



Quantification of lithium in hyper-stoichiometric lithium titanate by external (in air) particle induced gamma-ray emission (PIGE) method

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Abstract

Lithium titanate is one of the crucial breeder materials in nuclear fusion reactors. High lithium atomic density is the most desired property for this application. In view of this, advanced lithium titanate ($\text{Li}_{2+x}\text{TiO}_{3+y}$) ceramics with varying stoichiometry of Li were synthesized at temperatures in the range of 900–1100 °C and characterized using X-ray diffraction and scanning electron microscopy. External (in air) particle induced gamma-ray emission (PIGE) method was utilized for the quantification of lithium in the direct solid samples using ^{14}N (from air) as an external current normalizer. The method was validated using certified lithium titanate reference material. The obtained results are found to be in good agreement with the theoretical values. The present study highlights the advantages of the external PIGE as a simple non-destructive method of quantification of Li in ceramics over conventional methods.

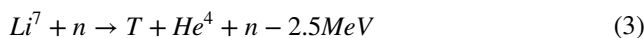
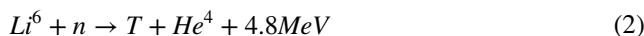
Keywords Lithium quantification · Hyper-stoichiometric lithium titanate · Li_2TiO_3 · External (in air) PIGE · Breeder material · Nuclear material

Introduction

Fusion energy is believed to be the potential energy source for the future. Two isotopes of hydrogen, namely deuterium and tritium are identified as feasible fuels for fusion reaction owing to their high reaction cross-section with the least energy requirement [1]. Deuterium and tritium fuse in the presence of plasma and yield 17.6 MeV of energy according to the reaction in Eq. 1.



Deuterium is available naturally in large quantities but due to the radioactive nature of tritium, it is not abundant in nature, thus it has to be synthesized. Generally, lithium is used for the production of tritium as per the reactions 2 & 3. Therefore, lithium-based ceramics are used as breeder material in nuclear fusion reactors.



Lithium titanate is a promising material for breeder application in nuclear fusion reactor, due to its superior properties such as minimal activation characteristics and good tritium release properties as compared with other ceramics [1, 2]. High Li density is one of the essential criteria for tritium breeding application [3]. Lithium content in the breeder material will decrease during operation due to the transmutation of lithium [2]. Additionally, lithium being volatile in nature, is lost from the ceramic during the high temperature synthesis process [4–6]. To compensate for lithium losses during the reactor operation and during the synthesis stage, extra lithium is added to lithium titanate. Thus, hyper-stoichiometric lithium titanate [$\text{Li}_{(2+x)}\text{TiO}_{(3+y)}$] with

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high Li/Ti ratio have been proposed [7–9]. Lithium titanate ceramics can be produced through different processing techniques. The conventional production route of lithium titanate includes solid state synthesis followed by high temperature sintering process to achieve the desired shape (e.g. pebbles) with the required density [3]. During production of lithium titanate, high temperature sintering step is associated with the loss of lithium due to its volatile nature. The lithium loss has been found to be a function of sintering temperature and time. Thus, it is important to quantify lithium content in the ceramic breeder material. Conventional chemical analysis techniques like Atomic absorption spectroscopy (AAS), Inductively coupled plasma mass spectrometry (ICP-MS) and Inductively coupled plasma optical emission spectroscopy (ICP-OES) require the ceramic sample to be in the solution form, which needs strong acids for dissolution for exact quantification of the element of interest. Although these methods have good accuracy and precision but are destructive in nature and the sample integrity is lost after the analysis. Any method which is capable of analysing the solid sample without dissolution is preferred over the conventional wet chemical techniques. On the other hand, analytical techniques namely particle induced X-ray emission (PIXE), X-ray fluorescence (XRF) and neutron activation analysis (NAA) are non-destructive in nature but not suitable for the quantification of low Z elements including lithium due to their unfavourable atomic and nuclear properties [10]. Nuclear analytical technique namely particle induced gamma-ray emission (PIGE) technique is very sensitive to low Z elements including lithium [10–13].

In the present study, stoichiometric (Li_2TiO_3) and hyperstoichiometric ($\text{Li}_{2+x}\text{TiO}_{3+y}$) lithium titanate ceramic samples have been synthesized at various temperatures ranging from 900–1100 °C and characterized by various techniques namely scanning electron microscopy and X-ray diffraction. Further, the external PIGE technique using nitrogen (from air) as an external current normalizer has been utilized to evaluate lithium concentration in stoichiometric and hyperstoichiometric Li_2TiO_3 samples. Compositional information obtained in the present study will be useful for the measurement of the net lithium concentration in lithium-based breeder ceramics for nuclear fusion reactors.

Principle of the PIGE technique

Particle induced gamma-ray emission (PIGE) is an isotope-specific nuclear analytical technique (NAT). It involves the interaction of energetically charged particles (p, d and α) with the target nuclei and results in the emission of prompt gamma rays from reactions such as inelastic-scattering (p, p' γ) or from nuclear reactions like (p, $\alpha\gamma$), (p, n γ) and (p, γ) [14–17]. PIGE method is very sensitive to the low Z

elements (usually $3 \leq Z \leq 16$) including Li in the wide spectrum of solid materials. The gamma-rays thus emitted are the characteristic signature of the isotopes of elements. Figure 1 represents the schematic diagram showing interaction between energetic proton beam and the target nucleus.

PIGE involves online measurement of prompt gamma rays emitted during de-excitation of excited nuclei of the isotope. The activity (A) produced in the PIGE method is given by Eq. 4 [18].

$$A = N \times I \times \int_{E_0}^0 \frac{\sigma(E)}{S(E)} dE \quad (4)$$

where, N is the number of target atoms per cm^3 , I is the beam current, $\sigma(E)$ and S(E) are the cross-section and the stopping power of the isotope of analyte in the target at a particular particle energy, respectively. The cross section of the relevant isotope for a given analyte will be the same for both the sample and the standard at a given proton beam energy. If the sample is thin and conducting, a Faraday cup can be placed behind it to measure the current directly. But if the sample is thick and insulator, then the beam is stopped by the sample and it is difficult to measure the beam current variation by the conventional approaches. Under these circumstances, current normalisation is carried out through the Rutherford Backscattering Spectroscopy (RBS) method [19, 20]. Since it is not necessary to measure absolute current in relative PIGE method, *in-situ* current normalization approach is an advanced method for monitoring the fluctuations of the beam current during the experiment. In this

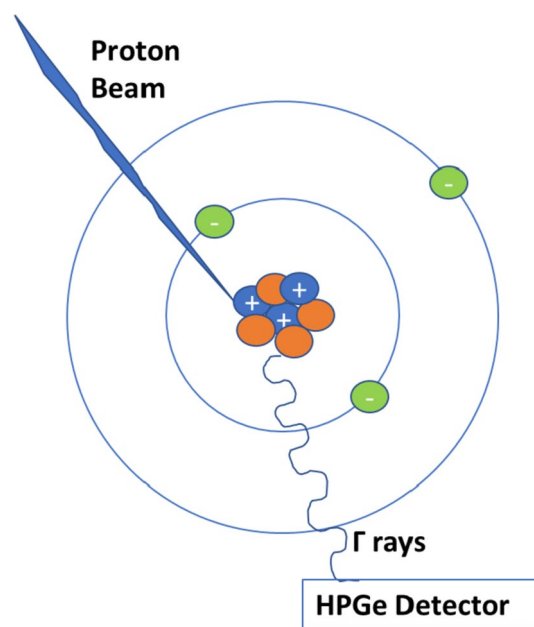


Fig. 1 Schematic diagram showing the interaction of proton beam with the nucleus of the target atom (Li)

method, the sample is supplemented with a known amount of an element that is highly sensitive to PIGE and is not present in the sample matrix. The count rate (counts per second, CPS) of the sample is normalized with sensitivity (CPS per unit mass) of the current normalizer to account for the current variation. This normalization process makes the analysis independent of beam fluctuation during irradiation [17]. In the *in-situ* current normalised PIGE method, the sample and the standard are pelletized in a similar matrix using a hydraulic press, resulting in a similar stopping power $S(E)$ in the sample and the standard. Thus, the ratio of count rate for an analyte ‘x’ present in sample and standard is given by Eq. 5 [19]

$$\frac{CPS_{x,sam}}{CPS_{x,std}} = \frac{C_{x,sam}}{C_{x,std}} \times \frac{I_{sam}}{I_{std}} \quad (5)$$

where, C_x is the concentration of the analyte ‘x’ in sample and standard and I is the corresponding beam current. In *in-situ* current normalisation process, the variation in the current is monitored through count rate of current normalizer (y). The ratio of absolute current in sample and the standard is proportional to the ratio of the sensitivity of the current normalizer ‘y’ in sample and standard as given by Eq. 6.

$$\frac{I_{sam}}{I_{std}} = \frac{S_{y,sam}}{S_{y,std}} = \frac{(CPS_{y,sam}/C_y)_{sam}}{(CPS_{y,sam}/C_y)_{std}} \quad (6)$$

where, S_y is the sensitivity of (y) and C_y is the concentration (mg kg^{-1} or % mass fraction) of the *in situ* current normalizer (y) in sample and standard and the Eq. 5 is modified as Eq. 7 [19].

$$C_{x,sam} = \frac{(CPS_{x,sam}/S_{y,sam})_{CN}}{(CPS_{x,std}/S_{y,std})_{CN}} \times C_{x,std} \quad (7)$$

In the present work, beam current was monitored through the count rate of gamma peak at 2313 keV from the $^{14}\text{N}(\text{p},\text{p}'\gamma)^{14}\text{N}$ reaction from the atmospheric nitrogen. Table 1 provides the relevant nuclear data of elements of interest and corresponding thick target gamma ray yield at 4 MeV proton energy.

Table 1 Nuclear data of the elements [21]

| Element | Nuclear reaction | Energy (keV) | γ -ray yield at 4 MeV (counts/ $\mu\text{C Sr}$) [#] |
|---------|--|--------------|---|
| Li | $^7\text{Li}(\text{p},\text{p}'\gamma)^7\text{Li}$ | 478 | 8.1×10^7 |
| | $^7\text{Li}(\text{p}, \text{n}\gamma)^7\text{Be}$ | 429 | 2.6×10^7 |
| N | $^{14}\text{N}(\text{p},\text{p}'\gamma)^{14}\text{N}$ | 2313 | NA |

NA, not available; #Thick target γ -ray yield

Experimental

Stoichiometric Li_2TiO_3 powder was produced through solid state reaction of Li_2CO_3 (> 99%, Sigma-Aldrich) and TiO_2 (AR Grade, M/s Travankore Titanium Products Ltd., India). Li_2CO_3 powder was mixed with TiO_2 powder using wet ball milling under ethanol media for 24 h. The wet mixture was dried in an oven for 2 h at 90 °C. The dried mixed powder was calcined at 700 °C for 2 h for phase formation. Particle size of the calcined powder was measured by particle size analyser in ethanol medium (Cilas 1090). Using similar processing technique, hyperstoichiometric lithium titanate with different Li/Ti ratio (Li/Ti = 2.06, 2.16, 2.20) was prepared and calcined at 700 °C for 2 h. The calcined powder phase purity was confirmed through X-ray diffraction (XRD; Inel XRG 3000). Stoichiometric and hyper-stoichiometric lithium titanate powders were compacted into green compacts (10 mm diameter and 1–2 mm height) using a uniaxial hydraulic press at ~150 MPa pressure. The stoichiometric Li_2TiO_3 pellets were sintered at different temperatures varying from 900 to 1100 °C for 4 h to investigate sinterability and lithium loss behaviour. Based on the sintering results of stoichiometric lithium titanate, hyper stoichiometric lithium titanate pellets were also sintered in air atmosphere at 1050 °C for 4 h. The phase purity of the sintered pellets was analysed through XRD. Mass loss during sintering was measured and the relative density of the pellets was determined by *Archimedes’* method. Microstructural characterisation of the sintered specimens was carried out using scanning electron microscopy (SEM Zeiss Evo 18). Lithium content in sintered ceramic specimens was measured using external PIGE.

In the present investigation, external (in-air) PIGE method using nitrogen as an external current normalizer was utilized for the quantification of Li in ceramic samples. A facility with 5 MeV proton beam from the FOLDED Tandem Ion Accelerator (FOTIA), Bhabha Atomic Research Centre (BARC), Mumbai, was already set up and optimised for external PIGE equipment. The collimated proton beam of 3 mm diameter and 5 MeV energy was extracted through a vacuum chamber through a window made of tantalum (Ta) metal with a thickness of 25 μm . Ta has been chosen as a window material because the other conventional window materials used such as Al, Ti, Si_3N_4 might contain one of the elements to be measured. This Ta window helps in sustaining the vacuum in the chamber however proton energy decreases by 1.25 MeV while passing through it which was calculated by the SRIM software [18–20]. Consequently, 3.75 MeV proton beam has been used in all the external PIGE experiment. Direct sintered pellets of samples and elemental standards were irradiated

with 3.75 MeV proton beam. The prompt gamma-rays at 429 and 478 keV from ${}^7\text{Li}(p, n\gamma){}^7\text{Be}$ and ${}^7\text{Li}(p, p'\gamma){}^7\text{Li}$ nuclear reactions, respectively, were measured using a P-type high purity germanium (HPGe) portable detector with 50% relative efficiency, having 1.9 keV resolution at 1332 keV of ${}^{60}\text{Co}$. The detector's energy calibration was carried out with reliable sources, such as ${}^{152}\text{Eu}$. Irradiation cum acquisition time per sample was 15 min or more depending upon the current which was maintained ~ 10 nA (approx. 9 μC charge). The counts under the peaks of 478 keV of Li and 2313 keV of N were more than 1,50,000 and 20,000, respectively. The acquired spectra were analysed by peak-fit method using Pulse Height Analysis Software (PHAST) developed at BARC. The samples and standards were irradiated in similar positions and geometrical configurations with regard to the detector in the current work, which used a relative approach of concentration calculation. Lithium titanate from Sigma-Aldrich (99.9% pure, AR grade) has been used for method validation and accuracy verification. The nitrogen (78%) contained in the air is employed for beam current normalisation using the relative technique of calculations, which quantifies the element in the sample using standards of known composition [20]. In the present studies, count rate under the prompt γ -ray peak (2313 keV) from nuclear reaction (${}^{14}\text{N}(p, p'\gamma){}^{14}\text{N}$) has been used for current normalization. In the relative method, the final Eq. 7 is reduced to Eq. 8

$$C_{\text{Li, sample}} = \frac{(CPS_{\text{Li}}/CPS_{\text{N,2313}})_{\text{CN, sample}}}{(CPS_{\text{Li}}/CPS_{\text{N,2313}})_{\text{CN, standard}}} \times C_{\text{Li, standard}} \quad (8)$$

where CPS is the count rate of Li and N of sample and standard and C is used for the concentration of Li in sample and standard and CN is the current normalizer [19].

Results and discussions

Phase purity of calcined stoichiometric lithium titanate (Li_2TiO_3) was confirmed through XRD (Fig. 2). All the observed peaks match with the monoclinic structure of $\beta\text{-Li}_2\text{TiO}_3$ phase (ICDD PDF 033–0831). The mean particle size $\beta\text{-Li}_2\text{TiO}_3$ was measured as ~ 3.7 μm .

The calcined samples were sintered at various temperatures, during sintering of lithium compounds, weight loss due to volatilisation of lithium was observed. In order to confirm this, mass of the sample pellets was measured before and after sintering and the corresponding calculated mass loss % values (difference between the mass taken before and after sintering) are tabulated in Table 2. It is observed that with increase in sintering temperature, the sintered density of the pellets increases with concomitant increase in mass loss. Since optimized pebble density

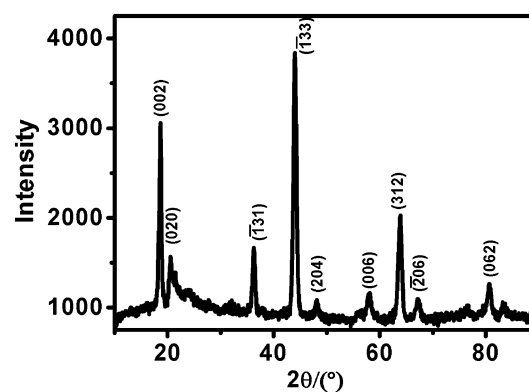


Fig. 2 XRD pattern of lithium titanate calcined at 700 °C for 2 h

Table 2 Mass loss and relative density of lithium titanate at different sintering temperatures

| Sintering temp (°C) | Mass loss(%) [#] ($\Delta m \cdot 100 / m_{\text{before sintering}}$) | Relative density (%TD) |
|---------------------|--|------------------------|
| 900 | 2.4 ± 0.03 | 66.98 ± 1.2 |
| 1000 | 2.5 ± 0.02 | 81.35 ± 0.8 |
| 1050 | 2.8 ± 0.04 | 91.07 ± 1.1 |
| 1100 | 4.3 ± 0.04 | 91.68 ± 0.3 |

[#]where $\Delta m = m_{\text{before sintering}} - m_{\text{after sintering}}$

for breeder application is between 85 and 90%, sintering of all hyper-stoichiometric compositions was done at 1050 °C for 4 h.

Figure 3 shows a representative gamma-ray spectrum of lithium titanate sample from external PIGE using 3.75 MeV proton beam and 10 nA beam current. Peaks at 429 keV and 478 keV represent high yield of lithium from the sample. Apart from lithium peaks, other peaks are due to titanium (${}^{48}\text{Ti}$, 889, 983, 1312 keV), nitrogen (${}^{14}\text{N}$, 2313 keV), background due to tantalum window (${}^{181}\text{Ta}$, 605, 705, 1047 and 1815 keV), iron structural material of beam tube (${}^{56}\text{Fe}$, 844, 1811 keV) and aluminium impurity (${}^{27}\text{Al}$, 1014 keV) [15, 16, 21]. As seen in the Fig. 3, there are no interference of these mentioned gamma-rays mainly due to Ta and Fe with gamma-rays of interest from Li and N.

Concentration of lithium in all the lithium titanate samples sintered at different temperatures was calculated by relative PIGE method as per Eq. 8 and the corresponding calculated mean concentrations (wt%) of Li are given in Table 3. The mean Li concentration was calculated from three replicate measurements with the individual propagated uncertainties within $\pm 0.73\%$ and the corresponding standard deviation ($N=3$) values within 0.09 wt%. Previous studies on quantification of lithium using PIGE in Li_2TiO_3 synthesised with different starting material and varying sintering temperatures reported lithium concentration in the range of

Fig. 3 Prompt gamma-ray spectrum of a lithium titanate sample irradiated with 3.75 MeV proton beam at ~ 10 nA current

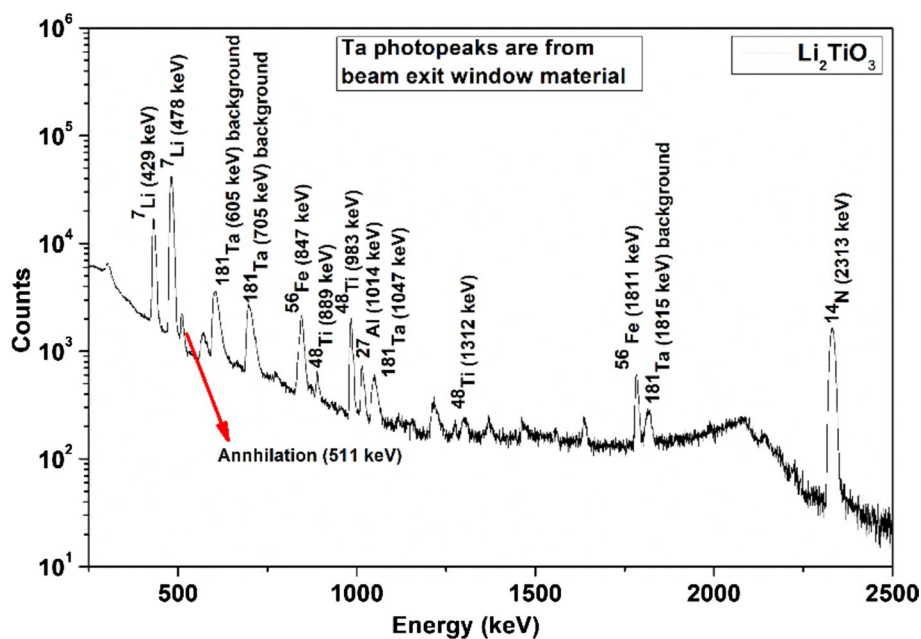


Table 3 Calculated Li concentration (wt%) in lithium titanate ceramic sintered at different temperatures for 4 h by external PIGE method

| Composition/sintering temperatures | Theoretical Li concentration (wt%) | Li concentration (wt%) by PIGE (Mean \pm SD; N = 3) | % Deviation (i.e., Loss%) [#] ($\Delta C^* 100/C_{\text{theoretical}}$) |
|---|------------------------------------|---|--|
| Li ₂ TiO ₃ -900 °C | 12.65 | 12.53 \pm 0.09 | 0.94 |
| Li ₂ TiO ₃ -1000 °C | 12.65 | 12.33 \pm 0.09 | 2.5 |
| Li ₂ TiO ₃ -1050 °C | 12.65 | 12.18 \pm 0.09 | 3.7 |
| Li ₂ TiO ₃ -1100 °C | 12.65 | 12.05 \pm 0.09 | 4.7 |

$$^{\#}\Delta C = C_{\text{theoretical}} - C_{\text{calculated}}$$

11.2–12.68% with $\pm 2\%$ uncertainty [22]. Other investigation on lithium-based ceramics such as Li₂TiO₃, LiAlO₂ and Li₂SiO₃ using ~ 4 MeV proton beam reported lithium concentration in the range of 10.1–15.8wt% with $\pm 5\%$ propagated uncertainty [20]. The results obtained in this investigation are in good agreement with previous results for lithium measurement using PIGE.

The deviation of calculated lithium concentrations with the theoretical Li content in lithium titanate is in the range of –0.9% to –4.7% as can be seen from Table 3. This deviation is due to increase in mass loss with increase in sintering temperature due to the volatile nature of lithium at high temperature (Table 3).

XRD pattern of hyper-stoichiometric lithium titanate (Li/Ti = 2, 2.06, 2.16, 2.20) calcined at 700 °C for 2 h are shown in Fig. 4(a). It is observed from the patterns that β -Li₂TiO₃ is the major phase in all the compositions along with the presence of residual Li₂CO₃ for samples with Li/Ti ratio as 2.16 and 2.20. Presence of Li₂CO₃ in higher stoichiometric lithium titanate is also reported in earlier studies [5, 23, 24]. Figure 4(b) shows XRD pattern of hyper-stoichiometric

lithium titanate (Li/Ti = 2, 2.06, 2.16, 2.20) sintered at 1050 °C for 4 h. It is observed that all compositions up to Li_{2.2}TiO_{3+y} have single phase β -Li₂TiO₃ and there are no additional peaks observed.

Figure 5 shows SEM images of hyper-stoichiometric lithium titanate with varying Li/Ti ratio sintered 1050 °C for 4h. The microstructures indicate liquid phase sintering caused due to the presence of excess Li₂CO₃ in the calcined powders of hyperstoichiometric lithium titanate samples.

The mean Li concentration was calculated by external PIGE method using nitrogen as external current normalizer from three replicate sample analysis with the individual propagated uncertainties within $\pm 0.73\%$ and the corresponding standard deviation (SD) (N = 3) values within $\pm 0.12\%$. Unlike the stoichiometric Li₂TiO₃ sample, the lithium loss is found to be more in hyper-stoichiometric sample, which is evident by mass loss calculation as well as lithium weight percent data obtained by external PIGE (Table 4). With the increase in lithium concentration in lithium titanate, lithium loss also increases significantly. At Li/Ti = 2.16, the lithium losses are around twice than that of stoichiometric

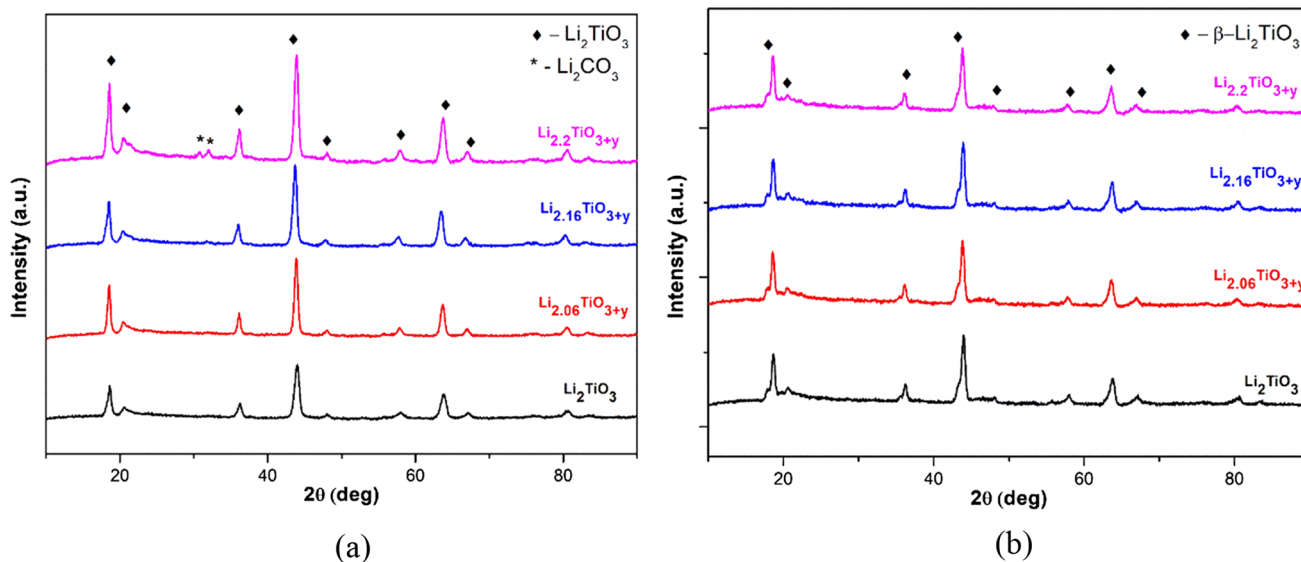


Fig. 4 XRD patterns of (a) 700 °C calcined and (b) 1050 °C sintered lithium titanate with different stoichiometries

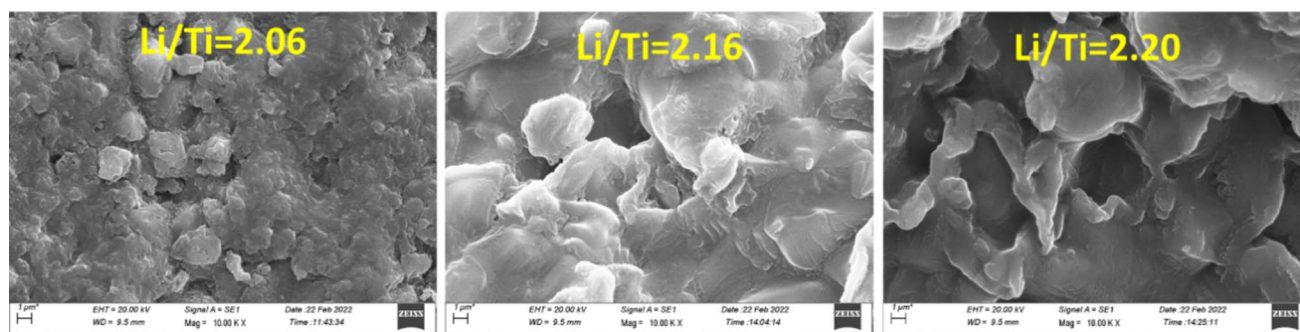


Fig. 5 SEM micrographs of $\text{Li}_{2+x}\text{TiO}_{3+y}$ sintered at 1050 °C for 4 h

Table 4 Calculated and measured Li concentration (wt%) in the hyper-stoichiometric lithium titanate ceramics sintered at 1050 °C for 4 h by external PIGE method

| Composition | Theoretical Li concentration (wt%) | Li concentration (wt%) by PIGE (Mean \pm std) | % Loss of $\text{Li}^\# (\Delta C \cdot 100 / C_{\text{theoretical}})$ |
|------------------------------------|------------------------------------|---|--|
| $\text{Li}_{2.06}\text{TiO}_{3+y}$ | 12.92 | 12.06 ± 0.11 | 6.6 |
| $\text{Li}_{2.16}\text{TiO}_{3+y}$ | 13.37 | 12.36 ± 0.11 | 7.6 |
| $\text{Li}_{2.2}\text{TiO}_{3+y}$ | 13.54 | 12.73 ± 0.12 | 5.9 |

$$\# \Delta C = C_{\text{theoretical}} - C_{\text{calculated}}$$

compound. The theoretical weight of non-stoichiometric composition ($\text{Li}_{2+x}\text{TiO}_{3+y}$) has been calculated taking $y = x/2$ to balance the overall charge of the compound.

Conclusions

Stoichiometric and hyper-stoichiometric Li_2TiO_3 , which are potential tritium breeder material in nuclear fusion reactors, have been prepared by solid state reaction and sintered at various temperatures. Non-destructive quantification of lithium present in these ceramic samples have been successfully carried out by relative external (in air) PIGE method using 3.75 MeV proton beam and ^{14}N as an external current normalizer. Losses incurred during different sintering temperatures in stoichiometric and hyperstoichiometric lithium titanates are quantified by comparing the results with the theoretical and calculated Li concentration values. Present study suggests that it is required to add 6–8% of excess lithium in the precursors during synthesis in order to avoid secondary phase formation and to increase the breeder lifetime. External PIGE method was

found to be simple, rapid and non-destructive method for quantification of Li in such lithium based ceramics.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest There is no conflict of interest in this manuscript.

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