistent multiple-scattering calculations. The spherical cluster size of electron wave function was increased until the spectra converged. The self-consistent calculations were performed in a cluster radius of 5.2 Å (about 40 atoms) around the absorbing Mn

atom. The full-multiple scattering calculations included all possible paths within a larger cluster radius of 7.5 Å (about 140 atoms) around the absorbing Mn atom. From the direct comparison with the measured Mn *K*-edge XANES features, the measured XANES is clearly consistent with the calculation of Mn³⁺ on Nb⁵⁺ site (Figure 4.8) and inconsistent with Mn other (not shown). This confirms that Mn³⁺ substituting on Nb⁵⁺ site in perovskite unit, due to the same oxidation state and the proximate ionic radius [46].

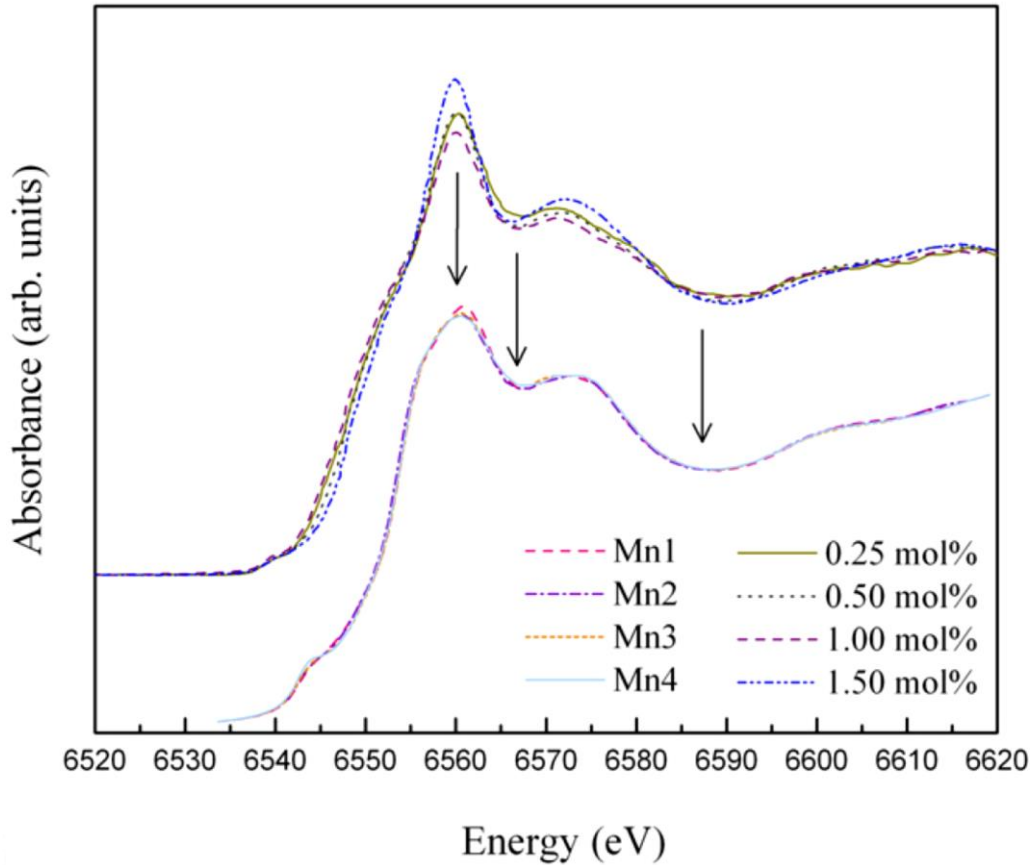


Figure 4.8 The measured and calculated Mn *K*-edge XANES spectra with Mn³⁺ substituted on Nb⁵⁺ site in KNNL [43].

4.2.2.3 Atomic distortions around Mn in KNNL

To investigate the effect of MnO₂ doping on local structure of ((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO₃ ceramics, the local structural distortion around the substituting Mn was calculated based on the density functional theory (DFT) using Quantum-Espresso package. The structural model was based on tetragonal (K_{0.3}Na_{0.7})NbO₃ host-structure (Figure 4.9(a)). The 3×3×3 supercell was constructed

with two lithium substituted on both sodium and potassium site i.e. $((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$. As the doping Mn atom changes its oxidation state from Mn^{4+} in MnO_2 to Mn^{3+} and substitutes on the Nb^{5+} in octahedral site, one manganese was substituted on one niobium site in the supercell, so there were a total of 90 atoms in one supercell, i.e. 8 potassium, 8 sodium, 2 lithium, 17 niobium and 54 oxygen atoms. However, the oxygen vacancy showed also generated in octahedral site due to the substituting of different oxidation states between Mn^{3+} and Nb^{5+} . Therefore, there are three possible structural models i.e. one oxygen vacancy in *ab*-axis, one oxygen vacancy in *c*-axis and no oxygen vacancy in octahedral site. In the structural relaxation, the exchange correlation energy functional was calculated using the generalized approximation (GGA). Only valence electrons were considered explicitly while core electronic states were represented via ultrasoft pseudo-potentials. The plane wave cut-off energy was set to 78 Ry and the Monkhorst-Pack grid consisted of $2 \times 2 \times 2$ points in Brillouin zone. The atomic positions of all atoms were allowed to vary to minimize the total energy and convergence was marked when the difference in total energies between the successive iterations is less than 10^{-4} Ry, while the lattice parameters were allowed to vary from the x-ray diffraction experimental value.

From the structural relaxation of $((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$ (Figure 4.9 (b)), the bond lengths between Nb^{5+} and O^{2-} in octahedral cell increases in *ab*-axis, due to that Li^+ has ionic radius smaller than those of Na^+ and K^+ ($r(Li^+) = 0.92 \text{ \AA}$, where $r(Na^+) = 1.18 \text{ \AA}$ and $r(K^+) = 1.51 \text{ \AA}$) [46] situated on A-site. Then, the bond lengths between Nb^{5+} and O^{2-} in *c*-axis changes and reduces electric force. From the structural relaxation of Mn-doped $((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$ (Figure 4.9 (c)), with the minimization of total energy, one oxygen vacancy presents in the longest bond length between Mn^{3+} and O^{2-} in *c*-axis, due to the weak bonding. Further, the bond lengths between Mn^{3+} and O^{2-} in both *ab*- and *c*-axis decrease due to Mn^{3+} has ionic radius smaller than that Nb^{5+} ($r(Mn^{3+}) = 0.58 \text{ \AA}$ and $r(Nb^{5+}) = 0.64 \text{ \AA}$) [46] in B-site. However, to calculate the structural distortion for the dilute Mn-doped $((K_{0.5}Na_{0.5})_{0.935}Li_{0.065})NbO_3$ with MnO_2 content = 0.25, 0.50, 1.00 and 1.50 mol%, the supercell has to be at least 20 Å in size (covering about 625 atoms). Furthermore, the atomic positions of each atom in the supercell need to be varied due to the possible lattice distortion caused by Mn^{3+} substitution and O vacancy. Therefore, how to effectively use DFT calculation to relax

these dilute doping structures is not trivial. Therefore, the EXAFS analysis was then used to demonstrate local structure of these dilute doping structures using DFT calculation as only a structural guideline.

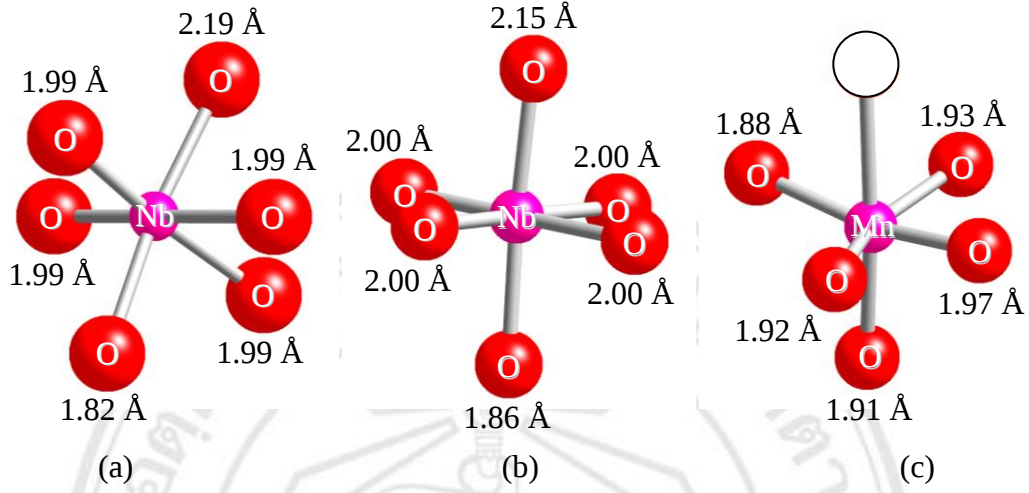


Figure 4.9 The relaxed octahedral structure of (a) $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$, (b) $((\text{K}_{0.5}\text{Na}_{0.5})_{0.935}\text{Li}_{0.065})\text{NbO}_3$ and (c) Mn-doped $((\text{K}_{0.5}\text{Na}_{0.5})_{0.935}\text{Li}_{0.065})\text{NbO}_3$ [47].

The radial distributions of the neighboring atoms around the absorbing Mn atom with the different Mn-doping contents were demonstrated by EXAFS analysis. The EXAFS Fourier transform of Mn K -edge in Mn-doped KNNL were compared in r -space (Figure 4.10). From Mn^{3+} octahedral site relaxation in KNNL, the average radial distances between Mn^{3+} and O^{2-} is about 1.92 Å. For Mn K -edge EXAFS Fourier transform in KNNL, the first and the second shells are presented by the backscattering of emitted photoelectron between Mn^{3+} and O^{2-} in both ab - and c -axis. It was found that the second shells shift which indicate shorter Mn^{3+} and O^{2-} radial distances with increasing Mn-doping contents. This means that the radial distances of Mn^{3+} and O^{2-} in both ab - and c -axis are more approximate and decrease with increasing Mn-doping contents, due to Mn^{3+} has ionic radius smaller than that of Nb^{5+} . From oxygen vacancies in the longest bond length between Mn^{3+} and O^{2-} in c -axis, the polarizations in opposite direction are produced and increased their polarization domains size, due to the approximate bond length between Mn^{3+} and O^{2-} in octahedral site with increasing Mn-doping contents. This is strong evidence that Mn-doping plays an important role in producing the polarization domains with opposite direction, which diminish remnant

polarization and decrease coercive field. This result is in good agreement with previous studies [48, 49].

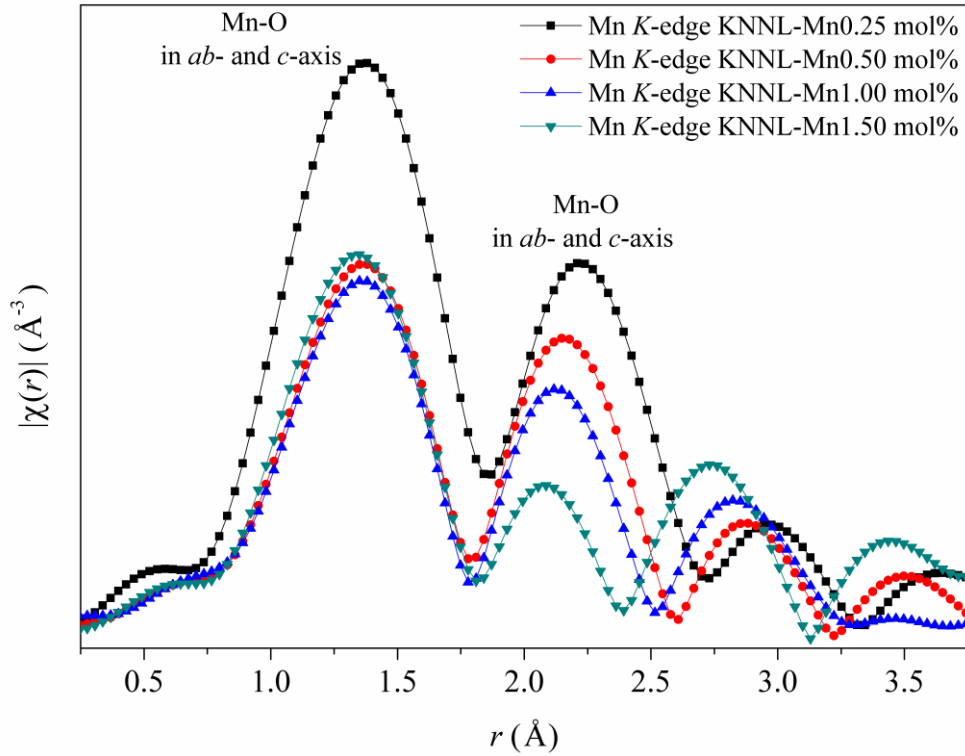


Figure 4.10 The Mn *K*-edge EXAFS Fourier transforms in *r*-space of Mn-doped KNNL with the different MnO₂ contents [47].

4.3 Lead Zine Niobate

Recently, much attention has been directed toward lead-based relaxor ferroelectric compounds with perovskite structure due to their excellent dielectric, piezoelectric and electrostrictive properties [50, 51]. They have been used as multilayer capacitor, actuator and transducer applications [52, 53]. However, these utilizations have some limitations, in particular on the reproducible preparation method for pure perovskite phase with consistent properties. It is well known that a single crystal of pure perovskite lead-based ferroelectric can be grown by the flux method [54]. Nevertheless, this method requires extremely complicated production techniques and expensive facilities, which is impractical in preparing a large amount of inexpensive practical uses. The conventional mixed-oxide method, known as simple and low cost to obtain usable quantities, is routinely used to synthesize pure perovskite phase ceramic [55]. Nevertheless, some lead-based ceramics cannot be synthesized by this method. The *B*-

site oxide precursor method is useful for producing the perovskite structure with higher amount of perovskite phase than that the conventional mixed-oxide method [56] or the columbite precursor method can produce. For instance, the *B*-site method can be used to produce pure perovskite phase of some lead-based ferroelectric ceramics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [57] and $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [58]. This is not, however, the case for $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [59]. The cubic pyrochlore phase, that is highly detrimental to dielectric and piezoelectric properties, has always been obtained via the methods mentioned above. Therefore, it is of great interest to investigate the instability, especially from the microscopic local structural distortion viewpoint. As a result, if the knowledge of how to enhance the stabilities of the perovskite phase is comprehensively obtained, one can therefore design applicable processing route in avoiding the pyrochlore phase and acquiring the pure perovskite phase. Consequently, this work employs a combination of the experimental x-ray absorption spectroscopy and the theoretical first-principles calculation to give more insight into the local structure configuration and the formation behavior in lead zinc niobate material.

From the information of microscopic local structure, the first-principles calculation can be employed to obtain the total energy and explain the atomic interactions within the local structural formation, to seek for the cause of the instability of the perovskite phase in lead zinc niobate material. This fundamental understanding of the total energy and structural distortion relationship can then be used as a guideline how to improve the preparation of perovskite lead zinc niobate ceramic with desired electrical properties.

4.3.1 Crystal structure of PZN

In this work, lead zinc niobate ceramic was synthesized by *B*-site precursor ($\text{Zn}_3\text{Nb}_2\text{O}_8$) mixed-oxide synthetic route. More details of the sample preparation were described elsewhere [60]. To verify the global crystal structure, x-ray diffraction pattern was measured using Philips PW 1729 diffractometer with Ni-filtered CuK_α radiation at room temperature. The x-ray diffraction pattern (Figure 4.11) indicates the formation of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ phase in matching with JCPDS file number 34-0374, which is cubic pyrochlore structure with cell parameter $a = 10.60 \text{ \AA}$ in space group $Fd\bar{3}m$.

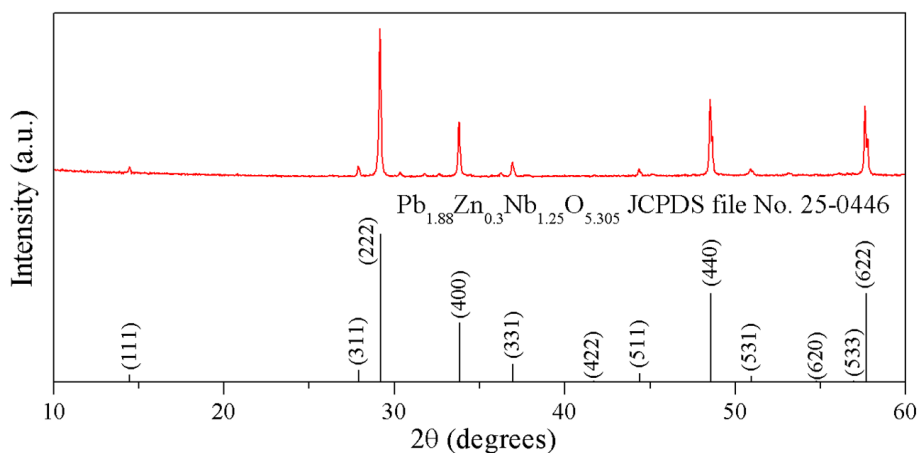


Figure 4.11 The x-ray diffraction pattern indicates the formation of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ phase in matching with JCPDS file number 34-0374, which is cubic pyrochlore structure with cell parameter $a = 10.60 \text{ \AA}$ in space group $Fd3m$.

The typical cubic pyrochlore $A_2B_2O_7$ structure (Figure 4.12) can be viewed as a framework of two types of cation-oxygen geometries. The corner sharing tetrahedral network composed of A atoms with $O1$ atom in the center of each tetrahedron that form cages filled with the corner sharing octahedral network composed of $O2$ atoms with B atom in the center of each octahedron.

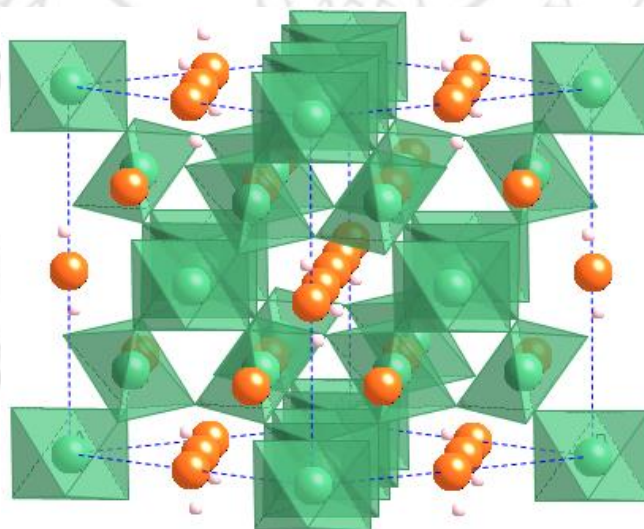


Figure 4.12 The structure of typical cubic pyrochlore $A_2B_2O_7$ with rings of BO_6 octahedral in green, A cations in orange and non-polyhedral oxygens in pink.

The atomic position of the typical cubic pyrochlore $A_2B_2O_7$ (Table 4.2) was used to create the starting model for subsequent refinement of the microscopic local structural configuration for the x-ray absorption spectroscopy analysis. In the typical cubic pyrochlore structure, it is known that $Pb_2Nb_2O_7$ has Pb on A-site and Nb on B-site. However, for $Pb_{1.83}Zn_{0.29}Nb_{1.71}O_{6.39}$, the substituting Zn site is yet to be experimentally elucidated. In this work, the atomic position of Zn atom in the sample was verified by XANES analysis, and then the radial distribution around Zn atom was extracted from EXAFS analysis.

Table 4.2 Atomic coordinate and Wyckoff position of $A_2B_2O_7$ in space group $Fd3m$ [61].

Atoms	Wyckoff position	Atomic coordinate		
		<i>x</i>	<i>y</i>	<i>z</i>
<i>A</i>	16 <i>d</i>	0.5	0.5	0.5
<i>B</i>	16 <i>c</i>	0	0	0
<i>O1</i>	48 <i>f</i>	0.3	0.125	0.125
<i>O2</i>	8 <i>d</i>	0.375	0.375	0.375

4.3.2 Local structure of PZN

The x-ray absorption spectra were measured at Beamline 8, Synchrotron Light Research Institute, Thailand, with the storage ring running at energy of 1.2 GeV and currents ranging from 120 to 80 mA. These spectra were recorded in the fluorescence mode with 13 Ge detectors at room temperature. The Zn *K*-edge of both XANES and EXAFS spectra were experimentally collected. These multiple scanned spectra were recorded and merged after performing an absolute energy calibration. The normalized spectra were obtained by first subtracting the spectra with the pre-edge jump height and later normalizing to unity. More details of the normalization procedure can be found elsewhere [33]. These Zn *K*-edge spectra were analyzed using the IFEFFIT package [15, 16]. Note that the XANES simulation was first performed to identify the qualitative picture of atomic position of the substituted Zn in the sample. After that, the EXAFS analysis was performed to extract quantitative structural distortion due to Zn substitution.

4.3.2.1 Atomic position of Zn in PZN

To identify atomic position of Zn atom in the sample, Zn *K*-edge XANES spectra were simulated with Zn located at different locations based on the typical cubic pyrochlore structure. Note that the simulated XANES spectrum can exactly reproduce the measured XANES spectrum (e.g., the use of MXAN approach [62]), by changing atomic configuration around the considered absorbing atom until the simulated XANES spectrum match well with the measured XANES spectrum. However, in this work, to generate atomic configuration of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$, the supercell has to be at least 30 Å in size (covering about 1000 atoms). Furthermore, to reproduce the measured XANES spectrum, atomic positions of each atom in the supercell have to be varied due to the lattice distortion caused by Zn substitutions and O vacancies. As the result, it is computational costly to generate the exact XANES spectrum of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$. Therefore, in this work, the typical cubic pyrochlore structure with one Zn atom was substituted on some considered sites (i.e. Zn substituting on Pb site (Zn_{Pb} known as *A*-site), Zn substituting on Nb site (Zn_{Nb} known as *B*-site), and Zn interstitial (Zn_{i})), where the rest of the typical cubic pyrochlore structure was preserved during the XANES simulation, was first investigated to check if it is possible to construct the XANES spectrum qualitatively comparable with those of the experiments.

The simulated XANES spectra were generated using the FEFF8.2 code, which employs a full-multiple scattering approach based on self-consistent overlapping muffin-tin potentials [22]. The spherical cluster size of electron wave function was increased until the spectra converged. The self-consistent calculations were performed in a cluster with a radius of 5.2 Å (about 40 atoms) away from the absorbing Zn atom. The full-multiple scattering calculations included all possible paths within a cluster with a radius of 7.5 Å (about 140 atoms) away from the absorbing Zn atom.

Results for the normalized absorbance of three possible Zn substitution models are presented in Figure 4.13 (left-sided). In addition, the normalized absorbance and the first derivative absorbance of three possible Zn substitution models were combined to find the best representative of the calculated spectrum. The linear combination fitting was performed with weight of three possible Zn substitution models ranging from 0 to

1. *R*-factor (which takes the form $R\text{-factor} = \frac{\sum (\text{data} - \text{fit})^2}{\sum (\text{data})^2}$) was used to determine the

fitting quality, where the smaller *R*-factor implies the better accuracy of the fitting. The best fitting results are presented in Figure 4.13 (right-sided) and in Table 4.3. The results clearly confirm Zn substitution on Nb site in the sample, which is due to that they share similar ionic radii [46]. The overall acceptable agreement between the XANES simulation and experiment spectra clearly indicate that the intact structure of typical cubic pyrochlore is good enough for identifying the qualitative picture of atomic position of Zn substituting in the sample. This model is thus suitable for further extracting local structural information by Zn *K*-edge EXAFS analysis.

Table 4.3 The fitting results of the normalized absorbance and the first derivative absorbance combinations of three possible Zn substitution models, presenting the weight of the fit that gives smallest *R*-factor.

Fitted data	Weight extracted from the best fit			Smallest <i>R</i> -factor
	Zn _{Pb} (A-site)	Zn _{Nb} (B-site)	Zn _i (Interstitial)	
The absorbance	0.00	1.00	0.00	0.0014
The first derivative	0.00	0.98	0.02	0.0943

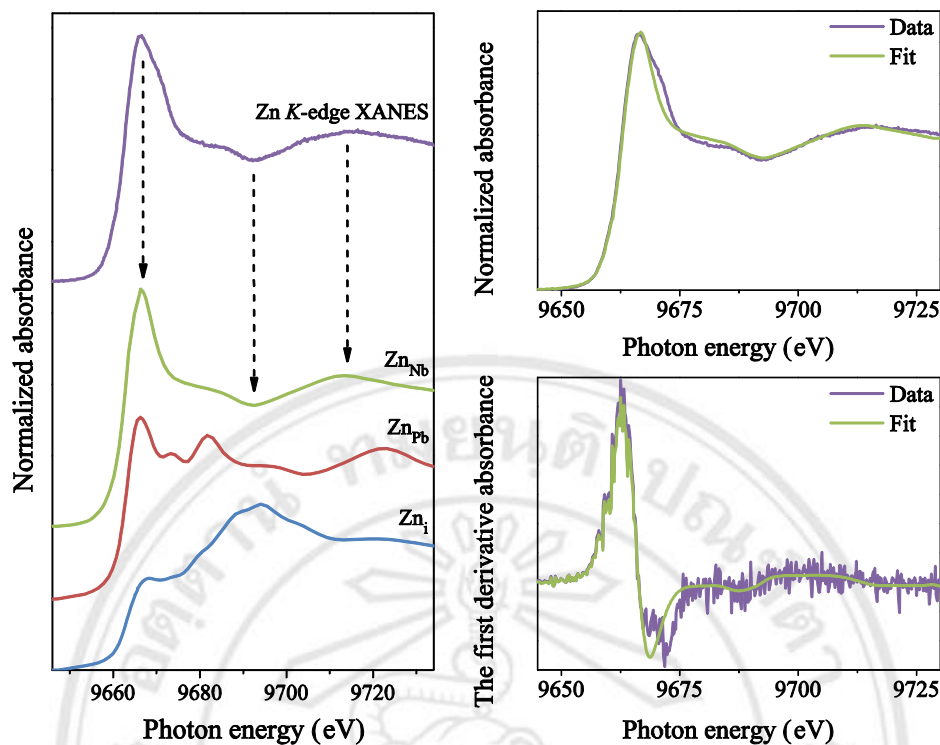


Figure 4.13 Results of the measured and the simulated Zn K-edge XANES spectra with Zn substituted at different locations in $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ (left-sided). The normalized absorbance (right-sided, top) and the first derivative absorbance (right-sided, bottom) are plotted from linear combination fitting using appropriate weight of three possible Zn substitution models in Table 4.3 [63].

4.3.2.2 Atomic distribution around Zn in PZN

The quantitative local structural information around Zn atom, including the average coordination number (N), the average distance (r), and the mean square variation (σ^2) of neighboring atoms, was obtained by Zn K-edge EXAFS analysis, to find the modeled EXAFS function that fits well with the measured EXAFS spectrum. The modeled EXAFS function was constructed from a set of the possible scattering paths of photoelectron scattered from distribution of neighboring atoms.

From atomic position of Zn in the sample, the radial distribution of neighboring atoms around Zn were generated by the program ATOMS, the scattering paths list was then calculated using the program FEFF [64] (also embedded in the program ARTEMIS) with Zn as central atom as shown in Table 4.4. The amplitude of the most

important scattering path is set to 100% and the amplitudes of the other paths are given in ratio with respect to the strongest. However, only atoms within the radial distance of 6 Å are taken into account to reduce the number of possible scattering paths, since usually the signals from atoms within a sphere with radius 6 Å are dominant in the spectrum.

Table 4.4 The scattering paths list of the program FEFF calculation with Zn as the central atom. The symbol [+] in the scattering path denotes the absorbing atom.

Path	Degeneracy	R_{eff} (Å)	Amplitude (%)	Scattering Path
1	6	1.947	100.00	[+] → O1 → [+]
2	12	3.259	9.73	[+] → O1 → O1 → [+]
3	12	3.387	7.25	[+] → O1 → O1 → [+]
4	6	3.691	20.15	[+] → O1 → [+]
5	1	3.748	3.40	[+] → Zn → [+]
6	6	3.748	27.62	[+] → Pb → [+]
7	5	3.748	24.10	[+] → Nb → [+]
8	2	3.821	3.94	[+] → Zn → O1 → [+]
9	10	3.821	28.86	[+] → Nb → O1 → [+]
10	6	3.895	15.20	[+] → O1 → O1 → [+]
11	6	3.895	7.46	[+] → O1 → [+] → O1 → [+]
12	6	3.895	6.07	[+] → O1 → [+] → O1 → [+]
13	5	3.895	12.13	[+] → O1 → Nb → O1 → [+]
14	24	4.131	14.62	[+] → O1 → O1 → [+]
15	24	4.262	9.63	[+] → Pb → O1 → [+]
16	6	4.394	12.44	[+] → O2 → [+]
17	12	4.571	6.59	[+] → O1 → O1 → O1 → [+]
18	20	4.693	4.71	[+] → Nb → O1 → [+]
19	12	4.696	20.59	[+] → O1 → [+]
20	24	4.698	6.33	[+] → O1 → O1 → O1 → [+]
21	24	4.761	34.13	[+] → O1 → O1 → [+]
22	20	4.766	7.61	[+] → O1 → Nb → O1 → [+]
23	12	4.826	6.11	[+] → O1 → O1 → O1 → [+]
24	12	4.826	16.08	[+] → O1 → O1 → O1 → [+]
25	12	4.893	3.90	[+] → O2 → O1 → [+]

26	24	5.087	5.44	[+]→ O2 → O1 → [+]
27	20	5.133	3.05	[+]→ Nb → O1 → O1 → [+]
28	20	5.195	2.81	[+]→ Nb → O1 → [+]
29	20	5.195	13.32	[+]→ O1 → Nb → [+]
30	24	5.219	3.28	[+]→ O2 → Pb → [+]
31	20	5.261	12.84	[+]→ Nb → O1 → O1 → [+]
32	20	5.261	2.72	[+]→ Nb → O1 → O1 → [+]
33	20	5.269	15.23	[+]→ O1 → Nb → O1 → [+]
34	6	5.300	11.53	[+] → Pb → [+]
35	24	5.442	2.92	[+]→ O1 → O1 → O1 → [+]
36	24	5.463	10.40	[+]→ O1 → O1 → [+]
37	24	5.478	8.27	[+]→ Pb → O1 → [+]
38	24	5.570	5.76	[+]→ O1 → O1 → O1 → [+]
39	24	5.574	4.15	[+]→ Pb → O1 → O1 → [+]
40	24	5.633	2.83	[+]→ O1 → O1 → [+]
41	24	5.638	3.03	[+]→ O1 → [+] → O1 → [+]
42	6	5.646	5.98	[+] → O1 → [+]

In the fitting, the Zn *K*-edge EXAFS spectrum was reduced to EXAFS oscillation in *k*-space $\chi(k)$ and *r*-space $\chi(r)$. The sum over scattering paths in EXAFS equation includes many scattering paths of absorbing atom scattered with distribution of neighboring atoms, while the amplitude reduction S_0^2 and the energy shift E_0 apply for all scattering paths. The amplitude reduction S_0^2 was fixed to 0.87 [65]. The energy shift E_0 was allowed to vary. The atomic species of neighboring atoms were recognized in the fit from their specific scattering amplitudes $F_j(k)$ and phase shifts $\delta_j(k)$. In the fitting, the scattering paths can be added into the fitting while maintain the condition of $N < N_{\text{idp}}$.

In the first shell fitting covering *r*-range from 0.8 to 2.1 Å, the first scattering path with approximate scattering distance, was included in the fitting (Table 4.5). Note that in this fit, the three parameters have to be defined, i.e. the change in effective path length (ΔR_{path}) and the mean square displacement (σ_{path}^2), with the path degeneracy (N_{path}) in Table 4.4.

Table 4.5 The atomic coordinate of neighboring atoms in the first scattering path including the first shell fitting.

Path	Atoms	Atomic coordinate			<i>r</i>
		<i>x</i>	<i>y</i>	<i>z</i>	
1	O1	0.530	-1.325	1.325	1.947

The first shell fitting result is shown in Figure 4.14 with *R*-factor = 0.0168. To further improve the overall fitting, the second and third shells fitting were performed. The most important scattering paths (those with single scattering or high amplitude) are needed to add into the fitting. From Table 4.4, the remaining scattering paths having single scattering or high amplitude e.g. the fourth, fifth, sixth, seventh, tenth, and sixteenth scattering paths are required to include in the fitting.

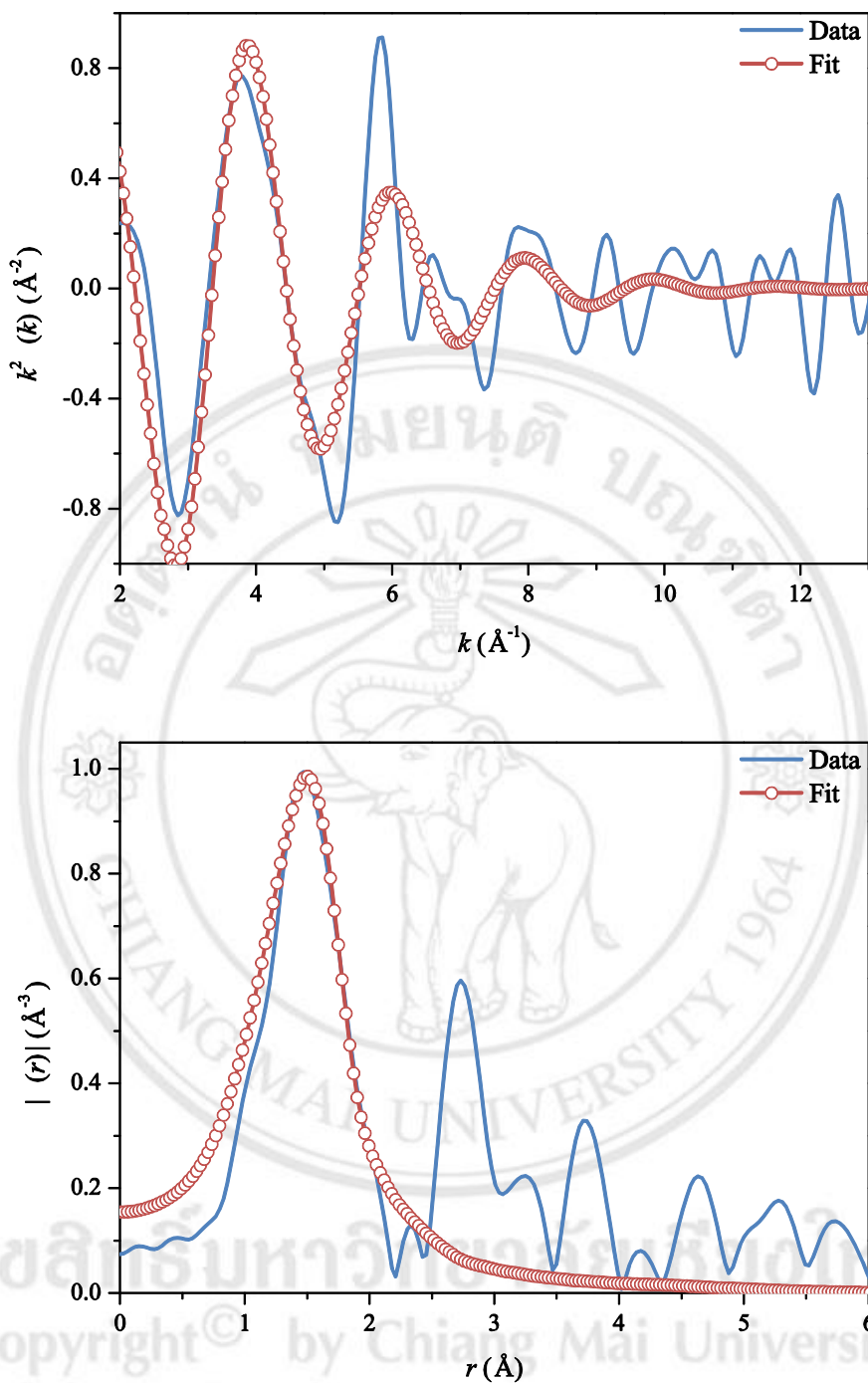


Figure 4.14 The first shell fitting to EXAFS oscillation of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ in k -space (top) and r -space (bottom).

In the second and third shells fitting covering r -range from 2.1 to 4.3 $\text{\AA}$, the fourth, fifth, sixth, seventh, tenth, and sixteenth scattering paths were included in the fitting (Table 4.6). The three parameters of each scattering path have to be defined, i.e.

the change in effective path length (ΔR_{path}) and the mean square displacement (σ_{path}^2), with the path degeneracy (N_{path}) in Table 4.4.

Table 4.6 The atomic coordinate of neighboring atoms in the fourth, fifth, sixth, seventh, tenth, and sixteenth scattering paths including the second and third shells fitting.

Path	Atoms	Atomic coordinate			r
		x	y	z	
4	O1	1.325	1.325	-3.180	3.691
5	Zn	2.650	2.650	0.000	3.748
6	Pb	-2.650	2.650	0.000	3.748
7	Nb	-2.650	0.000	2.650	3.748
10	O1	0.530	-1.325	1.325	1.947
	O1	-0.530	1.325	-1.325	3.895
16	O2	-1.325	-1.325	-3.975	4.394

Included to the fit with the second and third shells fitting, the fitting result is shown in Figure 4.15 with R -factor = 0.0027. To further improve the overall fitting, the fourth, fifth, and sixth shells fitting were performed. The most important scattering paths (those with single scattering or high amplitude) should be added into the fit. From Table 4.4, the remaining scattering paths having single scattering or high amplitude e.g. the nineteenth, twenty-first, thirty-fourth, and forty-second scattering paths are required in the fit.

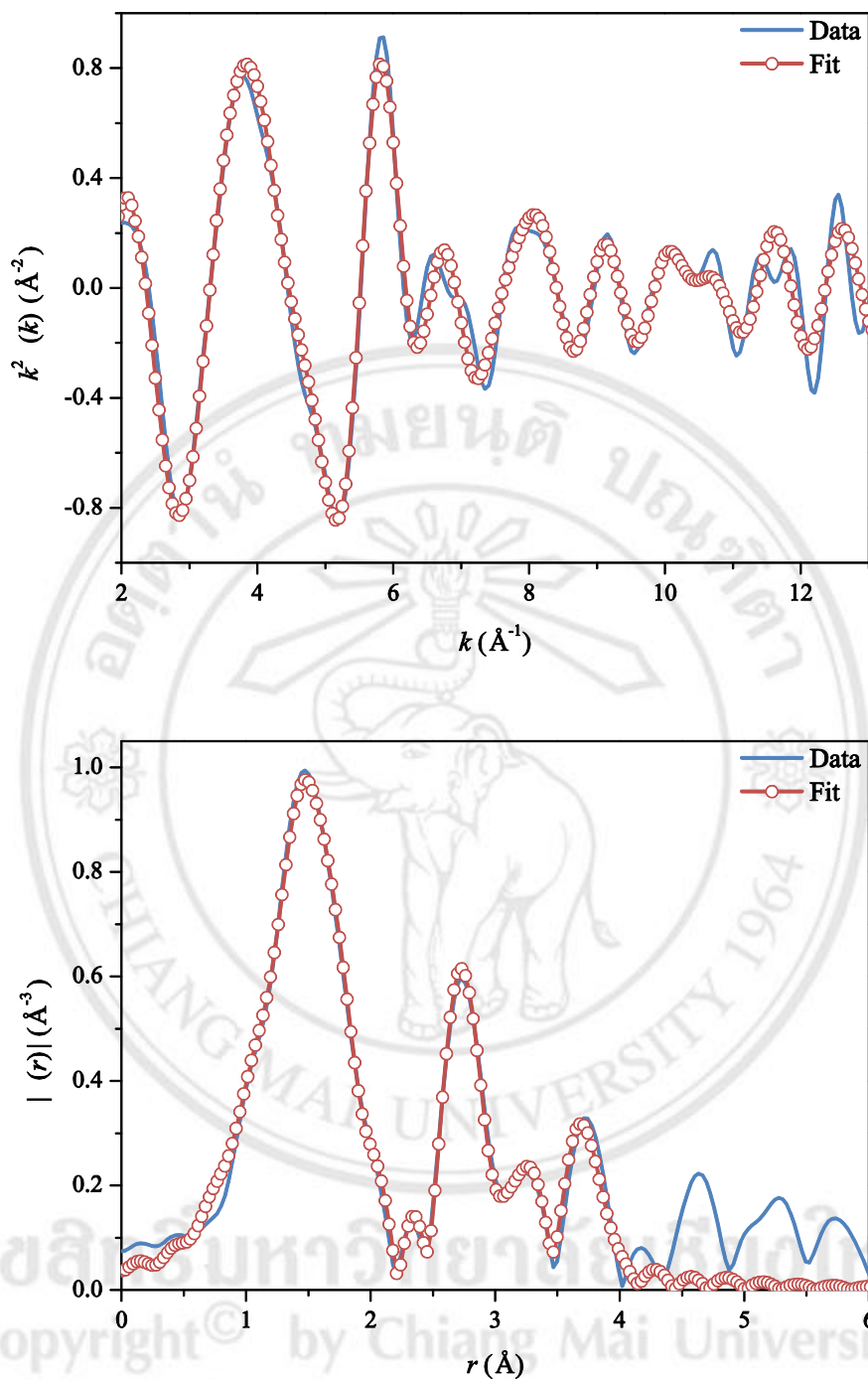


Figure 4.15 The first, second and third shells fitting to EXAFS oscillation of $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ in k -space (top) and r -space (bottom).

In the fourth, fifth, and sixth shells fitting covering r -range from 4.3 to 6.0 $\text{\AA}$, the nineteenth, twenty-first, thirty-fourth, and forty-second scattering paths were included in the fitting (Table 4.7). Again, the three parameters of each scattering path have to be

defined, i.e. the change in effective path length (ΔR_{path}) and the mean square displacement (σ_{path}^2), with the path degeneracy (N_{path}) in Table 4.4.

Table 4.7 The atomic coordinate of neighboring atoms in the nineteenth, twenty-first, thirty-fourth, and forty-second scattering paths including the fourth, fifth, and sixth shells fitting.

Path	Atoms	Atomic coordinate			r
		x	y	z	
19	O1	3.975	-1.325	-2.120	4.696
21	O1	-3.975	1.325	2.120	4.696
	O1	-1.325	0.530	1.325	2.879
34	Pb	0.000	0.000	5.300	5.300
42	O1	3.975	3.975	-5.300	5.646

Included to the fit with the fourth, fifth, and sixth shells fitting, the fitting result is shown in Figure 4.16 with R -factor = 0.0021. The number of variables ($N = 34$) is less than that of the independent points ($N_{idp} = 35$). The result from this fit gives the energy shift $E_0 = -7.2460 \pm 1.01423$ eV, the path degeneracy of the single scattering paths $N_1 = 5.0 \pm 0.1$, $N_4 = 1.1 \pm 0.1$, $N_5 = 5.0 \pm 0.2$, $N_6 = 5.9 \pm 0.3$, and $N_{16} = 6.0 \pm 0.8$, the change in effective path length of the single scattering paths $\Delta R_1 = 0.0236 \pm 0.0215$ Å, $\Delta R_4 = -0.6467 \pm 0.0147$ Å, $\Delta R_5 = -0.3036 \pm 0.0256$ Å, $\Delta R_6 = 0.0962 \pm 0.0113$ Å, and $\Delta R_{16} = -0.2746 \pm 0.0499$ Å, the mean square displacement factor of the single scattering paths $\sigma_1^2 = 0.0127 \pm 0.0306$ Å², $\sigma_4^2 = 0.0020 \pm 0.0020$ Å², $\sigma_5^2 = 0.0109 \pm 0.0045$ Å², $\sigma_6^2 = 0.0103 \pm 0.0277$ Å², and $\sigma_{16}^2 = 0.0038 \pm 0.0039$ Å².

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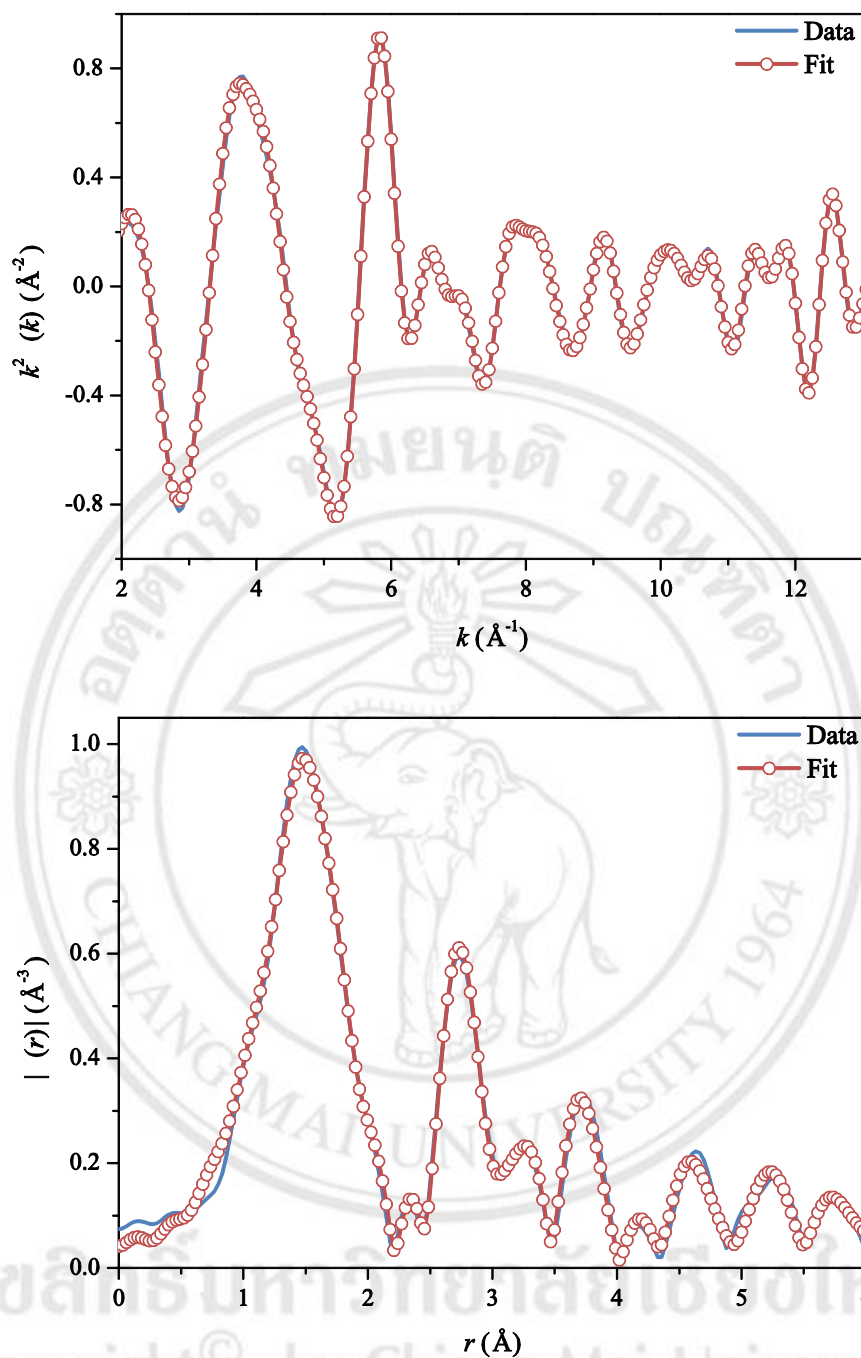


Figure 4.16 The EXAFS oscillation and fitting result in k -space (top) and r -space (bottom) for $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$. The fitting was performed in k -range from 2.0 to 12.9 $\text{\AA}^{-1}$, and R -range from 0.8 to 6.0 $\text{\AA}$ [63].

As mentioned, the effective path length R_{eff} equals to half scattering length of the given path, e.g. for the single scattering path, it is equivalent to the distance between central atom and neighboring atom. Therefore, the obtained parameters from the single

scattering path of the first, fourth, fifth, sixth, and sixteenth can be used to calculate the bond length of Zn-O1, Zn-Zn, Zn-Nb, Zn-Pb, and Zn-O2, respectively. The bond length of Zn-O is $R_1 + \Delta R_1 = (1.9470 + 0.0236) \pm 0.0215 = 1.9706 \pm 0.0215$ Å. The bond length of Zn-Nb is $R_4 + \Delta R_4 = (3.7480 - 0.6467) \pm 0.0147 = 3.1013 \pm 0.0147$ Å. The bond length of Zn-Nb is $R_5 + \Delta R_5 = (3.7480 - 0.3036) \pm 0.0256 = 3.4444 \pm 0.0256$ Å. The bond length of Zn-Pb is $R_6 + \Delta R_6 = (3.7480 + 0.0962) \pm 0.0113 = 3.8442 \pm 0.0113$ Å. The bond length of Zn-O2 is $R_{16} + \Delta R_{16} = (4.3940 - 0.2746) \pm 0.0499 = 4.1194 \pm 0.0499$ Å.

The fitting results are also presented in Table 4.8. It is found that the approximate bond length between Pb^{2+} and Zn^{2+} of pyrochlore phase is about 3.8442 Å, which is longer than that of perovskite phase (3.4391 Å) [66]. In addition, the approximate bond length between Pb^{2+} and Nb^{5+} of pyrochlore phase is about 3.6607 Å, which is also longer than that of perovskite phase (3.4413 Å) [66]. From these different radial distributions around Zn^{2+} atom, the total energies of both structures were calculated using the first-principles electronic structure calculation base on the Kohn-Sham equation [67].

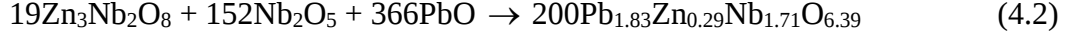
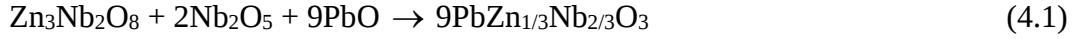
Table 4.8 The structural parameters of $Pb_{1.83}Zn_{0.29}Nb_{1.71}O_{6.39}$ obtained from the EXAFS analysis, where N is the coordination number, r is the average distance and σ^2 is the mean square variations of the nearest neighboring atom.

Path	N	r (Å)	σ^2 (Å ²)	R -factor
Zn - O1	5.0 ± 0.1	1.9706 ± 0.0215	0.0127 ± 0.0306	0.0021
Zn - Zn	1.1 ± 0.1	3.1013 ± 0.0147	0.0020 ± 0.0020	
Zn - Nb	5.0 ± 0.2	3.4444 ± 0.0256	0.0109 ± 0.0045	
Zn - Pb	5.9 ± 0.3	3.8442 ± 0.0113	0.0103 ± 0.0277	
Zn - O2	6.0 ± 0.8	4.1194 ± 0.0499	0.0038 ± 0.0039	

4.3.2.3 Formation energy of PZN

To find the reason why lead zinc niobate compound is always crystallized in pyrochlore phase rather than perovskite phase when prepared in normal atmospheric condition, the total energy along reaction path from the precursors $Zn_3Nb_2O_8$ with space group $C2/c$ (no. 15) [68], Nb_2O_5 with space group $Pbam$ (no. 55) [69] and PbO with space group $Pbcm$ (no. 57) [70] to perovskite $PbZn_{1/3}Nb_{2/3}O_3$ phase with space group

R3m (no. 160) [66] and to pyrochlore $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ phase with space group *Fd3m* (no. 227) was calculated using the following chemical reactions:



The first-principle calculations were performed within the framework of density functional theory (DFT) using the ABINIT package [71, 72]. The exchange correlation energy was defined under the local density approximation (LDA) as it usually provides good agreement with experimental data, e.g., the equilibrium lattice constants for metal oxide compounds [73]. Only valence electrons were considered explicitly while core electronic states were represented via a Troullier-Martins pseudo-potentials [74]. The plane wave cut-off energy was set to 10^3 eV, and the total energy is assumed to converge when the difference in total energies between the successive calculations is less than 10^{-5} eV.

From the DFT calculations of both reaction paths, due to the lowest melting point of PbO (about 886 °C) [75], PbO decomposes before reacting with Nb_2O_5 and $\text{Zn}_3\text{Nb}_2\text{O}_8$ to produce perovskite $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ phase and pyrochlore $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ phase as shown in Table 4.9. The total energy along reaction paths of perovskite and pyrochlore phases are shown in Figure 4.17. It is found that the formation energy of perovskite phase (E_{Per}) is noticeably higher than that of pyrochlore phase (E_{Py}). This is due to the fact that the shape of Pb^{2+} cation is not spherical arisen from the presence of the $6s^2$ lone pair. The steric hindrance of Pb^{2+} lone pair and the mutual interactions between Pb^{2+} lone pair and other cations are therefore the paramount factors in controlling structural formation. Nevertheless, the mutual interaction between Pb^{2+} lone pair and Zn^{2+} cation is stronger than that of Pb^{2+} lone pair and Nb^{5+} cation because the bonding energy between high valence Nb^{5+} and O^{2-} is larger than that of low valence Zn^{2+} and O^{2-} . From the x-ray absorption spectroscopy results, the approximate bond length between Pb^{2+} and Zn^{2+} of perovskite phase is then shorter than that of pyrochlore phase. Therefore, to compensate these mutual interactions, the perovskite phase requires higher formation energy than the pyrochlore phase. Note that, in the *B*-site oxide precursor method, Zn^{2+} and its neighboring O^{2-} in $\text{Zn}_3\text{Nb}_2\text{O}_8$ form the rutile-type structure (6-coordination) which is suitable for

perovskite structural, but Pb^{2+} and neighboring O^{2-} in PbO have the CsCl-type structure (8-coordination) which is inappropriate for perovskite structural formation [76]. As can be seen in Table 4.9, the major PbO contents in $\text{Zn}_3\text{Nb}_2\text{O}_8 + 2\text{Nb}_2\text{O}_5 + 9\text{PbO}$ then require high formation energy to produce the perovskite phase.

Table 4.9 The reaction path from the precursors $\text{Zn}_3\text{Nb}_2\text{O}_8$, Nb_2O_5 , and PbO to perovskite $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ phase and pyrochlore $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ phase.

Perovskite phase	Pyrochlore phase
$\text{Zn}_3\text{Nb}_2\text{O}_8 + 2\text{Nb}_2\text{O}_5 + 9\text{PbO}$	$19\text{Zn}_3\text{Nb}_2\text{O}_8 + 152\text{Nb}_2\text{O}_5 + 366\text{PbO}$
↓ I	↓ I
$\text{Zn}_3\text{Nb}_2\text{O}_8 + 2\text{Nb}_2\text{O}_5 + 9\text{Pb}^{2+} + 9\text{O}^{2-}$	$19\text{Zn}_3\text{Nb}_2\text{O}_8 + 152\text{Nb}_2\text{O}_5 + 366\text{Pb}^{2+} + 366\text{O}^{2-}$
↓ II	↓ II
$\text{Zn}_3\text{Nb}_2\text{O}_8 + 5\text{PbNb}_{4/5}\text{O}_3 + 4\text{Pb}^{2+} + 4\text{O}^{2-}$	$\text{Zn}_3\text{Nb}_2\text{O}_8 + 152\text{Pb}_2\text{Nb}_2\text{O}_7 + 62\text{Pb}^{2+} + 62\text{O}^{2-}$
↓ III	↓ III
$9\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$	$200\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$

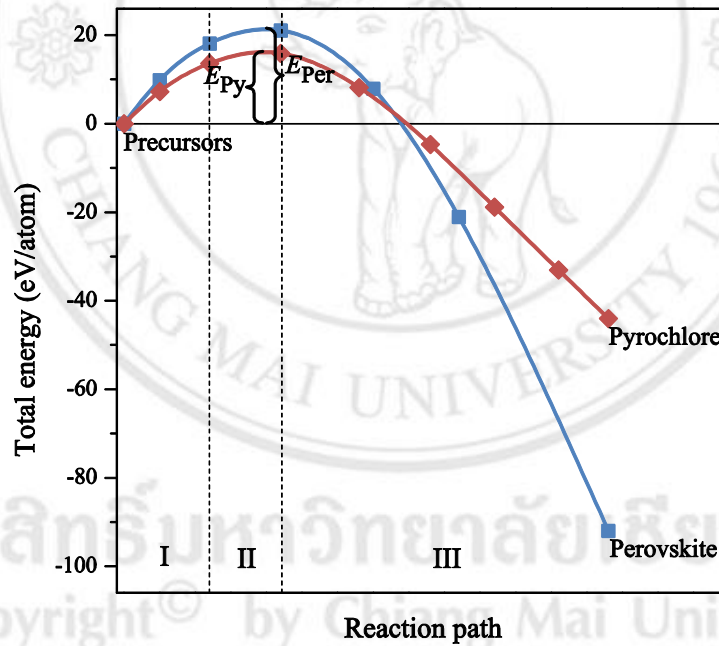


Figure 4.17 The total energy along reaction paths from the precursors $\text{Zn}_3\text{Nb}_2\text{O}_8$, Nb_2O_5 , and PbO to perovskite $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ phase and to pyrochlore $\text{Pb}_{1.83}\text{Zn}_{0.29}\text{Nb}_{1.71}\text{O}_{6.39}$ phase. Details of formations along reaction paths I, II, and III are presented in Table 4.9. The parameters E_{Per} and E_{Py} refer to formation energy or the energy barrier required and form perovskite phase and pyrochlore phase, respectively [63].

Consequently, the preparation method to obtain lead zinc niobate ceramic in perovskite phase should be focused on cancelling or decreasing the steric hindrance of Pb^{2+} lone pair and the mutual interaction between Pb^{2+} lone pair and Zn^{2+} cation. For instance, PZN can be synthesized under high pressure (from 1.5 to 3.5 GPa) and high temperature (about 1100° C to 1200 °C) [77, 78]. Under high pressure, the coordination number of Zn^{2+} with O^{2-} in ZnO transforms from the wurtzite-type structure (4-coordination) to rocksalt-type structure (6-coordination) [79], and the coordination number of Pb^{2+} with O^{2-} in PbO transforms from the CsCl-type structure (8-coordination) to the NaCl-type structure (6-coordination) [80] with shorter bond length. These geometric transforms are suitable for perovskite structural formation. Also, the temperature is high enough to compensate the mutual interaction between Pb^{2+} lone pair and Zn^{2+} cation. Moreover, PZN in perovskite phase can also be stabilized by partial substitution on *A*- or *B*-site cations using e.g. BaTiO_3 , SrTiO_3 , PbTiO_3 , and PbZrO_3 [81, 82]. The substituted *A*-site cations with spherical shape replace Pb^{2+} cations and the substituted *B*-site cations with high valence replace Zn^{2+} cations help decreasing the steric hindrance of Pb^{2+} lone pair and the mutual interaction between Pb^{2+} lone pair and Zn^{2+} cation. While these PZN preparation methods are useful for enhancing the stability of perovskite structure and increasing the amount of perovskite phase, the dielectric properties are still not as good as those of PZN single crystal obtained from PbO flux method [83]. Therefore, alternative preparation approach that employs the information of atomic local structural configuration may be useful to improve the preparation method of perovskite lead zinc niobate compound to yield excellent electrical properties.