論文の内容の要旨

論文題目　Behaviors of deuterium irradiated into ternary lithium oxides
（三元系Li酸化物中に照射された重水素の挙動）

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Controlled fusion has a potential to produce electricity in an environmentally benign way, meeting the needs of a growing world population. In fusion reaction the deuterium fuel can be separated from regular water, while tritium has to be manufactured - "bred". The lithium-containing "blanket" surrounding the reactor core absorbs neutrons from the fusion reaction and lithium is transformed into tritium and helium. The helium-cooled pebble-bed (HCPB in EU) and the water-cooled ceramic breeder (in Japan) concepts have been designed for the tritium blanket in fusion reactor. Ternary lithium oxides such as Li_2TiO_3 and Li_4SiO_4 are regarded as candidate breeders in solid blanket concepts.

Generally tritium generated by neutron irradiation exists as $–OT^-$ or T^-, then migrates to the surface, and gradually desorbs as hydrogen molecular form (HT, T_2) or water form (HTO, T_2O) by recombination process or by an exchange reaction with an H_2 molecule in the sweep gas. Both the migration of tritium to the surface and the release of tritium on the surface are affected by radiation defects. Therefore understanding on the interactions between tritium and radiation defects is needed.

The objective of the present research is to clarify the existence states and release behaviors of hydrogen isotopes affected by radiation defects in ternary Li-oxides (Li_xMO_y). For this purpose, IR absorption analysis and thermal desorption spectroscopy (TDS) were combined with the ion implantation technique. Since introduction of tritium enough to be detected by IR absorption analysis is difficult, the deuterium ion irradiation is applied, which can introduce not only hydrogen isotopes (deuterium), but also radiation defects (such as Li vacancies, M vacancies and F centers) simultaneously. Corresponding to $–OT^-$ or T^- induced by neutron irradiation, $-OD^-$ and D^- on/near the surface can be formed in deuterium irradiation. Various $–OD^-$ affected by proximate defects can be identified by FT-IR, and possible existence of non-O-D states such as D^- and release behavior of deuterium can be analyzed by TDS.

Powder and single crystals of ternary Lithium oxides (Li_xMO_y) including $LiAlO_2$, Li_2TiO_3, Li_2SiO_3, Li_4SiO_4, $LiNbO_3$ and $LiTaO_3$ were used as samples. The experimental system consists of FT-IR (Mattson, Infinity Gold) with an MCT detector, a mirror for the diffuse reflectance method, a Quadruple Mass Spectrometer (QMS), an ion gun, a vacuum chamber, a heating unit, a Faraday cup, and a cover to prevent any ion irradiation of the molybdenum sample holder.After the pretreatment, 3keV D_2^+ irradiation was performed, and in situ IR absorption analysis was conducted during the ion irradiation.. The ion implantation depth was about 50 nm according to calculation by SRIM2003 code. Some powder samples were irradiated at a flux of $4\sim16\times10^{16}$ D_2^+ m^{-2} s^{-1} up to the fluence level of $0.3\sim5\times10^{21}$ D_2^+ m^{-2}. The irradiation was directed towards the single crystal sample surface at an angle of 45°.

The release behavior of deuterium was detected by QMS during the heating process with a rate of 20 K min^{-1} up to 800 K after ion irradiation. The amount of deuterium released as different chemical forms were estimated based on the fundamental vacuum relationship of mass flow. For single crystals in-situ analysis was also applied during the heating after ion irradiation. All of FT-IR and TDS results of experimented Li_xMO_y samples are summarized in Table.1.

Deuterium irradiated into ternary lithium oxides exist as multiple O-D states and non-O-D states. Multiple O-D states can be indicated by different O-D vibration peaks observed in IR spectra. It is considered that there are three possible states of D^+ in Li_xMO_y after D_2^+ irradiation, namely sub.D^+_{Li}, sub.D^+_M and int.D^+. All of D^+ (whether sub.D^+ or int.D^+) are attracted by neighboring oxygen ions to form the O-D states of sub.D^+ or int.D^+. In addition, the isolated or hydrogen bonded $-OD^-$ exist on the surface (termed as surface $-OD^-$). Multiple O-D vibration peaks have been observed in D_2^+-irradiated lithium ternary oxides, corresponding to the above multiple O-D states. Their fractions are dependent on the sample shape (single crystal or powder), the irradiation fluence and the temperature of sample during irradiation.

It is observed that the O-D vibration peak corresponding to sub.D^+_M has higher frequency. It is considered that the production probability of M vacancy can be decreased with atomic weight of M increasing, due to the evaluation on that by a simplified binary collision approximation (BCA) model. Therefore the fractions of different O-D states can be affected by M, which is reflected by the average frequency (termed as $\overline{\nu}_{O-D}$) of all O-D vibration peaks weighted by weighted by each proportion. It is considered that $\overline{\nu}_{O-D}$ decreases with the increasing atomic number of M in Li_xMO_y. Based on a multiple states model it seems that Li_xMO_y with a heavier atom as M might be good choice from the respect in the diffusion of hydrogen isotopes.

The increase of O-D with desorption of deuterium during the heating after irradiation indicates the existence of non-O-D states, which has been observed in $LiAlO_2$ single crystal. The unpaired electron state is considered to be a trapping site for deuterium as non-O-D states.

Deuterium irradiated into Li_xMO_y (Li_2TiO_3, Li_2SiO_3, Li_4SiO_4, $LiTaO_3$, $LiAlO_2$ powder samples and $LiAlO_2$, $LiTaO_3$, $LiNbO_3$ single crystal samples) is released as four chemical forms: HD, D_2, HDO and D_2O. These release chemical forms can be divided into two groups, D_2/HD (termed as non-condensative forms) and D_2O/HDO (termed as condensative forms). In non-condensative forms, whether powder or single crystal, HD and D_2 can be desorbed at the same temperature. In condensative forms, desorption temperatures of HDO and D_2O are not always the same, for example desorption temperature of D_2O is higher that of HDO in $LiTaO_3$ and Li_4SiO_4 powder. In

Li_2SiO_3, Li_4SiO_4 and $LiTaO_3$ powder, desorption temperature of non-condensative forms is higher than that of condensative forms. However it is contrary in Li_2TiO_3 and $LiAlO_2$ powder. It reflects that desorption behaviors of deuterium are dependent on material.

HDO desorption is considered to be mainly due to the recombination reaction between $–OD^-$ and surface $–OH^-$ induced by the adsorption of water vapor on the sample. Desorption of non-condensative forms (D_2/HD) should be correlated to unpaired electron state indicated by the ESR signal peak. D_2O desorption is affected by the combination of HDO desorption and D_2 desorption. Deuterium desorbed as D_2 achieves the saturation at certain irradiation fluence, which suggests that concentration of unpaired electron state induced by irradiation is limited in the sample. It can be seen that D_2 is the predominant chemical form of deuterium (the fraction of deuterium released as D_2 in all forms > 60%) from the Li_xMO_y single crystal. Although HDO can almost not be detected in irradiated single crystal samples, it is one of the main chemical forms of deuterium released from irradiated powder samples (the fraction of deuterium released as HDO in all forms >30%). It reflects the influence of the sample shape that desorption behaviors of deuterium are different between powder and single crystal. Considering that the main difference between powder and single crystal is the area of surface, the fraction of different release chemical forms should be dependent on the surface condition of sample. Desorption behavior of deuterium is corresponding to the existence states of deuterium. O-D state with higher vibration frequency has a higher annihilation temperature, also corresponds to deuterium desorbed at a higher temperature

Finally, three factors appear to govern the release behavior of deuterium from ternary lithium oxides. The first is the corresponding vibration frequency of O-D state. It is considered that an O-D state with a higher vibration frequency has a higher annihilation temperature, also corresponds to deuterium desorption at a higher temperature. The second is the surface $–OH^-$ induced by the adsorption of H_2O vapor on the sample. In water forms (HDO and D_2O), deuterium desorbed as D_2O is much less than that as HDO. HDO desorption is considered to be mainly due to the recombination reaction between $–OD^-$ and surface $–OH^-$. D_2O desorption is partly dependent on the HDO desorption. The third is unpaired electron state induced by irradiation damage. Deuterium desorbed as hydrogen molecular forms (D_2/HD) is correlated to unpaired electron state indicated by the ESR signal peak.

The complexity observed in desorption behavior of deuterium from Li_xMO_y was considered to result from the combination influence of these three factors. The fractions of deuterium desorbed as different chemical forms are dependent on concentrations of O-D state, surface $–OH^-$ and unpaired electron state. The difference in desorption temperatures of deuterium as different chemical forms should be correlated to the potential energies of O-D state, surface $–OH^-$ and unpaired electron state.

Based on the multiple states model, it is considered that the existence states of deuterium in the bulk have no influence on the release chemical forms of deuterium. The fractions of different release chemical forms should be mainly dependent on the concentrations of deuterium as different existence states on the surface not in the bulk. Therefore the above conclusions on desorption behavior of deuterium from D_2^+ irradiated ternary lithium oxides can be partly applied for that of tritium after neutron irradiation.