

# Light element analysis of ceramics using in-air ERDA and TOF-ERDA

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## ABSTRACT

Ceramics such as  $\text{Li}_2\text{ZrO}_3$  and  $\text{Li}_4\text{SiO}_4$  have interesting features of water vapor and carbon dioxide absorption. However, the mechanism of absorption catalysis is not well understood. The element behavior in ceramics was measured using ion beam analysis. To measure the hydrogen and other light element quantities and distribution in ceramics, in-air and time-of-flight elastic recoil detection analyses were performed. Hydrogen quantity was compared with PET film by the in-air analysis. Carbon was observed in ceramics by the time-of-flight analysis, and lithium and oxygen distributions on the surface kept in air were compared with those of ceramics stored in a vacuum.

## 1. Introduction

Recently, global warming has become an urgent problem. Further reduction of carbon oxide emissions is necessary. Utilization of hydrogen as an energy source has also been promoted. Ceramics such as  $\text{Li}_2\text{ZrO}_3$  and  $\text{Li}_4\text{SiO}_4$  have functions of water vapor and carbon dioxide absorption. These ceramics also desorb hydrogen gas when heated up to 100–200 °C [1–3]. It is possible for hydrogen gas production to be carbon dioxide free. However, the mechanism of absorption catalysis is not yet well understood. Examining the behavior of hydrogen and other elements in ceramics is important for this understanding. In-air hydrogen analysis is required, because ceramics desorb water (hydrogen) in a vacuum. The quantity and distribution of hydrogen in ceramics have been measured using in-air elastic recoil detection analysis (ERDA) equipment, which was developed at the Wakasa wan Energy Research Center (WERC) [4]. Time-of-flight (TOF-)ERDA has also been used for distribution measurements of multi-elements [5].

## 2. Weight fraction of ceramics

Lithium zirconate ( $\text{Li}_2\text{ZrO}_3$ ; TYK Corporation, Japan) has high absorption ability for water vapor and carbon dioxide. First, two lithium zirconates,  $20 \times 14 \times 2$  mm in size, were heated to 350 °C to emit water and carbon dioxide. Their weight was thereby reduced to 1.29 g ( $2.3 \text{ g/cm}^3$ ). One lithium zirconate was then kept in air, and the other in a vacuum desiccator. The degree of vacuum was 1/10–1/100 of atmospheric pressure, and silica gels were installed in the desiccator to

remove water vapor. The weight ratios against initial weight as a function of exposure time are shown in Fig. 1. The weight of the lithium zirconate kept in air increased 10% after 900 h and 20% after 4500 h. The weight of the one kept in the vacuum increased 1% after 1000 h and 2.8% after 4500 h. After 5500 h, the weight of lithium zirconate in the air increased suddenly, because Japan entered its rainy season, and humidity rose to over 70%. Humidity during other seasons is 50–60%. This means that the weight gain depended on the humidity.

## 3. Hydrogen analysis in air

Lithium zirconates desorb water in a vacuum, and the water quantity will change conspicuously around the surface region. Since the effective area of the ion beam analysis corresponds to the same regions, our in-air ERDA system is suitable for this quantitative analysis.

A 5.1 MeV  $\text{He}^{2+}$  beam was used for the in-air hydrogen analysis. The setup of the experiment was the same as in reference [4]. Fig. 2 shows the hydrogen energy distributions of polyethylene terephthalate film (PET; black dashed line), lithium zirconate kept in air for 1100 h (blue dash-dotted line), lithium zirconate in vacuum for 1100 h (green line), and lithium zirconate in air for 7200 h (red dotted line). Hydrogen on the surface region corresponded to around 1500 channel events, and gradually decreased in the lower energy region on each spectrum. Very little hydrogen was observed in the lithium zirconate in the vacuum, but it increased when kept in air. Spectra shape of lithium zirconate in the air was almost the same as the PET one. In the PET film, the depth profile can be measured up to about 2.8  $\mu\text{m}$  from the surface.

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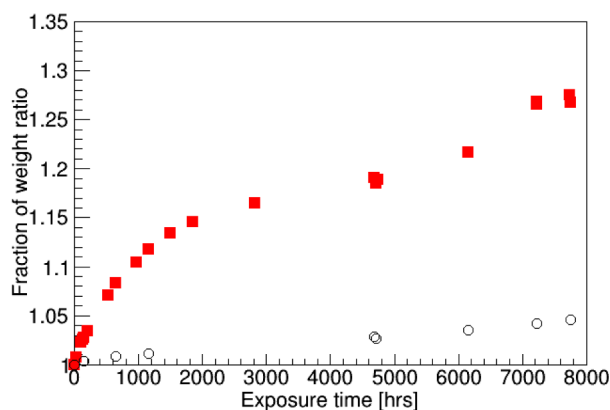


Fig. 1. The weight ratios of ceramics against initial weight as a function of exposure time. Ceramic weight ratios kept in air and in vacuum are shown as square and open circle symbols, respectively.

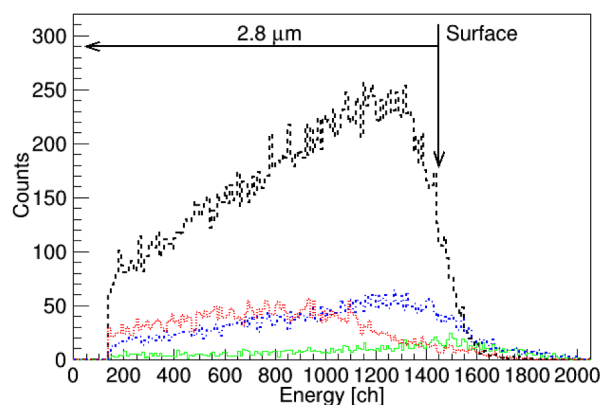


Fig. 2. The energy distribution of H from the in-air-ERDA analysis. The dashed (black), dotted (red), dash-dotted (blue), and continuous (green) lines correspond to PET, the lithium zirconate kept in air for 7200 h, and in air for 1100 h, and the one in vacuum, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Stopping range values of PET and lithium zirconate are same within 3% by SRIM2013 [6]. Thus the depth information for hydrogen is almost the same between PET and lithium zirconates. This means that hydrogen exists inside the lithium zirconate.

Distances between the beam window and target surface are not exactly the same, since targets cannot be set with same position for each measurement. The distance accuracy is below 0.5 mm because of visual confirmation of the setting position. This accuracy corresponds to about 30 channels in Fig. 2. However, the surface structure of ceramics in the air for 7200 h is very different from the others beyond the distance accuracy. This phenomenon will be addressed in the Discussion. To consider hydrogen quantity in this section, the comparison region used should be far from the surface; hence, hydrogen counts are summed up in the 300–600 channel (around 2 μm from the surface). Hydrogen quantities of lithium zirconates relative to PET were 4% (in the vacuum), 19% (1100 h in air), and 30% (7200 h in air).

Sometimes, hydrogen desorption will occur at beam irradiation. Total irradiation beam charges were several hundred nC at each in-air experiment. The stability of hydrogen quantity is shown in Fig. 3. Measurement data were recorded in list mode, and then data were divided to 5 sections. The first section (1) corresponds to the beginning of events, and the last section (5) corresponds to the end. The Y-axis shows the hydrogen quantity (summed up to 200–800 channels in Fig. 2) normalized by X-ray counts from the Si window. This method is the same as that in reference [4]. The normalized hydrogen quantity did

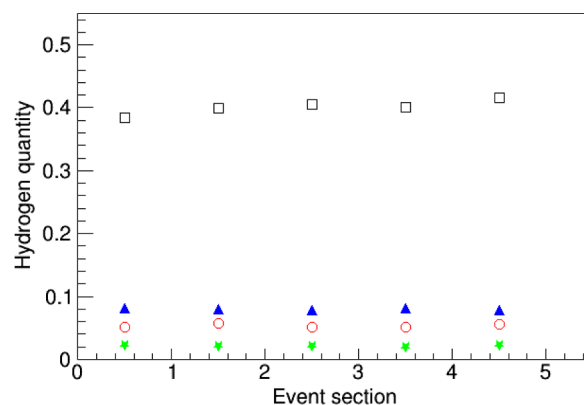


Fig. 3. The time dependence of hydrogen quantities. Measured data were divided into 5 sections, and hydrogen quantities were calculated in each section. The open squares (black), open circles (red), triangles (blue), and stars (green) correspond to PET, lithium zirconate kept in 7200 h, kept in air 1100 h, and in vacuum, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

not change in every section; therefore, hydrogen desorption was considered negligibly small between these measurements.

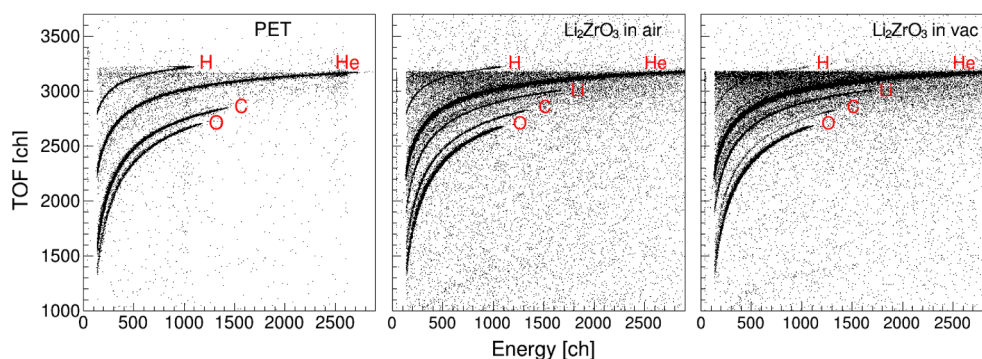
#### 4. Multi-element analysis using TOF-ERDA

Hydrogen quantity was shown to increase with greater exposure time in air by in-air ERDA measurements. The next interesting point is the behavior of other elements absorbed or constituent elements (carbon, oxygen, and lithium). TOF-ERDA can analyze multi-elements simultaneously [5,7]. However targets should be set in the vacuum for these measurements. Thus, the accuracy in determining element quantity deteriorates, even though the distribution of elements can be measured with nanometer-depth resolution [5].

TOF-ERDA measurements were performed using a 10 MeV  $\text{He}^{2+}$  beam at WERC. The target angle was 20 degrees, and TOF-ERDA detectors were set 40 degrees from the beam direction. TOF-ERDA measures energy and TOF of elements. The 2-dimensional (2-D) histograms of energy and TOF are very characteristic, and it is easy to separate the signals of multi-elements. Fig. 4 shows 2-D histograms of TOF vs. energy for PET, lithium zirconate in the vacuum, and lithium zirconate kept in air for 7700 h, respectively. Loci of H, He, C, and O can be clearly observed in the PET analysis. The Li is also observed in lithium zirconate samples.

To select events for object elements, mass spectrums were obtained. The element mass can be calculated by the equation  $E = 1/2 mv^2$ . The element velocity can be followed by  $v = L/T$  ( $L$ : the distance between two transmission detectors,  $T$ : TOF). Mass spectra are shown in Fig. 5. Peaks of H, He,  $^6\text{Li}$ ,  $^7\text{Li}$ , C, and O can be clearly observed. Quantities of H and C in the lithium zirconate in the vacuum were low compared to those in air. The mass peaks of C and O were smaller than 12 and 16. This mass decrease occurs on the energy loss of a dead layer in the energy detector of the TOF-ERDA system. Energy loss becomes bigger with mass number. Therefore the mass calculated by the equation  $E = 1/2 mv^2$  becomes small, especially for high-mass elements.

Energy distributions of H,  $^7\text{Li}$ , C, and O were obtained by event selection corresponding to each peak. Backgrounds were subtracted by sideband events. Fig. 6 shows energy distributions of H,  $^7\text{Li}$ , C, and O for PET, lithium zirconate kept in air for 7700 h, and lithium zirconate in vacuum, respectively. The mass resolution degenerated at the low-energy region (less than 500 channels), and as a result, event selection uncertainties increased. For this reason, the depth discussion considers regions with more than 500 channels. In these regions, possible detection ranges using the He 10 MeV beam are 15 μm, 2.9 μm, 0.9 μm, and 0.6 μm from the surface for H, Li, C, and O, respectively (see Fig. 6).



**Fig. 4.** The 2-D histograms of TOF vs. energy for PET (left), the lithium zirconate kept in air 7700 h (center), and lithium zirconate in the vacuum (right). Loci for H, He, Li, C, and O could be observed. Conversion factors for time and energy were 0.4 ns and 3.4 keV per channel, respectively.

The solid angle of the TOF-ERDA system was about 50 times smaller than that of the in-air ERDA. Therefore, beam irradiation times were long on TOF-ERDA measurements. Total irradiation beam charges were about 50  $\mu\text{C}$  at each measurement. Although the hydrogen quantity was stable for the in-air measurements, the quantity for the TOF-ERDA measurements might change due to long beam irradiation. To compare element quantities, the TOF-ERDA data of the lithium zirconate kept in air for 7700 h was divided in two (first half; second half). Counts of each element in the over-500-channels region are summed up in Fig. 6. Then, second half counts were divided by first half ones. The ratios were  $0.87 \pm 0.08$ ,  $0.91 \pm 0.03$ ,  $0.98 \pm 0.07$ , and  $0.96 \pm 0.03$  for H,  $^7\text{Li}$ , C, and O, respectively. Although the quantity of H decreased a little (about 10%), there were no large changes.

The H quantity around the region 2  $\mu\text{m}$  from the surface was 26% compared with PET. This was smaller than the amount in the in-air ERDA measurement of the lithium zirconate kept in air for 7200 h. However, this smaller hydrogen quantity would be effected by the hydrogen loss of beam irradiation discussed above. The weight of the lithium zirconate kept in air for 7700 h decreased about 0.5% after TOF-ERDA measurements. The total installation time in the vacuum between TOF-ERDA measurements was 24 h. Although the element loss was occurred while beam irradiation, the beam irradiation area is 50 times smaller than the total surface area. Therefore, the 0.5% weight decrease is mainly due to the effect of gas release in vacuum. To check this weight decrease, gas analysis was performed using a quadrupole mass spectrometer in vacuum:  $\text{H}_2\text{O}$  and a little  $\text{CO}_2$  were observed, and no significant signal was observed for the other elements, thus  $\text{H}_2\text{O}$  desorption was the main reason of the weight decrease.

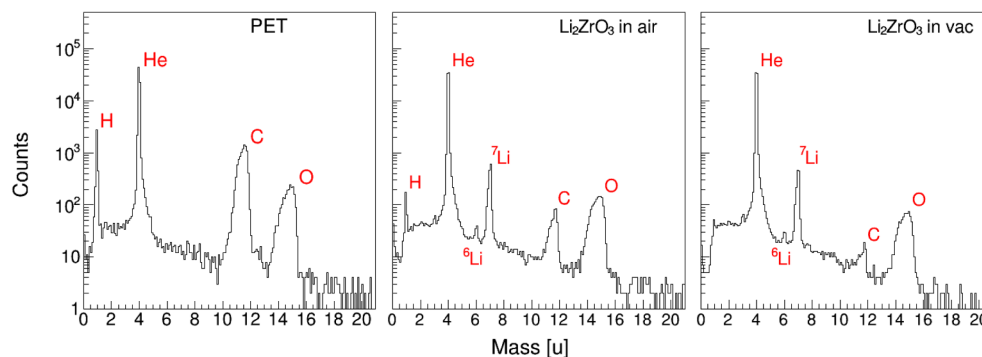
Rutherford backscattering spectroscopy (RBS) was performed simultaneously with TOF-ERDA measurements. A silicon surface barrier

detector was set at 135 degrees from the beam direction, and scattered He energy was measured. RBS spectrums of PET, the lithium zirconate kept in air for 7700 h, and the lithium zirconate in vacuum are shown in Fig. 7. Quantities of  $^7\text{Li}$ , C, and O of lithium zirconate in air were increased compared to those in vacuum. These results are consistent with the energy distributions of  $^7\text{Li}$ , C, and O discussed above. The maximum He energy scattered from Zr of the lithium zirconate in air (around 2650 channel) was smaller than that in the vacuum, and the rising slope became shallow.

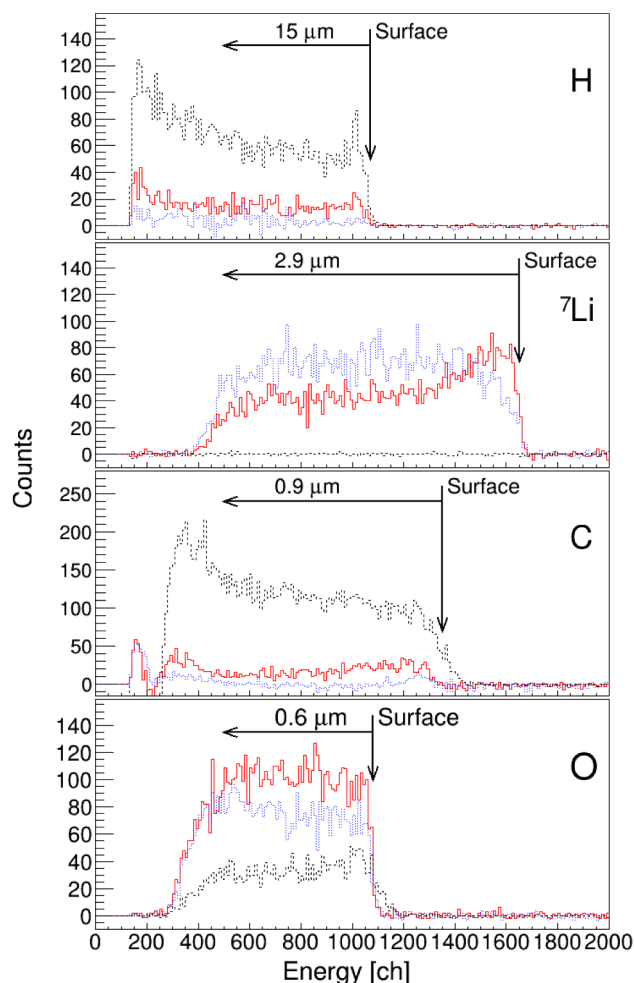
## 5. Discussion

In the in-air ERDA analysis, the structure of H distribution for the lithium zirconate in air was almost the same as that for PET. This means that H exists uniformly in the lithium zirconate up to 2.8  $\mu\text{m}$  from the surface. The lithium zirconate kept in air for 7200 h included 30% H compared with PET. This value corresponds to approximately 0.7% of the original weight of the lithium zirconate.

For the TOF-ERDA measurement, targets have to be set in the vacuum. Therefore, the element quantity for molecule release becomes low, even though element distributions can be determined with high depth resolution. From the TOF-ERDA analysis of lithium zirconate kept in air for 7700 h, H was shown to exist in deeper regions (more than 10  $\mu\text{m}$  from the surface); while C was observed at 600–1300 channels in Fig. 6, the quantity of C decreased gradually from the surface compared to the PET distribution. A few H events in the lithium zirconate in vacuum were observed up to 15  $\mu\text{m}$  from the surface, and a few C events were observed on just the surface region (just around 1200 channel in Fig. 6). These H and C distributions were similar to that of the lithium zirconate in air except for small quantities. The lithium zirconate was



**Fig. 5.** Mass spectrums for PET (left), the lithium zirconate kept in air 7700 h (center), and lithium zirconate in vacuum (right). Peaks for H, He, Li, C, and O were observed.

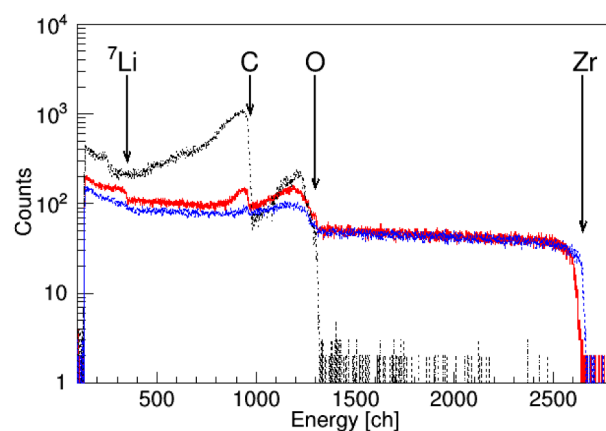


**Fig. 6.** Energy distributions for H,  $^7\text{Li}$ , C, and O. The dashed (black), continuous (red), and dotted (blue) lines correspond to PET, the lithium zirconate kept in air 7700 h, and in the vacuum, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

removed from the vacuum chamber several times for weight measurements. This meant that a little  $\text{H}_2\text{O}$  and  $\text{CO}_2$  could be absorbed. In terms of the O distribution, the O quantity increased around the surface region in the lithium zirconate in air comparing with that in vacuum (500–1100 channels in Fig. 6), and it seems that each O value was getting closer around 500 channel area. From above results, absorbed  $\text{CO}_2$  would be stacked around the surface region. The most interesting result was the Li distribution of the lithium zirconate in air. The peak structure was observed around the surface region (less than  $1\ \mu\text{m}$ ). This region was almost the same as the C increasing ranges.

The H/Li exchange has been reported on lithium compound materials [8–10]. From this H/Li exchange scenario, the Li in the material reacts with water  $\text{H}_2\text{O}$ , and  $\text{LiOH}$  will be generated on the surface region. H will then penetrate into the material. The wide-range distribution of H, and peak structure of the Li distribution, indicate that the same phenomenon will occur in lithium zirconates. The peak structure of Li may imply that  $\text{LiOH}$  condenses at the surface region. On the other hand, quantities of C and O increase at the same region as the Li peak.  $\text{LiOH}$  is a well-known carbon dioxide remover ( $2\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$ ). Therefore, lithium carbonates  $\text{Li}_2\text{CO}_3$  are generated on the surface. The water and carbon dioxide absorption of lithium zirconate can be explained by this discussion.

The H distribution of in-air measurements for the lithium zirconate kept in air for 7200 h and the RBS spectrum of the Zr surface structure



**Fig. 7.** RBS spectra. The dash-dotted (black), continuous (red), and dashed (blue) lines correspond to PET, the lithium zirconate kept in air 7700 h, and in the vacuum, respectively. Appearance points of Zr, O, C, and  $^7\text{Li}$  are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

support the scenario described above. The  $\text{Li}_2\text{CO}_3$  stayed within a  $1\text{-}\mu\text{m}$  region from the surface, and the amount of H in this region decreased. The 1000–1600 channel region of the lithium zirconate kept in air for 7200 h decreased more than the other distributions in Fig. 2. This 1000–1600 channel region corresponds to about  $1\ \mu\text{m}$  from the surface. The maximum energy of the RBS spectrum (Fig. 7) of the lithium zirconate kept in air for 7700 h was smaller about 50 channels than that in the vacuum. This energy decrease is equivalent to  $0.8\ \mu\text{m}$  thickness as  $\text{Li}_2\text{CO}_3$  layer. This thickness is consistent with the hydrogen decrease region (1000–1600 channel) of the in-air measurement. The shallow rising slope of the RBS spectrum of the lithium zirconate kept in air for 7700 h shows the energy straggling and the mixing of the interface region.

## 6. Conclusions

The quantitative H analysis in air was performed with lithium zirconates using the in-air ERDA system at WERC. H existed uniformly in the lithium zirconate up to  $2.8\ \mu\text{m}$  from the surface. ToF-ERDA was performed to analyze the behavior of H, Li, C, and O. The H existed more than  $10\ \mu\text{m}$  from the surface by the ToF-ERDA analysis. For the Li distribution, the peak structure was observed around the surface region. Quantities of C and O increased in the same Li condensation region. These studies suggest one scenario for the mechanism of water vapor and carbon dioxide absorption by lithium zirconates.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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