Proton Induced Gamma-ray Emission Reaction for Quantification of Lithium in Lithium Titanate Samples

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Introduction

Lithium based ceramic materials like Li_2O, Li_2SO_4, Li_2TiO_3, Li_2SiO_3, Li_2ZrO_3 are proposed as tritium breeding materials in fusion reactors based on D-T reaction [1]. Lithium titanate (Li_2TiO_3) is considered as one of the best candidates for blanket in this type of reactors due to the properties like high efficiency of tritium production, high chemical and mechanical stability and good tritium release [2]. Presently studies are being carried out using natural lithium in these materials. As lithium content of ceramic breeder directly related to the production of tritium, accurate determination of its content by a suitable technique in this ceramic material is necessary for chemical quality control.

Since it is difficult to dissolve the titanium based ceramic material, wet chemical methods like AAS, ICP-MS and ICP-AES are not preferred for Li quantification. X-ray based techniques like XRF and PIXE are not used for this low Z element. Among the nuclear analytical techniques, particle induced gamma-ray emission (PIGE) using proton beam is found to be suitable for Li determination in this matrix due to its non-destructive nature and low matrix effect. In addition to Li, this method is unique for the determination of other low Z elements like Be, B, F, Na, Mg, Al and Si. This technique utilizes measurement of characteristic gamma-rays emitted from proton induced nuclear reactions such as (p,p'γ), (p,γ), (p,$\alpha\gamma$) and (p,nγ) using particle accelerators.

In the present work a PIGE method using proton beam has been standardized for lithium determination in lithium titanate samples. The work was carried out using 4 MeV proton beam obtained from Folded Tandem Ion Accelerator (FOTIA), BARC, Mumbai. Li_2TiO_3 samples were prepared by sol-gel route using HMTA, urea as gelating agent. The element F, which has got higher sensitivity in PIGE, was used as an internal current normalization standard. Prompt gamma ray of 478 keV from ^{7}Li (p, p'γ) ^{7}Li reaction was used for Li quantification. The 197 keV gamma-ray from ^{19}F (p, p'γ) ^{19}F reaction was used for monitoring relative beam current that may occur during the experiment. The count rates of 478 keV peaks of Li (in standards and samples) were normalized with sensitivity (cps/ppm) of F using count rate of 197 keV peak. The Li amounts in the samples were calculated using relative method.

Experimental

Samples of lithium titanate were prepared by sol-gel route [4]. The sintering temperatures were in the range of 500-1250 ºC. The standards were prepared by homogenously mixing fixed amount of CaF_2 (~25 mg), varying amount of $Li_2SO_4.H_2O$ (10-100mg) and required amount of cellulose to make the pellet (1g). Similarly the synthetic sample pellets (1 g) were prepared by mixing constant amount of CaF_2 (30 mg), TiO_2 (50 mg) and known amount of Li_2SO_4 with cellulose. The sample pellets were prepared by mixing the sample (75-80mg) along with fixed amount of CaF_2 and cellulose. The standard and samples were irradiated for about 10 minutes with 4 MeV proton beam (current ~5 nA). A typical γ-ray spectrum obtained from one of the lithium titanate samples is shown in Fig. 1. The prompt gamma rays were assayed using a 30% HPGe detector coupled to 4k-MCA.

Results and discussion

From the gamma ray spectrum of sample (Fig. 1), it is observed that there is no γ-ray interference for the two characteristic peaks. The results of Li contents in four synthetic and five samples are given in Table 1. The uncertainties are in the range of 1-2%, which are due to counting statistics and peak fitting errors. The determined Li concentrations in synthetic samples were found to be in good agreement (within ± 4%) with the expected values. The results of five samples are found to be in fare agreement (except for sam-5) with expected Li content (12.67%), assuming formation of stoichiometric Li_2TiO_3 compound. Further work in this regard is in progress in optimizing preparation of stoichiometric compounds and also evaluating Ti concentration as well as Li to Ti ratios. In conclusion, a simple non-destructive PIGE method has been standardized for Li estimation in lithium titanate samples and this method keeps promise for simultaneous estimation of Li, Si and Al in other breeding materials.

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Table: 1 Results of Li contents in synthetic and actual Li_2TiO_3 samples by PIGE

Synthetic Sample			
S. No.	Li amount expected (mg kg^{-1})	Li amount obtained (mg kg^{-1})	% Deviation
Syn-1	31063	32236	0.4
Syn-2	49349	49168	-2.4
Syn-3	72050	73807	-3.6
Syn-4	101871	98988	2.9
Samples			
Sample (Sintering Temp ºC)	Li amount expected (mg kg^{-1})	Li amount obtained (mg kg^{-1})	% Difference
Sam-1 (500 ºC)	126700	119805	-5.0
Sam-2 (700 ºC)	126700	126815	0.1
Sam-3 (800 ºC)	126700	124130	-2.0
Sam-4 (1000 ºC)	126700	123844	-2.3
Sam-5 (1250 ºC)	126700	111568	-12.0

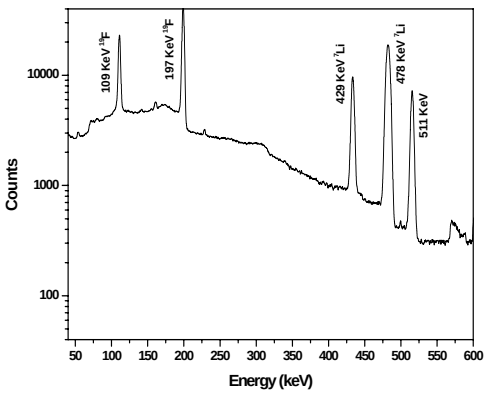

Fig. 1: Typical gamma-ray spectrum of Li_2TiO_3 sample in PIGE using 4 MeV proton beam