



Short communication

Electrical conductivity and charge compensation in Ta doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$

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ABSTRACT

Ta doping in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) as function of different heat-treat atmospheres (oxidizing/reducing) was investigated and compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to determine its effect on ionic/electronic conductivity and the charge compensating defects. Under oxidizing conditions $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ was primarily an ionic conductor where the extra charge of Ta was compensated by Ti vacancies. Under reducing conditions $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ was primarily an electronic conductor where the extra charge of Ta was compensated by an electron. The charge compensating defects were confirmed by sintering data.

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1. Introduction

Recently, there has been considerable interest in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a potential anode for use in Li-ion batteries [1–5]. It has many advantages compared to the currently used graphite. For example, it is a zero-strain lithium insertion host suggesting virtually unlimited cycle life. It features a flat, operating voltage of about 1.5 V versus lithium, above the reduction potential of common electrolyte solvents thus, it does not form a solid electrolyte interface based on solvent reduction which should be a favorable property for high rate and low temperature operation. However, several disadvantages exist compared to graphite. These include low electronic conductivity. As a result several methods have been used to increase electronic conductivity with the intent of improving rate-capability. These include forming a composite of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and a conductive second phase (Ag) [6], doping $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with Mg^{2+} on the Li^+ sites and then heating under reducing conditions [7] and heating pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under a reducing atmosphere [8].

Another possibility to increase the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is to substitute a M^{5+} ion (i.e., Ta^{5+}) on a Ti^{4+} site, which should lead to an increase in electron concentration, for heat-treatment under reducing conditions, according to the charge neutrality condition (Kroger–Vink [9] notation is used) given in Eq. (1) and hence, an increase in electronic conductivity.

$$[e'] = [\text{Ta}_{\text{Ti}}^{\bullet}] \quad (1)$$

where an electron, e' , corresponds to Ti^{3+} on a Ti^{4+} site.

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For the case of oxidizing conditions, the extra charge of Ta should be compensated by lattice defects [9–11]. It is likely that charge compensation can be accomplished by either a Li vacancy or a Ti vacancy, as given below in Eqs. (2) and (3), respectively. It should be noted that for the case of Li it could sit on tetrahedral and octahedral sites, whereas Ti sites only on octahedral sites in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure [2,3,5].

$$[V_{\text{Li}}]_{\text{tetrahedral}} + [V_{\text{Li}}]_{\text{octahedral}} = [\text{Ta}_{\text{Ti}}^{\bullet}] \quad (2)$$

$$4[V^{\prime\prime\prime}_{\text{Ti}}] = [\text{Ta}_{\text{Ti}}^{\bullet}] \quad (3)$$

For the case charge compensation by a Li vacancy, an increase in Li-ion conductivity would be expected compared to undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$, in this case the defect model is of the form $\text{Li}_{1-x}\text{V}_x^{\text{Li}}[\text{Li}_{1/3-y}\text{V}_y^{\text{Li}}\text{Ti}_{5/3-z}\text{Ta}_z]\text{O}_4$ in spinel notation ((2) and (5)) whereas for the case of charge compensation by a Ti vacancy no significant increase in Li-ion ionic conductivity would be expected compared to undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the defect model is of the form $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3-z}\text{Ta}_{z/5}\text{V}_{4z/5}^{\text{Ti}}]\text{O}_4$. Thus, a comparison of the ionic conductivity of Ta to undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be used to determine the charge compensating lattice defect.

It is the purpose of this paper to investigate the effects of Ta doping on the ionic/electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a function of heat-treatment atmosphere (reducing and oxidizing conditions). The results will be compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under similar heat-treatment conditions to allow for a determination of the charge compensating defects under reducing/oxidizing conditions.

2. Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were prepared using a solid-state method from TiO_2 (rutile structure) and Li_2CO_3 [12]. The Ta doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared also using a solid-state method with TiO_2 (rutile structure), Li_2CO_3 and Ta metal. In both cases three weight percent excess Li_2CO_3 was used to compensate for lithia volatilization during the high temperature heating. A 1% Ta doping level was selected, which yields the following composition, $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ assuming that Ta sits on a Ti site. This is probably a good assumption in that the volume change is about a factor of ~ 3.8 times greater if Ta^{5+} sits on Li^+ tetrahedral sites and ~ 3.3 times greater if Ta^{5+} sits on Li^+ octahedral sites rather than on Ti^{4+} octahedral sites [13]. This Ta doping level was selected because it has been observed that 1% doping of Nb^{5+} into TiO_2 increased the electronic conductivity from about $\sim 10^{-13}$ to $10^{-2} \text{ S cm}^{-1}$ [14]. The starting materials were ground with an alumina mortar and pestle with enough methanol to form a slurry. The dried and mixed reactant mixture was pelletized and then heated at 800°C for 12 h in air (oxidizing) or 3 vol.% H_2/Ar (H_2/Ar) (reducing). The sample was reground, pelletized and heated for another 24 h at 800°C in air or H_2/Ar . The powders were reground and uniaxially pressed into cylindrical specimens 13 mm in diameter with a thickness between 2 and 4 mm at pressure of 200 MPa. A 5 wt.% polyvinyl alcohol binder used. The pellets were then sintered at 800°C for 12 h in air or H_2/Ar . The density of the sintered pellets was measured using the Archimedes method with methanol as the immersion medium.

The samples were characterized by X-ray diffraction. Lattice constants were determined by fitting the data using Rietveld refinement [15]. DC and AC room temperature conductivity were determined on sintered and polished disk samples using the two probe method. Silver paste electrodes were applied to the top and bottom surfaces of the disk. DC resistances were measured using a Keithly 6517A Electrometer/High Resistance Meter with a Model 8009 Resistivity Test Fixture capable of measuring volume resistivities as high as $1018 \Omega \text{ cm}$. High resistance samples required equilibration times of about 18–24 h to ensure steady-state was achieved. AC impedance was measured using a Solatron 1260 Impedance Analyzer in the frequency range 1–106 Hz.

3. Results and discussion

Both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ samples that were heated under air were white colored, indicative of an electronic insulator. Whereas, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ samples heated under H_2/Ar were purple colored. Previous results [8] based on X-ray photoelectron spectroscopy had shown that the color change from white to purple for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was a result that some of the Ti^{4+} ions had been reduced to Ti^{3+} ions during heat-treatment under reducing conditions.

X-ray diffraction pattern(s) of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under air or H_2/Ar are shown in Fig. 1. From Fig. 1 it can be observed that the patterns for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air or H_2/Ar are similar. They both represent a single-phase cubic material with a $\text{Fd}3\text{m}$ space group.

The room temperature AC conductivity results for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under air using Li-ion blocking silver electrodes are shown in the complex impedance plot in Fig. 2. From Fig. 2 several important points are observed. Firstly, the data separates into a high frequency region which contains a semicircle and low frequency region which contains a spike. For this case, since we have Li blocking electrodes the shape of the curve represents a material which is predominately a Li-ion conductor with very low electronic conductivity [16–19]. Secondly, the low frequency intercept of the semicircle on the Z' axis gives the total ionic resistance, which for the case of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$

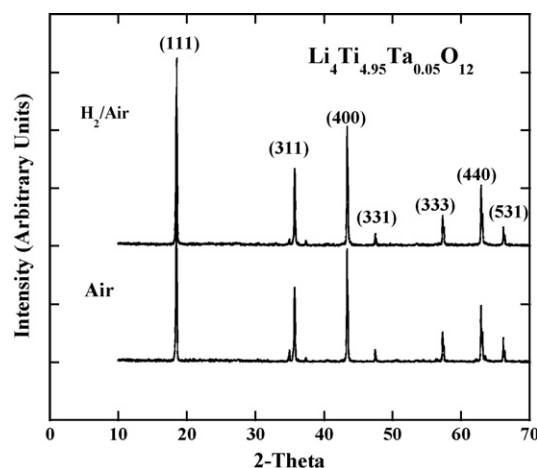


Fig. 1. X-ray diffraction pattern of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ synthesized under air or 3 vol.% H_2/Ar (H_2/Ar).

yields an ionic conductivity of $\sim 3 \times 10^{-8} \text{ S cm}^{-1}$. The shape of the curve and value of the ionic conductivity for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air was similar to that for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$. The DC electronic conductivity for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ was $\sim 1 \times 10^{-9} \text{ S cm}^{-1}$ and for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ $\sim 8 \times 10^{-10} \text{ S cm}^{-1}$, both heat-treated under air. The electronic conductivity values for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air are in close agreement. The ionic conductivity values for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of $\sim 3 \times 10^{-8} \text{ S cm}^{-1}$ are in good agreement with ionic conductivity values in the literature for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air by Porotnikov et al. [20] ($6 \times 10^{-8} \text{ S cm}^{-1}$) and Hayashi and Hatano [21] ($7 \times 10^{-8} \text{ S cm}^{-1}$) and a factor of 3 higher than by Leonidov et al. [22] ($\sim 10^{-9} \text{ S cm}^{-1}$) and Prosini et al. [23] ($\sim 10^{-9} \text{ S cm}^{-1}$) and about an order of magnitude lower than that observed by Huang et al. [24] ($2 \times 10^{-7} \text{ S cm}^{-1}$). The DC electronic conductivity values for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ ($\sim 1 \times 10^{-9} \text{ S cm}^{-1}$) and for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\sim 8 \times 10^{-10} \text{ S cm}^{-1}$) heated under air are in good agreement with results of Huang et al. [25] who measured $\sim 4 \times 10^{-9} \text{ S cm}^{-1}$ for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air. The ionic transport number (ionic conductivity/total conductivity) for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ is ~ 0.97 and for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is ~ 0.97 heated under air. This result suggests that $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ when heated under oxidizing conditions are predominately ionic conductors.

A comparison of the ionic conductivity results for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air can allow for a determination of the charge compensating lattice defect for

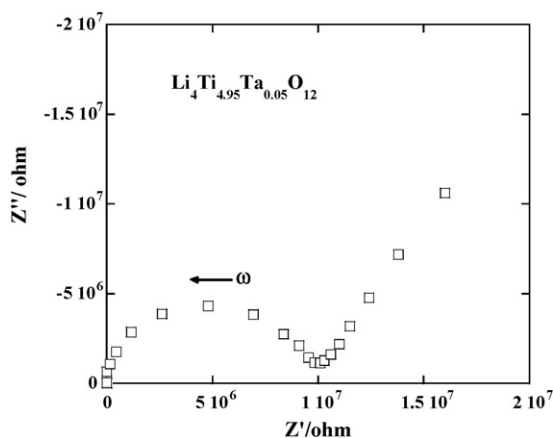


Fig. 2. Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under air.

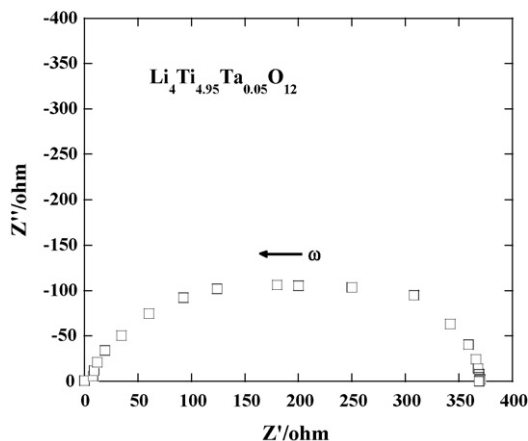


Fig. 3. Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under H_2/Ar .

Ta. According to Eqs. (2) and (3) under oxidizing conditions, the extra charge of Ta should be compensated by a Li vacancy (Eq. (2)) or a Ti vacancy (Eq. (3)). For the case of compensation by a Li vacancy an increase in ionic conductivity would be expected whereas, for compensation by a Ti vacancy no change in ionic conductivity would be expected. Since the ionic conductivity value of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air are the same ($\sim 3 \times 10^{-8} \text{ S cm}^{-1}$), this suggests that under oxidizing conditions the extra charge of Ta is compensated by Ti vacancies rather than by Li vacancies.

The complex impedance plots for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under reducing conditions are shown in Figs. 3 and 4, respectively. A comparison of Fig. 2 with Fig. 3 reveals quite a difference in the shape of the complex impedance plot exhibited by $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under oxidizing (Fig. 2) and reducing (Fig. 3) conditions. The complex plot for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ under reducing conditions reveals only a semicircle, suggesting a mixed ionic and electronic conductor [16,17]. The electronic conductivity determined from the low frequency intercept of the semicircle on the Z' axis yields $\sim 8 \times 10^{-4} \text{ S cm}^{-1}$. The electronic conductivity determined from DC measurements $\sim 1 \times 10^{-3} \text{ S cm}^{-1}$, is in excellent agreement with the AC results. This is about a 106 increase in electronic conductivity for same material when heated under reducing conditions instead of oxidizing conditions. The high electronic conductivity value of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$

for heat-treatment under reducing conditions is a result that some of the Ti^{4+} ions have been reduced to Ti^{3+} ions to compensate for the extra charge of the Ta^{5+} (Eq. (1)), increasing the number of electrons and hence, electronic conductivity. The electronic conductivity ($\sim 1 \times 10^{-3} \text{ S cm}^{-1}$) for 1% Ta^{5+} doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is in good agreement with the electronic conductivity value for 1% doping of Nb^{5+} into TiO_2 [14] ($\sim 3 \times 10^{-3} \text{ S cm}^{-1}$), where in this case charge compensation of Nb^{5+} also occurs by the reduction of some Ti^{4+} ions into Ti^{3+} ions to increase the number of electrons and hence, electronic conductivity.

The electronic conductivity of Ta doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can also be compared to Mg doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The electronic conductivity ($\sim 1 \times 10^{-3} \text{ S cm}^{-1}$) for 1% Ta^{5+} doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) is higher than for $\text{Li}_{3.95}\text{Mg}_{0.05}\text{Ti}_5\text{O}_{12}$ ($\sim 1 \times 10^{-7} \text{ S cm}^{-1}$). It would be expected in a first approximation that the electronic conductivity of these two materials to be similar since, the dopant level (i.e., the concentration of the electrons) and electron mobility for both materials should be the same. One possible reason for this difference is that at low concentrations for both the Nb and Mg materials it was observed that there is a very large change in conductivity with dopant concentration at low dopant levels [7,14]. Thus, it is possible that the dopant levels in the starting compositions (i.e., $\text{Li}_{3.95}\text{Mg}_{0.05}\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) are not the actual dopant levels, which will lead to different dopant concentrations and hence, different electron concentrations and electronic conductivity values.

The complex plot (Fig. 3) for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under reducing conditions also reveals only a semicircle, suggesting a mixed ionic and electronic conductor [16,17], similar to that for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$. For the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ the low frequency intercept of the semicircle on the Z' axis is greater than that for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$, revealing a lower electronic conductivity value. The electronic conductivity value for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ determined from the low frequency intercept of the semicircle on the Z' axis yields $\sim 4 \times 10^{-5} \text{ S cm}^{-1}$. The electronic conductivity for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ determined from DC measurements $\sim 2 \times 10^{-5} \text{ S cm}^{-1}$, in good agreement with the AC results. These results are in very close agreement with the electronic conductivity results of Huang et al. [6], who observed a value of $\sim 1 \times 10^{-5} \text{ S cm}^{-1}$ for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere. For the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ unlike $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$, the increase in electron concentration (reduction of some Ti^{4+} ions into Ti^{3+}) and hence, the electronic conductivity results from nonstoichiometry of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at low oxygen partial pressures (Eq. (4)). For the case of nonstoichiometry the charge neutrality condition is given by Eq. (5).



$$[\text{e}'] = 2[\text{V}_\text{o}^{\bullet\bullet}] \quad (5)$$

where O_o^\times represents an oxygen ion and $\text{V}_\text{o}^{\bullet\bullet}$ represents an oxygen vacancy. A comparison of the electronic conductivities, reveals that the electronic conductivity of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ ($\sim 1 \times 10^{-3} \text{ S cm}^{-1}$) is about 100 times higher than that for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\sim 3 \times 10^{-5} \text{ S cm}^{-1}$) suggesting that at the temperature, oxygen partial pressure and dopant level used in this investigation, the electronic conductivity of the Ta doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is controlled by the Ta dopant (Eq. (1)) rather than by nonstoichiometry (Eq. (5)).

A comparison of the relative densities of sintered $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ under oxidizing and reducing conditions can also be used to confirm the charge compensating defects in $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$, determined previously based on conductivity measurements. This is because sintering (relative densities) like conductivity is also controlled by the concentration and mobility of point defects [9–11,26]. However, unlike conductivity which is usually controlled by the concentration and mobility of the fastest species, sintering is controlled by the concentration and mobility

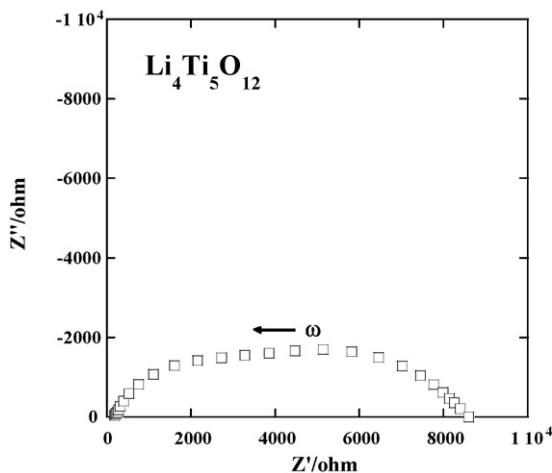


Fig. 4. Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under H_2/Ar .

of the slowest species [9–11,26]. For the case of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ it is highly likely that the oxygen ion is the slowest moving species and moves via a vacancy mechanism and hence, controls sintering [26–29]. Using this fact along with the charge neutrality equations given earlier (Eqs. (1)–(3) and (5) and assuming that the ionic defects form Schottky defects (vacancies) rather than Frenkel defects (interstitials), the relative densities of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under oxidizing and reducing conditions can be compared to confirm the charge compensating defects in $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ determined from the conductivity data.

From Eqs. (4) and (5) the dependence of the oxygen vacancy concentration on oxygen partial pressure for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under reducing conditions can be determined and is given in Eq. (6).

$$[V_{\text{O}}^{\bullet\bullet}] \propto P_{\text{O}_2}^{-1/6} \quad (6)$$

Eq. (6) suggests that as oxygen partial pressure decreases the oxygen vacancy concentration increases. From Eqs. (5) and (6) it can be seen that under reducing conditions for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ that charge compensating defects are electrons and oxygen vacancies. For $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ under reducing conditions the conductivity results suggest that charge compensation of Ta by takes electrons, whose concentration is determined by the Ta doping level (Eq. (1)). In this case there is no effect of Ta on the oxygen vacancy concentration. Thus, it is expected that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ would have a higher oxygen vacancy concentration than $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and hence, a higher sintering rate for heat-treatment under reducing conditions. This is in agreement with the experimental results. The relative density for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was 83% versus 76% for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under reducing conditions.

For the case of heat-treatment under an oxidizing atmosphere based on the conductivity results it is expected that $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ would have a lower sintering rate (relative density) compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. For the case of Schottky defects, the product of the cation vacancy concentration times the anion vacancy concentration is fixed at given temperature. Thus, at a given temperature if the cation vacancy concentration is increased the anion vacancy concentration must decrease to keep the product constant. The ionic conductivity results suggest that the extra charge of Ta under oxidizing conditions is compensated by a Ti vacancy (Eq. (3)). In this case $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ will have a higher Ti vacancy concentration compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which will lead to a lower oxygen vacancy concentration in $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and hence, a lower sintering rate is expected for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$. This is in agreement with the experimental results. The relative density of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ was 71% versus 76% for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, both heated under oxidizing conditions. Thus, confirming that under oxidizing conditions Ta doping is compensated by a cation lattice defect. Based on the ionic conductivity results it is suggested that this cation lattice defect is most likely a Ti vacancy.

4. Conclusions

The effects of a 1% Ta doping level in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) as function of different heat-treat atmospheres (oxidizing/reducing) was investigated to observe the effect of Ta doping on the ionic/electronic conductivity and to determine the charge compensating defects in this material. The ionic conductivity value of the white colored $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$

heated under an oxidizing atmosphere was $\sim 3 \times 10^{-8} \text{ S cm}^{-1}$ with a DC electronic conductivity value of $\sim 1 \times 10^{-9} \text{ S cm}^{-1}$. These values are similar to values observed for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the same oxidizing atmosphere. These results suggest that both materials are predominately ionic conductors, with the extra charge of Ta compensated by a lattice defect, most likely Ti vacancies. For the case of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under a reducing atmosphere it was purple colored with an electronic conductivity value of $\sim 1 \times 10^{-3} \text{ S cm}^{-1}$. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere was also purple colored with an electronic conductivity value of $\sim 3 \times 10^{-5} \text{ S cm}^{-1}$. These results suggest both of these materials are predominately electronic conductors where the electronic conductivity is a result of the reduction of some Ti^{4+} ions into Ti^{3+} ions. For $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ this reduction is a result of the extra charge of the Ta whereas for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ it is a result of nonstoichiometry. The sintering results are in agreement with the conductivity results, in that Ta charge compensation in $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ takes by electrons under reducing conditions and cation lattice defects under oxidizing conditions.

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