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## Synthesis, Structure and Electrical Properties of N-doped $\text{Li}_3\text{VO}_4$

Bo Dong<sup>1</sup>, Rouzbeh Jarkaneh<sup>1</sup>, Stephen Hull<sup>2</sup>, Nik Reeves-McLaren<sup>1</sup>, Jordi Jacas Biendicho<sup>3</sup> and Anthony R West<sup>1</sup>

<sup>1</sup> University of Sheffield, Department of Material Science and Engineering, Mappin Street, Sheffield S1 3JD, U.K.

<sup>2</sup> The ISIS Facility, STFC, Rutherford-Appleton Laboratory, U.K.

<sup>3</sup> Catalonia Institute for Energy Research, Jardins de les Dones de Negre 1, 08930 Sant Adrià del Besos, Spain.

### Abstract

N-doped  $\text{Li}_3\text{VO}_4$  of general formula  $\text{Li}_{3+x}\text{VO}_{4-x}\text{N}_x$  was prepared by solid state reaction of  $\text{Li}_3\text{N}$ ,  $\text{V}_2\text{O}_5$  and either  $\text{Li}_2\text{CO}_3$  or  $\text{LiOH}\cdot\text{H}_2\text{O}$ . A solid solution based on the low temperature  $\beta$  polymorph of  $\text{Li}_3\text{VO}_4$  was obtained with composition  $0 \leq x \leq 0.2$ . Structural studies by x-ray and neutron powder diffraction confirmed the partial replacement of oxygen on the O(1) sites by N together with creation of an equal number of  $\text{Li}^+$  ions which are located off-centre in adjacent octahedral Li(3) sites. Electrical property measurements on sintered pellets using impedance spectroscopy showed that the solid solutions are modest conductors of  $\text{Li}^+$  ions, consistent with the partial occupancy of  $\text{Li}^+$  ions in the interstitial octahedral sites. The activation energy for conduction of samples prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\sim 1.91$  eV, is much greater than for samples prepared at higher temperature, using  $\text{Li}_2\text{CO}_3$ ,  $\sim 0.78$  eV; it is speculated that this is due to ion trapping in  $\text{Li}_i^+ / \text{N}_0^-$  defect clusters. This study represents a relatively new method for doping  $\text{Li}^+$  ions into a structure by aliovalent anion doping: partial replacement of O by N is compensated by creation of interstitial  $\text{Li}^+$  ions.

## Introduction

With the increasing demand for high energy and power density lithium batteries for charge storage and electric vehicle applications, there is a need for new high-capacity electrode materials, as well as high conductivity solid electrolytes for possible all-solid-state batteries<sup>1</sup>.  $\text{Li}_3\text{VO}_4$  has been proposed as a possible anode material, since it shows a reversible capacity of about  $300 \text{ mAhg}^{-1}$  in the potential range from 0.2 to 3.0 V. Its theoretical energy density is 2.5 times greater than that of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  which is widely used as a lithium intercalation anode<sup>2</sup>.  $\text{Li}_3\text{VO}_4$  has also been used as a surface coating on  $\text{LiCoO}_2$  which is the cathode in many lithium ion batteries<sup>3</sup>.

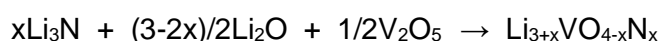
$\text{Li}_3\text{VO}_4$  shows temperature-dependent polymorphism with a low temperature  $\beta$  polymorph that is isostructural with  $\beta \text{ Li}_3\text{PO}_4$ , an intermediate temperature, T polymorph whose structure is not known and a high temperature  $\gamma$  polymorph isostructural with  $\gamma \text{ Li}_3\text{PO}_4$ <sup>4</sup>. At the highest temperatures, prior to melting, a fourth polymorph has been identified from thermal analysis but no structural information is available. The  $\beta$  and  $\gamma$  polymorphs belong to the family of tetrahedral structures; the  $\beta$  structures are ordered wurtzite superstructures derived from ZnO in which cations occupy one set of tetrahedral sites within a hexagonal close packed, HCP, oxide ion array<sup>5</sup>. The  $\gamma$  structures are related to the  $\beta$  structures but cations are now distributed over both sets of tetrahedral sites leading to edge-sharing of some tetrahedra. The oxide array is derived from HCP but the layers are more buckled than in the  $\beta$  structures. The oxide packing arrangement in the  $\gamma$  structures may also be regarded as tetragonal packed, TP, which in its ideal form is characterised by four fold symmetry, as in the case of rutile,  $\text{TiO}_2$ .<sup>6</sup> The  $\gamma$  family of tetrahedral structures, including  $\text{Li}_3\text{YO}_4$ : Y = P, As, V, Cr and  $\text{Li}_2\text{MXO}_4$ : M = Mg, Zn; X = Si, Ge are the parent structures for a range of materials known as "lisiscons" which have high  $\text{Li}^+$  ion conductivity that are generated by forming solid solutions with phases  $\text{Li}_4\text{ZO}_4$ : Z = Si, Ge, Ti. More recently, there has been much interest in new cathode materials,  $\text{Li}_2\text{MSiO}_4$ : M = Mn, Fe in the same structural family since it is possible to de-intercalate  $\text{Li}^+$  ions and activate redox couples associated with Mn and Fe<sup>7</sup>.

There is also much recent interest in a new family of sulphur-based analogies of the lisicons known as thio-lisicons which are characterised by high levels of  $\text{Li}^+$  ion conductivity at room temperature, giving possibilities of use as electrolytes in all-solid-state Li batteries<sup>8</sup>.

Most studies on lisicon materials as either  $\text{Li}^+$  ion conductors or as mixed conducting electrodes, focus on compositional modification by cation doping within a fixed oxide ion sublattice. Our interest here is to investigate the possibility of anion, specifically N, doping, with creation of interstitial  $\text{Li}^+$  ions for charge compensation. It follows on from work by the Oakridge group on LIPON materials which are nominally N-doped  $\text{Li}_3\text{PO}_4$  but which are often glassy materials containing condensed phosphate anions rather than the isolated  $\text{PO}_4$  tetrahedra of  $\text{Li}_3\text{PO}_4$ <sup>9</sup>. In this work we report a first study on the possible N doping of crystalline  $\text{Li}_3\text{VO}_4$  and structural and electrical properties of the products. For the syntheses, two sources of Li were used:  $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}\cdot\text{H}_2\text{O}$ ;  $\text{LiOH}\cdot\text{H}_2\text{O}$  has the potential advantage that reaction occurs at significantly lower temperature than using  $\text{Li}_2\text{CO}_3$ .

## Experimental

Solid solutions of general formula,  $\text{Li}_{3+x}\text{VO}_{4-x}\text{N}_x$ , were synthesised by the following solid state reaction:



where the source of  $\text{Li}_2\text{O}$  was an equivalent amount of  $\text{LiOH}\cdot\text{H}_2\text{O}$  or  $\text{Li}_2\text{CO}_3$ . Reagents used were  $\text{Li}_3\text{N}$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$  and  $\text{V}_2\text{O}_5$ .  $\text{Li}_2\text{CO}_3$  and  $\text{V}_2\text{O}_5$  were dried at 180 °C before use; other reagents were used directly from the bottle. When using  $\text{LiOH}\cdot\text{H}_2\text{O}$ , this was mixed with  $\text{V}_2\text{O}_5$  in the required amounts and the mixture was heated at 150 °C in  $\text{N}_2$  to remove water. For the preparation of N-containing samples, the dried mixtures were placed in an Ar atmosphere in a Mbraun Labstat glovebox to continue with the preparations. All weighing, mixing and pellet-pressing was carried out in the glovebox; weighed powders were mixed dry with an agate mortar and pestle and then pressed into pellets using a small hand press. Samples were reacted in molybdenum boats since there was some evidence of reaction with

Li<sub>3</sub>N if gold foil boats were used. Mixed powders were placed in the Mo boats which were inserted into glass tubes closed at one end. The other end was sealed with scotch tape and the tubes, with contents, were removed from the glovebox and placed in a horizontal tube furnace in flowing N<sub>2</sub>. After purging the furnace atmosphere for 30 mins, the furnace temperature was increased at 5 °C/min to either 650 °C if Li<sub>2</sub>CO<sub>3</sub> was used as the source of lithium or 450 °C using LiOH·H<sub>2</sub>O and held at that temperature for 10 h. During heating, at ~150 °C the scotch tape cover of the glass tubes decomposed. At the end of the heat treatment, the furnace was cooled at 5 °C/min, still under flowing N<sub>2</sub>.

In order to prepare samples for impedance measurements, pellets were reheated at 750 °C for 10 h under N<sub>2</sub>. Samples for x-ray powder diffraction, XRD, were prepared in air and analysed using CuKα<sub>1</sub> radiation with a linear position sensitive detector on a STOE STADI P diffractometer. For powder neutron diffraction, ND, the HRPD diffractometer at the Rutherford-Appleton Laboratory, U.K was used in time of flight, TOF, mode with incident wavelength in the range 0.5 to 5.1 Å. Rietveld refinement used the EXPGUI interface of the GSAS suite of programmes<sup>10-11</sup>.

For impedance measurements, pellets were coated on opposite faces with Au paste which was dried and hardened by heating at 800 °C for 2 h. Impedance data were collected with a Solartron analyser at 100mV ac over the frequency range 10<sup>-2</sup> to 10<sup>6</sup> Hz in N<sub>2</sub> atmosphere.

## Results and Discussion

Samples of Li<sub>3</sub>VO<sub>4</sub> and N-doped solid solutions of formula Li<sub>3+x</sub>VO<sub>4-x</sub>N<sub>x</sub>; 0 ≤ x ≤ 0.2 appeared to be single phase by XRD after synthesis at either 450 °C using LiOH·H<sub>2</sub>O or 650 °C using Li<sub>2</sub>CO<sub>3</sub> as shown in Fig. 1. Patterns were fully indexed on the unit cell of β Li<sub>3</sub>VO<sub>4</sub> with slightly smaller lattice parameters for N-doped Li<sub>3</sub>VO<sub>4</sub>. Compositions with higher nitrogen content contained small amounts of Li<sub>2</sub>CO<sub>3</sub>, Fig. 1. From these data, the similarity in lattice parameters of x=0.2 and 0.4 and the conductivity data discussed later, we estimate the solid solution limit to be ~ x = 0.2. Similar results were obtained using either LiOH·H<sub>2</sub>O or Li<sub>2</sub>CO<sub>3</sub>

as the source of  $\text{Li}_2\text{O}$  but reaction was achieved at significantly lower temperatures using  $\text{LiOH}\cdot\text{H}_2\text{O}$ , primarily because of the thermal stability of  $\text{Li}_2\text{CO}_3$ .

Structure refinement on two compositions  $x = 0$  and  $x = 0.2$  prepared using  $\text{Li}_2\text{CO}_3$  was carried out using a combination of XRD and ND data. Initially, the thermal parameter, or  $U_{\text{iso}}$  for each atom was set to a default value ( $0.025 \text{ \AA}^2$  for V and  $0.01 \text{ \AA}^2$  for other atoms). The background (6 terms of shifted Chebyshev function), scale factor and lattice parameters were refined first followed by zero point and peak profile coefficient which were fixed after convergence. Then, the atomic coordinates of V were refined using XRD data and those of other atoms using ND data; these were fixed after convergence. Finally, the thermal parameters of all atoms were refined. The starting model was the reported structure of  $\beta$   $\text{Li}_3\text{VO}_4$  with space group  $\text{Pmn}2_1$ . Results for stoichiometric  $\text{Li}_3\text{VO}_4$ ,  $x = 0$ , Table 1, were similar to those reported in the literature<sup>12</sup> and gave reasonable  $U_{\text{iso}}$  values for all positions with full site occupancy.

For the refinement of composition  $x = 0.2$ , scale factor, cell parameter, zero point, instrumental parameters and atomic parameters were refined in turn. It was assumed initially that the sample contained no nitrogen or interstitial lithium ions; occupancies of oxygen sites were refined giving a value for site O(1) significantly greater than unity, which was a strong indicator that oxygen may be partially replaced by nitrogen on that site since nitrogen is a stronger scatterer of neutrons than is oxygen. At this stage,  $\chi^2 = 5.248$ ,  $\text{Rwp} = 9.54\%$  for ND and  $3.38\%$  for XRD; the occupancy of site O(1) was therefore refined allowing mixed occupancy by oxygen and nitrogen within a constraint of full occupancy, giving occupancy values of  $0.12(2)$  for N and  $0.88(2)$  for O with improved statistical parameters:  $\chi^2 = 4.933$ ,  $\text{Rwp} = 9.50\%$  for ND. The occupancies of sites O(2) and O(3) remained as unity within errors and therefore, there is no indication of significant nitrogen occupancy on these sites. In order to look for the presence of interstitial lithium ions, Fourier difference maps were constructed and a site Li(3) identified, Table 1. Its occupancy was set to 0.2, consistent with the value  $x = 0.2$  in the starting composition and the value of the nitrogen content

determined from the O(1) site occupancy, and remained at 0.19(2) on refinement. The atomic coordinates of Li(3) were refined followed by occupancy of Li(3) to give a value of 0.19(3) when convergence was reached ( $\chi^2 = 4.916$ , Rwp = 9.48% for ND). Then,  $U_{iso}$  values of all atoms except Li(3) were refined ( $\chi^2 = 4.618$ , Rwp = 7.95% for ND and 3.56% for XRD). In the final refinement, using combined ND and XRD data, the occupancies of O(1), N(1), Li(3) and the atomic coordinates of O(1), N(1), O(2), O(3), V, Li(1) and Li(2) were refined with fixed  $U_{iso}$  values ( $\chi^2 = 4.210$ , Rwp = 7.95% for ND and 3.25% for XRD). An attempt was made to carry out a simultaneous refinement which included the  $U_{iso}$  values of all atoms apart from Li(3). The refinement converged with similar atomic coordinates but the  $U_{iso}$  of all three oxygens and nitrogen were zero within 3 esds although they had slightly negative values.

Final refined parameters are listed in Table 1 for compositions  $x = 0$  and 0.2, together with selected bond lengths and bond angles.

The partial substitution of N for O on the O(1) sites has little effect on the overall atomic coordinates of the crystal structure of  $x = 0.2$  compared with  $x = 0$ . The new site for Li(3) is a distorted octahedral site with 3 short Li-O bonds typical of usual Li-O bond distances and 3 longer bonds in the range 2.56 to 2.70 Å, Fig 3. In the  $\beta$  structure of  $\text{Li}_3\text{VO}_4$ , all the cations occupy sets of tetrahedral sites,  $T^+$ , that point “up” in figure 3(a), whereas those that point “down”,  $T^-$ , are empty. The off-centre displacement of Li(3) in octahedral sites, (b), reduces the repulsions from cations in the adjacent occupied  $T^+$  tetrahedral sites since the Li(3) ions are displaced towards the empty  $T^-$  tetrahedral sites.

The preference of N to substitute for O on the O(1) sites may be understood by considering the coordination environments of the three oxygen sites, Table 2. Bond lengths to the four tetrahedrally-coordinated atoms V, Li(1), Li(1)' and Li(2) are comparable for all three O sites and the difference is therefore associated with the possible coordination to Li(3). The O(1) site is coordinated to Li(3) with a reasonable Li – O, N bond length of 1.965 Å. However the

corresponding O(2) bond to Li(3) length is significantly greater, 2.062 Å and O(3) is not coordinated at a reasonably short distance to Li(3). Given the higher nominal charge on nitrogen, 3<sup>-</sup>, compared with that on oxygen, 2<sup>-</sup>, the extra positive charge associated with Li(3) is balanced by substitution of N on adjacent O(1) sites. Consequently, coupled substitution of N on O(1) sites with an equivalent occupancy of adjacent Li(3) sites occurs leading to defect association.

A typical impedance dataset for N-doped Li<sub>3</sub>VO<sub>4</sub> is shown in Fig. 4. Data are presented in four different complementary formats. In (a), impedance complex plane plots show a high frequency arc, which passes through the origin and a low frequency spike which becomes an arc at high temperatures. Using the same data, plots of capacitance, C' against frequency, (b), show a high frequency plateau with value ~ 1-2 pFcm<sup>-1</sup> which is a typical value for a bulk capacitance with an associated permittivity in the range 10 – 20. At lower frequencies, the C' data increase to values as high as 10 μF at a frequency of 10<sup>-2</sup> Hz; such a high capacitance is indicative of electrode double layer phenomena, such as would be associated with ionic conduction of, in this case, Li<sup>+</sup> ions. Plots of log conductance, Y' against log f, (c), show a frequency independent plateau over a wide frequency range; at lower frequencies a dispersion to much lower conductivities occurs and is associated with the charge blocking at the sample-electrode interface. At high frequencies, a second dispersion to higher conductivity values is observed and is attributable to Jonscher power law behaviour of the sample bulk conductivity. Combined spectroscopic plots of Z''/M'', (d), show overlapping peaks at high frequencies which are attributable to the sample bulk response and the tail of a large peak at low frequencies in the Z'' spectrum associated with the blocking electrodes. The conclusion from these results is that the sample is electrically homogeneous with no evidence of a significant grain boundary impedance and that the sample is an ionic conductor whose bulk conductivity is given either from the intercept on the Z' axis (a) or from the frequency-independent Y' plateau in (c).



For undoped  $\text{Li}_3\text{VO}_4$ , the impedance data are similar to those for N-doped  $\text{Li}_3\text{VO}_4$  but the main difference is that the low frequency electrode spike is much less pronounced. Overall conductivity values are also 1-2 orders of magnitude lower. Pure  $\text{Li}_3\text{VO}_4$  is expected to be an ionic and electronic insulator and the measured conductivity may therefore be attributed to either residual  $\text{Li}^+$  conduction associated with slight departure from stoichiometry or the presence of, as-yet unidentified, electronic impurities.

Bulk conductivity data are presented in Arrhenius format in Fig 5 for both undoped and doped  $\text{Li}_3\text{VO}_4$ , prepared using the two different sources of  $\text{Li}_2\text{O}$ . In both cases, the conductivity of  $\text{Li}_3\text{VO}_4$  increased by 1-2 orders of magnitude on doping with N. The increase in conductivity is attributed to  $\text{Li}^+$  ion conduction, consistent with (i) the creation of interstitial  $\text{Li}^+$  ions within the parent  $\text{Li}_3\text{VO}_4$  structure and (ii) the presence of the low frequency spike in the impedance data, Fig 4(a). There is no reason to expect an increase in electronic conduction on N doping, since V stays in the +5 oxidation state and N doping is compensated by an ionic charge balance mechanism. The conductivity is a maximum for composition  $x=0.2$ ; similar conductivity was obtained for  $x=0.4$ , which is further evidence that the solid solution limit is close to  $x=0.2$ . Composition  $x=0.1$  had conductivity (not shown) intermediate between those of  $x=0$  and 0.2.

The conductivities of both undoped and doped  $\text{Li}_3\text{VO}_4$  are somewhat higher for materials prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ ; this is attributed to the presence of unidentified electronic impurities in the  $\text{LiOH}\cdot\text{H}_2\text{O}$  starting materials. An additional difference between the two sets of N-doped  $\text{Li}_3\text{VO}_4$  samples is the activation energy for  $\text{Li}^+$  ion conduction, which is much greater for samples prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ . We speculate that this may be due to strong defect association, involving  $\text{Li}(3)$  and N, leading to a higher activation energy for  $\text{Li}^+$  ion conduction, in materials prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ . Possibly this is because the higher synthesis temperature which was necessary using  $\text{Li}_2\text{CO}_3$ , led to reduced defect association and therefore, easier  $\text{Li}^+$  ion conduction. If we assume that the activation energy of 0.78 eV for the sample prepared using  $\text{Li}_2\text{CO}_3$  represents the activation energy for  $\text{Li}^+$  ion migration,

then that for the sample prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ , 1.74 eV, contains an additional 0.96 eV that may represent the dissociation energy of  $\text{Li}(3)\text{-N}$  defect complexes. Further work, including conductivity measurements over a wider temperature range, is required to better understand the possibility of defect association and its consequences.

The impedance data clearly show an increase in  $\text{Li}^+$  ion conductivity on doping  $\text{Li}_3\text{VO}_4$  with N. This correlates well with the crystallographic data which, for composition  $\text{Li}_{3.2}\text{VO}_{3.8}\text{N}_{0.2}$ , show the presence of an additional 0.2  $\text{Li}^+$  ions on the  $\text{Li}(3)$  site and the substitution of 0.2 N atoms on the  $\text{O}(1)$  site, in accord with the expected composition and assuming that no loss of Li and/or N occurs during synthesis.

The mechanism of  $\text{Li}^+$  ion migration may involve direct interstitial migration between adjacent  $\text{Li}(3)$  sites, either in the *ac* plane or in adjacent *ac* planes, or an interstitialcy (or knock-on) mechanism involving the displacement of  $\text{Li}(1)$  or  $\text{Li}(2)$  ions from their regular lattice sites. In the *ac* plane, adjacent  $\text{Li}(3)$  sites are separated by empty tetrahedral, T, sites, through which a migrating  $\text{Li}^+$  ion must pass. These T, sites share faces with occupied  $\text{LiO}_4$  or  $\text{VO}_4$  tetrahedra and strong cationic repulsions would prevent simultaneous occupation of adjacent T, and  $\text{T}_+$  sites, especially if one of these contains vanadium. The T, sites, therefore, represent a saddle position in the  $\text{Li}^+$  ion migration pathway between adjacent  $\text{Li}(3)$  sites. Alternatively, an interstitialcy or knock-on mechanism may operate which requires the ejection of a  $\text{Li}^+$  ion from its occupied  $\text{T}_+$  site which is then occupied by the incoming  $\text{Li}^+$  ion.

In the *b* direction, direct interstitial migration between, face-sharing octahedral sites appears to be possible, as one step in the migration pathway between  $\text{Li}(3)$  sites in adjacent *ac* planes. We conclude that 3D conduction of  $\text{Li}^+$  ions in N-doped  $\text{Li}_3\text{VO}_4$  should be feasible although there may be a certain degree of anisotropy between conduction in the *b* direction and within the *ac* plane. It could be useful to probe the details of the migration mechanism and pathway by modelling studies.

## Conclusions

Many examples of  $\text{Li}^+$  conductivity in “lissicon” materials are known but, to date, these all involve solid solutions based on the parent  $\gamma$  polymorph of end-member phases, such as  $\text{Li}_3\text{PO}_4$  and  $\text{Li}_2\text{ZnGeO}_4$ , and contain either  $\text{Li}^+$  vacancies or interstitial  $\text{Li}^+$  ions that are generated by aliovalent cation doping. The present study concerns the  $\beta$  polymorph of  $\text{Li}_3\text{VO}_4$  and is the first example of a  $\text{Li}^+$  ion conducting solid solution based on a  $\beta$  tetrahedral structure.

Combined ND/XRD studies confirm the substitution of O by N together with the creation of an equal number of interstitial  $\text{Li}^+$  ions; defect pairs form by electrostatic attraction between N located on O(1) sites and occupied adjacent Li(3) interstitial sites. The composition determined by refinement of XRD/ND data matches that expected from the target stoichiometry and indicates the usefulness of the synthetic procedure developed for N-doping.

Impedance data show enhanced  $\text{Li}^+$  ion conductivity in the N-doped materials. Variation in activation energy between different samples may indicate whether or not the Li(3) ions are trapped by adjacent nitrogen atoms. Although anion doping, by N, represents a relatively untried method of modifying the Li content of a structure, trapping of interstitial  $\text{Li}^+$  ions within defect complexes, and the associated increase in activation energy for conduction, may limit the usefulness of this method for generating a high level of  $\text{Li}^+$  ion conductivity. Further studies on the general applicability of this doping method are planned.

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## Figure and Table Captions

**Figure 1** X-ray diffraction patterns of  $\text{Li}_{3+x}\text{VO}_{4-x}\text{N}_x$ :  $x = 0, 0.2, 0.4$ . Samples used  $\text{Li}_2\text{CO}_3$  as source of Li and were reacted at 750 °C for 10 h in  $\text{N}_2$ ; composition  $x=0.4$  had a residual amount of  $\text{Li}_2\text{CO}_3$

**Figure 2** Observed, calculated and difference profiles from refinement of (a, b)  $\text{Li}_3\text{VO}_4$  and (c, d)  $\text{Li}_{3.2}\text{VO}_{3.8}\text{N}_{0.2}$  using XRD and ND data. Inserts in (b) and (d) show expanded d-space region from 2.2 to 2.6 Å.

**Figure 3** Polyhedral structure of  $\text{Li}_{3.2}\text{VO}_{3.8}\text{N}_{0.2}$ . Blue and yellow tetrahedra are  $\text{Li}(1,2)\text{O}_4$  and  $\text{VO}_4$  respectively; green spheres are Li(3) in off-centre octahedral sites. Purple and red spheres are O, N(1) and O(2, 3) respectively.

**Figure 4** Impedance data for  $\text{Li}_{3.2}\text{VO}_{3.8}\text{N}_{0.2}$ , prepared using  $\text{Li}_2\text{CO}_3$ . (a) Impedance complex plane plots at 332, 387, 449 °C. Spectroscopic plots of  $C'$  (b),  $Y'$  (c),  $-Z''$  and  $M''$  (d). Inset in (a) shows impedance data prepared using  $\text{LiOH}\cdot\text{H}_2\text{O}$ .

**Figure 5** Arrhenius plots of  $\text{Li}_{3+x}\text{VO}_{4-x}\text{N}_x$ :  $x = 0, 0.2$ ; Sample prepared using (a)  $\text{Li}_2\text{CO}_3$ , (b)  $\text{LiOH}\cdot\text{H}_2\text{O}$ . Activation energies are noted beside each data set.

**Table 1**(a) Refined structural parameters, (b) Bond lengths, (c) Bond angles.

**Table 2** Bond lengths to O(1), O(2) and O(3).

Figure 1

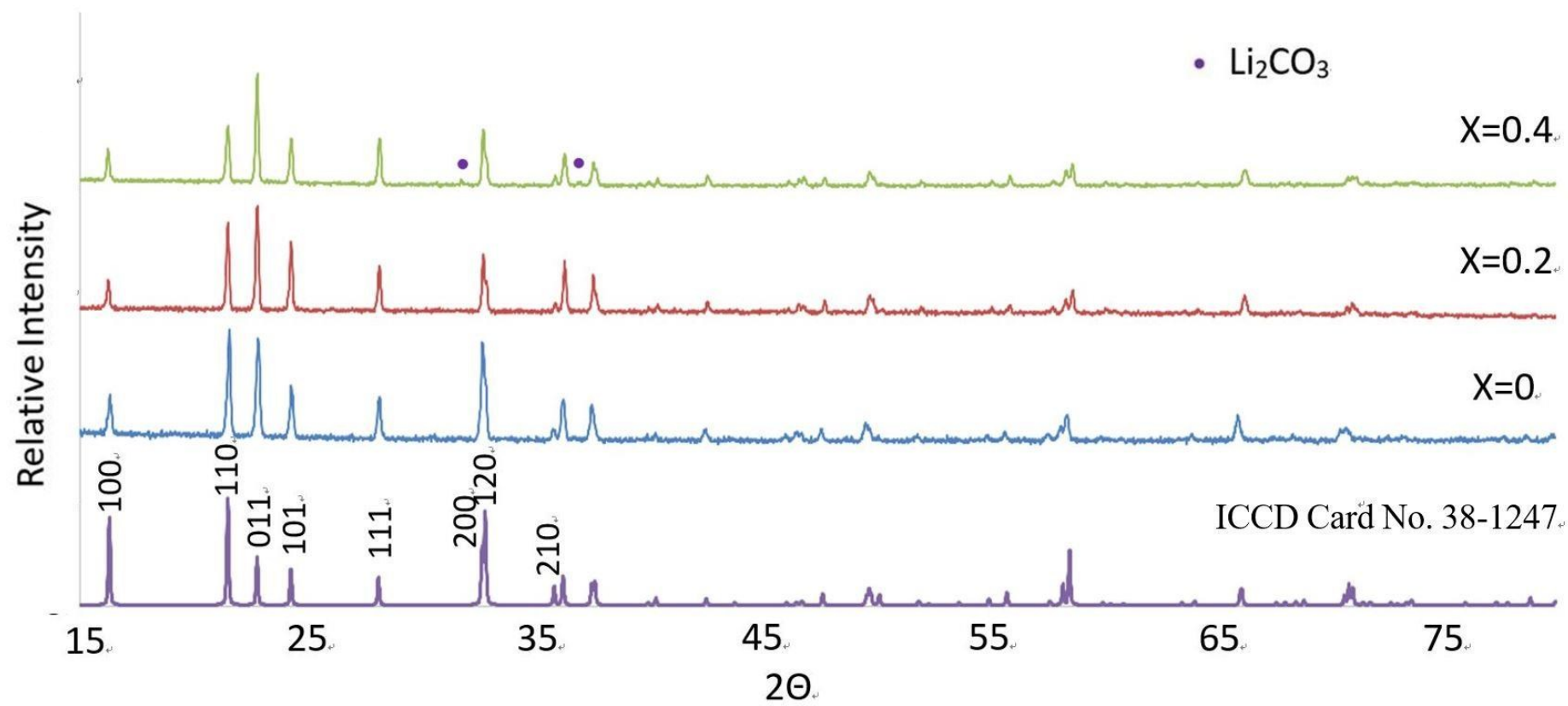
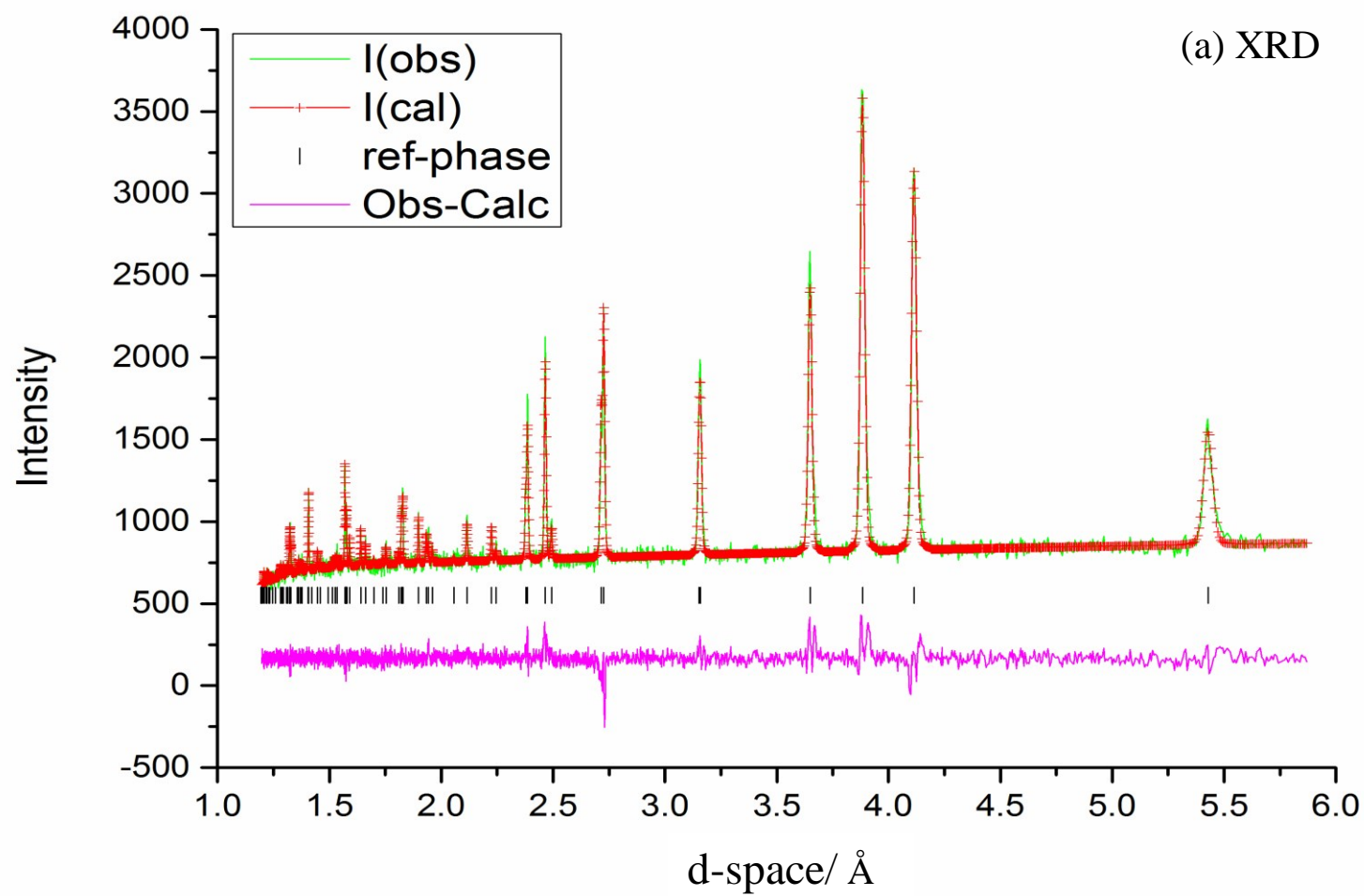
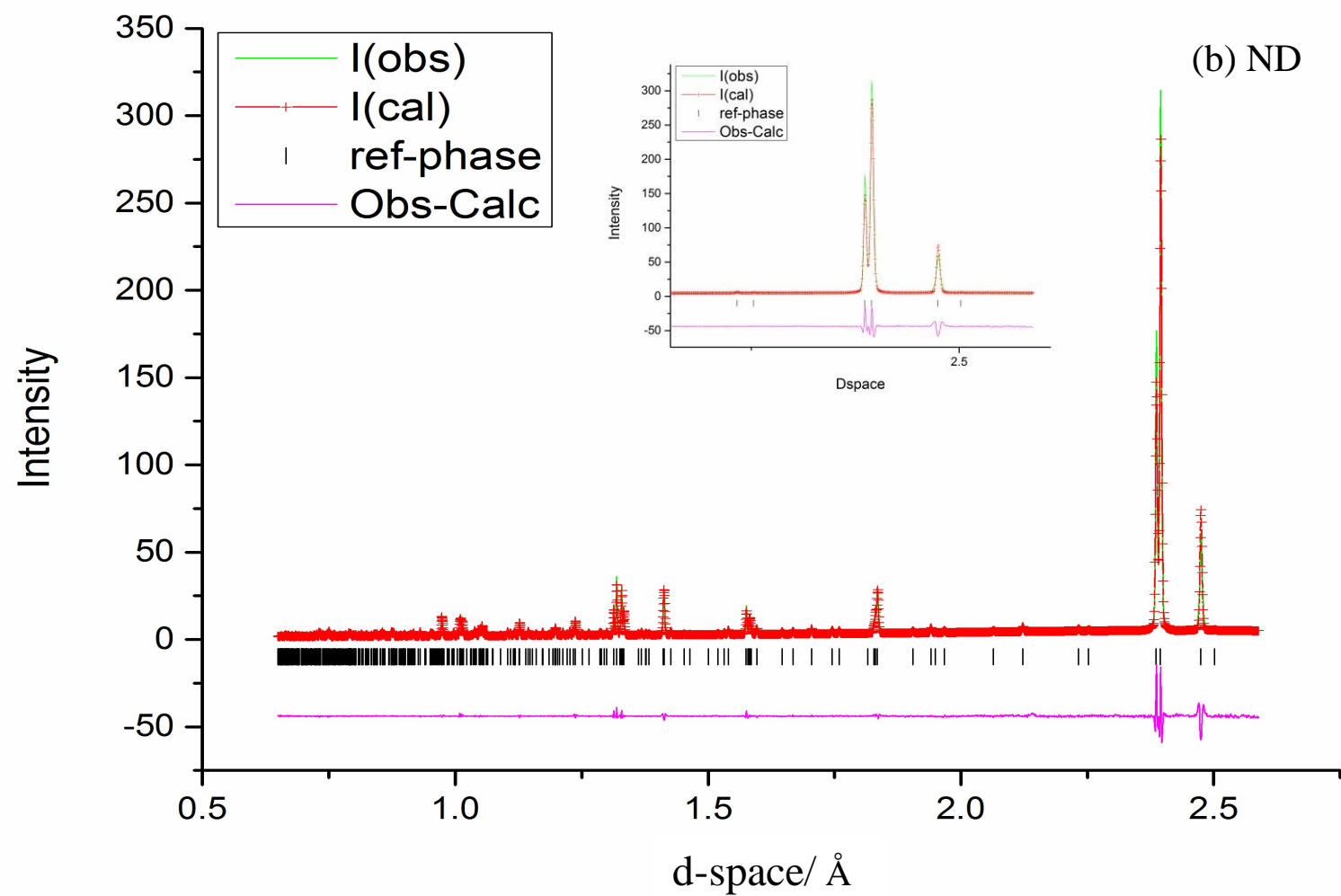
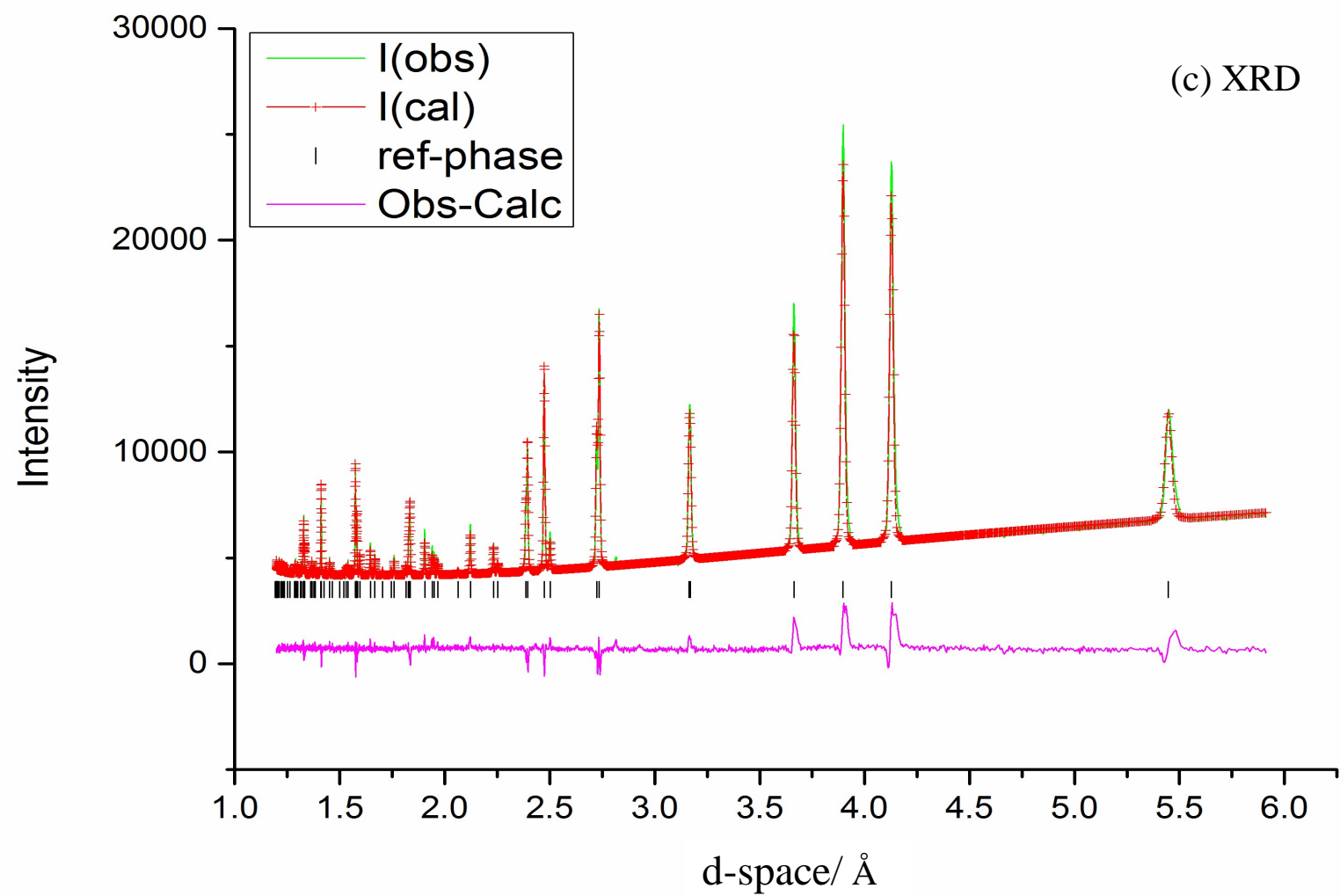


Figure 2









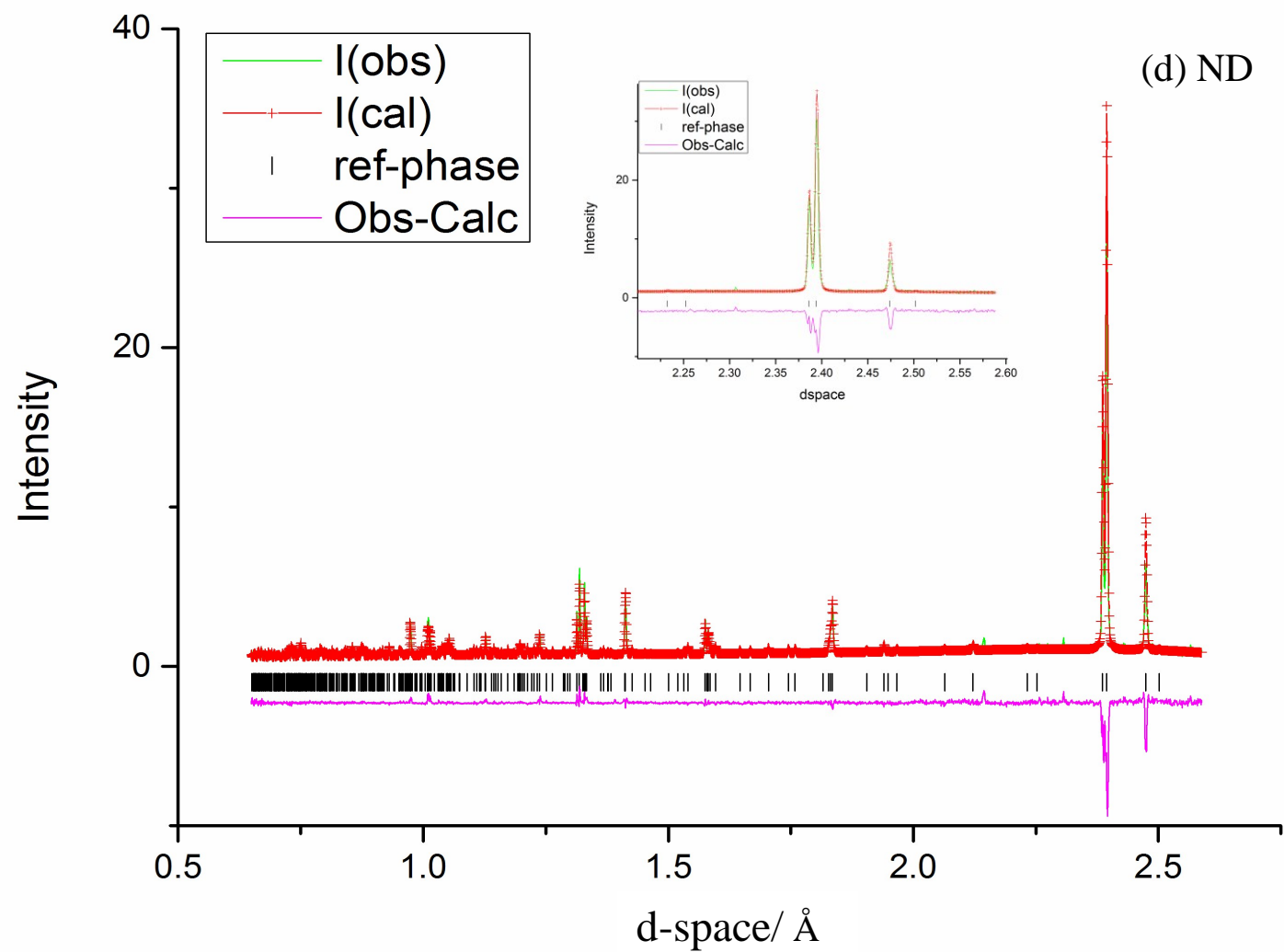


Figure 3

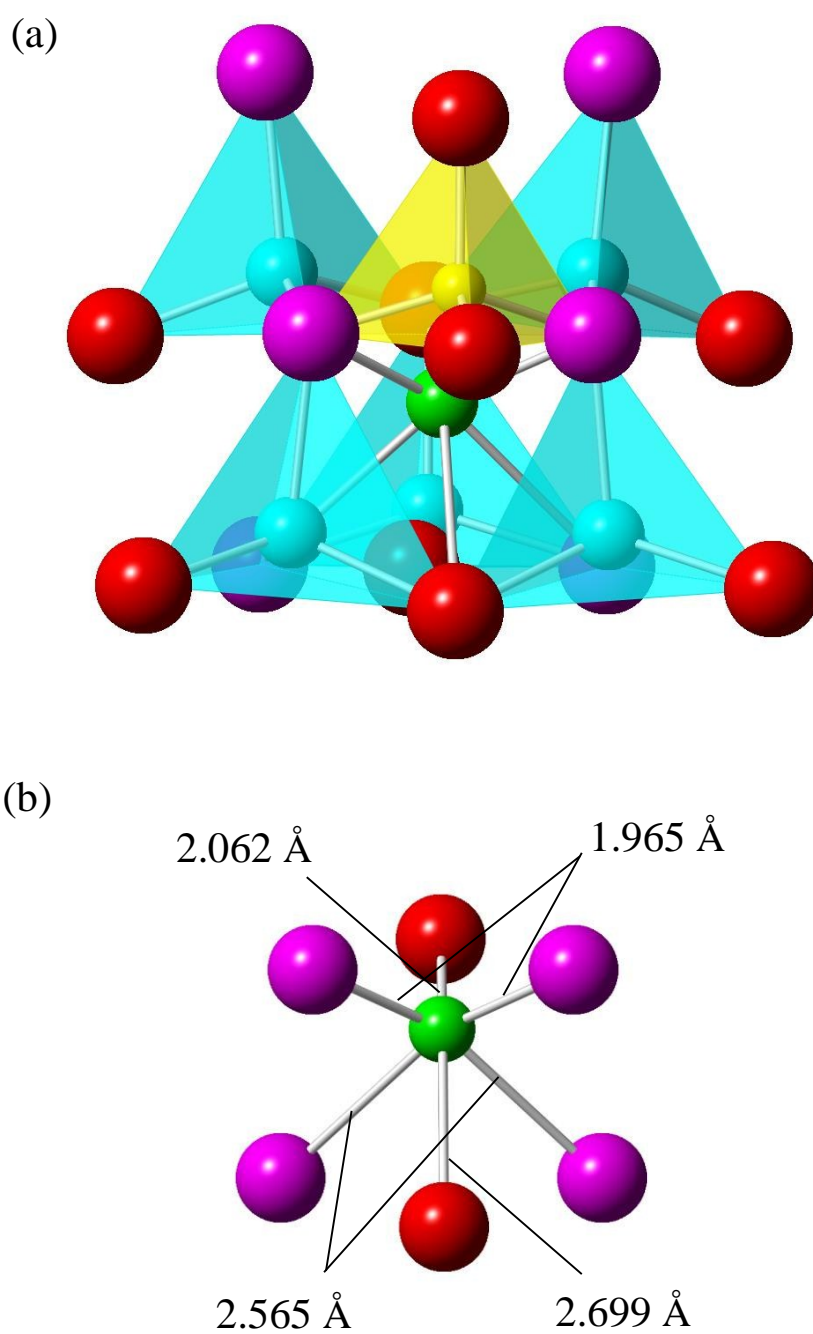


Figure 4

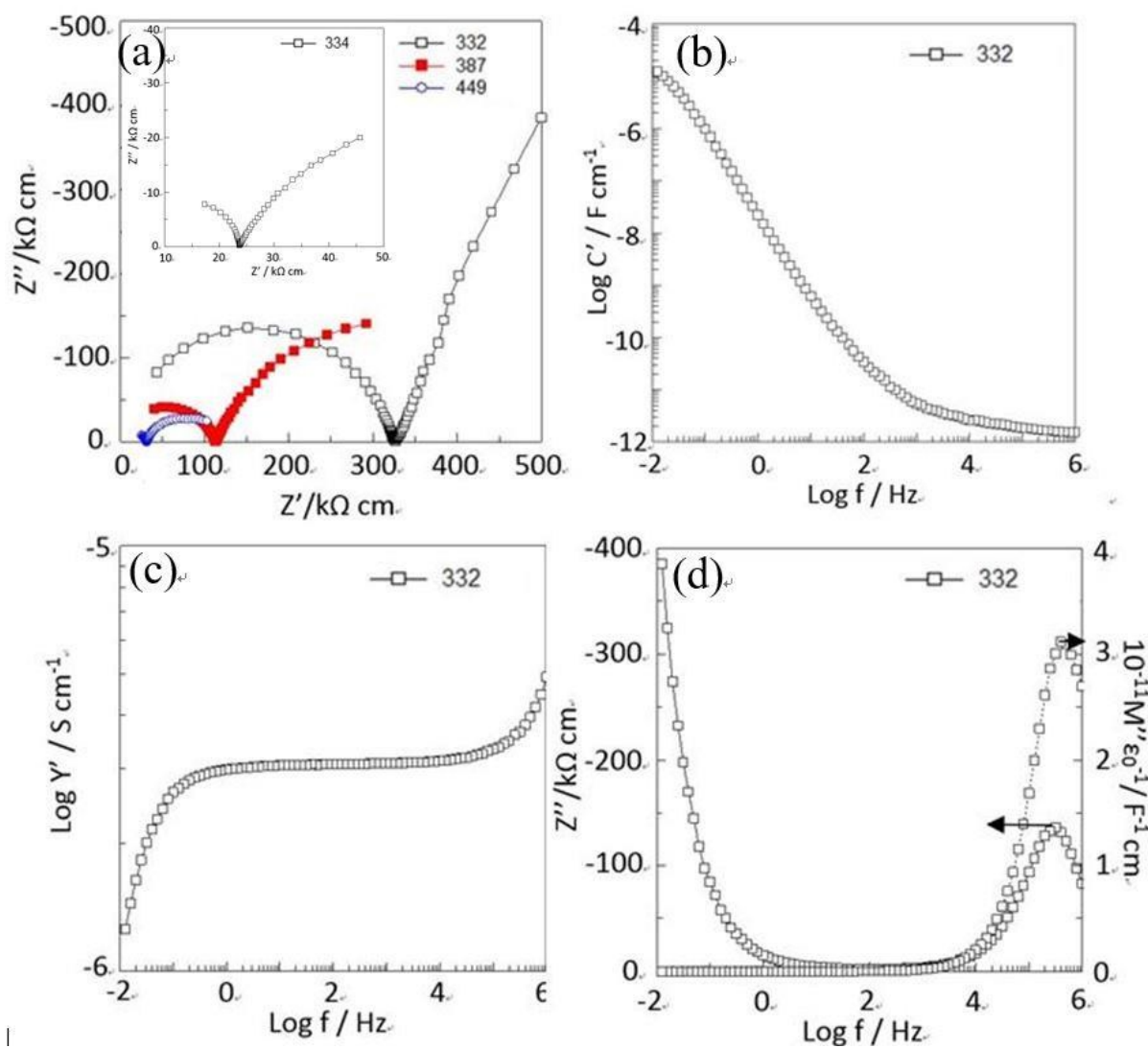


Figure 5

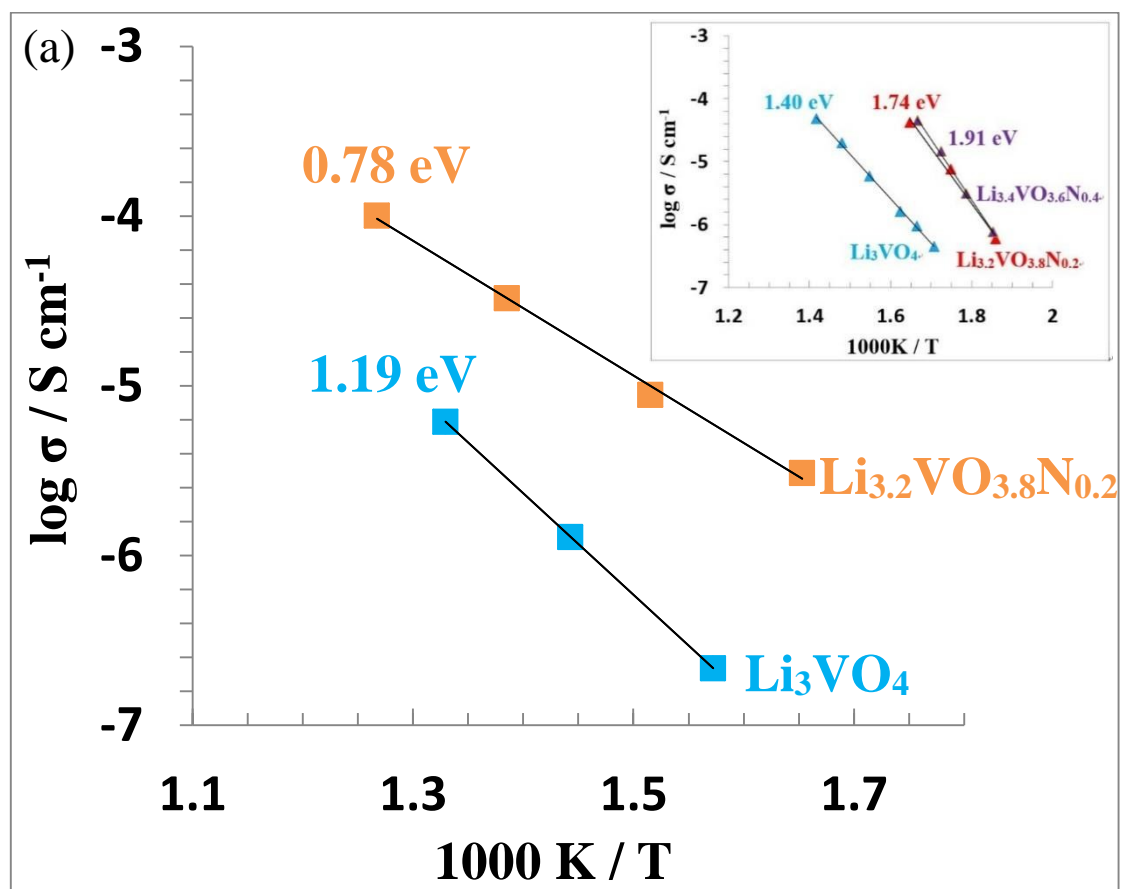


Table 1(a)

Atom and multiplicity	Parameter	Li <sub>3</sub> VO <sub>4</sub> (x=0)	Li <sub>3.2</sub> VO <sub>3.8</sub> N <sub>0.2</sub> (x=0.2)
Li(1), 4	x	0.246(1)	0.247(1)
	y	0.331(1)	0.331(2)
	z	0.986(6)	0.991(2)
	Occupancy	1	1
	$U_{iso} \times 100 / \text{\AA}^2$	1.50(8)	0.24
Li(2), 2	x	0.5	0.5
	y	0.836(1)	0.832(3)
	z	0.985(6)	0.995(2)
	Occupancy	1	1
	$U_{iso} \times 100 / \text{\AA}^2$	1.8(1)	1.39
Li(3), 2	x	--	0.5
	y	--	0.523
	z	--	0.235
	Occupancy	--	0.19(3)
	$U_{iso} \times 100 / \text{\AA}^2$	--	1.0
V, 2	x	0	0
	y	0.828(1)	0.829(1)
	z	0	0
	Occupancy	1	1

	$U_{iso} \times 100 / \text{\AA}^2$	2.4(2)	2.67
O(1), 4*	x	0.224(1)	0.224(1)
	y	0.680(1)	0.679(1)
	z	0.888(6)	0.896(1)
	Occupancy	1	O1 0.88(2) N1 0.12(2)
	$U_{iso} \times 100 / \text{\AA}^2$	1.36(2)	0.01
O(2), 2	x	0	0
	y	0.123(1)	0.129(1)
	z	0.890(6)	0.899(1)
	Occupancy	1	1
	$U_{iso} \times 100 / \text{\AA}^2$	1.39(3)	0.13
O(3), 2	x	0.5	0.5
	y	0.174(1)	0.175(1)
	z	0.843(6)	0.847(1)
	Occupancy	1	1
	$U_{iso} \times 100 / \text{\AA}^2$	1.27(4)	0.34
For x=0, a=6.3288(1) \AA, b=5.4475(1) \AA, c=4.9483(1) \AA, V=170.602(4) \AA <sup>3</sup> , $\chi^2$ = 2.920, Rwp=5.90%, Rp=6.88% for ND, Rwp=4.59%, Rp=3.35% for XRD.			
For x=0.2, a=6.3271(1) \AA, b=5.4470(1) \AA, c=4.9478(1) \AA, V=170.518 (2) \AA <sup>3</sup> , $\chi^2$ = 4.093, Rwp=7.88%, Rp=8.47% for ND, Rwp=3.21%, Rp=2.04% for XRD.			

\*For  $\text{Li}_{3.2}\text{VO}_{3.8}\text{N}_{0.2}$ , the O(1) site contained a disordered mixture of 11% N and 89% O.

Table 1(b)

	Li <sub>3</sub> VO <sub>4</sub>	Li <sub>3.2</sub> VO <sub>3.8</sub> N <sub>0.2</sub>
Vector	Length (Å)	Length (Å)
Li1-O1	1.968(5)	1.958(8)
Li1-O1	2.004(4)	2.013(7)
Li1-O2	1.961(4)	1.963(7)
Li1-O3	1.952(4)	1.952(7)
Li2-O1	2.000(3)	1.994(7)
Li2-O1	2.000(3)	1.994(7)
Li2-O2	2.013(6)	2.008(13)
Li2-O3	1.973(7)	2.007(13)
V1-O1	1.720(10)	1.713(2)
V1-O1	1.720(10)	1.713(2)
V1-O2	1.730(10)	1.712(4)
V1-O3	1.70(3)	1.717(4)
Li3-O1	--	1.965(3)
Li3-O1	--	1.965(3)
Li3-O2	--	2.062(2)
Li3-O1	--	2.565(2)
Li3-O1	--	2.565(3)
Li3-O3	--	2.699(4)



Table 1(c)

Angle	Degree(°)	Degree(°)
O1-Li1-O1	106.2(2)	105.8(4)
O1-Li1-O2	115.1(2)	115.6(4)
O1-Li1-O3	113.2(2)	113.2(4)
O1-Li1-O2	107.3(2)	106.8(4)
O1-Li1-O3	105.6(2)	105.9(3)
O2-Li1-O3	108.8(2)	108.8(4)
O1-Li2-O1	121.8(3)	122.1(7)
O1-Li2-O2	106.1(2)	106.9(4)
O1-Li2-O3	108.0(2)	107.3(4)
O1-Li2-O2	106.1(2)	106.9(4)
O1-Li2-O3	108.0(2)	107.3(4)
O2-Li2-O3	105.7(3)	105.4(6)
O1-V1-O1	110.9(1)	111.8(2)
O1-V1-O2	110.2(1)	111.4(1)
O1-V1-O3	108.5(1)	107.2(2)
O1-V1-O2	110.2(1)	111.4(1)
O1-V1-O3	108.5(1)	107.2(2)
O2-V1-O3	108.6(1)	107.5(3)
O1-Li3-O1	--	92.4(1)
O1-Li3-O2	--	110.89(1)
O1-Li3-O2	--	110.89(1)

Table 2

Bond Length(Å)	O(1)	O(2)	O(3)
V(1)	1.713(2)	1.712(4)	1.717(4)
Li(1)	1.958(8)	1.963(7)	1.952(7)
Li(1)'	2.013(7)	1.963(7)	1.952(7)
Li(2)	1.994(7)	2.008(13)	2.007(13)
Li(3)	1.965(3)	2.062(2)	--
Li(3)	2.565(2)	--	2.699(4)