

Interaction of Hydrogen Isotopes with Defects in Li₂O Analyzed by FTIR

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Abstract

We have investigated interaction between hydrogen isotopes and defects in bulk Li₂O, using the Fourier transform infrared absorption spectroscopy (FT-IR). Multiple peaks were observed in the O–D stretching vibration region with Li₂O single crystals which were treated by thermal absorption and quenching. These peaks had different dependence on temperature and were attributable to the stretching vibrations of O–D in bulk Li₂O with or without defects.

I. INTRODUCTION

A series of works on solid breeder materials shows that defects affect tritium migration in the bulk and desorption from the surface. It is reported that the most of hydrogen isotopes in Li₂O exist as H⁺ to form a hydroxyl group coupling with the oxygen ion. Therefore, it is required to understand the interaction of –OH with defects. In the present work, the existing state of hydrogen isotopes in Li₂O was analyzed by the measurement of O–D vibrations especially emphasizing on the interaction with defects. Stretching vibrations of O–D in Li₂O are considered to be affected by defects around –OD. The O–D stretching vibrations in Li₂O with defects were measured by the infrared spectrum analysis, where defects were produced by quenching from high temperature.

II. EXPERIMENTAL

Single crystal of Li₂O was used for investigations. Deuterium was introduced into specimens by thermal absorption. Into specimens treated with thermal absorption, defects were introduced by the quenching. Specimens were maintained at 973 K under D₂ of 0.5 atm for 6 hours. After thermal absorption, they were cooled down to room temperature at four cooling rates: in 10, 3, 1 and 0.5 minute from 973 K down to 293 K. It is known that the quenching of oxides usually leads to increase of the density of oxygen vacancies or its variations (F-center etc.) in crystals. The larger cooling rate leads to the larger density of the oxygen vacancy. Additionally, the quenching treatment stops relaxation such as the relaxation of the lattice strain. Therefore, it is considered that difference in cooling rates results in the change of interactions between hydroxyl groups and defects. Infrared absorption spectra were recorded by the FT-IR under the air atmosphere at room temperature.

III. RESULTS AND DISCUSSION

Fig.1 shows the infrared absorption spectra of Li₂O recorded before and after the thermal absorption of D₂. For all samples with various cooling rates, a large peak was observed around 2710 cm⁻¹. This peak is independent of the cooling rate. It was attributed to stretching vibration of bulk –OD which was little or not affected by defects. In the lower wave number region than 2710 cm⁻¹, multiple peaks were observed (Fig.2). Intensities of these peaks increase with increasing cooling rates of the sample. Therefore, it was considered that these peaks were attributable to bulk –OD affected by oxygen vacancies. In the bulk of Li₂O, an oxygen vacancy has positive electricity relatively. When an oxygen lattice point around hydroxyl group becomes vacant, electrons of hydroxyl group are attracted by the vacancy. It results in decrease of the charge in the hydroxyl group, hence decrease of the bond energy of O–D. This leads to the shift of the O–D peak to the lower wave number region.

The sample with the largest cooling rate, 680 K / 0.5 min, was heat treated again, and the change of the peak intensity was observed (Fig.3). The sample was heated under the N₂ gas

atmosphere. After the heat treatment, infrared absorption spectra were recorded in the air at room temperature. After the heat treatment at 373 K for 6 hours, positions and intensities of all peaks did not change. By additional heating at 473K for 3 hours, the peak at 2651 cm^{-1} disappeared and intensity of the peak at 2566 cm^{-1} decreased largely. At the same time, intensity of the peak at 2610 cm^{-1} increased. After heating at 573K for 3 hours, the peak at 2610 cm^{-1} also disappeared, but several small peaks still existed. The peak at 2710 cm^{-1} also existed (Fig.4). This peak disappeared only after heating above 673 K. It is known that the oxygen vacancy in Li_2O is recovered above 570 K. Therefore, disappearance of these peaks at 573 K shows that these peaks are from $-\text{OD}$ affected by oxygen vacancies. Multiple peaks are considered to be also caused by oxygen vacancies which are not in the nearest or which have different charge state (F-center etc.). Furthermore, other kinds of defects such as Li vacancy or interstitial atom are presumably given as reasons of multiple peaks.

IV. CONCLUSION

In this study, we observed infrared absorption spectra of Li_2O single crystals which were treated by the thermal absorption and the quenching. Multiple peaks attributed to $-\text{OD}$ in Li_2O were observed and intensities of these peaks had different dependence on cooling rates or annealing temperature. This is considered to show that oxygen vacancies affected an existing state of hydroxyl group in Li_2O .

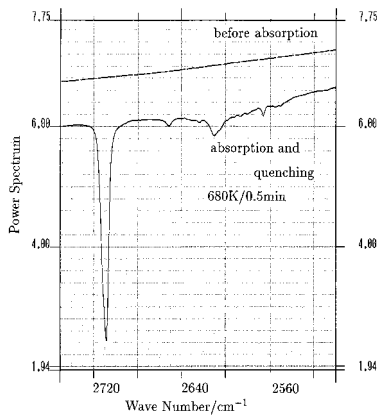


Fig.1 Infrared absorption spectra of O-D region.

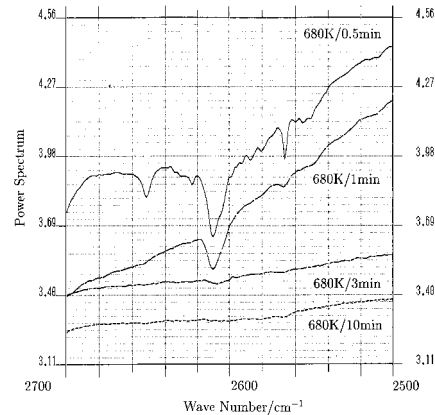


Fig.2 Dependence on cooling rates of infrared spectra.

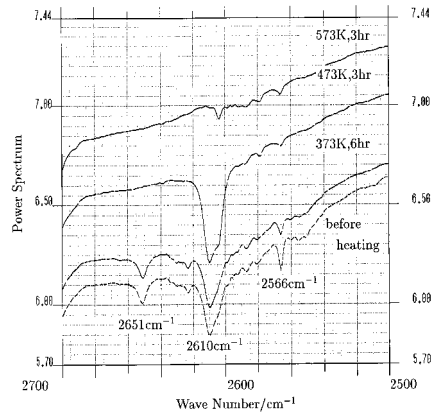


Fig.3 Change of absorption spectra with heating.

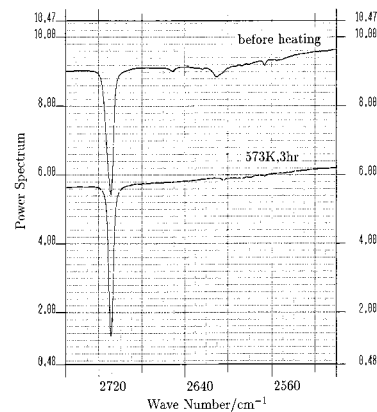


Fig.4 Change of absorption spectra with heating.