Shape effects of forsterite particles on infrared spectra

Osaka University, *Ritsumeikan University, **Subaru Telescope, NAOJ
Many sharp peaks were detected

↓

Compare with laboratory data (absorption of particles, reflectance)

↓

Identified as minerals forsterite, enstatite, diopside, melilite, calcite, """

ISO observation
In circumstellar

NGC 6302

Waters et al.
(1998, Nature 391)

Molster et al. 2001
Infrared Absorption of dust (fine particles) depend on

- size
- composition (olivine, pyroxene, ...)
- shape (Fo)
- coagulation (aggregate)
- temperature (cooling at RT, 200K, 100K, 50K, 20K, 8K)
- crystallinity (degree of crystallinity)
- medium (KBr, PE)

We investigate about forsterite particles on the shape and coagulation
(Koike et al. 2010, Koike et al. in preparation)

forsterite: Mg$_2$SiO$_4$
Sample Preparation for Forsterite $\text{Mg}_2\text{SiO}_4$ particles

$\text{Mg(OH)}_2 + \text{SiO}_2$  
(Mg / Si = 2 / 1)

\[\text{evaporation & condensation}\]

spherical amorphous particles

\[\text{annealing and crystallization}\]

spherical, and irregular forsterite particles

commercial products

in plasma method

@ Nisshin Engineering Inc.
Infrared spectra of annealed forsterite particles

Starting products

original amorphous of Nissin products (by XRD)
- NiA average size 11 nm: coagulated
- NiB average size 80 nm: isolated

↓ annealing at various temperature

shape depend on annealed temperature
- NiA spherical and coagulated → irregular shape
- NiB spherical → irregular shape

how to change infrared spectra

(KBr & PE) (in wide wavelength region)
- $11 \mu m$, $33 \mu m$ band
- $69 \mu m$ band

NiA (Nissin A)

NiB (Nissin B)
### Condition for annealing of amorphous products (NiA & NiB)

**Low temperature**
- ≤ 1200 °C

<table>
<thead>
<tr>
<th>NiA</th>
<th>550°C</th>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
<th>800°C</th>
<th>1000°C</th>
<th>1100°C</th>
<th>1150°C</th>
<th>1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3h</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>24h</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
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<tr>
<td>48h</td>
<td>○</td>
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</tr>
</tbody>
</table>

**NiB**

<table>
<thead>
<tr>
<th>600°C</th>
<th>650°C</th>
<th>700°C</th>
<th>800°C</th>
<th>1100°C</th>
<th>1130°C</th>
<th>1150°C</th>
<th>1200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6h</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24h</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

**High temperature**
- ≥ 1200 °C

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Annealing time</th>
<th>protoenstatite (by XRD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200 °C</td>
<td>3 h</td>
<td></td>
</tr>
<tr>
<td>1300 °C</td>
<td>3, 16, 18, 60, 96</td>
<td>16 – 96 h</td>
</tr>
<tr>
<td>1400 °C</td>
<td>3 h</td>
<td></td>
</tr>
<tr>
<td>1500 °C</td>
<td>2, 3, 4, 10, 14.3, 45.5</td>
<td>2 – 45.5 h</td>
</tr>
<tr>
<td>1600 °C</td>
<td>3 h</td>
<td></td>
</tr>
</tbody>
</table>

| NiB | 1500 °C | 3 h | 2, 3, 4, 10, 14.3, 45.5 | 2 – 45.5 h |
| 1600 °C | 3 h | 2, 3, 4, 10, 14.3, 45.5 | 2 – 45.5 h |

Red: IR measured
NiB_original

NiB_800C1d

NiB_1100C3h

NiB_1200C1d

NiB_SEM

Spherical & isolate ↓ Irregular ↓ Plate-like including

Single crystal
NiA_TEM

Spherical & Coagulation
↓
Irregular
↓
Plate-like including

NiA_800C1d

NiA_1200C3h

NiA_AS

NiA_1150C1d

NiA_1600C3h

NiA_1000C1d

NiA_1200C3h

Single crystal
All spectra of two Ni products
For annealed samples
Annealing at 600 °C
Some broad peaks appear at each band and depend on original products

Annealing at 700 °C
All spectra show sharp peaks
Spectra are depend on original products
Annealing temperature $\geq 1200$ °C

All spectra became similar to that of Fo fine (Koike et al. 2006). Fo fine

Fo fine

(ground from bulk Fo synthesized by Czochralski method)
(irregular shape)
Both of products have similar spectra for annealing at above 1200 °C as that of Fo fine.
The diagram shows the absorption coefficient (k) in cm²/g as a function of wavelength (μm) for two different sets of samples: NiA and NiB.

For NiA, the temperature and time conditions are as follows:
- Original
- NiA800°C1d
- NiA1600°C3h

For NiB, the temperature and time conditions are as follows:
- Original
- NiB800°C1d
- NiB1200°C1d

Key observations:
- There is a strong absorption peak at 11 μm band for NiA800°C1d.
- The absorption coefficient decreases with increasing temperature and time for both NiA and NiB.
- The absorption coefficient for NiB1200°C1d is weak compared to other conditions.

Note: The images of NiA and NiB at 800°C1d and 1200°C1d temperatures provide visual representations of the material's morphology.
labo data

9.95 \( \mu \) m and 11 \( \mu \) m

peak intensity

strong \( \rightarrow \) weak

spherical &

coagulate

↓

irregular (\( \geq 1200 \) C)

Calculation (in KBr)

spherical

9.95 \( \mu \) m

sharp peak

11 \( \mu \) m peak

double peak

irregular

broad,

peak position shift

CDE1: Continuous Distributions of Ellipsoids  (CDE2: near-spherical particle shapes)
NiA compare to NiB
9.95 \( \mu m \) & 11 \( \mu m \)
broad due to coagulation

NiA & NiB for high annealing temperature
peak position shifts to long wavelength
due to irregular shape
$33 \, \mu \text{m band}$

Annealing at $650 \, \text{C} - 800 \, \text{C}$ increase

Annealing at $650 \, \text{C} - 1200 \, \text{C}$ increase

NiB

$\kappa$ (cm$^2$/g)

wavelength (μm)

- 600C1day
- 650C1day
- 700C1day
- 800C1day
- 1150C1day
- 1200C1day
- Fo fine
spherical & coagulation

NiB800°C1d

NiB1200°C1d

CDE (irregular shape)
16 – 28 μm region

The graph shows the absorption coefficient (κ) as a function of wavelength (μm) for various samples. The samples include NiB800C1d, NiB1200C1d, NiB1600C3h, and a calculation. The graph includes peaks at different wavelengths, indicating absorption properties at specific wavelengths. The image at the bottom right shows a spherical and coagulation structure with a scale of 10μm.
How to change intensity, peak position, and FWHM of 69 um band
These may be depend on shape of particles?
Calculation (in PE)

Peak intensity
- sphere: strong
- CDE1, CDE2: weak

Annealing
- sphere: irregular
- CDE2: weak
- CDE1: strong
- 5:1:5: weak
- 100:1:100: strong

Calculation
- sphere
- CDE2
- CDE1
- 5:1:5
- 100:1:100
Difference of Peak intensity due to shape effects & coagulation (irregular & only small part of plate-like)

Difference of peak position among labo data and calculation may be due to refractive index of PE?
LDPE $n = 1.46$ (here assume 1.50), HDPE $n = ?$
Peak intensity of 69 um band

peak intensity

annealing temperature 650 °C → 1200 °C → 1600 °C

crystal growth & shape effects

strong

weak

Peak positions are nearly same
$69 \text{ \( \mu \) m band at each cooling temperature}$

![Graph showing the 69 \( \mu \) m band at each cooling temperature with various labels and curves representing different samples.

- NiB1200C1d
- NiA1500C3h
- NiA1600C3h
- NiB1600C3h

Wavelength (\( \mu \)m) and Thermal Conductivity (\( \kappa \) (cm\(^2\)/g))
All peak positions shift shorter than that of Fo fine lower 200 K

Samples of annealing at 1500C and 1600C
Peak positions shift to a little shorter wavelength than spherical
this may be due to increase plate-like shape?  It is not clear.
Peak position
plate like : shift to shorter wavelength than spherical
Cooling temperature ↓ : FWHM (Full Width of Half Maximum) ↓
At low temperature : high annealing temperature samples
FWHM became a little sharp
: may be due to similar size ?
Marusu Fo: band is very sharp due to similar size ?
Cooling temperature became low
Peak position & FWHM: correlation
The tendency is same as for annealed sample and Fo fine except for marusu
Summary

Annealing temperature

- Below 1200 °C for both products
  - spectra depend on shape (spherical & coagulation)
    - 11 μm, 19 μm, 23 μm, 33 μ, 69 μm band
      - for spherical ---- each peak became sharp and strong

- above 1200 °C for both products (irregular)
  - all spectra became similar to that of Fo fine

69 μm band for cooling
- peak strength
  - depend on shape (annealing temperature) & coagulation