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Quantitative analysis of Li by PIGE technique

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ABSTRACT

In this work, the cross section of the reactions ^{7}Li(p,pγ)^{7}Li (γ – 478 keV) at the proton energy range 2.0–4.2 MeV was measured. The measurements were carried out at the 3 MV Tandem Accelerator at the CTN/IST Laboratory in Lisbon. To validate the obtained results, calculated gamma-ray yields were compared, at several proton energy values, with experimental yields for thick samples made of inorganic compounds containing lithium. In order to quantify the light elements present in the samples, we used a standard free method for PIGE in thick samples, based on a code – Emitted Radiation Yield Analysis (ERYA), which integrates the nuclear reaction excitation function along the depth of the sample. We also demonstrated the capacity of the technique for analysis of Li ores, as Spodumene, Lithium Muscovite and Holmquistite, and Li-alloys for plasma facing materials showing that this is a reliable and accurate method for PIGE analysis of Li in thick samples.

1. Introduction

The booming sales of clean energy vehicles is increasing the demand for lithium ion batteries and is intensifying the production of new sources of lithium raw materials. The prices of the industrial chemical lithium carbonate used in lithium ion batteries have increased suddenly 47 percent in 2016. Hence, the mining companies, the auto industry and industrial technology, would gain with the ability to determine with accuracy the concentration of lithium in a variety of samples, for example in Li ores.

Lithium is not detectable by the most commonly used Ion Beam Analysis (IBA) techniques, Proton-induced X-ray analysis (PIXE) and Rutherford Backscattering (RBS). Hence, Proton-induced γ-ray analysis (PIGE) is an advantageous alternative.

In order to use a standard free method for PIGE thick sample analysis, for which cross sections of the relevant reactions are needed, and improve the sensitivity and the multi-elemental character of the technique, it is necessary to have cross sections for proton energies up to 4.0 MeV.

This is particularly important for Li ores which are mostly silicates, as the ones employed in this work, or phosphates. In order to be able to quantify phosphorus and silicon simultaneously with Li, proton energies above 3 MeV must be used.

Moreover, with a higher energy range, the PIGE technique will be particular useful in new research domains, since we may follow the segregation of Li in a matrix as a solute or in lithium alloys. A new concept in nuclear fusion devices points to the use of liquid metals as plasma facing materials (PFM) to take advantage of the regenerative properties of liquid walls, while PFM will be exposed to high neutron loads induced by the ^{3}H(^{2}H,n)^{4}He reaction. Sn-Li alloys are natural candidates to be used as liquid PFM if the contamination by heavy Sn (detrimental to the plasma) is mitigated by a fast segregation of Li towards the exposed surfaces.

In the present work we extended [1] the energy range of available cross sections of the reaction ^{7}Li(p,p'γ)^{7}Li (γ – 478 keV) to 4.0 MeV. This was done in the context of a IAEA Concerted Project, concerning PIGE data [2].

In order to validate the standard free method for Li, gamma-ray yields for Li inorganic compounds were also measured and compared with the calculated ones by the ERYA code.

As case studies, we applied this method to Li ores, Spodumene, Lithium Muscovite and Holmquistite and to Sn-Li alloys.

2. Experiment

2.1. Experiment conditions

The proton beam was accelerated by a 3 MV Tandetron accelerator at the CTN/IST Laboratory in Lisbon. The proton energy was calibrated by the 1645.1 and 1930.7 keV resonances of the reaction

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$^{23}Na(p,p'\gamma)^{23}Na$ and by the 3470 keV resonance of the $^{16}O(p,p)^{16}O$ reaction.

The reaction chamber is electrically insulated from the beam line working together with the target holder and beam stopper as one Faraday cup for beam charge collection [3].

Gamma-rays were detected by a 45% Ge(HP) detector located at 130° in relation to the incident beam direction and at a distance of 55.5 mm from the target. The absolute efficiency versus gamma-ray energy was obtained by measuring the yields of gamma-rays produced by radioactive sources (^{133}Ba and ^{152}Eu) calibrated in activity as well as by Monte Carlo simulations using GEAN [4] and PENELOPE [5].

2.2. Cross section measurements

For cross section measurements, the target consisted of a thin film of LiF deposited over a thin self-supporting film of Ag. The measurements were performed with a proton beam at energies from 1940 to 4175 keV with an energy step of around 10 keV, as the cross section is rather smooth. Proton beam currents of the order of 50 nA were employed. The referred beam currents assured dead time corrections of the collected spectra under 4%.

As the stoichiometry of the target was impossible to measure, the absolute differential cross section was obtained by normalization to the results measured previously for energies lower than 2350 keV and published in [1]. A table of cross section values obtained in this work is available in IBANDL [6]. These values correspond to total cross section, as the 478 keV γ-ray line is isotropic. The uncertainty budget for cross section measurements is shown in Table 1.

2.3. Thick target yields

For thick target yield measurements, one of the targets was a pressed pellet made of LiF powder mixed thoroughly with silver powder, yielding an isotopic ^7Li fraction of 3.7% and the other a pressed pellet made of pure Li_2WO_4. Proton beam currents of the order of 20 nA were employed. Usually more than 4×10^4 counts were collected in the characteristic 478 keV gamma-ray emission for Li. The uncertainty budget for the measurements of the inorganic compound yields is shown in Table 2.

Additional uncertainties must be considered for pure Li target yields which were deduced from these measurements – uncertainties of the target stoichiometry and stopping powers used in the calculation. For LiF/silver mixture there is a target stoichiometry uncertainty related to the homogeneity of the mixture, of around 10%. For chemically pure Li_2WO_4 the uncertainty of the stoichiometry is negligible. In relation to the ratio of the stopping powers of pure Li to the used targets, the uncertainty is 10%. Thus, pure Li target yields deduced from the LiF/silver mixture have an overall uncertainty of 18% and pure Li target yields deduced from Li_2WO_4 have an overall uncertainty of 15%.

2.4. Case studies

The PIGE technique was used to analyse the Li content of geological sample and Li-alloys, by using incident 3470 keV H^+ ions.

Table 1
Uncertainty budget for cross section measurement.

γ-ray peak area	γ-ray detector efficiency	Reproducibility of collected charge	Previous values for normalization	Overall uncertainty
1%	5%	3%	4%	7%

Table 2
Uncertainty budget for the measurements of thick target yields.

γ-ray peak area	γ-ray detector efficiency	Absolute value of the collected charge	Overall uncertainty
1%	6%	10%	12%

Proton beam currents of the order of 12 nA were employed, resulting a dead time correction lower than 6%. Usually more than 10^4 counts were collected in the pertinent gamma-ray lines.

Geological samples were Spodumene (single-crystal), Lithium Muscovite (mixed with other minerals in a rock sample) and Holmquistite (mixed with other minerals, as for example Feldspars, in a rock sample). The referred minerals obey generally the following stoichiometric formulas $LiAlSi_2O_6$, $K_2Li_3Al_3Si_6Al_2O_{20}(OH)_2$ and $Li_2Mg_3Al_2(Si_8O_{22})(OH)_2$, respectively. Some variations may occur as Li may be replaced by Mg or K and Si by Al, and the group $(OH)_2$ by F.

Due to the main properties of the Sn-Li alloys, used as liquid PFM, the PIGE technique allows the evaluation of the segregation of Li towards the exposed surfaces. A virgin Sn-Li sample and a melted Sn-Li sample irradiated at the edge of deuterium plasma over 3 s were analysed.

In order to quantify Li, and also F, Na, Mg, Si, Al for geological samples, we used a standard free method for PIGE in thick samples, based on a code – Emitted Radiation Yield Analysis (ERYA) [1,7–9], which allows a simultaneous fit of all the light elements present in the spectra. The results given by ERYA due to the calibration [10] of the system are expected to be lower than 7% (mainly from the stopping power uncertainty).

3. Results and discussion

3.1. Total cross-sections of the reaction $^7Li(p,p'\gamma)^7Li$

The total cross sections of the reaction $^7Li(p,p'\gamma)^7Li$ are presented in Fig. 1. Total cross-sections were calculated assuming an isotropic angular distribution of the gamma rays [11]. As shown, for the energy range used in this work, the total cross sections are rather smooth. Comparing our values (referred as this work) with previous measurements [9–11], we note that our values agree, within the quoted experimental uncertainties, with those of Caciolli et al. [12], Boni et al. [13] and Guzhovskij et al. [14].

3.2. Thick target yields

To validate the obtained results, values for thick pure Li target yields were calculated from experimental gamma-ray yields of thick samples made of inorganic compounds containing lithium. In Fig. 2, our results (referred as this work) are compared with previous measurements. Deviations are within the quoted uncertainties; at 2400 keV our value is 3% lower than Kiss et al. [15] and 10% lower at 3800 keV. Regarding of Savidou et al. [16] our values are 25% higher at 2400 keV, coincident at 3620 keV and 12% higher at 3800 keV. Note that between 3800 and 4000 keV Savidou et al. curve has a wrong slope.

3.3. Geological samples

Gamma-ray spectrum for the Holmquistite at 3470 keV is shown in Fig. 3. The relevant gamma-ray lines are well separated from other lines, with a consequent small uncertainty in the extracted area. The atomic fractions calculated by ERYA are given in the table below for all the analysed samples (Table 3).

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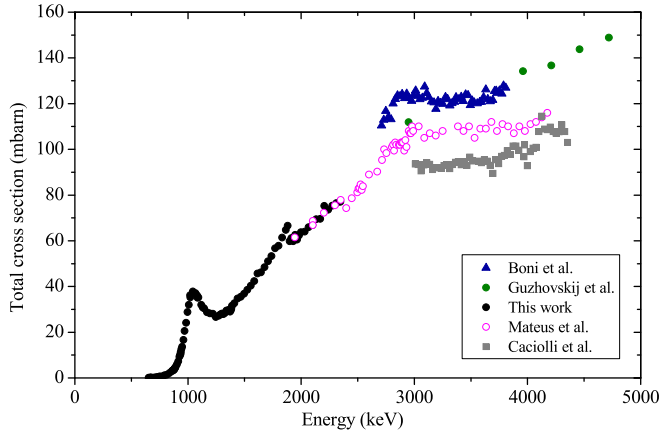

Fig. 1. Total cross section of the reaction ^{7}Li(p,p'γ)^{7}Li, E_γ = 478 keV, as measured in this work together with data from [12–14]. The cross section is rather smooth at this energy range showing the resonance at 1030 keV and the dip at 1880 keV related to the threshold of the reaction ^{7}Li (p,n) ^{7}Be.

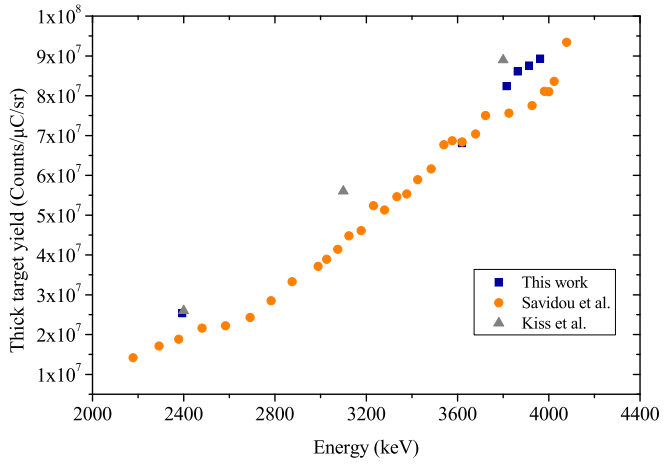

Fig. 2. Thick pure Li target yields measured in this work together with data from [15,16]. The error bars related to experimental statistical and area extraction uncertainties are smaller than the point symbol dimensions.

Considering that the Spodumene is a single-crystal of $LiAlSi_2O_6$, no impurity originating peaks, as expected, and the calculated at.% agree with the ones from the chemical formula within the uncertainties.

For the other samples, as there are a mixture of minerals, no prediction of the sample contents can really be made. Hence, it is not strange the results do not follow the formulas. Here, only a semi-qualitative analysis is obtained.

For example, the calculated atomic fractions of Li and Mg are below as expected, due to the inhomogeneity of the sample, and maybe the mixture with Feldpars (for example $KAlSi_3O_8$ – $NaAlSi_3O_8$) as Al is higher than expected and Na is present in the spectra. Also, the group (OH) is partially or totally replaced by F.

Even for the case of natural rocks with Li minerals mixed with other minerals, PIGE is useful for a pre-evaluation of the sample giving a first hint of its richness in Li. Of course for a true evaluation, the sample should be milled and homogenized and pressed as a pellet. For PIGE the sensitivity is mostly sample dependent and Li, F, Al, Si and O due to higher gamma-ray lines contribute with Compton to the background under the 478 keV Li peak. Even so, the sensitivity may be estimated [17] to be between 20 and 60 ppm for these geological samples.

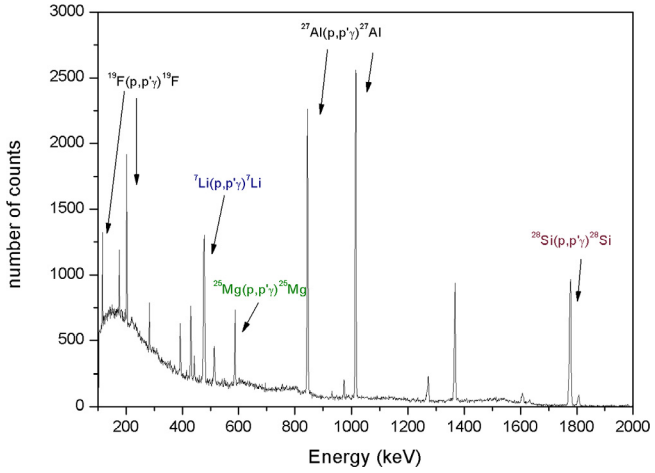

Fig. 3. Energy spectrum of γ-radiation produced by the bombardment of a Holmisquite sample by 3470 keV protons. The gamma-ray lines related to the quantified elements used in this work are labeled in the Figure. As for the other gamma-ray lines, they refer to ^{7}Li(429 keV), ^{27}Al(171, 1369 keV), ^{25}Mg(390, 585, 975, 1369 keV) and ^{26}Mg(1809 keV).

Table 3
Atomic fraction calculated by ERYA for Spodumene ($LiAlSi_2O_6$), Muscovite ($K_2Li_3Al_3Si_6Al_2O_{20}(OH)_2$) and Holmquistite ($Li_2Mg_3Al_2(Si_8O_{22})(OH)_2$). These values have 7% uncertainty. The atomic fractions in brackets are calculated from the geological formulas.

Element	Spodumene	Muscovite	Holmquistite
F	–	0.115 (0.059)	0.002 (0.026)
Na	–	–	0.001 (0.001)
Li	0.097 (0.1)	0.063 (0.059)	0.01 (0.052)
Mg	–	–	0.016 (0.079)
Al	0.093 (0.1)	0.068 (0.176)	0.072 (0.052)
Si	0.215 (0.2)	0.142 (0.353)	0.160 (0.211)

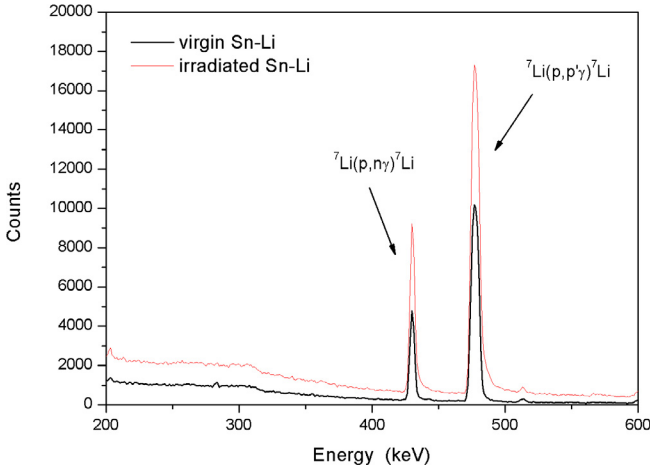

Fig. 4. Gamma-ray emission spectrum obtained for a melted Sn-Li sample irradiated at the edge of deuterium plasma over 3 s and a virgin Sn-Li sample bombarded by proton beams of 3470 keV. The characteristic 478 keV gamma-ray yield for Li was higher in the exposed surface.

3.4. Li-alloys

The chemical modifications in Sn-Li alloys are being investigated at the ISTTOK tokamak [18]. The composition of the exposed surface (deuterium retention and Li contents) was compared with

that one of a virgin Sn-Li sample by nuclear reaction analysis (NRA) by using ^{3}He ion beams. A higher Li content was found in the exposed surface due to an increment of the emission proton yields induced by the ^{2}H(^{3}He,p)^{4}He and ^{7}Li(^{3}He,p)^{9}Be reactions. Nevertheless, ^{3}He gas sources are very expensive and the reported cross-section data involving ^{6}Li and ^{7}Li reactions are too distinct. In this work, a better quantification for Li is achieved by PIGE. Fig. 4 presents new spectra collected from the Sn-Li samples by using incident 3470 keV H^{+} ions. The characteristic 478 keV gamma-ray yield for Li was found to be 1.89 higher in the exposed surface, confirming the occurrence of the segregation mechanism. The evaluated Sn:Li ratios were 79:21 and 66:33 at.% in the virgin and exposed surfaces, respectively.

4. Conclusions

The present work extended the energy range of available cross sections of the reaction ^{7}Li(p,p′γ)^{7}Li (γ – 478 keV) to 4.0 MeV and the obtained values are in agreement with previous measurements in similar conditions. This extension to 4 MeV has been done for PIGE analysis purposes. Standard-less PIGE bulk analysis was again demonstrated as a reliable and accurate method for PIGE analysis of Li in thick samples. For the studied geological samples, a sensitivity between 20 and 60 ppm was estimated, which is by far lower than 1%, which is the relevant value from the mining economic point of view.

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References

[1] R. Mateus et al., Nucl. Instrum. Methods B 190 (2002) 117.
[2] P. Dimitriou et al., Nucl. Instrum. Methods B 371 (2016) 33.
[3] P. Cabanelas et al., Nucl. Instrum. Methods B 381 (2016) 110.
[4] S. Agostinelli et al., Nucl. Instrum. Methods A 506 (2003) 250.
[5] F. Salvat, J.M. Fernández-Varea, J. Sempau, OECD NEA Data Bank/NSC DOC, (2011) 5.
[6] IAEA, 2014 at http://www-nds.iaea.org/ibandl/.
[7] R. Mateus et al., Nucl. Instrum. Methods B 229 (2005) 302.
[8] R. Mateus et al., Nucl. Instrum. Methods B 219–220 (2004) 519.
[9] M. Fonseca et al., Nucl. Instrum. Methods B 268 (2010) 1806.
[10] http://www.itn.pt/sec/fis/rn/uk_rn_erya.htm.
[11] A.A. Kraus, Phys. Rev. 93 (1954) 1308G.
[12] A. Caciolli et al., Nucl. Instrum. Methods B 249 (2006) 98.
[13] C. Boni et al., Nucl. Instrum. Methods B 35 (1988) 80.
[14] B. Ja. Guzhovskij et al., Jour. Izv. Kaz. Akad. Nauk, Ser. Fiz.-Mat. 4 (1984) 24.
[15] A.Z. Kiss, J. Radioanal. Nucl. Chem. 89 (1985) 123.
[16] A. Savidou et al., Nucl. Instrum. Methods B 152 (1999) 12.
[17] R. Mateus et al., Nucl. Instrum. Methods B 264 (2007) 340.
[18] J.P.S. Loureiro, H. Fernandes, F.L. Tabarés, G. Mazzitelli, C. Silva, R. Gomes, E. Alves, R. Mateus, T. Pereira, H. Figueiredo, H. Alves, Deuterium retention in tin (Sn) and lithium–tin (Li–Sn) samples exposed to ISTTOK plasmas, Nucl. Mater. Energy (2016), http://dx.doi.org/10.1016/j.nme.2016.12.026.

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