

Abstract of the thesis

(論文の内容の要旨)

論文題目 Release behavior of hydrogen isotopes in ternary lithium oxides
 (三元系リチウム酸化物における水素同位体放出挙動)

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1. Introduction

In order to sustain the tritium self-sufficiency for fusion reaction, it is important to minimize the tritium inventory in the blanket. Accordingly, the understanding of tritium migration and release process in ceramic breeder materials is indispensable. The tritium release from ceramic breeder materials is understood to be composed by multiple fundamental processes including diffusion in the bulk, surface processes, migration along grain boundaries, percolation in the interconnected open pores and convection by purge gas. The previous experiments indicate that the tritium release is influenced by temperature, purge gas condition, irradiation, microstructure of materials, etc. However, the influence of material microstructure (grain size, surface condition, and open and closed pores) has not been fully understood.

The objective of the present work is to study the influence of microstructure (grain size, surface condition, and open and closed pores) on the release behavior of hydrogen isotopes in ternary lithium oxides systematically by changing the samples from single crystal to poly crystal. In order to achieve the objective, LiNbO_3 and Li_2TiO_3 are chosen as the researching materials.

2. Experiment

2.1 Sample preparation

LiNbO_3 single crystal cubic samples ($4.7 \times 4.7 \times 4.7 \text{ mm}^3$, $1.5 \times 1.5 \times 1.5 \text{ mm}^3$, $0.46 \times 0.46 \times 0.46 \text{ mm}^3$) are cut from a block by using a diamond cutter. LiNbO_3 single crystal powder samples with size of around $50 \text{ }\mu\text{m}$ (av.) and around $5 \text{ }\mu\text{m}$ (av.) are prepared by crushing a part of the same block and meshing with a set of sieves: $45 \text{ }\mu\text{m}$ and $53 \text{ }\mu\text{m}$ sieves for the former, and $5 \text{ }\mu\text{m}$ and $6 \text{ }\mu\text{m}$ sieves for the latter. LiNbO_3 poly crystal powder sample with size of around $50 \text{ }\mu\text{m}$ (av.) is prepared by meshing the as-received material.

Li_2TiO_3 single crystal plate samples are synthesized by a flux method with B_2O_3 as the flux agent. Li_2TiO_3 single crystal powder samples with size of around $50 \text{ }\mu\text{m}$ (av.) and around $5 \text{ }\mu\text{m}$ (av.) are prepared by crushing single crystal plates and meshing. Li_2TiO_3 poly crystal pellets are prepared by pressing the starting materials of as-received Li_2TiO_3 poly crystal powder, PVA (5 wt%) and stearic acid (5 wt%) and sintering at 1173 K, 1223 K, 1273 K, 1373 K, and 1473 K for 12 h in air to obtain five pellet samples with certain apparent density (% of theoretical density): 76% T.D., 83.5% T.D., 86.6% T.D., 88.6% T.D. (1373 K) and 88.6% T.D. (1473 K). These apparent densities were evaluated by measuring the mass and size of pellets.

2.2 Experiment procedure

Samples put in a Ni sample holder are heated at 1073 K for 1 h in 100 Pa D_2O vapor for deuterium absorption in absorption system. After cooling down and evacuation, samples are transferred to a high-vacuum TDS system without exposure to air by using a transfer rod. In TDS system samples are heated at 5 K/min to high temperatures (1173 K for cubic and plate sample, 973 K for powder and pellet samples) for desorption. The species and amount of gases released from the samples during heating process are monitored by a quadrupole mass spectrometer (QMS). The correlation of QMS signal versus the temperature or time, namely TDS spectrum is obtained.

3. Release behavior of hydrogen isotopes in LiNbO₃ single crystal cubic and powder

The release behavior of hydrogen isotopes in LiNbO₃ single crystal cubic (4.7×4.7×4.7 mm³, 1.5×1.5×1.5 mm³, 0.46×0.46×0.46 mm³) and powder (50 μm av.) samples was studied by TDS. The deuterium thermally sorbed was mainly released in HDO and D₂O.

In the large-size cubic samples, two peaks were observed for HDO: low-temperature peak (590~600 K) related to recombination desorption of hydroxyl groups chemically adsorbed on the surface (surface hydroxyl groups) and high-temperature peak (> 800 K) related to diffusion of hydroxyl groups in the bulk. With the sample size decreasing, the peak related to bulk diffusion was clearly observed to move to lower temperature regions, which is due to the shorter diffusion path, while the peak related to recombination desorption did not change much.

In the small-size powder (50 μm av.) sample, two peaks were observed for HDO: (i) around 350 K due to desorption of molecules physically adsorbed on the surface; (ii) around 635 K, with H₂O peak observed at the same temperature, due to recombination desorption of hydroxyl groups chemically adsorbed on the surface. The bulk diffusion in single crystal was modelled by using the simple diffusion model. It was shown that the rate-controlling step is the bulk diffusion at high temperatures (> 800 K) in the large-size cubic sample, and moves to surface processes at low temperature region (590~635 K) in the small-size powder sample.

4. Release behavior of hydrogen isotopes in Li₂TiO₃ single crystal plate and powder

The release behavior of hydrogen isotopes in Li₂TiO₃ single crystal samples was studied by TDS. Similar to LiNbO₃, the deuterium thermally sorbed in Li₂TiO₃ was mostly released in HDO and D₂O. In single crystal plate sample (thickness of 0.2~0.4 mm), three peaks were observed for HDO:

Peak (1): due to desorption of water molecules physically adsorbed on the surface (around 345 K)

Peak (2): due to recombination desorption of surface hydroxyl groups (around 625 K)

Peak (3): due to recombination desorption of hydroxyl groups diffused from the bulk (around 1000 K)

In small-size powder samples (50 μm av., 5 μm av.), no obvious peak (3) was observed, which is considered to be due to (i) the sample amount is too small to observe this peak, (ii) the rate-controlling step has moved from the bulk diffusion to surface processes.

A broad peak was observed at 400~600K in 5 μm (av.) powder sample:

Peak (4): the peak between peak (1) and peak (2) (400~600K), which is considered to be the release of molecules (HDO, D₂O) physically adsorbed on the surface of inner open pores created by agglomeration through gas migration along narrow open pore channels with different shapes and sizes.

By comparing the TDS spectra of LiNbO₃ and Li₂TiO₃, it was found that surface hydroxyl groups have the similar environment in LiNbO₃ and Li₂TiO₃ and both bonded to Li atoms. The diffusivity of hydroxyl groups in the bulk of grains is smaller in Li₂TiO₃ than that in LiNbO₃.

5. Influence of surface condition on hydrogen isotopes release behavior in LiNbO₃ cubic (single crystal) and powder (single and poly crystal)

The release behavior of hydrogen isotopes in LiNbO₃ single and poly crystal samples with different surface condition was studied by TDS. The surface morphology was observed by SEM and the specific surface area of powder samples was measured by BET.

In single crystal cubic sample (1.5×1.5×1.5 mm³), HDO, D₂O and H₂O peaks related to recombination desorption of surface hydroxyl groups (peak (2)) disappeared after high-temperature pretreatment (at 1233 K for 1 h in vacuum and followed at 1073 K for 1 h in air), while the peak related to bulk diffusion (peak (3)) did not largely change. Meanwhile, the surface roughness of cubic sample created by cutting was greatly smoothed by high temperature pretreatment. The decrease in the amount of surface hydroxyl groups is considered to result from the decrease of the surface area and recovery of surface defects induced by high-temperature pretreatment.

In 50 μm (av.) single and poly crystal powder samples, the amount of surface hydroxyl groups per gram is

proportional to the specific surface area measured by BET. While in 5 μm (av.) single crystal powder sample, smallest amount of surface hydroxyl groups was observed in contrast of the largest theoretical and BET specific surface areas, which is considered to be related to agglomeration of this powder sample, for example the access of hydroxyl groups to the surface was decreased due to agglomeration.

By assuming that the surface area for one hydroxyl groups ($-\text{OH}$ or $-\text{OD}$) is half of the surface area for one water molecule with Van der Waals radius of around 1.4 \AA and considering the distance between two oxygen atoms of around 2.7~3 \AA in LiNbO_3 crystallographic frame, the amount of hydroxyl groups per m^2 adsorbed in the monolayer was calculated (calculation result). The experiment results for the amount of hydroxyl groups per m^2 were estimated from the TDS results and BET measurement. It was found that the experiment results are around two orders of magnitude larger in the 50 μm (av.) powder samples and one order of magnitude larger in the 5 μm (av.) single crystal powder sample by comparing with the calculation result. It reveals that hydroxyl groups are densely formed on the surface region.

For peak (2) at 590~635 K related to recombination desorption of surface hydroxyl groups, H_2O peaks have almost two orders of magnitude higher level than HDO and D_2O , which is mainly due to the $-\text{OH}$ formed by isotope exchange reaction between $-\text{OD}$ on the sample surface and H_2O residue in the system.

6. Release behavior of hydrogen isotopes in Li_2TiO_3 poly crystal pellet

The release behavior of Li_2TiO_3 poly crystal pellet samples with different microstructure was studied by TDS. The grain size and pore morphology were observed by SEM. The open porosity, open pore size distribution and specific surface area of open pores were measured by mercury intrusion porosimetry.

The amount of molecules physically adsorbed (peak (1)) and hydroxyl groups chemically adsorbed (peak (2)) on the surface are not totally proportional to the specific surface area of open pores measured by mercury intrusion porosimetry, which could not reflect the real surface area of pellet samples due to that pores smaller than 168 nm could not be detected. More precise method should be used to measure the specific surface area of pellets.

The peak (4) related to the release of molecules physically adsorbed on the surface of inner open pores was observed at 400~650 K and similar to that was observed in 5 μm (av.) LiNbO_3 and Li_2TiO_3 single crystal powder samples with obvious agglomeration. It is considered that the release of peak (4) is mainly due to the Knudsen diffusion and interaction between gas molecules and walls of narrow open pore channels with several (tens) nm.

A new peak - peak (5) was observed at 650~900 K in high-density ($\geq 83.5\%$ T.D.) pellet samples, for which pores with dead end were observed by SEM. It is due to the release of hydroxyl groups absorbed in the bulk of grains with size of several (tens) μm , which was delayed due to the existence of closed pores. The “effective grain size” is defined to be an effective diffusion length needed to reach the surface (or open pores) and calculated from temperature of peak (5) by using the simple diffusion model. It is found that the “effective grain size” is several (tens) times larger than the real grain size decided by SEM observation. It is considered that the hydroxyl groups absorbed in the bulk of high density pellet samples have to undergo bulk diffusion in multi-grains and trapping in closed pores before arriving at the surface or open pores.

7. Conclusion

As the sample size of single crystal decreases from several hundreds μm to 50 μm and smaller, the rate-controlling step moves from the bulk diffusion at high temperatures (> 800 K) to surface processes at lower temperature region (590~635 K).

The amount of surface hydroxyl groups, which can influence the tritium release behavior by acting as tritium trapping, is found to decrease with the surface area decreasing induced by the smoothing of surface roughness at high temperatures. It was revealed that isotope exchange reaction between surface hydroxyl groups and H_2O residue in system occurs easily.

The release of hydroxyl groups absorbed in the bulk of grains with size of several (tens) μm is delayed by the existence of closed pores to high temperature region (650~900 K). Before arriving at the surface or open pores, these hydroxyl groups have to undergo bulk diffusion in multi-grains and trapping in closed pores several times.

The migration of gas along narrow open pore channels occurred at relatively high temperature of 450~600 K due to the Knudsen diffusion and interaction between gas molecules and walls of narrow open pore channels of several (tens) nm.