IR Spectra of Enstatite with Lattice Defects

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Overview of crystallization experiments

1. $\text{Mg}_{1.1}\text{Fe}_{0.9}\text{SiO}_4$
   - Formulation of crystallization process
   - Crystallization dependency on nucleation process

2. $\text{Mg}_{1.1}\text{Fe}_{0.4}\text{SiO}_{3.5}$
   - Fractionation of Mg/Fe between crystal & amorphous phases

3. $\text{Mg}_{1.1}\text{SiO}_{3.1}$
   - Activation energy (→ Tsuchiyama’s talk)
   - Implication to observations
$1 \text{ Mg}_{1.1}\text{Fe}_{0.9}\text{SiO}_4$ (Murata et al. 2007)

Formulation of Crystallization

$C_{IR}$ : Degree of crystallization

$$\kappa_{im} = (1 - C_{IR}) \kappa_{as} + C_{IR} \kappa_{xt}$$

Fig. 7—IR spectra of the samples heated at a constant temperature (680°C) for different durations.
1 $\text{Mg}_{1.1}\text{Fe}_{0.9}\text{SiO}_4$ (Murata et al. 2007)

Time evolution of crystallization

JMA (Johnson-Mehl-Avrami) eq.

$$C_{IR} = C_\infty \{1 - \exp[-(t / \tau)^n]\}$$

n = 1.5: constant number of nuclei
n = 2.5: constant nucleation rate
Mg$_{1.1}$Fe$_{0.4}$SiO$_{3.5}$ (Murata et al. 2009a)

Fractionation of Mg/Fe between crystal & amorphous phases
3 $\text{Mg}_{1.1}\text{SiO}_{3.1}$ (Murata et al. 2009b)

![Graph showing the relationship between $T$ (K) and $T^{-1}$ (K⁻¹) on a logarithmic scale, with data points and a line of best fit. The equation is $\tau = t_0 \exp \left( \frac{E_a}{k_B T} \right)$, with $E_a/k_B = 1.12 \times 10^5$ K (900 kJ/mol) and $t_0 = 10^{-40}$ s.]
3 $\text{Mg}_{1.1}\text{SiO}_{3.1}$ (Murata et al. 2009c)  
Chondritic Enstatite with lattice defects

Sample preparation

Amorphous silicate ($\text{Mg}/\text{Si} = 1.07$) with Si-alkoxide (TEOS) by Sol-Gel method

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
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</thead>
<tbody>
<tr>
<td>Hydrolysis</td>
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<tr>
<td>$n\text{Si(OR)}_4 + 4n\text{H}_2\text{O} \rightarrow n\text{Si(OH)}_4 + 4n\text{ROH}$</td>
</tr>
<tr>
<td>Poly-condensation</td>
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<tr>
<td>$n\text{Si(OH)}_4 \rightarrow n\text{SiO}_2 + 2n\text{H}_2\text{O}$</td>
</tr>
</tbody>
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Heating at 790°C $\rightarrow$ Crystallized Enstatite
Advantages of Sol-Gel method

Very promising method to produce functional glass materials in industrial fields!

- Homogeneity within the molecular scale
- Required temperature is low
- Molding is possible
- Extremely porous $\rightarrow$ chemically active
Time evolution of crystallization

![Graph showing time evolution of crystallization at 790°C](chart)

- **790°C**

- **clinoenstatite** (Chihara et al. 2002)

- **Time evolution of crystallization**
  - 1 h
  - 3 h
  - 4 h
  - 6 h
  - 18 h

**Graph Details**
- X-axis: Wavelength (μm)
- Y-axis: \( \kappa + \text{offsets (cm}^2/\text{g}) \)

**Key Points**
- The graph illustrates the changes in \( \kappa + \text{offsets} \) over time at 790°C.
- Clinoenstatite is identified as a significant crystallization phase.
- The chart likely pertains to spectral analysis or infrared spectroscopy, indicating the presence of specific minerals or phases that are formed during heat treatment.
Spectra at room temperature & comparison with single crystals

790°C 72 hours
Spectra at lower temperature

\[
\kappa \text{ (cm}^2/\text{g)}
\]

\[
\text{wavelength (\mu m)}
\]

- 9 K
- 50 K
- 100 K
- 150 K
- 200 K
- RT

Inset graph showing spectral data at various temperatures.
Summary of spectral features

- Far-IR features are different from both of ortho- and clino- enstatite.
- Some peak strengths are weaker than those of single crystals (19, 26 micron).
- At lower temperature prominent feature appear at 48 micron.
- Broad 69um feature.
A. Crystallized enstatite from sol-gel material

B. Clinoenstatite single crystal

Stacking faults along to (100) direction
Implication to observations

Fig. 10. A fit (dotted line) to the continuum and amorphous silicate subtracted spectrum (solid line) of HD 45677. $T_1 = 140$ K and $T_0 = 140$ K.

Fig. 13. A fit (dotted line) to the continuum subtracted spectrum (solid line) of HD 44179. $T_1 = 135$ K and $T_0 = 135$ K. Below 15 µm the spectrum is dominated by PAH features.

F.J. Molster et al. 2002
Ferrarotti et al. (2000) proposed that FeSi may be possible carrier of the unidentified the 48 μm feature under a peculiar abundance condition.

Fig. 1. Stability limits of condensates of some of the most abundant elements for varying C/O abundance ratio. The pressure is fixed at $P = 10^{-4}$ dyn cm$^{-2}$.

Fig. 4. Upper Part: Spectrum of AFGL 4106 (taken from Molster et al. 1999) in the far infrared wavelength region $28 \lesssim \lambda \lesssim 54$ μm. The strong bands are due to forsterite and enstatite. Lower part: Absorption efficiency $Q_\lambda$ of FeSi grains with 0.1 μm radius at $T_{\text{dust}} = 120$ K. A broad distribution of grain radii would broaden the absorption bands.
Figure 4. Comparison of the continuum-subtracted spectrum of HD 44179 with the model (1) (SCE + forsterite, thin line) and (2) (HAS + forsterite, thick line) multiplied by the Planck function of 150 K and normalized to 1.

Figure 5. Comparison of the continuum-subtracted spectrum of MWC 922 with the model (1) (SCE + forsterite, thin line) and (2) (HAS + forsterite, thick line) multiplied by the Planck function of 150 K and normalized to 1.
Traces of similar features in previous studies

Enstatite crystallized from glass

Fabian et al., 2000
IR spectrum of the sample shows different features from those of single crystals (in particular at 19, 26, 48 & 69 um).

Lattice defects (stacking faults) is thought to be the cause of the spectral discrepancies.

Existence of enstatite with lattice defects is suggested in circumstellar environment.