Spectral diversity of enstatite polymorphs

A relevance with Heated Amorphous Silicate

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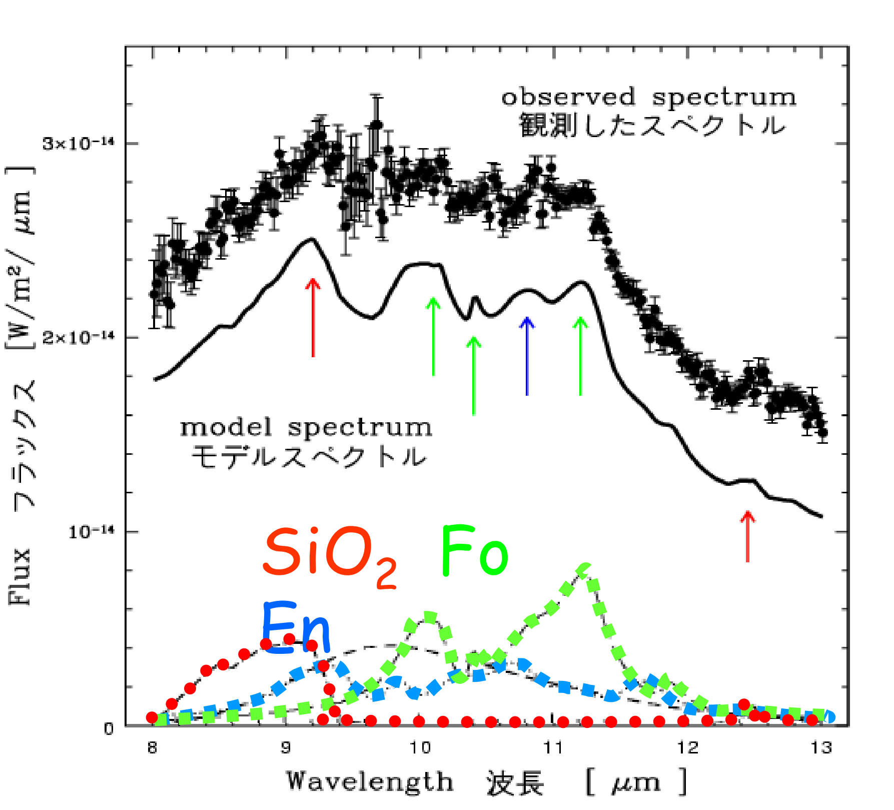
Crystalline silicates in cosmic dust

- Together with olivine, pyroxene is one of the most important mineral species in the context of astronomy.
- Many spectroscopic research in laboratory were carried out
- Particularly, existence of highly Mg-rich members of these minerals are confirmed by combination of observational and laboratory studies.

Example of identification of pyroxene



Subaru / COMICS N-band
Honda et al. 2003, ApJ 585 L59

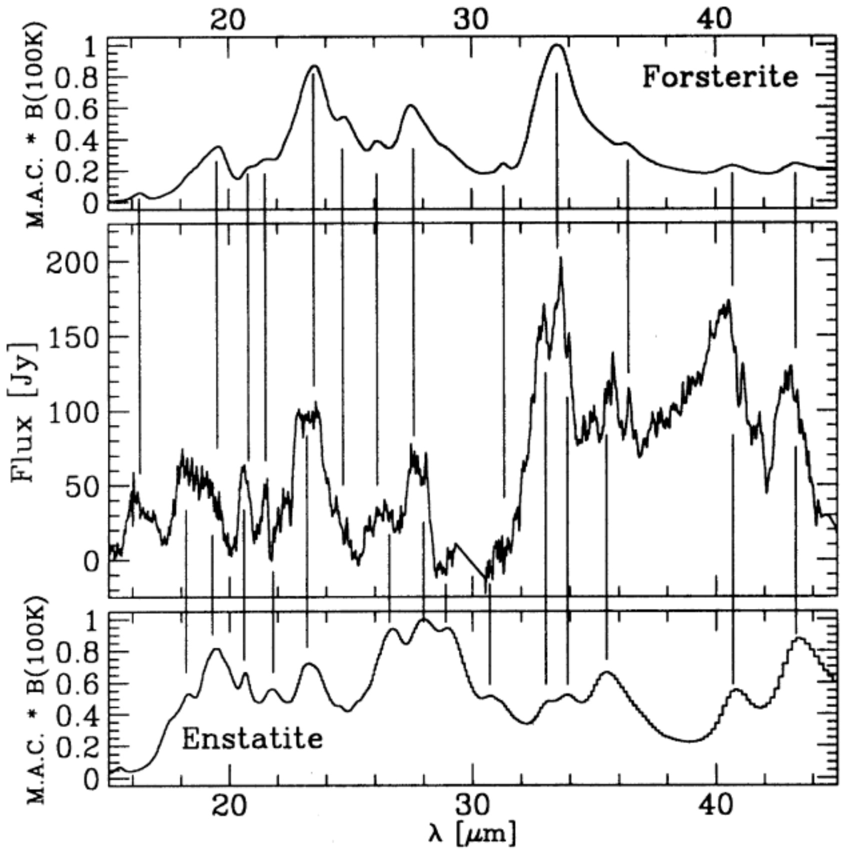


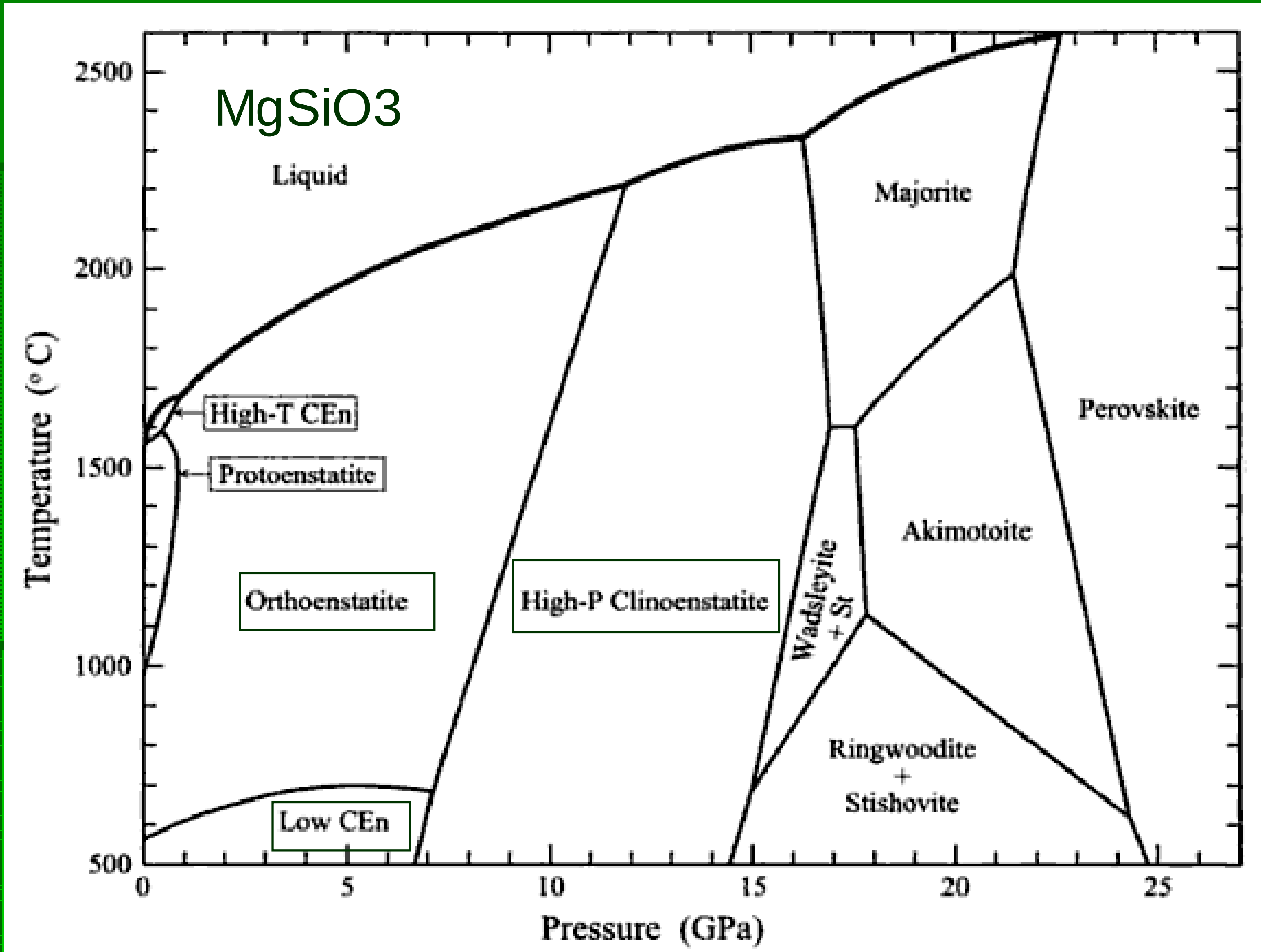
Fig. 8. Comparison of the continuum subtracted spectrum of AFGL 4106 with the MAC of forsterite and clinoenstatite multiplied by a Planck curve of 100 K and normalized to one.

ISO / SWS
Jäger et al. 1998 A&A 339 904

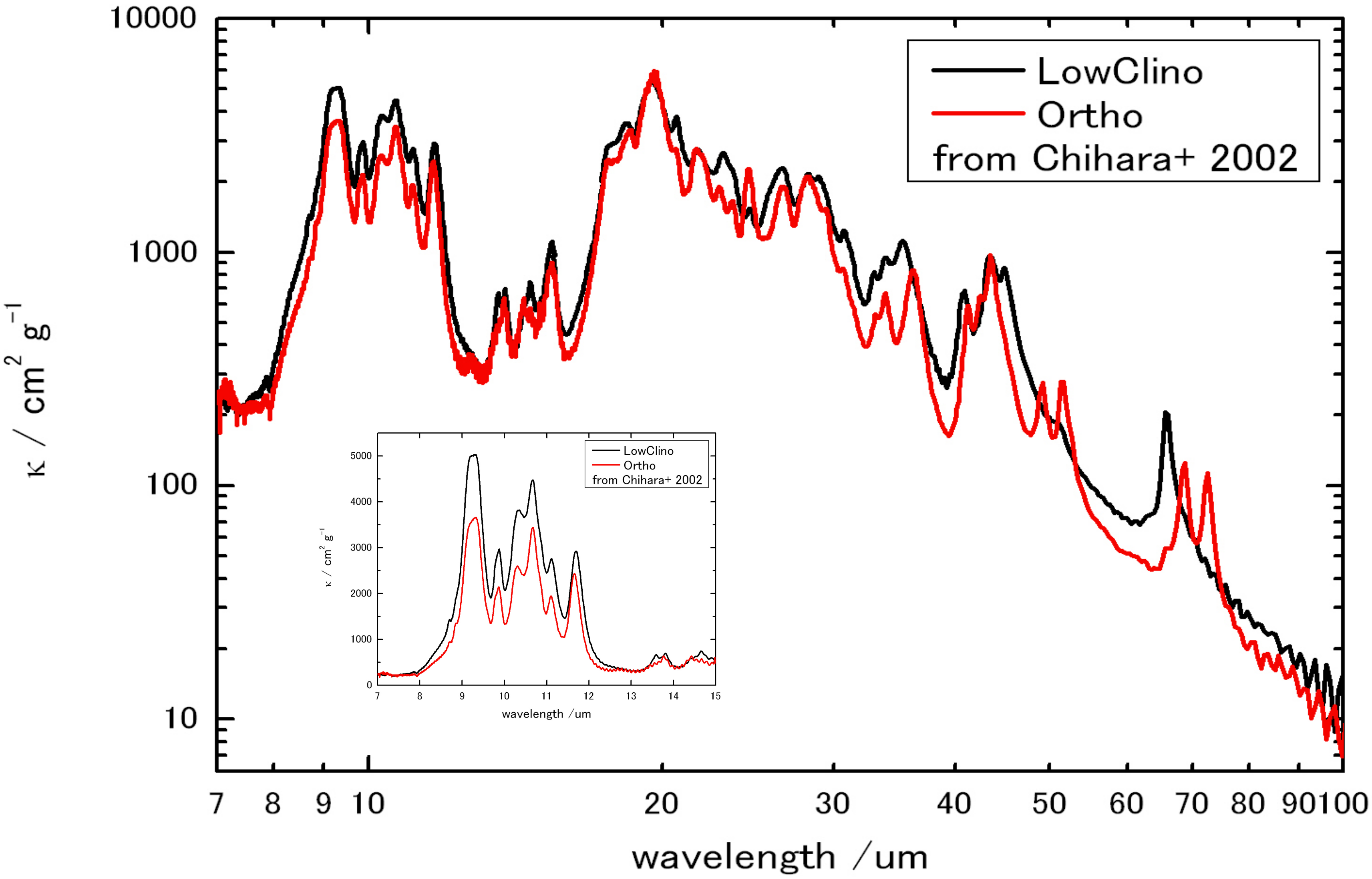
Polymorphs of enstatite

- Protoenstatite (Pen) *Pbcn* > ~1275 K
  orthorhombic, unquenchable at RT
- Orthoenstatite (Oen) *Pbca*
  orthorhombic, most common, occur in slow cooling
- Clinoenstatite (Cen) monoclinic
  - High-Temp. clinoenstatite *2c/c* > ~1450 K
    unquenchable at RT
  - High-Pressure clinoenstatite *2c/c* > ~6GPa
  - Low-clinoenstatite $P2_1/c$
    most common, occur in rapid cooling

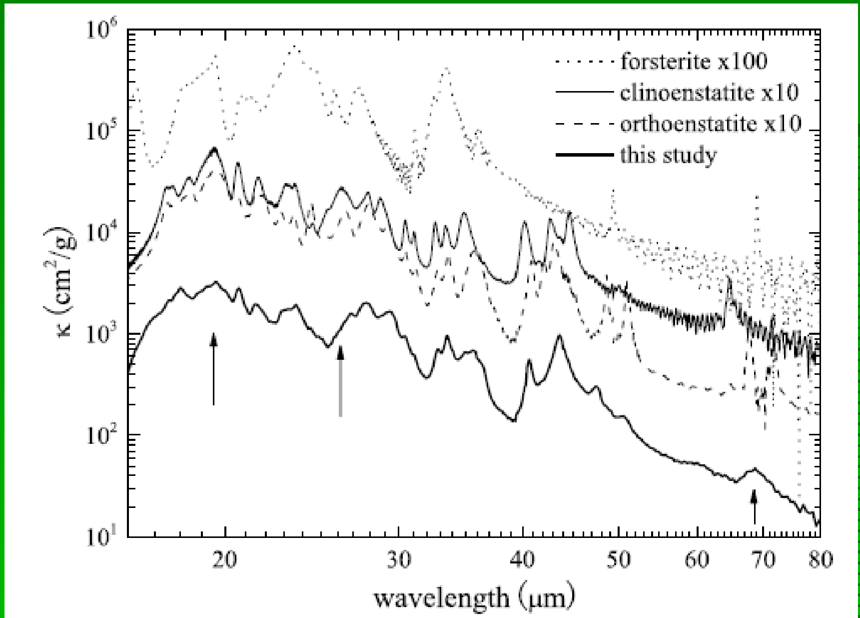
Phase diagrams

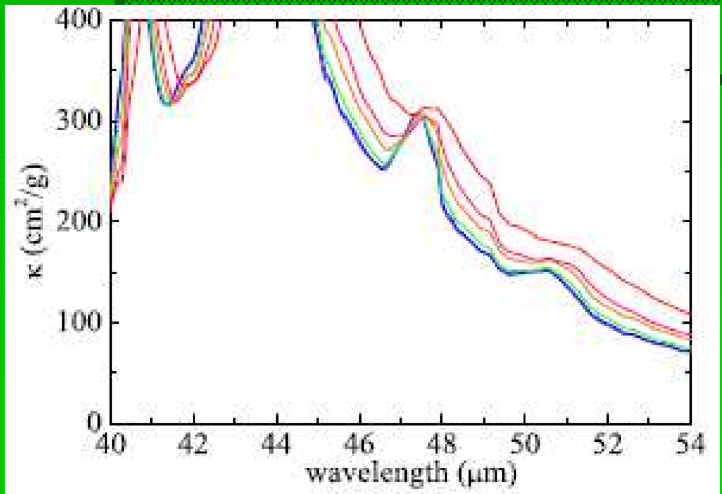


Difference between Oen & Cen



Heated Amorphous Silicate (HAS)
Murata et al. 2009 ApJ 698 1903





- Synthesized by Sol-Gel method and crystallized by heating at 790 °C for several days.
- FIR feature resembles neither orthoenstatite nor clinoenstatite
- Peak intensities at 19 & 26 um are weaker than ortho- & clino-enstatite
- Broad feature at around 70 um
- At cryogenic temperature, small but prominent feature appear at 48 um

HAS can fit observation better

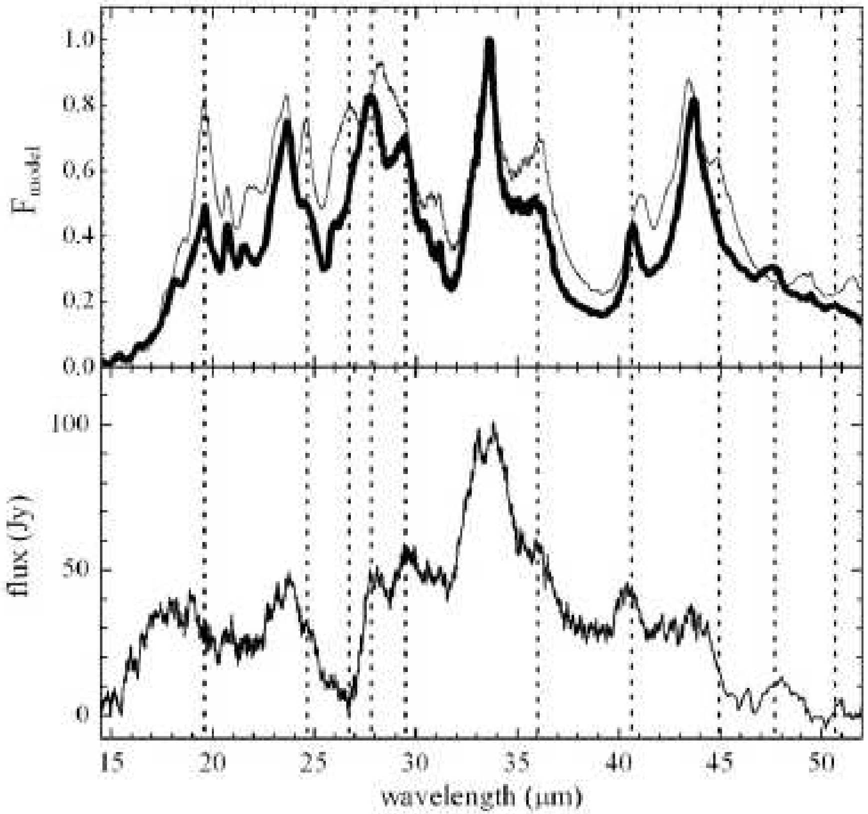


Figure 4. Comparison of the continuum-subtracted spectrum of HD 44179 with the model (1) (SCE + forsterite, thin line) and (2) (HAS + forsterite, thick line) multiplied by the Planck function of 150 K and normalized to 1.

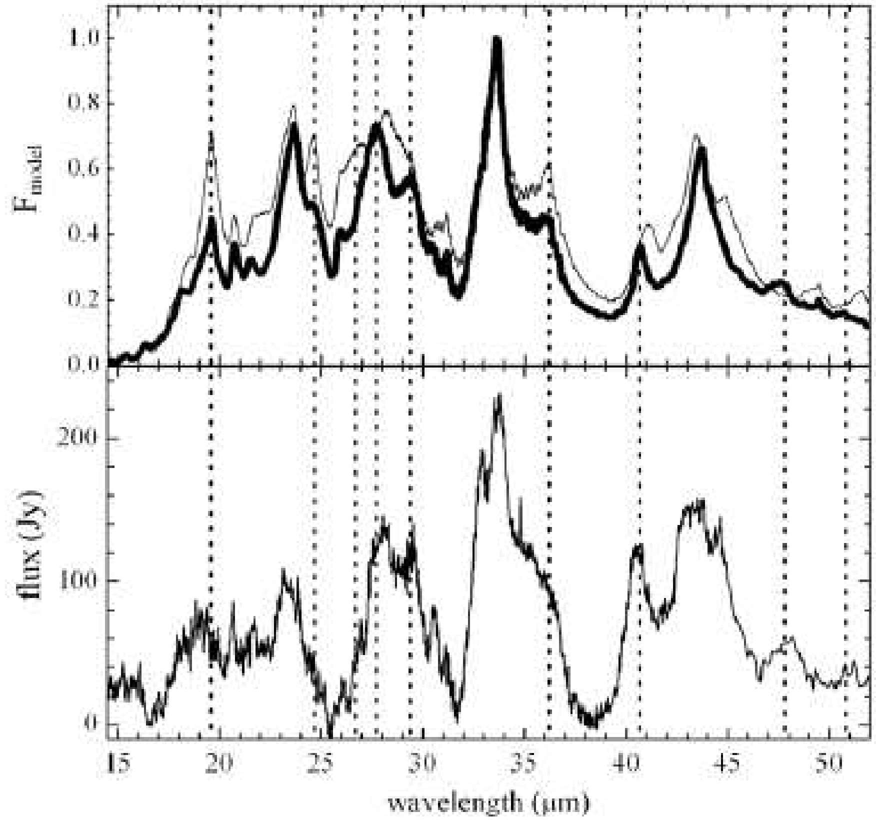
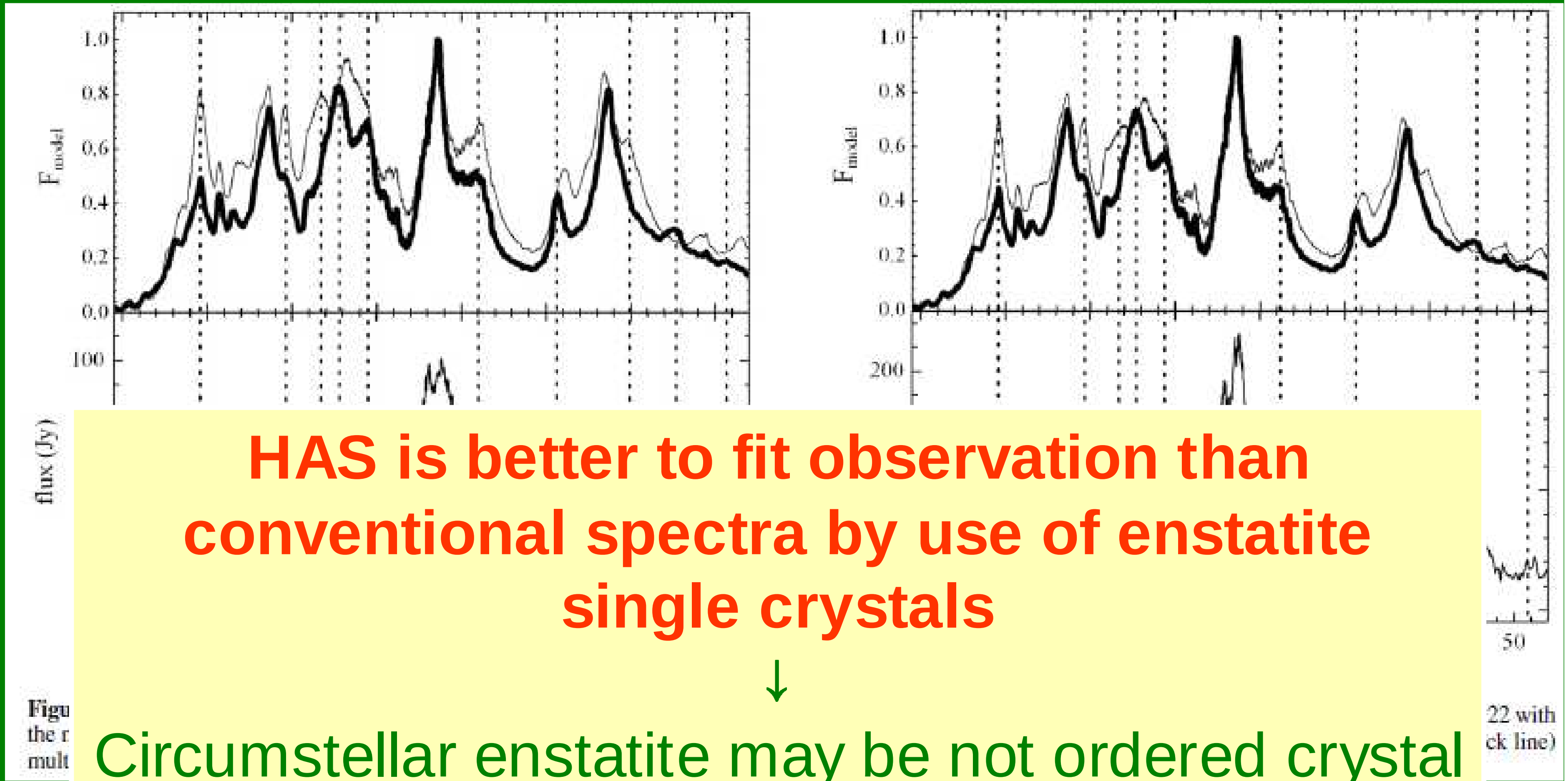


Figure 5. Comparison of the continuum-subtracted spectrum of MWC 922 with the model (1) (SCE + forsterite, thin line) and (2) (HAS + forsterite, thick line) multiplied by the Planck function of 150 K and normalized to 1.

Murata et al. 2009

HAS can fit observation better



HAS is better to fit observation than conventional spectra by use of enstatite single crystals

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Circumstellar enstatite may be not ordered crystal

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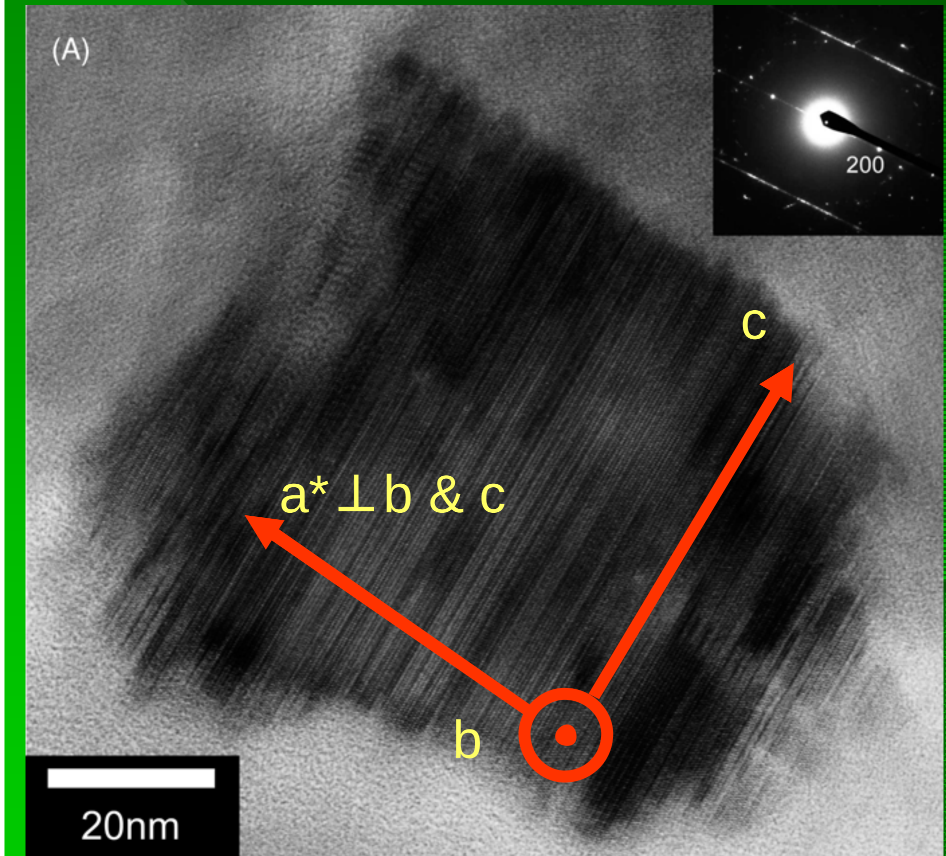
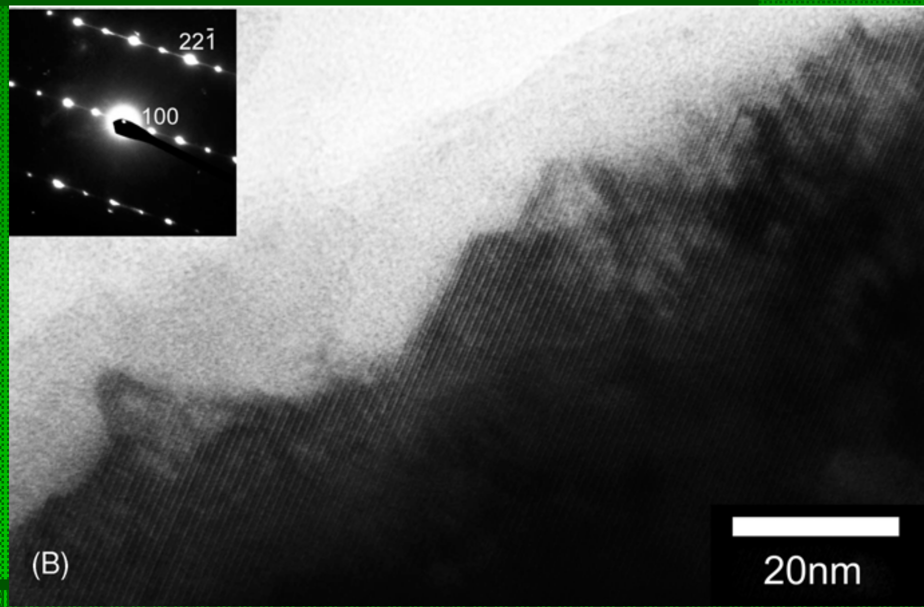
Its may affect estimation of amount of enstatite

High density stacking faults in HAS



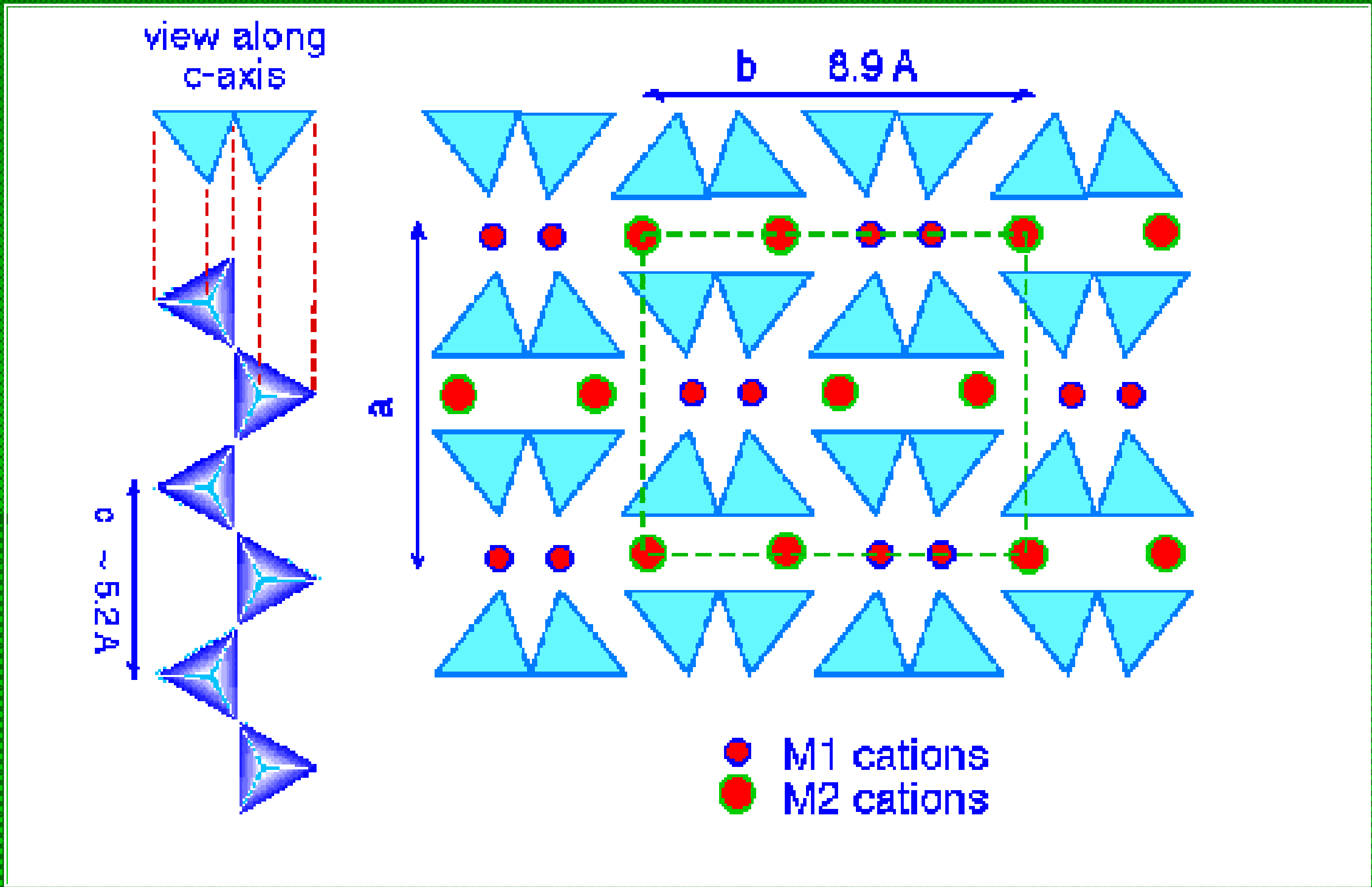
Murata et al. 2009



Transmission electron microscope images and selected area electron diffraction patterns of (A) enstatite in the sample in this study and (B) fine powdered single crystal of clinoenstatite viewed parallel to *a-axis.**

Basic structure of pyroxene

SiO_4 tetrahedra form liner single chains with two bridging oxygen atoms per tetrahedron



Stacking sequence along to a*-axis

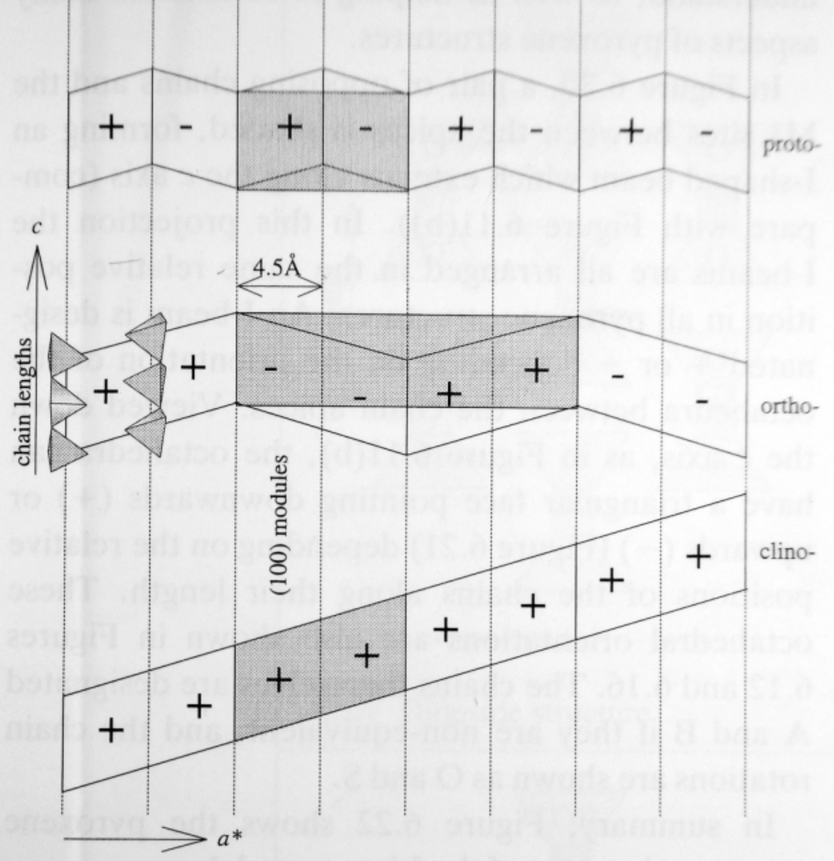


Figure 6.18. The relationship between the structures of proto-, ortho-, and clino-pyroxenes in terms of the stacking of layers of chains which form modules of the structure parallel to (100) planes. The modules are 4.5Å thick. There are two possible positions for each module, corresponding to relative displacements of adjacent chains along their length. These positions are labelled + and −. The unit cell for each structure is shaded. (After Buseck *et al.*, 1982.)

→VICS-II

Inversion mechanism

- proto-clino inversion
  - martensitic transition

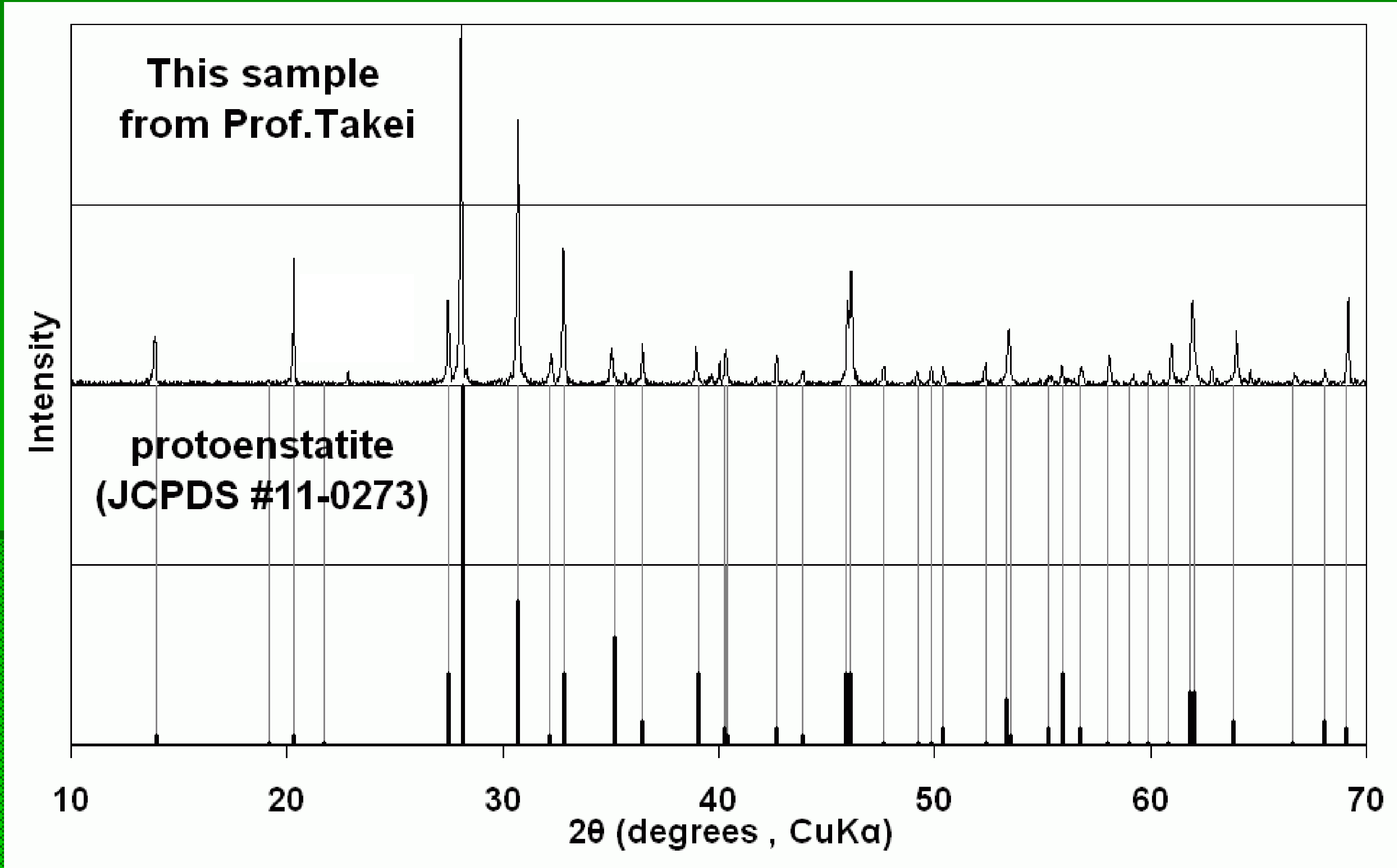
    instantaneous (rapid cooling) , diffusionless, stress inducible and reversible
- proto-ortho inversion
  - order-disorder transition

    sluggish time scale (slow cooling)
- clino-ortho inversion
  - prolonged annealing between 900-1200K produces OE via CE-OE inversion(Smyth 1974)

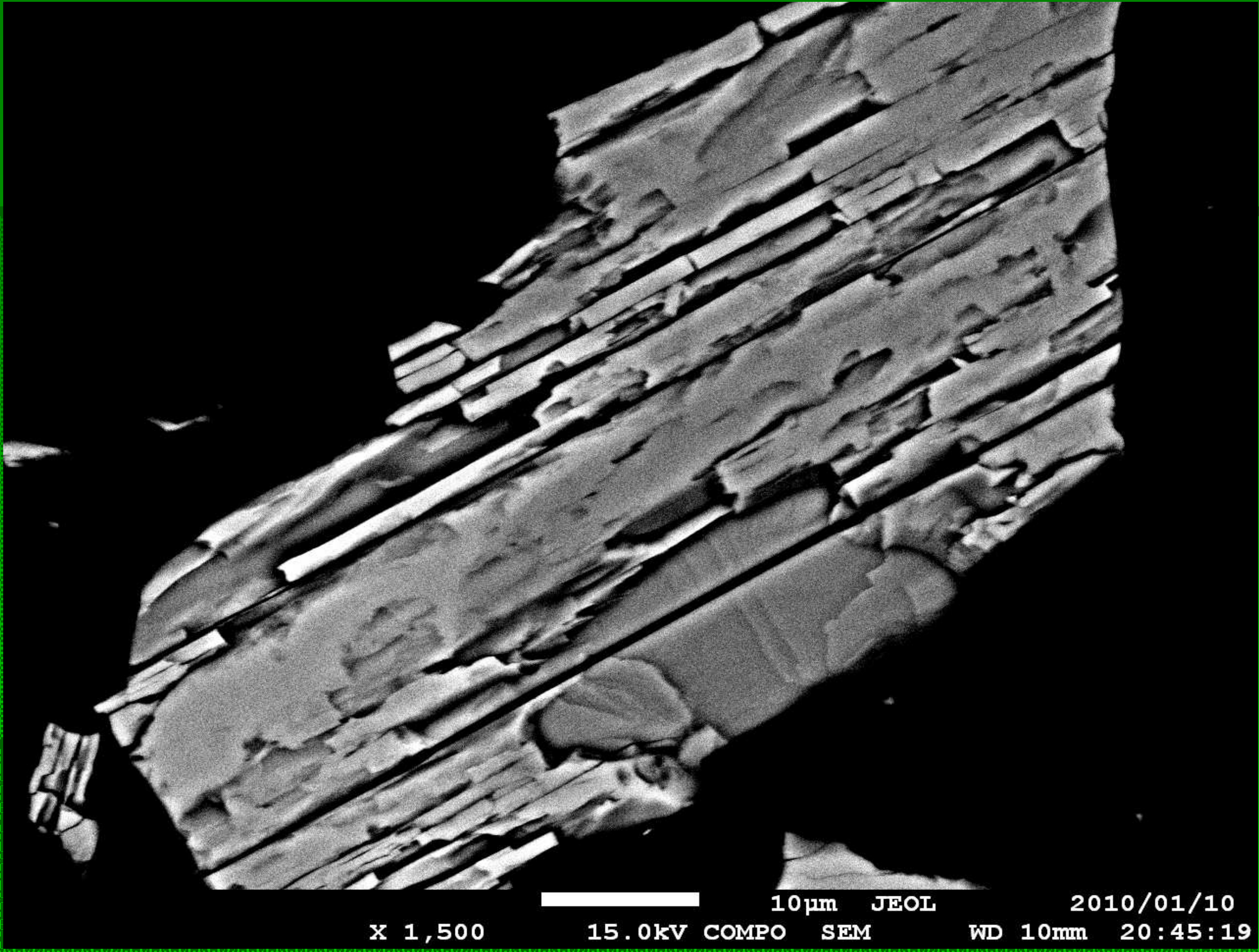
Single phase of protoenstatite sample was found in stack of sample assets of Prof. Takei

1 mm

X-ray Diffraction pattern indicate almost single phase protoenstatite



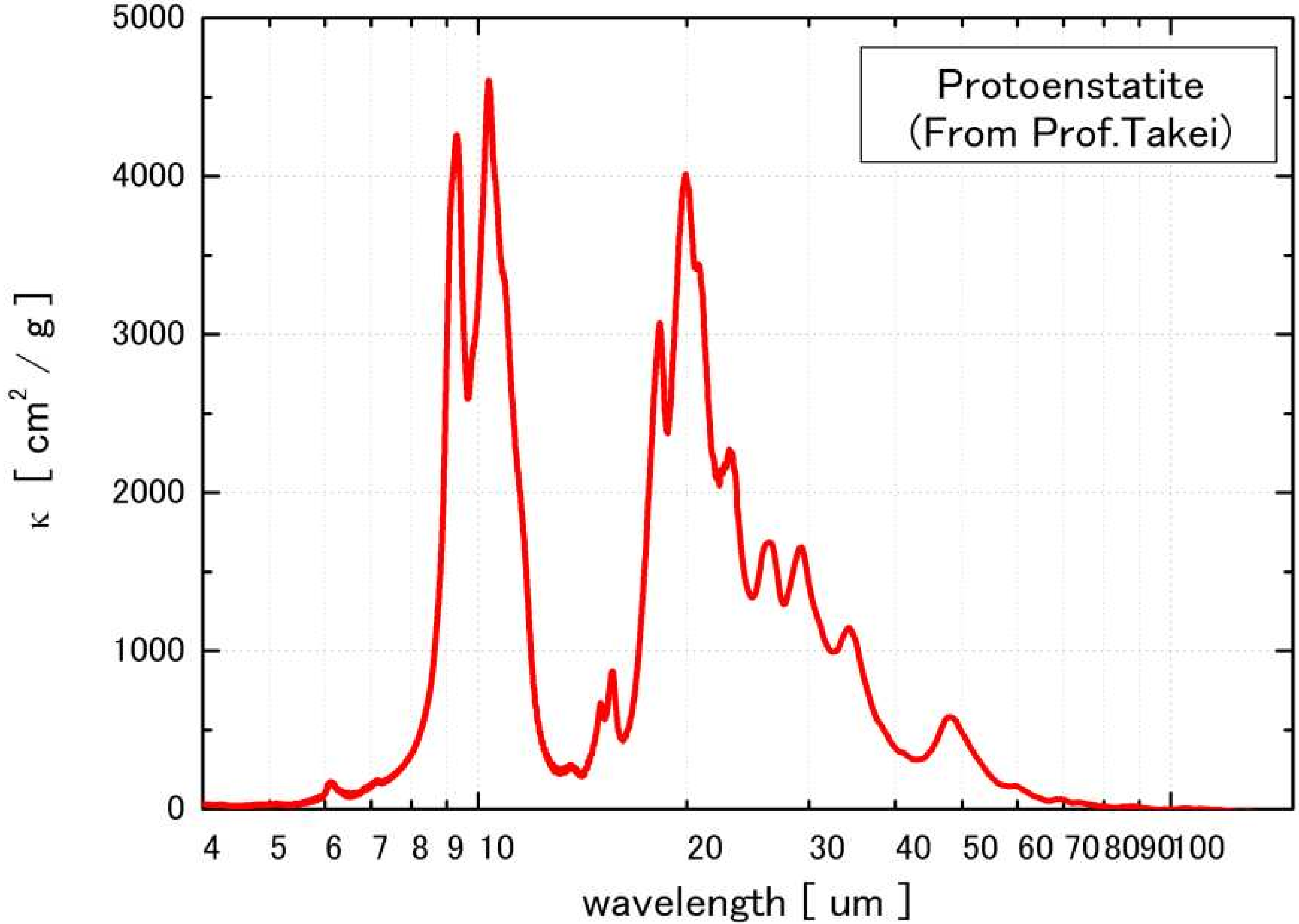
Chemistry : SEM/EDS



Iron concentration ~ 4.1 wt%

$En_{95} = Mg_{0.95}Fe_{0.05}SiO_3$

IR mass absorption coefficient

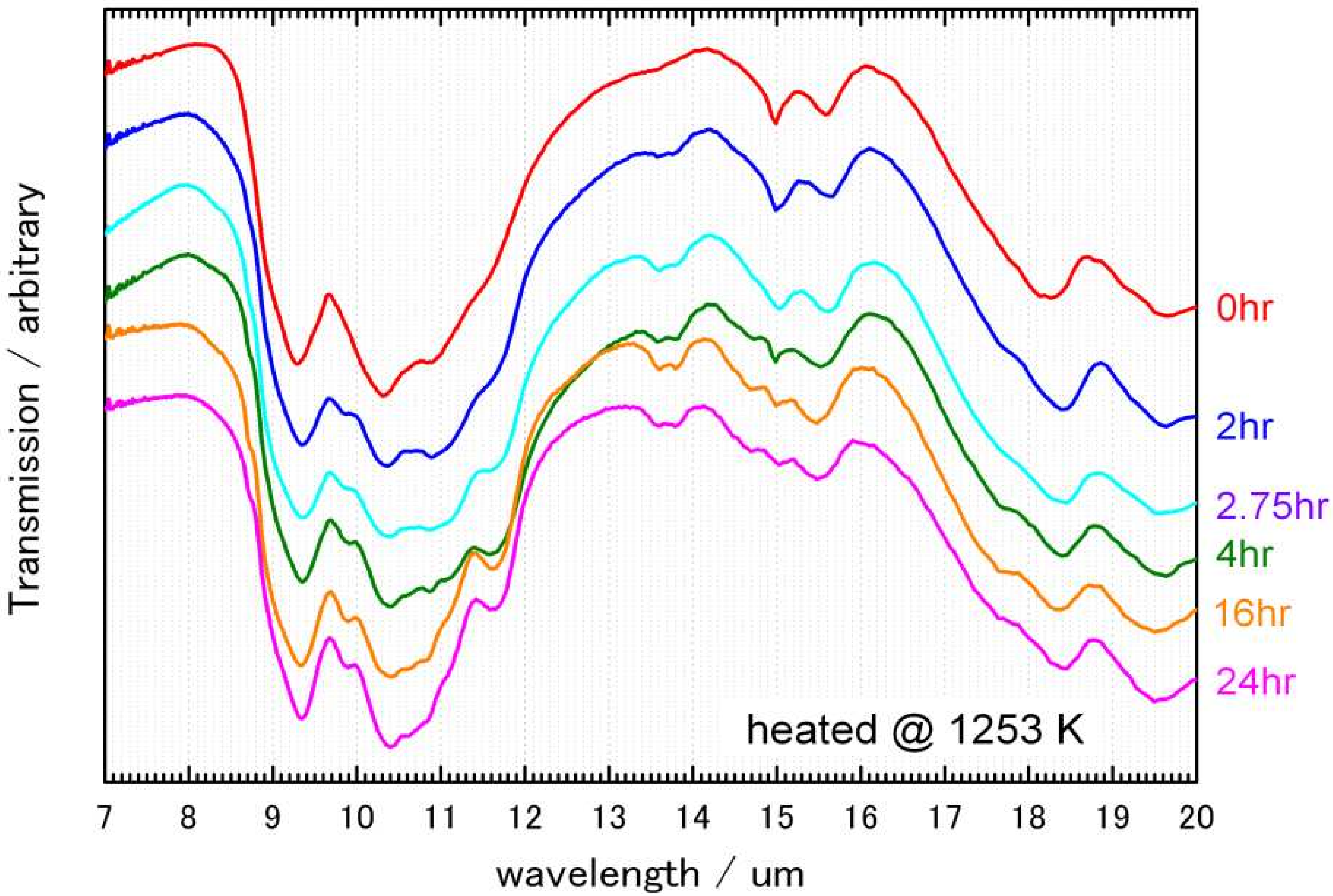


Annealing experiment and IR spectroscopy

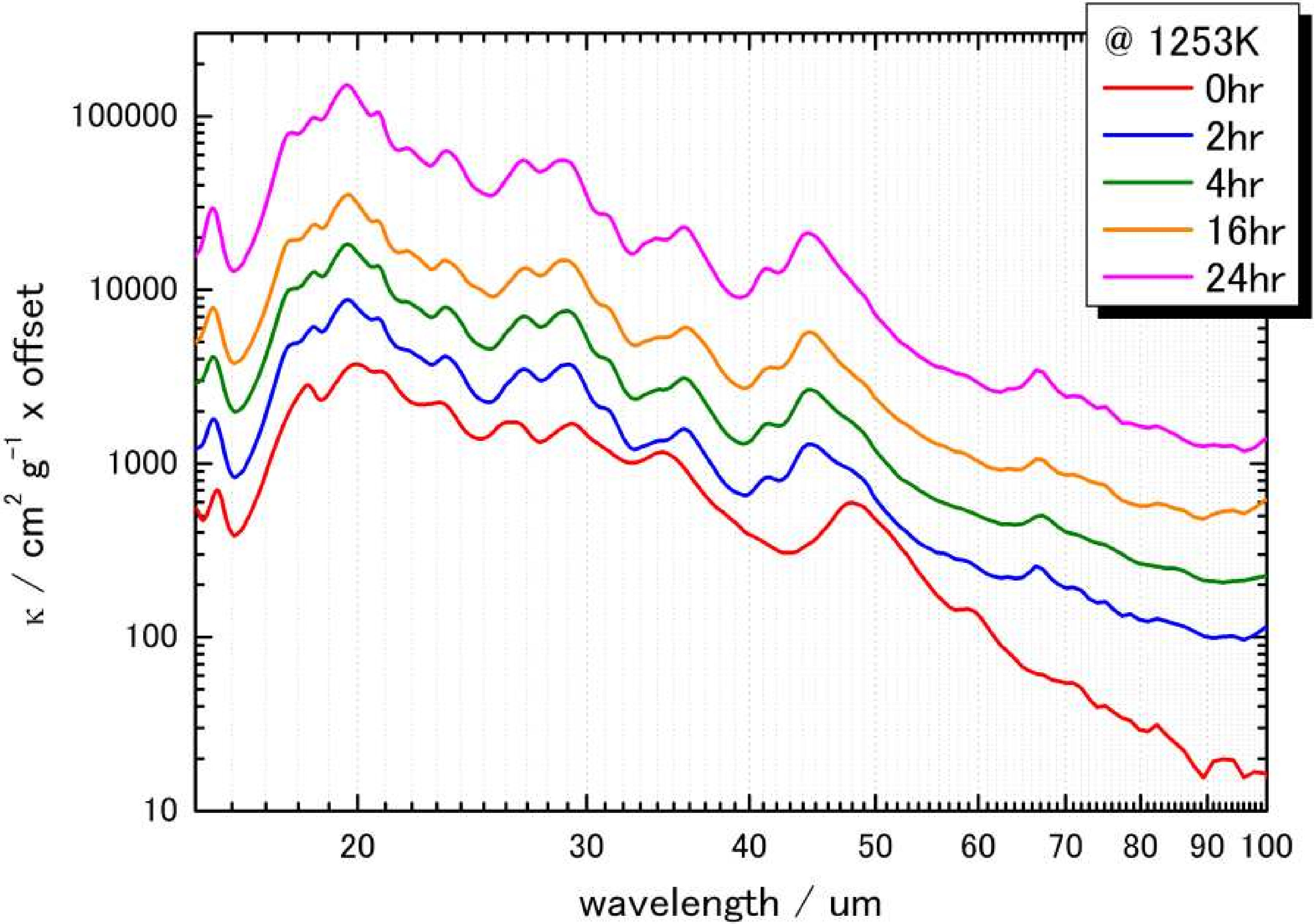
Temp.	1253 K (980℃)
heating duration at 1 atm under IW buffer	2 hr
	2.75 hr
	4 hr
	16 hr
	24 hr

MIR 4000-400 cm^{-1}	FIR 700 - 50cm^{-1}
IR microscopy (qualitative) ↓ only transmission	Polyethylene pellet method (quantitative) ↓ κ

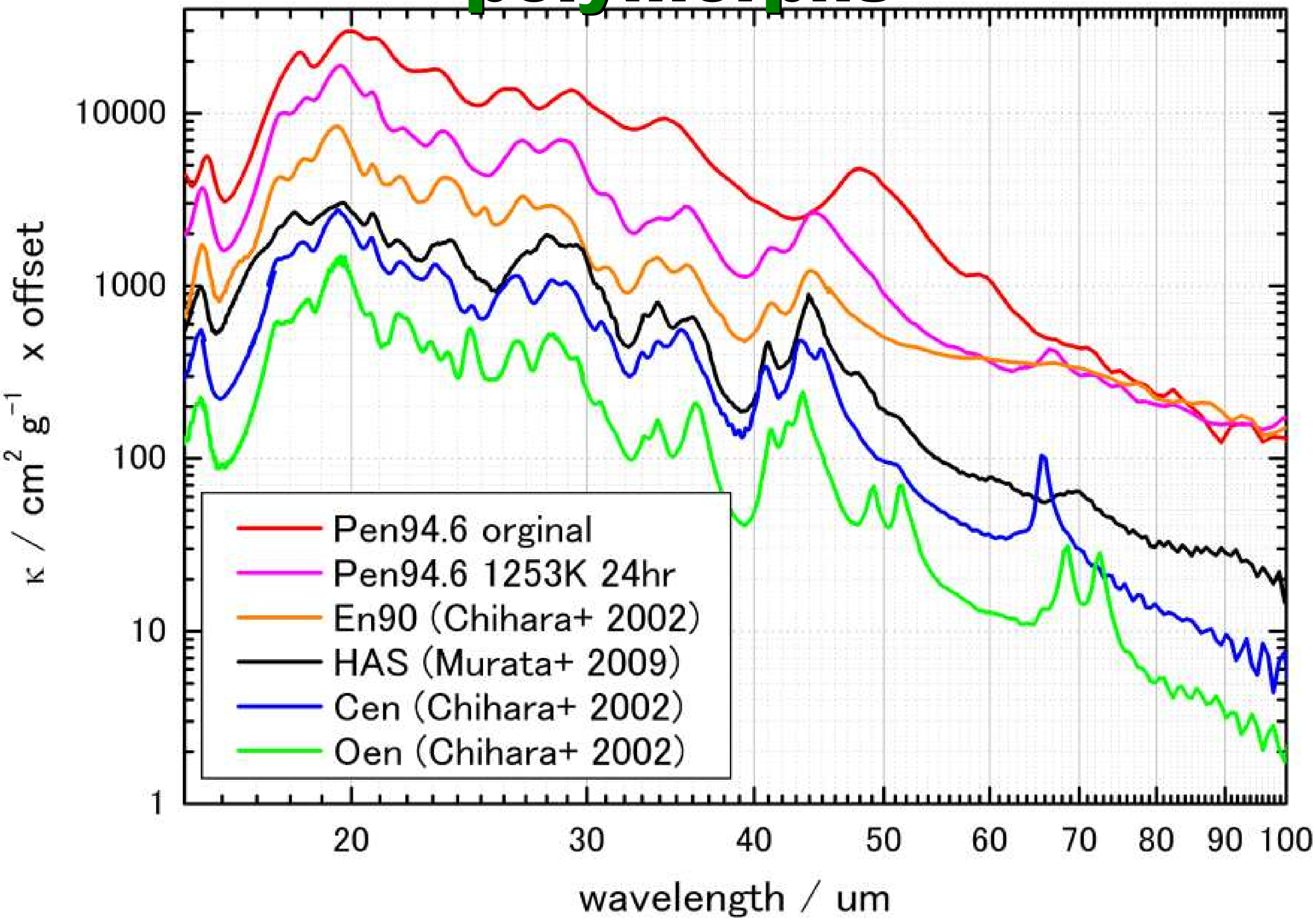
MIR-micro spectroscopy @ 1253 K



FIR spectroscopy @ 1253 K



Spectral variety of enstatite polymorphs



Experimental sumary for protoenstatite

- Infrared spectroscopy revealed transition of protoenstatite to clinoenstatite (probably) for the first time.
  - Spectral feature of protoenstatite is unique and different from both of clino- and orthoenstatite
  - Protoenstatite has weak 19 um feature, and position of 26 um feature is slightly shorter than others.
  - Transition seems completed during 16-24hr in MIR spectra, while in FIR spectra it seems more rapid.
  - After transition complete, it can be concluded that crystal structure is clino-phase due to the existence of ~66 um feature (but XRD analysis will be required).

Astrophysical implication

- Stacking sequence along to a*-axis causes pyroxene polymorphs
- Direction of stacking fault of HAS is also along to a*-axis. Therefore it can be presumable that HAS is mixture of enstatite polymorphs
- HAS spectrum seems blend of protoenstatite and clinoenstatite, indeed.
- HAS can fit observation better

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Circumstellar enstatite may be mixture of clinoenstatite and protoenstatite ?