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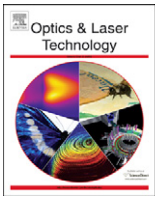

Research Note

The use of laser induced breakdown spectroscopy for the determination of Li in organic wash solutions during the preparation of lithium based oxide ceramics by sol–gel

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ABSTRACT

Laser induced breakdown spectroscopy (LIBS) has been investigated for the determination of lithium in various streams generated during the preparation of lithium titanate microspheres employing internal gelation in Sol–gel. Important parameters including laser energy and acquisition delay were optimized to achieve the best signal to noise ratio during the LIBS analysis using filter paper as a solid support. The usefulness of different analytical emission lines of lithium was investigated. The developed LIBS methodology was found to be useful in developing the sol–gel process for preparing the lithium based microspheres for fusion based R&D programs.

1. Introduction

The world-wide projects on the development of future fusion reactor (FR) power plants are based on the overall nuclear fusion reaction (Eq. (1)). The role of the ^{6}Li fuel is to generate tritium by the ^{6}Li(n, α)T nuclear reaction inside the blanket of a thermonuclear reactor by exploiting the fast neutrons (n) generated from the D–T fusion [1].

$$^6\text{Li}+\text{n}\rightarrow{}^4\text{He}+\text{T}+4.8\ \text{MeV} \qquad (1)$$

Lithium (40–60% ^{6}Li) based oxide ceramics, such as Li_2TiO_3, Li_2ZrO_3 and Li_4SiO_4, have been proposed as tritium breeding materials for fusion reactor blankets [2–5]. Among them, lithium titanate (Li_2TiO_3) shows the best chemical stability in air and the most excellent tritium release characteristics at lower temperature. Moreover, it displays acceptable mechanical strength and low activation [6–8]. For the preparation of lithium-containing ceramic powders, several synthetic techniques including solid state reaction, co-precipitation, solution combustion process and sol–gel process are available [9–11]. In Bhabha Atomic Research Centre (BARC), sol–gel is one of the well studied processes for the preparation of gel microspheres of UO_2, ThO_2, (U, Pu)O_2, (Th, U)O_2, etc. [12]. Sol–gel process was hence developed for the preparation of Li containing ceramic materials of required size and characteristics [13].

In the sol–gel process, the gel particle consists of a Ti–hydroxide network in which Li ion is trapped. The concentration of Li ion needs to be optimum (1.65 M) in the gel so that the ultimate product is stoichiometric Li_2TiO_3. The gel particle once produced is washed with ^{6}Li containing organic solution to remove unreacted and unused materials, while maintaining Li/Ti stoichiometry in the gel. The number of washings required needs be standardized so that the Li concentration in the gel does not deviate from the expected value. The washed solutions, which contain enriched ^{6}Li also need be analyzed for Li content prior to the recovery process.

The process requires a simple and robust technique, which is capable of online determination of Li to standardize the number of washings required in the various steps of the sol–gel process. Determination of inorganic constituents in an organic matrix (HMTA, urea, etc.) by conventionally used techniques such as ICPMS, ICP-OES, TXRF, etc. requires the removal of organics. When it proves difficult to remove the organic components by conventional methods such as evaporation, combustion methods are employed, which can lead to loss of volatile inorganic components like Li, which is unacceptable in the sol–gel process. Moreover, the mixture containing HMTA and NH_4NO_3 becomes explosive in nature upon heating [14]. Among the other methods, acid–base titration or flame photometer [15] method can be used, but is not suitable as a fast approach and the solution also needs be diluted to ppm level. It was, therefore, considered worthwhile to investigate the possibility of employing laser induced breakdown spectroscopy (LIBS) for the determination of Li concentration.

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2. Experimental

2.1. Apparatus

The Spectrolaser 1000 M, from M/s Laser Analysis Technologies Pvt. Ltd (now known as XRF Scientific), Victoria, Australia was used in this work. The details of the instrument are given elsewhere [16,17]. The instrument is equipped with a high power Q-switched Nd: YAG laser, which yields up to 200 mJ of pulse energy at the fundamental IR wavelength of 1064 nm in a 7 ns pulse width with a repetition rate of 10 Hz. The laser energy is focused to a spot size of 500 μm. The emitted light is fed to a spectrograph (Czerny–Turner configuration) equipped with CCD detectors.

2.2. Sample preparation and analysis

The Li_2TiO_3 microspheres were obtained by the internal gelation process as described by Vittal Rao et al. [18]. Enriched $^6LiNO_3$ and $TiCl_3$ solutions were mixed with 3 M solution of HMTA (hexamethylenetetramine) and urea mixture at 0 °C to obtain feed solution. This feed solution was then dispersed as droplets through a stainless steel capillary having an internal diameter of 0.8 to 1.0 mm into hot silicone oil (silicone oil ~90 °C) kept in a glass column. These droplets on contact with hot oil make gel microspheres and become hard as they travel down the column. After separating the gel microspheres from the oil, they are washed initially with CCl_4 (3/4 times) to remove the adhering silicone oil and then they were dried. After the particles are dried, they were digested in 1.55 M LiOH at 333 K in an air oven for 18 h. Finally these particles were washed to remove the unreacted materials and unused chemicals from the microspheres to prevent their cracking during sintering of the microspheres. Since the microspheres are made of ^{6}Li, washing is also done with ^{6}Li containing solution so that leaching of Li from the sol–gel particles during washing can be minimized. A ^{6}Li containing organic mixture (0.54 M NH_4NO_3+0.24 M NH_4Cl+0.075 M HMTA+0.075 M Urea+LiOH) was used for washing. In order to study the pickup/leaching of Li from the microspheres during the washing, 16 wash samples from different stages were collected and analyzed.

11 synthetic samples of Li in the concentration range 33 mM–2 M were prepared by dissolving analytical grade $LiNO_3$ in the same organic composition as stated earlier. Membrane based Whatman-42 filter paper was used as the sample substrate in this work. The data reported on the concentrations of different trace elements in the Whatman-42 membrane filter paper show that no Li is present in the filter paper. Also no observable spectral lines for Li were seen during the LIBS analysis of blank filter paper, which was selected as substrate to minimize the blank contribution [19].

Volumetric pipette (Eppendorf, Germany) was used to transfer 20 μL of solution drop wise to the Whatman-42 membrane filter paper. The solution spread circularly over the filter paper with a radius of approximately 1 cm. The solution was evaporated to dryness with the help of a hot air blower. Subsequently, the paper was allowed to cool to room temperature and was then mounted in the sample holder. The spatial extent of the sample was marked on the filter paper so that the analysis could be performed over a region of 1 cm diameter where Li is expected to be uniformly distributed. Triplicate analyses were performed on all samples including the calibration samples as well as the unknowns.

3. Results and discussion

Initially, by carefully studying the spectra, 5 lithium emission lines were selected for this work. These are Li(I) 670.79 nm, Li(I) 610.364 nm, Li(I) 812.644 nm, Li(I) 497.174 nm and Li(I) 460.288 nm. Spectroscopic data of these emission lines are listed in Table 1. All these emission lines selected are doublet and were not completely resolved with the existing instrument resolution (0.6 nm at 300 nm) available in our laboratory. Hence the gross intensity under the peak area was used for construction of calibration curves. One of the samples was used to study the effect of laser fluence and acquisition delay, in order to obtain the optimum analysis conditions for Li determination. Fig. 1 shows the dependence of signal to noise ratio (SNR) on incident laser fluence as well as on acquisition time delay for Li present in a test sample. 100 mJ laser energy and 2.5 μs acquisition time delay were found to be the best conditions.

Maintaining the above optimized conditions, calibration curves were constructed as shown in Fig. 2. Li(I) spectral line of 670.79 nm was found to be very sensitive and provided a linear calibration up to 0.54 M Li concentration. But in view of the

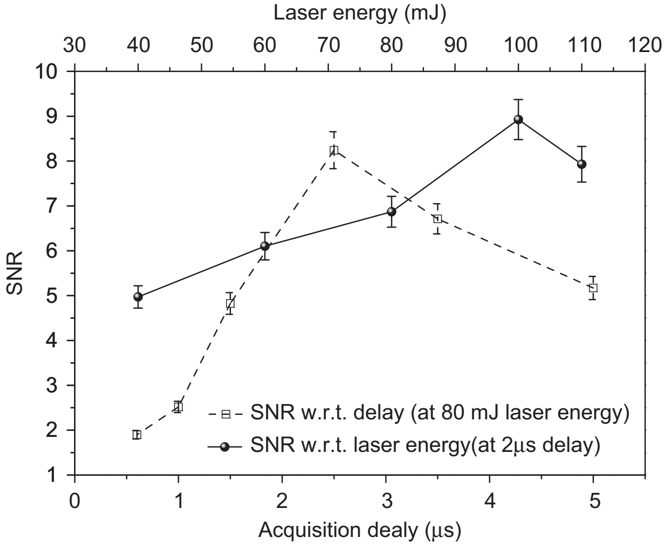

Fig. 1. Dependence of the signal to noise ratio (SNR) of the Li(I) 670.79 nm emission line on laser fluence and acquisition delay.

Table 1
Characteristics of spectral lines employed for LIBS analysis of Li along with their fitted parameters obtained from calibration curves.

Species	Wavelength λ_{ij} (nm)	A_{ij} (10^8 s^{-1})	E_j (cm^{-1})	E_i (cm^{-1})	Slope	Intercept
Li(I)	460.288	0.223	14903.957	36623.312	1483	−682
Li(I)	497.174	0.673	14903.957	35012.06	352	−168
Li(I)	610.364	0.686	14903.957	31283.053	–	–
Li(I)	670.790	0.369	0	14903.622	10241	18
Li(I)	812.644	0.349	14903.957	27206.066	651	−3.9

λ_{ij} is the transition wavelength, A_{ij} is the transition probability and E_i and E_j are the energies of the upper and lower levels, respectively.