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Isotope separation of silicon and molybdenum using a free electron laser

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Abstract

The isotope separation of silicon and molybdenum was studied with a free electron laser (FEL). The FEL was used to irradiate flowing Si_2F_6 between 1000 and 800 cm^{-1} wavenumbers and to irradiate MoF_6 at 740 cm^{-1}. Enrichments of ^{29}Si and ^{30}Si were detected by 1000 cm^{-1} irradiation. A similar tendency with the ^{29}Si and ^{30}Si concentration as a function of the wavenumber resulted with a CO_2 laser irradiation. The maximum concentration occurred at around 950–955 cm^{-1} for ^{30}Si and 960 cm^{-1} for ^{29}Si. The concentration of ^{29}Si was also detected at 800 cm^{-1} band. $^{98}MoF_6$ and $^{100}MoF_6$ were selectively decomposed and ^{92}Mo and ^{94}Mo were concentrated in the residual gas after the FEL irradiation at 728 cm^{-1} but the enrichment was small.

1. Introduction

Silicon is a main constituent of heat resisting ceramic materials such as SiC and Si_3N_4, and it is widely used as a semiconductor. However, natural silicon is composed of the three isotopes ^{28}Si(92.23%), ^{29}Si(4.67%) and ^{30}Si(3.1%). If Si is isotopically purified, several improved or new properties can be expected for silicon and its compounds. For example, ^{30}SiC or ^{29}SiC are expected to provide excellent low induced radioactivity under fusion neutron irradiation because of the suppression of formation of the long-lived isotope ^{26}Al.

We have successfully separated ^{28}Si and ^{30}Si using the selective decomposition of Si_2F_6 with a pulsed CO_2 laser [1]. However, emission lines of a CO_2 laser are limited to 1000 cm^{-1} wavenumbers where Si_2F_6 has an asymmetric stretching vibration. However, Si_2F_6 has symmetric stretching and bending modes at 800 and 400 cm^{-1}, respectively, where the CO_2 laser has no emission lines as shown in Fig. 1. Moreover, the emission band of a CO_2 laser itself is composed of four branches, and the lines of 956–966, 983–1033 and 1057–1069 cm^{-1} are absent. Among several lasers with emissions over a wide wavenumber region, the free electron laser (FEL) has no limitation in wavenumber and has a high power density equal to that of a CO_2 laser.

We reported the first observation of selective isotope decomposition of Si_2F_6 by the irradiation with an FEL laser at static conditions [2]. In the present study, the Si isotope selective decomposition of Si_2F_6 under a flowing system had been examined by considering the application of an FEL for practical isotope separation. Furthermore, irradiation of MoF_6 with the FEL was also explored for molybdenum isotope separation. ^{92}Mo and ^{94}Mo, two of the stable isotopes in molybdenum are not desirable from the viewpoint of induced activity because they produce long-lived radioactive nuclides such as ^{92}Nb and ^{94}Nb under the fusion neutron spectrum.

2. Experimental procedures

Free electron laser for infrared experiments (FELIX) of Fundamenteel Onderzoek der Materie (FOM)

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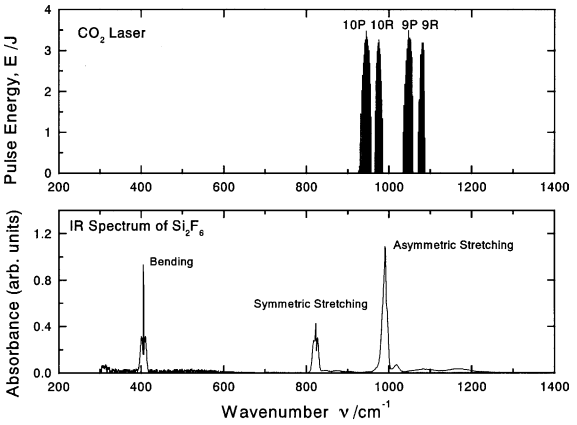

Fig. 1. Infrared spectrum and CO_2 pulse laser lines of Si_2F_6.

Institute Rijnhuizen of The Netherlands was used as a laser source. In Table 1, the beam characteristics of FELIX are described in comparison with a CO_2 pulse laser [3].

The wavenumber of the laser is in the range of 333–2000 cm^{-1}. The beam is composed of micropulses of 1 ps and macropulses of 4 μs with an energy for macropulses of 15–33.3 mJ at the front of the cell. The wavenumber resolution is about 1–2%, which is inferior to that for CO_2 lasers of 0.003%. However, the energy fluence is comparable to that for a CO_2 laser. The beam of 3 mm ∅ was focused at the end of the cell with a ZnSe lens of 254 mm in focal length and was irradiated with a repetition of 10 Hz. The reaction cell was a Pyrex glass tube of 10 mm in inner diameter and 100 mm in length. Since the beam is focused and the shape is conical, all gas inside the cell has not necessarily reacted during irradiation. The reaction volume was measured by changing the focus position through the cell containing the static gas and was estimated to be 0.0152 cm^3 which is only 0.2% of the total volume of the cell. This reaction volume was used for correcting the concentration of each isotope since the Si_2F_6 source contained 0.06% SiF_4 as an impurity, and the background subtraction is required.

Table 1
Characteristics of the FELIX laser beam and a CO_2 pulse laser

	FELIX	CO_2 laser
Spectral width ($\delta\lambda/\lambda$)	1–2%	0.003%
Wavenumber	2000–333 cm^{-1}	1092–907 cm^{-1}
Micropulse duration	1 ps	
Intervals	1 ns	
Energy	60–133 μJ	
Macropulse duration	4 μs	104 ns
Intervals	200 ms	
Energy	15–33.3 mJ	0.5–3.12 J
Repetition rate	5–10 Hz	1–10 Hz
Beam size	3 mm ∅	30 × 30 mm
Fluence	2.1–4.7 kJ/m^2	0.83–5.2 kJ/m^2

The Si_2F_6 gas with a purity of 99.94% was supplied at 8.3 mm^3/s and 10–13.3 Pa. The SiF_4 produced by the laser irradiation for 600 ks according to the equation

$$Si_2F_6(gas) + nh\nu \rightarrow SiF_4(gas) + SiF_2(solid) \quad (1)$$

was collected by vacuum distillation and the isotopic ratio of ^{28}Si, ^{29}Si and ^{30}Si in the SiF_4 was measured by a mass spectrometer.

The amount of SiF_4 produced in the flowing system was estimated by IR measurements of the peak intensities of the SiF_4 and Si_2F_6 spectra from the irradiated gas. In the present study, the irradiation experiments were conducted at 1000 and 800 cm^{-1} wavenumbers.

In the case of MoF_6, the irradiation was at 600–780 cm^{-1}, 8.3 mm^3/s and 13.3 Pa. The focus position of the beam was set at the center of the cell. The gas was decomposed as

$$MoF_6 + nh\nu \rightarrow MoF_4 + F_2 \quad \text{or} \quad Mo + 3F_2 \quad (2)$$

The isotope ratios in the residual gas of MoF_6 after irradiation were measured.

3. Results and discussions

3.1. Si isotope separation

Silicon isotope concentrations produced in SiF_4 were measured and corrected by subtracting the background value of SiF_4 contained in the Si_2F_6 source as discussed above. Then the enrichment factor, β_i, is defined as:

$$\beta_i = [^iSiF_4]_{irrad}/[^iSiF_4]_{natural}, \quad (3)$$

where $[^iSiF_4]_{irrad}$ is the concentration of isotope i after irradiation and $[^iSiF_4]_{natural}$ is the natural abundance of isotope i in SiF_4.

The enrichment factor β for each silicon isotope after irradiation at various wavenumbers in the 1000 cm^{-1} band is shown in Fig. 2. The results using a CO_2 laser [1] are also plotted for comparison in this figure. ^{30}Si was enriched with a maximum at about 960 cm^{-1}, a wavenumber that cannot be emitted by a standard CO_2 laser. The data shown in this figure are in good agreement with the previous results of the IR measurements [2,4]. In the case of ^{30}Si concentration, the β value of the CO_2 laser irradiation is higher than that of FEL. As seen in Table 1, the spectral width of FEL is much wider and the macropulse is longer than those of the CO_2 laser. For these reasons, it is concluded that FEL irradiation is not as selective as the CO_2 laser, and as a result, a low β

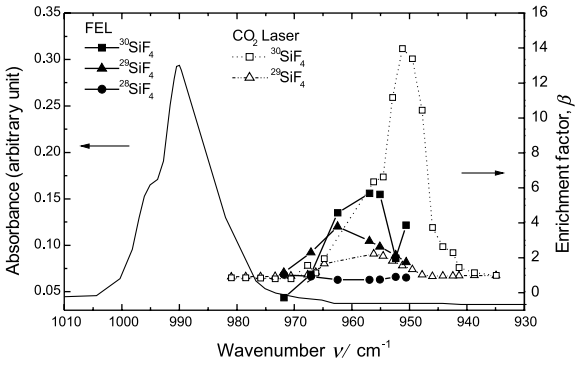

Fig. 2. Enrichment factor β of silicon isotopes in comparison with that by a CO_2 laser [1] and IR spectrum of Si_2F_6 in the 1000 cm^{-1} band.

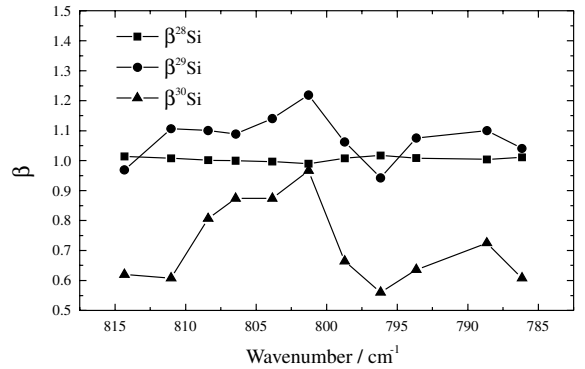

Fig. 3. Enrichment factor β of silicon isotopes irradiated in the 800 cm^{-1} region.

value was observed for the FEL irradiation. The wavenumber with a maximum selectivity for FEL does not coincide with that of the CO_2 laser. The low value is probably also due to the wide spectral width of FEL. For ^{29}Si, we could first observe an increase in concentration at around 960 cm^{-1} which was expected from the CO_2 laser irradiation experiment. Fig. 3 shows the results for the 800 cm^{-1} region. A small enrichment of ^{29}Si is observed at around 810–800 cm^{-1}. For ^{30}Si and ^{28}Si, no apparent enrichment in the SiF_4 product was detected because the β values equal 1 or are below 1.

Since the reaction volume was so small in the present experiment, the SiF_4 included as an impurity in the Si_2F_6 source affected the measurement of isotope concentrations and gave some error for the small change of concentration as seen in Figs. 2 and 3. It is necessary to increase the power and widen the beam size of the FEL to make the reaction volume larger in order to reduce the effect of the SiF_4 background.

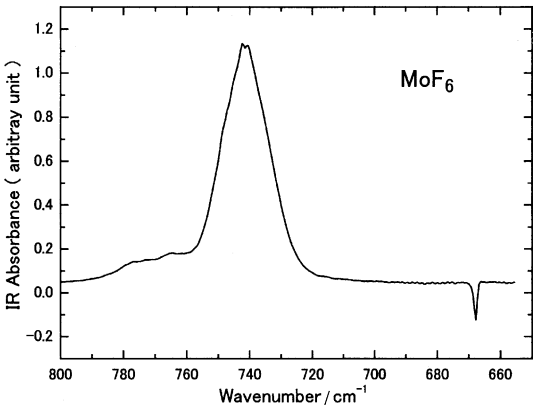

Fig. 4. IR spectrum of MoF_6.

3.2. Mo isotope separation

Fig. 4 shows the IR spectrum of MoF_6. A strong absorption peak at around 742 cm^{-1} of the $\nu 3$ band [5] is observed. The mass spectrum for each isotopic MoF_5^+ ion was measured after irradiation. Although the data were rather scattered, there was a tendency for a decreased in concentration of heavy ions at smaller wavenumbers than 727 cm^{-1}. The enrichment factor at 727 cm^{-1} plotted against molybdenum isotope mass is shown in Fig. 5. The lighter isotopes are concentrated in the residual MoF_6. This result is in good agreement with the previous result using a H_2 Raman laser at 728 cm^{-1} [6] as indicated in this figure. The enrichment of light molybdenum isotopes was also reported for the $\nu 3$ and $\nu 5$ bands at 1050 cm^{-1}, which is the first experiment of molybdenum isotope separation [7]. For the irradiation at lower wavenumbers, heavier isotopes are expected to

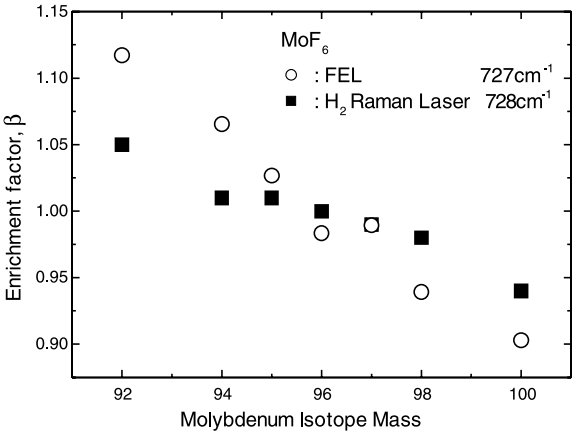

Fig. 5. Enrichment factor β of molybdenum isotopes after FEL irradiation at 727 cm^{-1} in comparison with β by a H_2 Raman laser at 728 cm^{-1} [6].

concentrate in MoF_6. However, it was not clearly observable in the present study probably because of the broad spectrum of FEL as seen in Table 1. The light stable isotopes of molybdenum such as ^{92}Mo and ^{94}Mo are not preferable from the viewpoint of induced activity since these isotopes are transmuted to long-lived radioactive nuclides such as ^{92}Nb and ^{94}Nb in a fusion neutron spectrum. It is necessary to narrow the spectrum width of FEL, for example, by using gratings and to search a better irradiation condition in order to concentrate heavier molybdenum isotopes in MoF_6.

4. Conclusion

From the experimental results on the enrichments of Si_2F_6 and MoF_6 by TEL irradiation under flowing conditions, the following conclusions are drawn:

(1) Successive isotope separation of ^{29}Si and ^{30}Si was successful at the 1000 cm^{-1} band.
(2) The enrichment factor of ^{29}Si was maximized at around 960 cm^{-1}.
(3) Isotope enrichment of ^{29}Si using the 800 cm^{-1} bands was also observed.
(4) The lower enrichment of ^{30}Si using FEL that was observed compared to the CO_2 laser operating in the 1000 cm^{-1} band was expected to be mainly due to its broader spectrum width.
(5) ^{92}Mo and ^{94}Mo could be concentrated in MoF_6 by the FEL irradiation at 727 cm^{-1} but the enrichment was small. In order to concentrate the molybdenum isotopes in MoF_6, it is necessary to narrow the spectrum width of FEL and to search further a better irradiation condition.

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References

[1] H. Suzuli, H. Araki, T. Noda, J. Jpn. Inst. Metals 61 (1997) 145.
[2] J.L. Lyman, B. Newnam, T. Noda, H. Suzuki, J. Phys. Chem. A 103 (1999) 4227.
[3] H. Suzuki et al., 12th Symp. MRS Jpn. K1-011 (2000) 198.
[4] M.E. Jacox, K.K. Irikura, W.E. Thompson, J. Chem. Phys. 103 (1995) 5308.
[5] R.S. McDowell, R.J. Sherman, L.B. Asprey, R.C. Kennedy, J. Chem. Phys. 62 (1975) 3974.
[6] T. Oyama, S. Satooka, S. Kato, K. Midorikawa, H. Tashiro, K. Takeuchi, Laser Chem. 8 (1988) 235.
[7] S.M. Freund, J.L. Lyman, Chem. Phys. Lett. 55 (1978) 435.