Optical Properties of Non-stoichiometric Amorphous Silicates with Application to Circumstellar Dust Extinction

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Abstract

We determine the optical constants of non-stoichiometric amorphous magnesium-iron silicates and demonstrate that they can well reproduce the observed mid-infrared emission spectra of evolved stars. Stoichiometric and non-stoichiometric amorphous magnesium-iron silicate films are fabricated by pulsed laser deposition. Transmittance and ellipsometry measurements are performed in the wavelength range between 2 and 200 μm and 1.7 and 33 μm, respectively. Optical constants are derived from transmittance and ellipsometric Ψ and Δ spectra by means of oscillator models. These newly obtained optical constants are applied in radiative transfer models for examining reproducibility of the observed spectral features of circumstellar dust shells around supergiants. The spectra of four selected supergiants are dominated by amorphous silicate dust emission in the wavelength range between 9 and 25 μm. To obtain a good fit to the observed spectra, we take into account amorphous corundum and metallic iron particles as additional dust components to the model calculations to rationalize the dust emission at λ < 8 μm. For each of the objects, a set of model parameters (dust mass and condensation temperature) is derived by an automated optimization procedure that reproduces the observation well. Consequently, our model spectra using new optical data reveal that the silicate bands at ~10 and ~18 μm depend on the magnesium and iron ratio in the silicate system, and that a good fit requires a significant iron content of the amorphous silicate dust component to reproduce the observed peak positions and shape of the silicate bands.

Key words: circumstellar matter – stars: AGB and post-AGB – stars: mass-loss – stars: winds, outflows

1. Introduction

The standard cosmic element mixture found almost everywhere in space is rich in oxygen. The oxygen abundance typically exceeds that of carbon by a factor of about two (see, e.g., Asplund et al. 2009; Lodders et al. 2009), in which case carbon is chemically blocked in the CO molecule. If refractory minerals formed from such matter, the resulting mixture of condensed phases is strongly dominated by the magnesium-iron (hereafter Mg-Fe) silicates (e.g., Gail 2010). Silicate dust is therefore ubiquitous in space if conditions are such that solids can resist the ever-present destroying mechanisms. Mg-Fe silicates form the dominating dust component in circumstellar environments such as protostellar accretion disks or dust shells of evolved late-type stars (if these are not rich in carbon), and in addition to carbon dust, it forms the main dust component of interstellar matter.

The nature of the dust material in space is inferred from the wavelength dependence of the interstellar extinction or the infrared (IR) emission spectrum from circumstellar environments. In particular, some strong IR bands from lattice vibrations are indicative of the nature of the material, and they have been extensively used for remote sensing of the dust composition in space (see Molster et al. 2010, for a review on observations). For silicate dust, in particular their absorption bands from stretching and bending vibrations of the SiO4-tetrahedron around 10 μm and 18 μm, respectively, are used, and when the silicates are crystalline, there are many additional absorption bands up to 100 μm (e.g., Koike et al. 2003) that can be observed.

Since the earliest days of research on dust in space, it is known (see Li 2005 for a historical review) that the interstellar silicate dust component has an amorphous lattice structure. This is recognized by the broad and smooth shape of the IR bands around 9.7 and 18 μm that do not show the characteristic substructures that are seen for crystalline silicates, and it is also shown by the absence of far-infrared (FIR) bands ≥ 25 μm of crystalline materials. Crystalline silicate dust also has been found in space, but this is limited to special environments: circumstellar dust shells and protostellar accretion disks (Molster et al. 2010). While for accretion disks, it is quite common to have part of the silicate dust in crystalline form and most of it as amorphous materials (e.g., Oliveira et al. 2011), for circumstellar dust shells the presence of some fraction of crystalline silicate dust is restricted to only a small fraction of the objects (cf. Jones et al. 2012). The greater part of the silicate dust in accretion disks and circumstellar envelopes is seen to have an amorphous lattice structure like interstellar medium (ISM) dust.

The analysis of the observed dust features requires a detailed knowledge of the optical properties that are largely ruled by the complex dielectric function ε(ω) of the dust grains. Since silicate dust in space mostly has an amorphous structure, much effort has been undertaken to determine the variation of ε(ω) for amorphous silicates with different compositions and prepared by various fabrication techniques. Colangeli et al. (2003) have reviewed the experimental work and its main results some time ago.

Optical data of olivine-like amorphous silicates with different Fe content are of special importance for astronomical applications. While crystalline silicate dust formed from a cosmic element mixture under near-equilibrium conditions, which are a mixture of almost Fe-free forsterite and enstatite (e.g., Grossman 1972; Gail 2010), the amorphous cosmic dust

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seems to have a different composition that is due to strongly deviating formation conditions in non-equilibrium condensation processes. Interstellar silicate dust seems to be dominated by an amorphous material with a composition approximately equal to MgFeSiO$_4$ (Draine 2003). In accretion disks, the amorphous dust component seems to be a more complex mixture of materials with olivine-like (Mg$_{2-3}$Fe$_{2+3}$Si$_{2-5}$O$_{10}$) and pyroxene-like (Mg$_x$Fe$_{1-x}$SiO$_3$) composition with a considerable iron content ($1-x \approx 0.3$) (see Pollack et al. 1994), but high fractions of crystalline olivine and pyroxene have also been reported in some cases (e.g., Watson et al. 2009). In circumstellar dust shells, the amorphous dust component also seems to consist of olivine- and pyroxene-like materials with varying iron content (Molster et al. 2010).

Laboratory-measured optical properties of various amorphous silicates have been reported previously. Day (1979, 1981) fabricated amorphous Mg$_2$SiO$_3$ and Mg$_2$SiO$_4$ and Fe$_{1-2}$SiO$_3$ and Fe$_2$SiO$_4$ silicate thin films on KBr (potassium bromide) disks by means of reactive sputtering for transmission measurements in IR regions. Optical constants of these films were derived using classical dispersion theory. Amorphous silicate glasses with different proportions of Fe and Mg in both pyroxene- and olivine-like systems were produced using quenching-melts technique, and both transmittance and reflectance measurements were carried out with KBr pellet and thin slab methods, respectively, in the wavelength range between 0.19 and 500 $\mu$m (Dorschner et al. 1995). Dorschner and collaborators derived the optical constants of each amorphous silicate glass by Kramers–Kronig relations. Likewise, Jäger et al. (2003) adopted the sol-gel technique to fabricate non-stoichiometric pyroxene samples of the composition Mg$_2$SiO$_3$ ($x = 0.7, 1, 1.5, 2, 2.4$; $y = 2.7, 3, 3.5, 4, 4.4$), and reflectance spectra of dense pellets embedded in epoxy resin and transmittance spectra of KBr (for MIR) and PE (polyethylene for FIR) were measured as functions of wavelength in the range 0.2–200 $\mu$m. These optical constants were obtained by either the Lorenz-oscillator fit method or Kramers–Kronig relations, or both. In most cases, experimentally measured optical properties are represented by absorption, transmission, or reflection (Koike & Hasegawa 1987; Tamanai et al. 2006; Speck et al. 2011). In fact, highly accurate optical constants of various materials are an essential prerequisite for astrophysical modeling of, e.g., interstellar dust, accretion disks around young stars, planetary atmospheres, and cometary dust tails. However, optical constants of diverse chemical compositions are not readily available, especially of amorphous materials with different conditions such as temperature and pressure dependence (e.g., high temperature $\geq 1273$ K), and morphological aspects including particle irregularity in shape, aggregate/agglomerate states, and various individual particle sizes.

In this paper, we describe the optical properties of non-stoichiometric amorphous silicates with a composition between olivine-like and pyroxene-like and varying iron content, fabricated by pulsed laser deposition (PLD) technique in the MIR and FIR regions to characterize the effect of metals (Mg and Fe) on the silicate absorption. To cross-check the optical constants of each investigated silicate, we carried out both spectroscopic transmittance and ellipsometry measurements. As an application, the newly derived optical constants are used to compare synthetic spectra of dust shells around supergiants to observed MIR spectra of four objects.

2. Silicate Stardust

Information on the composition and size of silicate dust grains from circumstellar dust shells enshrouding highly evolved stars can be obtained in two ways.

The standard way is to compare IR spectra from the objects of interest with template spectra calculated from measured optical properties of laboratory made analogous minerals and with models for the source regions (see, e.g., Colangeli et al. 2003; Henning 2010, and Molster et al. 2010 for reviews).

The second possibility is to analyze specimens of cosmic dust in the laboratory. This has become possible by the detection in the 1980s that primitive meteorites contain a small fraction of stardust grains of different composition from different stellar sources (see, e.g., the collection of articles in Bernatovich & Zinner 1997 or the review of Lodders & Amari 2005), the presolar dust grains, which are identifiable by their suspicious isotopic anomalies found for some elements. This allows a direct study of their properties and composition in the laboratory. Since the detection by Nguyen & Zinner (2004) that silicates from stellar sources are also present in meteorites, it has also become possible to analyze presolar silicate dust grains. Vollmer et al. (2009), Bose et al. (2010, 2012), and Nguyen et al. (2010) have provided direct information on the size and composition for 145 such presolar silicate grains.

We concentrate here on silicate grains from the meteorite ACFER 094, a primitive ungrouped carbonaceous chondrite, because the matrix material in this meteorite seems to be only slightly metamorphosed. The matrix material has not been subject to high temperatures where the material would equilibrate, and the presolar silicate grains in this meteorite show only indications of minor aqueous alteration and oxidation of Fe metal on the parent body (e.g., Keller et al. 2012). Hence, the compositions of the silicate grains probably largely resemble their composition at formation time in the dust shell of an asymptotic giant branch (AGB) star.

The fractional abundance of the six main rock-forming elements (O, Si, Mg, Fe, Ca, and Al) was studied in Vollmer et al. (2009), Bose et al. (2010), Nguyen et al. (2010), and Bose et al. (2012). We try to derive from the laboratory derived fractional abundances of the elements given in these papers the corresponding abundances of the oxides SiO$_2$, SiO, MgO, FeO, CaO, and Al$_2$O$_3$ and of solid iron in the dust grains, which reproduces their observed elemental composition and also considers the stoichiometry of the elements.

The oxide SiO is added to the set because complex silicate structures exist (e.g., chains of rings) in which the O/Si ratios formally correspond to an oxide component SiO$_x$ with $1 \leq x \leq 2$ such that the astronomical silicates may deviate in their composition from the usually assumed olivine or enstatite stoichiometry. To account for a more complex stoichiometry, the SiO is included.

We add metallic iron to the set of oxide components since it is known that presolar silicate dust grains may contain iron grains as nanometer-sized inclusions, at least in some cases. Iron-sulphide particles are also commonly found as nanometer-sized inclusions when iron particles are present. These inclusions are found in GEMS, a class of subgrains in interplanetary dust particles that are characterized by the presence of iron and iron-sulphide inclusion embedded in a glassy ground matrix. While most of such grains seem to be of interstellar or solar system origin, a few percent show oxygen isotopic anomalies, which indicates an origin as stellar or
supernova condensate (e.g., Messenger et al. 2003; Matzel et al. 2008; Keller & Messenger 2011). We cannot take FeS particles into account because no S abundance was measured. Additionally, we consider Fe₂O₃ as a possible component. It is unlikely that iron can be oxidized to the Fe³⁺ state under the strongly reducing circumstellar conditions, but the presolar material may be oxidized during its residence on the parent body of the meteorite or on the Earth’s surface before being collected.

This set of components does not cover all possibilities for the composition of presolar material from oxygen-rich parent stars, but it does include the most important possibilities. The relative abundances of the components are determined by a least-squares minimization such that the relative abundance of the sum of all elements in the mixture fits the measured elemental abundances as well as possible. Figure 1(a) shows the resulting value of χ² as a function of the fractional abundance of the sum of all elements contained in the particle (in the figure: the percentage). Ideally, this should sum up to 1.0 or to 100%. For most particles a solution can be found by breaking down the material into the fundamental oxides and the additional Fe that fits the experimental data with an accuracy better than 10⁻²; in many cases, the fit is even much better. This suggests that the corresponding particle is likely composed of minerals (and free iron) that contain the seven oxide components SiO₂, SiO, MgO, FeO, Fe₂O₃, CaO, and Al₂O₃. For particles where the optimum fit fails to reproduce the measured elemental abundances within the limits of 10⁻², the grains either contain significant fractions of additional elements or components with an alternate composition, or the measurements are inaccurate for some reasons. We exclude these particles from further considerations.

With respect to iron-bearing components found in the fit, the following holds: metallic iron must be an inclusion in the silicate or be attached to its surface, and any portion of Fe₂O₃ must be a secondary product of oxidation of iron metal during the residence time on the parent body or on Earth. Only the fraction of Fe that is not contained in these two components can be part of the silicate material. Figure 1(b) shows the fraction of the total Fe content that seems to have been built into the presolar silicate grains as iron metal during particle formation. Surprisingly, the laboratory-determined composition of the silicate grains can be best explained if a high fraction of the Fe contained in the presolar grains is not part of the silicate lattice, but is contained as metallic iron particles, either as inclusions within the grains or attached to its surface. The size of such iron particles must be generally below the resolution limit of the nano-SIMS (∼ 50 nm) used for the investigations (Vollmer et al. 2009; Bose et al. 2010, 2012; Nguyen et al. 2010) because it is not reported in the papers that such inclusions are detected in all or most of the grains. Atom ratios Fe/Si up to 0.3 are frequent, which converts into metal/silicate volume ratios of up to about 0.15.

Part of the particles contain some fraction of Al and Ca. This indicates heterogeneous composed particles of silicate and aluminum-calcium minerals or a complex chemical composition of the grains. To avoid any ambiguity resulting from this, we do not consider Ca-Al-bearing particles. The remaining particles are (more or less) pure magnesium-iron-silicate particles where part of the iron seems to be present as metallic iron.

Figure 2(a) shows the correlation between the cation-to-silicon ratio in the presolar grains. The vertical gray lines correspond to the O/Si ratios in different mineral structures varying from O/Si = 2 for framework silicates to O/Si = 4 for island silicates and intermediate values for chain and ring silicates, and for solid SiO (O/Si = 1). The presolar silicates cover the whole range, with no preference for one of the specific values, corresponding to well-defined mineral structures. This suggests the amorphous character of circumstellar silicates does not solely refer to a disorder in the arrangement
of the SiO$_4$-building blocks in a material with an otherwise well-defined composition as for mineral compounds, as was obtained by melt-quenching (Dorschner et al. 1995). This type of disorder will also manifest itself in broad smeared-out $\sim 10$ $\mu$m and $\sim 18$ $\mu$m silicate bands. The silicates condensed in stars seem to have more than that: compositions with highly variable fractions of bridging bonds between the SiO$_4$-tetrahedrons that do not correspond to any of the regular structures of minerals. They may resemble the “chaotic silicates” discussed by Nuth & Hecht (1990), and this type of material may also form during the rapid quenching of vapor by the vapor-deposition fabrication method that is used to prepare the amorphous thin films we used (see Section 3.1).

Figure 2(b) shows the iron content of the silicate material according to our calculation. Significant iron contents seem to be frequent, but iron-poor silicates seem not to be rare either. This probably means that the iron fraction of silicates that formed in the outflow from stars is variable, but since the presolar grains are a mix from many different stellar sources, we cannot draw any conclusion on the circumstances that determine the iron content. Additionally, we have to be aware that our calculated FeO fraction may contain some contributions from rusting of iron when Fe$_2$O$_3$ is also found to have non-negligible abundance.

3. Experiments

3.1. Non-stoichiometric Amorphous Silicate Samples

Non-stoichiometric amorphous samples were prepared by means of the PLD technique at the Institute of Geology, Mineralogy, and Geophysics of the Ruhr-University Bochum (RUB) (e.g., Dohmen et al. 2002). Floating-zone Si (111) crystal structure substrates with size of $10 \times 10$ mm and thickness of 740 $\mu$m (SILTRONIX) were employed since the Si wafer is highly transparent in the IR region.

An Excimer-Laser with nanosecond pulses of 193 nm wavelength at a frequency 10 Hz was used to ablate a synthesized target pellet material under high vacuum condition ($10^{-4}$ mbar) in the PLD chamber. The laser fluences were between 1 and 5 J $cm^{-2}$, which typically yielded a film thickness of about 50 nm after 10 minutes. The different stoichiometry of each olivine target pellet was prepared by thoroughly mixing in a mortar three synthetic powders, which were 99.99% pure SiO$_2$, MgO, and Fe$_2$O$_3$ with the nominal ratio, and this mixed powder was cold-pressed into a pellet of 8 mm diameter. The fabricated target pellets were then annealed in a furnace for approximately 20 hr at temperatures of 1500, 1300, 1225, and 1100°C under an oxygen fugacity $f_O^*$ of 1, $10^{-9}$, $10^{-10}$, $10^{-11}$, and $10^{-12}$ bar for Mg$_2$SiO$_4$, Mg$_{0.8}$Fe$_{1.2}$SiO$_4$, Mg$_{0.4}$Fe$_{1.6}$SiO$_4$, and Fe$_2$SiO$_4$, respectively. The $f_O^*$ was controlled by the flow of gas mixture (CO and CO$_2$) during the annealing processes (e.g., Dohmen et al. 2002). The T$_2$O$_2$ conditions were selected for the Fe-bearing pellets such as to reduce the Fe$^{++}$ to Fe$^{+}$ and to be within the stability field of the respective olivine composition according to Nitsan (1974).

In the PLD chamber, the $10 \times 10$ mm Si substrate was placed on a substrate holder that was mounted directly in front of the target material on a rotating holder. This Si substrate was first heated to 400°C under a pressure of $10^{-5}$ mbar for 15 minutes in order to remove unnecessary volatile absorbents on the surface, especially H$_2$O. The deposition was carried out at approximately room temperature and a background gas pressure of around $10^{-6}$ mbar. When an incoming laser beam hit the target, a plasma cloud containing a mixture of neutral and ionic atoms was created in an anterior direction of the mounted Si substrate. Hence, the particles in the plasma are deposited on the mounted Si substrate (more details in Dohmen et al. 2002)).

The chemical compositions of the deposited silicate films were determined by Rutherford backscattering spectroscopy (RBS). The RBS measurements were carried out at the RUBION facility of the RUB using the dynamitron tandem accelerator to produce a 2 MeV beam of alpha particles. The measurements were performed with a final aperture of 1 mm, a beam current typically between 20 and 50 nA, a detecting angle of 160° with a silicon particle detector at an energy resolution of about 16–20 keV, and the sample surface was tilted at about 5° relative to the beam direction to avoid channeling. The RBS spectra were simulated using the software RBX (Version 5.18 Kotai 1994) assuming a density of the amorphous silicate layers as of the respective crystalline olivine. The thin film thickness was not completely homogeneous over the sample; it was maximum for the central area. Uncertainties are $\pm 5$ nm minimum related to the energy resolution of the detector. However, the fabricated silicate films are chemically homogeneous at least down to the 10 nm scale and totally amorphous, which has been demonstrated by TEM investigations of thin films with similar compositions (Dohmen et al. 2002; Le Guillou et al. 2015). The oxidation state of Fe is mainly 2+, as shown by Le Guillou et al. (2015). Table 1 shows the physical and chemical characteristics of the deposited amorphous silicate samples analyzed by the RBS.

3.2. FTIR Spectroscopy

The IR spectroscopic transmittance measurements have been performed in order to examine the optical properties of the deposited amorphous silicates. A Bruker IFS66 v/s Fourier transform infrared (FTIR) spectrometer with deuterium triglycine sulfinate (DTGS) detector was employed for the MIR transmittance measurements in the frequency range between 500 and 5000 cm$^{-1}$ ($20–2\mu$m), as well as a Bruker Vertex80v with a special FIR-DTGS detector together with a Mylar beam splitter for the FIR measurements in the frequency range between 50–600 cm$^{-1}$ ($200–16.7\mu$m). The sample compartment of both FTIR spectrometers was evacuated to a pressure below 4 mbar for all measurements. All transmittance spectra were normalized to the spectrum of the bare Si(111) wafer and obtained with a spectral resolution of 4 cm$^{-1}$. As shown in Figure 3, the transmittance spectra measured in both MIR and FIR regions overlapped each other at around 500 cm$^{-1}$ and were feasible to connect (more details in Wetzel et al. 2012a, 2012b). Hence, it is possible to determine the optical constants through the incorporated transmittance spectra that can cover a wide spectral range within the IR region.

The measured transmittance spectrum of Si-film3 together with a Brendel oscillator model fit (Brendel & Bornemann 1992) for the dielectric function

$$
\varepsilon(\omega)_{\text{IR}} = \varepsilon_{\infty} + \sum_{j=1}^{N} \frac{1}{\sqrt{2\pi} \sigma_j} \int_{-\infty}^{\infty} dz \frac{e^{-(\omega_0)^2}}{2\sigma_j} \frac{\omega_{p,j}^2}{z^2 - \omega^2 + i\gamma_j \omega}
$$

4
using five oscillators is shown in Figure 4. This model accounts for the amorphous structure of a material by assuming that the different IR modes can be represented by Lorentz-oscillators with randomly shifted resonance frequencies distributed according to Gaussian probability distributions. We performed the spectral fits in the range between 100 and 1400 cm⁻¹ using the software package SCOUT (Theiss 2011). To model the transmittance spectrum, the value of ε₁∞ has to be used as an input parameter. However, no values for ε₁∞ obtained from amorphous silicates equivalent to our non-stoichiometric samples are available.

Fundamentally, the optical properties are sensitively influenced by chemical compositions (Koike et al. 2003; Tamanai et al. 2009), and thus the value of ε₁∞ also varies with different concentrations of Fe and Mg in the silicate system. Consequently, the values of the high-frequency dielectric constant (ε₁∞) derived from the ellipsometric fitting have been applied for the transmittance modeling in order to determine the accurate dielectric function (see Section 3.3). Since the oscillator damping constant γ cannot properly be determined from the fits for vibrational spectra of disordered solids (cf. Ishikawa et al. 2000), we fixed the value of γ to the resolution of our measurement 4 cm⁻¹. Nearly the same type of procedure has previously been reported in the literature (Naiman et al. 1985; Grosse et al. 1986; Brendel & Bormann 1992; Ishikawa et al. 2000). Our parameters of the best fit for the oscillator model are given in Table 2. The Brendel oscillator model provides a reasonable fit to the experimental transmittance spectra of our amorphous silicate samples.

### Table 1

**RBS Analysis of Amorphous Magnesium-Iron Silicates**

| Sample | Film Thickness (nm) | Target Composition | Thin Film Properties | Chem. Formula | Mg/(Fe+Mg) | (Mg+Fe)/Si |
|--------|---------------------|--------------------|----------------------|---------------|------------|------------|
| Si-film1 | 235                | Fo100              |                      |               | 1.00       | 0.85       |
| Si-film2 | 210                | Fo80Fa20           |                      |               | 0.64       | 0.91       |
| Si-film3 | 235                | Fo40Fa60           |                      |               | 0.32       | 1.89       |
| Si-film4 | 70                 | Fa100              |                      |               | 0.00       | 1.50       |

Figure 3. Relative transmittance measurement of the Si-film3 sample in the MIR and FIR region.

Figure 4. Comparison of composite transmission spectrum of Si-film3 with the best fit of a Brendel oscillator model with the oscillator parameters given in Table 2. The oscillator positions are indicated by dashed lines.

### Table 2

**Parameters for the Brendel Oscillators**

| Osc. | Param. (cm⁻¹) | Si-film1 | Si-film2 | Si-film3 | Si-film4 |
|------|--------------|----------|----------|----------|----------|
| 1    | ω₀           | 377      | 372      | 366      | 307      |
|      | ωₚ           | 514      | 625      | 614      | 391      |
|      | σ             | 125      | 139      | 135      | 94       |
| 2    | ω₀           | 502      | 525      | 520      | 493      |
|      | ωₚ           | 390      | 410      | 401      | 452      |
|      | σ             | 75       | 73       | 61       | 61       |
| 3    | ω₀           | 739      | 721      | 708      | 687      |
|      | ωₚ           | 223      | 181      | 191      | 174      |
|      | σ             | 70       | 42       | 56       | 74       |
| 4    | ω₀           | 972      | 942      | 921      | 920      |
|      | ωₚ           | 692      | 752      | 670      | 628      |
|      | σ             | 77       | 77       | 67       | 62       |
| 5    | ω₀           | 1118     | 1098     | 1064     | 1062     |
|      | ωₚ           | 212      | 299      | 268      | 396      |
|      | σ             | 63       | 74       | 58       | 79       |

ε₁∞ = 2.43, 2.67, 3.15, 3.69

Note. The values of ε₁∞ are obtained from the IRSE modeling.

### 3.3 Infrared Spectroscopic Ellipsometry

To obtain the real and the imaginary part of the optical constants of the amorphous silicate samples, we carried out infrared spectroscopic ellipsometry (IRSE) as well. IRSE is a characterization technique for obtaining physical (e.g., thickness
and surface roughness) and optical properties of both anisotropic and isotropic materials. Fundamentally, ellipsometry measures in the polarization state of light when it is reflected from a surface of a sample. As a result, \( \Psi \) (relative amplitude change) and \( \Delta \) (relative phase change) spectra can be obtained from the measurements. In this investigation, the measurements of \( \Psi \) and \( \Delta \) spectra have been carried out in the frequency range between 300 and 6000 cm\(^{-1}\) within an angle of incidence for 60° and a resolution of 4 cm\(^{-1}\) under dry air (IR-WASE: J.A. Woollam Col, Inc.). These \( \Psi \) and \( \Delta \) parameters correspond to the Fresnel reflection coefficients \( R_p \) (p-polarized; parallel to the plane of incidence) and \( R_s \) (s-polarized; perpendicular to the plane of incidence). So the complex reflectance ratio \( \rho \) as the basic equation for ellipsometry can be described as

\[
\rho = \frac{R_p}{R_s} = \tan(\Psi) e^{-i\Delta},
\]

where \( \tan(\Psi) \) denotes the ratio of reflected amplitudes, and \( \Delta \) is the phase shift of p- and s- linearly polarized components as a result of reflection.

A dielectric function that is derived from the ellipsometry measurements for uniform and isotropic bulk materials is described as a “pseudo-dielectric function” that can be derived from the measured values of \( \Psi \) and \( \Delta \) spectra,

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2 = \sin^2(\Phi_f) \left\{1 + \tan^2(\Phi_f) \left(\frac{1 - \rho}{1 + \rho}\right)\right\},
\]

where \( \varepsilon_1 \) is the real part, \( \varepsilon_2 \) is the imaginary part of the complex dielectric function, and \( \Phi_f \) is the angle of the incident radiation (Fujisawa 2007).

Because of the inhomogeneous line broadening of the amorphous samples, the Gaussian oscillator model of the ellipsometry software is applied to model the IR vibrational modes of the amorphous silicates. The spectral line shape of the measured \( \Psi \) and \( \Delta \) spectra is approximated by a Gaussian line profile, which can be expressed by the Kramers–Kronig relations. The real part \( \varepsilon_1 \) of the complex dielectric function is related to the imaginary part \( \varepsilon_2 \) at all frequencies and is represented as

\[
\varepsilon_1(\omega) = \frac{2}{\pi} P \int_0^{\infty} \frac{\varepsilon_2(\Omega)}{\Omega^2 - \omega^2} d\Omega,
\]

where \( P \) is the Cauchy principal part (Peiponen & Vartiainen 1991).

The imaginary part describes each Gaussian oscillator mathematically,

\[
\varepsilon_2(\Omega) = A e^{-\frac{(\Omega - \Omega_0)^2}{2\sigma^2}} - A e^{-\frac{(\Omega + \Omega_0)^2}{2\sigma^2}},
\]

where \( A \) denotes the amplitude, \( \Omega_0 \) is the center/resonance energy, and \( \sigma \) is related to the broadening \( Br \) of a band by

\[
\sigma = \frac{Br}{2\sqrt{2\ln(2)}}
\]

(De Sousa Meneses et al. 2006). All three parameters, \( A \), \( \sigma \), and \( \Omega_0 \), are ellipsometry model fit values that are summarized in Table 3.

| Osc. | Param. (cm\(^{-1}\)) | Si-film1 | Si-film2 | Si-film3 | Si-film4 |
|------|-----------------------|----------|----------|----------|----------|
| 1    | \( \omega_0 \)       | ...      | ...      | 369      | ...      |
|      | \( A \)               | ...      | ...      | 4.36     | ...      |
|      | \( \sigma \)          | ...      | ...      | 1.39     | ...      |
| 2    | \( \omega_0 \)       | 461      | 448      | 501      | 412      |
|      | \( A \)               | 3.83     | 4.51     | 1.66     | 4.61     |
|      | \( \sigma \)          | 96       | 106      | 65       | 134      |
| 3    | \( \omega_0 \)       | 776      | 751      | 746      | 910      |
|      | \( A \)               | 0.72     | 0.44     | 0.59     | 2.57     |
|      | \( \sigma \)          | 39       | 26       | 20       | 54       |
| 4    | \( \omega_0 \)       | 964      | 931      | 903      | 981      |
|      | \( A \)               | 3.62     | 3.61     | 3.43     | 2.09     |
|      | \( \sigma \)          | 87       | 88       | 70       | 123      |
| 5    | \( \omega_0 \)       | 1157     | 1129     | 1021     | ...      |
|      | \( A \)               | 0.36     | 0.29     | 0.76     | ...      |
|      | \( \sigma \)          | 47       | 56       | 77       | ...      |

\( \varepsilon_{\infty} \):

\[
2.43, 2.67, 3.15, 3.69
\]

Note. “A” has the unit “1”.

There are several discrepancies between the oscillator data of Tables 2 and 3. Whereas transmittance at normal incidence measures only vibrational dipoles parallel to the layer, ellipsometry is also sensitive to those perpendicular to the layer. In our fit we assumed isotropic and smooth layers, and hence, any small anisotropy and inhomogeneity is not taken into account in the ellipsometric analysis. Nevertheless, ellipsometry delivered accurate \( \varepsilon_{\infty} \) values, the use of which improved the transmittance analysis.

4. Experimental Results

4.1. Absorbance Behavior

In Figure 6 the measured transmittance spectra have been converted into absorbance spectra by the equation

\[
\text{absorbance} = -\log(T)
\]
(T is the transmittance). Figure 6 shows these absorbance spectra in the wavelength range between 8 and 25 \( \mu m \) for four various stoichiometries of amorphous silicate samples. Table 4 lists the positions of the two strongest absorbance features. They mainly include Si-O-Si stretching and bending vibrations, respectively. As obvious in Figure 6, the Si-O asymmetric stretching vibration band undergoes a redshift as the Fe concentration in the amorphous silicate system increases. However, this tendency is not systematic up to Si-films4 because of the different behavior of the two modes that contribute to this peak, see Table 2. A weak Si-O-Si symmetric stretching vibration band around 13–14 \( \mu m \) has been observed for Si-film1, Si-film2, and Si-film3.

4.2. Derived Optical Constants

As mentioned in Sections 3.2 and 3.3, we have derived the optical constants of each amorphous silicate film by two different methods. We inspect whether these methods deliver corresponding optical constants and how we can combine the results for further astronomical simulations in this section.

A comparison of the real and imaginary parts derived from modeling the ellipsometric and transmittance spectra of the Si-film3 sample is shown in Figures 7(a) and (b), respectively.

Since we employed the value of \( \varepsilon_{\infty} \) derived from the ellipsometric model for the transmittance, the spectral fit could be improved significantly. Concerning the imaginary part, the
peak positions of the resonance frequency around 10 μm as well as the peak around 20 μm are located at almost the same positions. However, an obvious difference is observed around 12.5 μm: absorption due to the Si-O symmetric vibration clearly appears as a shoulder in the ε₂ spectrum derived from the ellipsometric modeling, but in the transmittance fit, it appears only as a plateau between two strong features. The fit parameters for this resonance position are different for the two methods, see Tables 2 and 3. The same result has been obtained for the Si-film1 and Si-film2 samples. These deviations are related to the very weak IR activity of this mode, which together with the inhomogeneous line broadening complicates the spectral analysis. The strong disparity at the longer wavelength side (≥20 μm) is related to the limited measurement range of the IRSE, which is 1.7–33 μm. When we approach the limit of the measurement range (≥20 μm), the signal-to-noise ratio decreases, see this spectral range in Figure 5. In this noisy range, the ellipsometric data are no longer used for further simulations.

The two derived data sets were combined at reasonable points in order to cover a broad spectral range between 2 and 200 μm for astronomical simulations. In Figure 7 the short dashed line exhibits the combined dielectric function. For both the real and imaginary parts, there were some points of contact where it was easy to connect these data sets without critically losing accuracy. Figure 7(a) shows the real part of Si-film3. The transmittance data were used at the short wavelength between 1.25 and 4.17 μm. The ellipsometric model data were integrated at 4.17 μm up to 14.3 μm because the Si-O-Si symmetric stretching vibration band appears more clearly in this region. The ellipsometric data were again combined with the transmittance data at the point of 15.4 μm. Because there was no exact intersection point between those two data sets, we here interpolated the ellipsometric data between 14.3 and 15.4 μm where the ellipsometric data line was descended along the transmittance line curve up to 15.4 μm. Then the transmittance data were selected from 15.4 to 200 μm. As mentioned in Section 3.3, the Δ spectra are highly sensitive to thin films; therefore, we selected the ellipsometric data in the MIR region where the Si-O-Si asymmetric and symmetric vibration bands appear clearly. A similar modification of the complex dielectric function data sets was performed for Si-film1, Si-film2, and Si-film4.

### 5. Application to Circumstellar Dust Shells

We calculate synthetic spectra for dust-enshrouded evolved stars using the newly derived optical constants for non-stoichiometric amorphous silicate materials with compositions intermediate between olivine and pyroxene and compare the results with observed IR spectra from stellar sources taken with the ISO satellite. We aim to check how well we can match the observed emission properties of circumstellar dust with models for the infrared emission based on our newly determined optical constants.

#### 5.1. Choice of Model Stars

Dust associated with highly evolved cool stars is freshly formed in the massive outflows that evolve as the stars ascend the red giant branch in the Hertzsprung–Russell diagram (HR) of stellar evolution toward very high luminosities. Depending on whether the oxygen-to-carbon abundance ratio remains ≤1 or exceeds this value, the stars form mineral dust from the abundant rock-forming elements (Mg, Si, Al, Ca, and Fe) or they form soot and carbides, respectively.

The low- and intermediate-mass stars (with initial masses ≤8 M☉ a⁻¹) are in their dust-forming phase on their second giant branch, the AGB, where they have a degenerated carbon–oxygen core and alternatively burn hydrogen and helium in two shell sources. Some of them become carbon stars (with C/O ≥ 1 at their surface) if some of the freshly produced carbon is dredged up to the stellar surface. The massive supergiants (with initial masses ≥8 M☉ a⁻¹ and ≤40 M☉ a⁻¹) are on their first giant branch, where they burn hydrogen in a shell source on top of their helium core. Owing to their different mass and internal structures, the properties of AGB stars and supergiants are somewhat different during their final evolution. The most important differences in our context are that supergiants (i) retain their initial abundances of refractory dust forming elements during their whole evolution until they explode as a supernova, and (ii) they have much higher luminosities and slightly higher surface temperatures than AGB stars, such that they do not cross one of the instability strips in the HR-diagram where stars become large-amplitude pulsators. These differences makes supergiants better suited as test cases for investigations of dust condensation in stars than AGB stars.

First, the critical factor ruling the chemistry in the outflow, the C/O abundance ratio, does not increase by mixing substantial amounts of carbon from the core region to the surface as in AGB stars, but instead, it slightly decreases by mixing CNO-cycle equilibrated material in which most C is converted into 14N to the surface. This guarantees that there is always a sufficient excess of oxygen over carbon that all the refractory rock-forming elements can be oxidized. This leaves no doubt about the chemical nature and composition of the dust mixture that could be formed.

Second, although the supergiants are variable to some extent as all stars in the upper right part of the HR-diagram, they do not show the high-amplitude visual magnitude variations characteristic of the pulsationally unstable stars found on or close to the AGB (Arroyo-Torres et al. 2015). For this reason, the hydrodynamic structure of the outflow from supergiants is expected to be much simpler than for their lower-mass relatives on the AGB because there are no strong shock waves running through the atmosphere and the inner part of the dust envelope, as in the case of Miras or semi-regular variables. A simple steady-outflow model represents the density structure of the dust shell sufficiently accurately for our purpose.

We restrict our considerations to objects with optically thin dust shells. This prevents radiative transfer effects and scattering from being important for the formation of the IR-emission spectrum, which complicates the interpretation of the spectra.

| Samples  | Asymmetric Stretching (μm) | Bending (μm) |
|----------|----------------------------|--------------|
| Si-film1 | 10.2                       | 21.4         |
| Si-film2 | 10.0                       | 20.6         |
| Si-film3 | 10.0                       | 20.0         |
| Si-film4 | 10.8                       | 20.5         |

Table 4: Si-O-Si Vibrational Assignments of the Strongest Bands

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Tamanai et al. 2015, The Astrophysical Journal, 845:6 (18pp), 2017 August 10
Dust in the environment of supergiants has been studied by Speck et al. (2000) and Verhoelst et al. (2009) for a large sample of stars for which ISO-spectra are available. We select from these studies a small number of objects that satisfy the following requirements:

1. The dust shells are clearly optically thin in the IR region. For this, we consider only objects of the category 2.SEc as defined by Kraemer et al. (2002).
2. The spectra show marked but not very strong emission bands around 10 and 18 μm that are typical for amorphous silicate dust. This serves to ensure that the optical thickness in the bands is \( \frac{1}{1} \).
3. The spectra show no obvious indication of the presence of crystalline silicates to avoid a significant contribution of such material to the bands around 10 and 18 μm.
4. The spectra show low noise in the spectral region \( \lambda \leq 25 \) μm.

The objects that fulfill these requirements such that they are suited for our purpose belong to the objects of the category 2. SEc as defined by Kraemer et al. (2002), which is essentially defined as satisfying the properties of items 1–3. Our set of objects selected from the database of Sloan et al. (2003) is shown in Table 5 together with some basic parameters of the star and the outflow. Completely reduced ISO-spectra for these four stars, as used in Verhoelst et al. (2009), were kindly provided to us by S. Hony.

We fit the MIR spectral data of these four test objects with calculated spectra from a model for an optically thin circumstellar dust shell. The properties of the dust shell including the dust mixture are determined by an optimization procedure where we vary the parameters of the problem such as to obtain the best possible fit between observed and synthetic spectrum.

### 5.2. Model Assumptions

We do not model in this study the formation of dust in the stellar outflow and the acceleration of the outflow by radiation pressure on the dust particles and subsequent momentum transfer from dust to gas by frictional coupling. Instead, we follow the practice of most other laboratory studies that compare their results with observed stellar spectra and assume a spherically symmetric dust density distribution around the star and instantaneous condensation of dust when the dust temperature drops below a given condensation temperature. For optically thin dust shells, this simple model is not as unrealistic as it looks at a first glance, either, because the details of the spatial distribution of the dust are of minor importance (see the Appendix).

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**Table 5**

The Sample of Supergiants and Their Basic Data

| Name | Spectral Type | Variable Type | Period (day) | \( T_{eff} \) (K) | \( L^{*} \) (\( L_\odot \)) | \( M_{gas}^{\infty} \) (\( M_\odot \) a\(^{-1}\)) | \( \gamma_{exp} \) (km s\(^{-1}\)) | Distance (pc) | \( A_V \) |
|------|--------------|---------------|--------------|-----------------|-----------------|-----------------|-----------------|--------------|-----|
| \( \mu \) Cep | M2Ia | SRc | 730 | 3700 | \( 3.4 \times 10^{5} \) | \( 5.0 \times 10^{-6} \) | 20 | 870 | 2.01 |
| RW Cyg | M3lab | SRc | 550 | 3600 | \( 1.45 \times 10^{5} \) | \( 3.2 \times 10^{-6} \) | 23 | 1320 | 4.49 |
| W Per | M3lab | SRc | 485 | 3550 | \( 5.5 \times 10^{4} \) | \( 2.1 \times 10^{-6} \) | 16 | 1900 | 4.03 |
| RS Per | M4lab | SRc | 245 | 3550 | \( 1.4 \times 10^{5} \) | \( 2.0 \times 10^{-6} \) | 20 | 2400 | 2.63 |

**Notes.**

\( ^{a} \) Taken from SIMBAD database.
\( ^{b} \) Levesque et al. (2005).
\( ^{c} \) Mauron & Josselin (2011).
\( ^{d} \) Jones et al. (2012).
are the result of agglomeration of corundum grains that condense earlier than silicates in a stellar outflow, which later become overgrown by silicate material as the temperature drops in the outflow, or they are the result of agglomeration of corundum grains and silicate grains. To model the opacity, we have to include corundum grains either as a separate dust component, or as inclusions within silicate grains, or in both variants. Practically, we found that including the corundum only in the form of a separate dust component resulted in slightly better fits than also including silicate particles with corundum inclusions. The difference is, however, only marginal such that we cannot clearly distinguish between the possible cases on the basis of spectral modeling alone. We consider in our modeling corundum and amorphous silicate as separate dust components.

Furthermore, metallic iron particles seem to be present as inclusions in the silicate grains. They are required to explain the NIR opacity of real circumstellar dust (Ossenkopf et al. 1992) and the elemental composition of presolar silicate grains (see Section 2). The contribution of such inclusions to the opacity of the composed particles is low in the diagnostically important spectral region at wavelengths longer than 9 \( \mu \)m, and they cause only an almost constant upward shift of dust opacity in this region that cannot be separated from the effect of a slight increase in silicate dust abundance. The main effect of these iron inclusions is their strong contribution to the optical-to-NIR dust opacity, which rules the dust temperature. This effect of the iron inclusions becomes important only for an iron-free silicate matrix, however. If the silicate material already contains a significant iron content, the influence of possible iron metal inclusions becomes moderate. We found that we cannot clearly distinguish from the quality of fit between models with and without iron grains because of a degeneracy between the a wavelength range where the silicate opacity is very low, such that it contributes neither to dust heating nor to emission from dust. This choice is somewhat arbitrary, but it influences only the calculated radius of the inner edge of the dust shell for a given condensation temperature, but not the infrared model spectrum at given condensation temperature and dust mass.

In principle, it would be desirable to use in the fitting process only the amorphous silicate dust material studied in this paper since we are interested in the first place whether it is possible to already obtain reasonable fits with these materials alone. However, we also find in most oxygen-rich objects a non-negligible contribution to emission from an additional dust component, which is identified with amorphous corundum (Onaka et al. 1989a, 1989b; Little-Marenin & Little 1990; Jones et al. 2014). Unfortunately, the emission from corundum contributes to the spectral range between 10 and 15 \( \mu \)m is such that it interferes with the silicate dust emission. In particular, it fills up the deep absorption minimum between the two silicate features. For this reason, we include amorphous corundum as a dust component in the modeling.

Optical constants for the corundum for \( \lambda \geq 7.8 \mu \)m are taken from Begemann et al. (1997) (the constants for porous amorphous aluminium oxide). For shorter wavelengths they are augmented by data from Palik (1985).

Interferometric observations have shown that the corundum dust seems to be formed much closer to the star than the silicate dust (e.g., Danchi et al. 1994; Karovska et al. 2013; Wittkowski et al. 2015, and references therein), as could be expected because of its much higher thermal stability (Salpeter 1977). The grains may then either be heterogeneously composed of corundum grains that condense earlier than silicates in a stellar outflow, which later become overgrown by silicate material as the temperature drops in the outflow, or they are the result of agglomeration of corundum grains and silicate grains. To model the opacity, we have to include corundum grains either as a separate dust component, or as inclusions within silicate grains, or in both variants. Practically, we found that including the corundum only in the form of a separate dust component resulted in slightly better fits than also including silicate particles with corundum inclusions. The difference is, however, only marginal such that we cannot clearly distinguish between the possible cases on the basis of spectral modeling alone. We consider in our modeling corundum and amorphous silicate as separate dust components.

The main purpose is to check how well the amorphous silicates for which we determined optical constants can reproduce the observed MIR emission spectrum of our test stars. The amorphous silicate dust generally dominates the IR emission from circumstellar dust in the 9–20 \( \mu \)m spectral region where the diagnostically important resonances from stretching vibrations of the Si-O bond (~10 \( \mu \)m) and O-Si-O bending (~18 \( \mu \)m) vibrations are located as well. To fit the synthetic method, we therefore use the spectral region between 9 and 25 \( \mu \)m. Furthermore, we consider in the fitting procedure the spectral region between 3 and 4.5 \( \mu \)m because (i) in this range the shape of the observed spectrum shows no suspiciously strong molecular absorption bands that render it difficult to find the level of stellar continuum emission, and (ii) the absorption of silicate dust in this range is very low such that we observe the unattenuated stellar radiation. This NIR spectral range helps to fix the baseline of zero dust emission.

Figure 8 shows the mass-absorption coefficients calculated for the four different amorphous silicate materials discussed in Section 4.1. To average over particle sizes, a MRN distribution between a minimum diameter of 10 nm and a maximum of 500 nm in 10 bins is used for all species. In applications to circumstellar dust shells, it usually turns out that the assumption of spherical grains is not suited to reproduce observed band profiles. These are much better reproduced by using, e.g., a continuous distribution of ellipsoids (CDE) (Bohren & Huffman 1983), which is therefore used in our calculations for all species, except for iron, for which we use the Mie theory. We compare the absorption coefficient calculated for our amorphous silicates with absorption coefficients using data for optical constants of amorphous silicates from Dorschner et al. (1995) and Jäger et al. (2003), which are synthesized by methods different from ours.

To calculate dust temperatures, we need to also know the optical properties in the range \( \lambda < 2 \mu \)m, where we have no measured data for our silicate materials. For the purpose of calculating the dust temperature, we use in the 0.2 \( \leq \lambda < 4 \mu \)m wavelength range the \( x = 0.5 \) data from Dorschner et al. (1995). The cut at \( \lambda = 4 \mu \)m is chosen such that it is located in

\[ \frac{x_{\text{abs}}}{x_{\text{abs}}(\lambda = 4 \mu \text{m})} \]

\[ \lambda_{\text{[\mu m]}} \]

\[ \begin{array}{ll}
10^1 & 10^2 \\
10^3 & 10^4 \\
\end{array} \]

**Figure 8.** Mass absorption coefficient \( x_{\text{abs}}(\lambda) \) for an ensemble of spherical silicate particles with composition Si-\( \text{flm1} \) (black line), Si-\( \text{flm2} \) (red line), Si-\( \text{flm3} \) (green line), and Si-\( \text{flm4} \) (blue line; all shown as full lines). For comparison, the \( x = 0.5 \) data from (Dorschner et al. 1995; dotted dillac line) and the \( x = 0.7 \) (dashed gray line) and \( x = 1.0 \) (dash–dotted cyan line) data from Jäger et al. (2003) are shown.
content of iron inclusions and the amount of dust that is present. We therefore neglect iron inclusions.

Another possibility is that iron forms as a separate dust component. This follows from considerations on thermal stability (e.g., Salpeter 1977; Gail & Sedlmayr 1999) and has been found to be a likely contributor to opacity in circumstellar dust shell in the $\lambda < 8 \mu m$ spectral region by Kemper et al. (2002) and Verhoelst et al. (2009). This case differs from the case of iron inclusions in so far as inclusions are thermally coupled to the silicate matrix, while separate iron particles have their own temperature distribution. In effect, this results in significant differences in the calculated model spectra compared to the case of iron inclusions. We also consider iron grains in our modeling. The optical constants are taken from Ordal et al. (1988).

5.3. Individual Fits

We fit the MIR spectral data of the four test objects with calculated spectra from circumstellar dust shell models (also called synthetic spectra) by an optimization procedure described in Appendix.

The stellar luminosities and effective temperatures of the objects are taken from the literature; the corresponding values and references are given in Table 5. No dereddening was finally performed for the ISO-spectra because it turned out that the corresponding correction is very small in the wavelength range of interest for all our objects.

The dust temperature in the models drops below 100 K at a distance of about $10^3$ stellar radii. Regions farther out do not contribute significantly to the infrared spectral region $\lambda < 30 \mu m$ we used in our comparison of observed with synthetic model spectra. The outer radius of the dust shell therefore cannot be pinned down by our model optimization; it was set to a fixed value of $10^4$ stellar radii in all cases.

5.3.1. Fits with Two Dust Components

In the following models, we consider two dust species, amorphous silicate particles and corundum particles, as opacity sources.

**W Per:** A fit to W Per was tried first using the optical constants of Si-film1, Si-film2, and Si-film3 for the silicate component. The results are shown in Figure 9. The iron-free Si-film1 can be excluded because the resonance at $\sim 10 \mu m$ does not fit the data. The optical data of Si-film2 result in a good fit for the resonance at $\sim 18 \mu m$ and a reasonable fit to the peak and the long-wavelength flank of the $\sim 10 \mu m$ resonance. The short-wavelength flank is too extended, however. The dust model Si-film3 gives a low-quality fit, but it deviates from the ISO data just in the opposite direction than the Si-film2 model. This means that an amorphous silicate of the type studied in this paper with an intermediate iron content between Si-film2 and Si-film3 would fit the observed spectral energy distribution.

A linear interpolation of the data for Si-film2 and Si-film3 using a fraction of 0.6 of Si-film2 and a fraction of 0.4 of Si-film3 results in an rather good fit between the ISO data and the corresponding synthetic spectrum. The corresponding model is shown in Figure 10. The correspondence between observed spectrum and optimized synthetic spectrum appears almost perfect, except in the range between about 6–8 $\mu m$. In particular, the two silicate bands are well reproduced by the model.

We discuss the missing flux shortward of 8 $\mu m$ below.

**RW Cyg:** In the case of RW Cyg, the observed stellar spectrum is embraced by the optimized models using the data of Si-film2 or Si-film3. A model using a weighted mean of the opacity data with a fraction of 0.4 from Si-film2 and 0.6 from Si-film3 results in a model that fits the observational data well. This model is shown in Figure 10.

**RS Per:** Although the observed stellar spectrum is again embraced by the optimized models using the data of Si-film2 or
There is a noticeable discrepancy in the model spectrum slightly shortward of the peak in the observed spectrum, and here there is also a noticeable discrepancy in the model flux at wavelengths longward of 20 μm.

### 5.3.2. Fits with Three Dust Components

In the following models, metallic iron as a separate dust component is added to the amorphous silicate and corundum particles in order to provide opacity in the λ < 8 μm spectral region where the silicate and corundum dust components are transparent. For the optimization we also included the wavelength range between 5.5 and 7.5 μm in the calculation of χ² because iron dust is the sole source of the emission from the dust shell in this region.

**W Per:** The addition of a third dust component changes the relative abundances of amorphous silicate and corundum, and additionally, the iron content of the amorphous silicate dust required to obtain a good fit. An interpolated dielectric function using a fraction of 0.5 for Si-film2 and Si-film3 results in a close fit between observed and synthetic spectrum. The resulting model spectrum is shown in Figure 11. Now the flux deficit in the 5–8 μm spectral region of the two-component models seen in Figure 10 has completely disappeared. The remaining slight flux excesses of the synthetic spectrum over the observed spectrum at around 4.8, 6.8, and 8 μm are obviously due to molecular absorption bands of CO, H2O, and SiO, respectively. The stretching and bending modes at 10 and 18 μm of the amorphous silicate are well reproduced by the model spectrum.

**RW Cyg:** In this case, a linear interpolation of the optical constants of Si-film2 and Si-film3 with weights 0.2 and 0.8, respectively, is required for a best fit. The resulting model spectrum is shown in Figure 11. The correspondence between observed spectrum and model spectrum is very close.

**RS Per:** In this case, a linear interpolation of the optical constants of Si-film2 and Si-film3 with weights 0.3 and 0.7, respectively, is required for a best fit. The resulting model spectrum is shown in Figure 11. Again, the correspondence between observed spectrum and model spectrum is good in the range between about 9–20 μm. At longer wavelengths, the model flux is slightly lower than the stellar flux.

**μ Cep:** A similar situation is encountered for μ Cep. A compromise here is to use a weighted mean of the opacity data using a fraction of 0.8 from Si-film2 and 0.2 from Si-film3. The resulting model spectrum is shown in Figure 10. Again, the peak position of the 18 μm band in the model appears at a position slightly shortward of the peak in the observations, and here there is also a noticeable discrepancy in the model flux at wavelengths longward of 20 μm.

### 5.3.3. The 10 μm Silicate Band

The 10 μm band often attracts particular attention in discussions of the quality of the fit between radiative transfer...
models and observed spectra, therefore we consider this feature in more detail.

Figure 12 shows details of the fits between observed and synthetic spectra of our comparison stars for the wavelength range around the 10 μm band corresponding to the Si-O stretching vibrations. The models using the optical data of the set of amorphous silicates synthesized and investigated by us result in fits that are able to reproduce the width, peak position, and general shape of this silicate band with considerable accuracy when they are combined with the dust materials corundum and iron. They also reproduce the change in slope of the long-wavelength flank at ~12 μm, which seems to be present in most supergiants (Speck et al. 2000). In our model this particular detail results from the weak Si-O-Si symmetric stretching band in the amorphous silicate absorption in this region and the broad maximum of the corundum absorption. This weak silicate feature is lacking in other data sets for silicate dust absorption because the corresponding vibration mode cannot be easily separated from the background because its absorption strength is much weaker than that of the asymmetric band (see Sections 3.3 and 4.2).

The fits are not perfect, however, and the observed spectra show more structure than the calculated spectra, which may be associated with the presence of some minor additional dust components. It is not necessary, however, to include other minerals than the components used by us to explain the main structure of the observed 10 μm band. In particular, it is not necessary to invoke substantial amounts of Ca-Al-silicates (melilite) to fit the observed shape of the profile, as in Verhoelst et al. (2009). Such a compound is unlikely to exist as widespread dust component because if it were, it would be found in meteorites as presolar dust grains like other aluminum oxide particles, which is not the case.4 The overall fit is, however, substantially improved when an iron dust component is included, as has been found in Verhoelst et al. (2009).

The quality of the fit of the 10 μm feature is nearly the same for the models with or without iron dust particles. The properties of the model with respect to dust content or iron content of the silicate material are slightly changed by including or omitting an iron dust component (cf. Table 6), but in both cases, a parameter combination can be found that

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4 This argument would fail, however, if most of the dust produced by massive supergiants were destroyed if it is overrun by the final supernova blast wave.
reproduces the 10 $\mu$m feature. The presence of iron dust is inconsequential in this respect.

5.3.4. The 18 $\mu$m Silicate Band

Figure 13 shows details of the fits between observed and synthetic spectra of our comparison stars for the wavelength range around the 18 $\mu$m band corresponding to the Si-O stretching vibrations. The quality of the data for the observed flux is not as good for the feature at 10 $\mu$m, but the band profiles are clearly marked, and this second important emission band of silicate minerals is also reasonably well fit by the three-component mixture of our silicate materials augmented with corundum and iron, although slightly worse than the 10 $\mu$m band.

One problem is, however, that the model flux in the spectral range $\lambda > 20$ $\mu$m is slightly but systematically below that of the stellar spectrum (cf. Figures 10 and 11) when most weight is given to the peaks by the optimizing procedure. One reason for this deficit may be that a value of $p = 2$ as assumed in our models for the density variation $\rho \propto r^{-p}$ is unrealistic because of, e.g., variable mass-loss rate or outflow velocity. Including $p$ as an additional variable in the optimization procedure, however, returns a value of $p \approx 2.02$ and only slightly improves the situation. The flux deficit seems to be related to a deficit of the extinction coefficient of the dust mixture at long wavelength for at least one of the three dust components.

5.3.5. Discussion

From these results we conclude that it is possible to completely explain the silicate dust emission of supergiants by the presence of some type of amorphous silicate material with a non-standard stoichiometry corresponding to a composition between olivine and pyroxene. We only have to add corundum and iron dust particles in order to supply the required opacity in the range between the two silicate bands and for $\lambda < 8$ $\mu$m to account for the observed emission from the dust shell in these regions, which cannot result from the silicate dust. Experiments with additional dust components (e.g., spinel or iron oxide) resulted in low abundances that were assigned to such additional components by the optimization algorithm.

The formation of a non-stoichiometric amorphous silicate material can be expected under the conditions of an outflow from a supergiant. Because of the high stellar atmospheric temperature, the silicate dust condensation commences at considerable distances from the star when the equilibrium temperatures of the dust drop sufficiently low for the dust to become stable against vaporization. In fact, the temperature of the inner edge of the dust shell, $T_i$, in our radiative transfer model is substantially lower than an estimated vaporization temperature of 1100 K, except for one case (RS Per, the model with three dust components, see Table 6), where it is close to the limit. This means that the dust is formed under conditions that resemble the vapor deposition on a cold substrate to some extent, where growth species attached to the surface almost immediately become immobile at the surface of the condensed phase.

For the type of dust shell models calculated by us it remains open, however, whether a low temperature at the inner edge, $T_i$, well below the stability limit of silicates as found in most of our models results (i) from slow particle growth in the continuously diluting and cooling gas, or (ii) from an onset of silicate dust condensation at these low temperatures. In the first case, silicate dust formation commences at higher temperature, but dust grows only slowly in the outflowing gas, such that the dust density peaks at large distances, i.e., low temperature, when sufficient dust has formed for a rapid acceleration of the dusty gas. This then results in a rapid density decrease with increasing distance from the star. In the second case, we possibly have an onset of dust formation at rather low temperatures (e.g., Gail et al. 2013). More detailed models considering dust particle growth are required to choose one of these possibilities, which is beyond the scope of this paper, however.

For all our sample stars a considerable iron content of the silicate material is required to obtain a satisfactory spectrum fit. The iron content is determined by interpolation between the Fe/(Fe + Mg) ratio of our four amorphous silicate samples. The fit quality of the peak position of the two silicate bands and of the short-wavelengths flank of the 10 $\mu$m feature allows us to fix the relative contribution of the two components between...
Table 7: Estimated Dust Mass-loss Rates

| Object | Silicate | Corundum | Iron | 
|--------|----------|----------|------|
|        | $M_{\text{dust}}$ | $f$ | $M_{\text{dust}}$ | $f$ | $M_{\text{dust}}$ | $f$ | $M_{\text{gas}}$ |
| W Per  | 18.3     | 1.6     | 9.0  | 14.3 | 40.3  | 10.9 | 2100 |
| RW Cyg | 10.0     | 0.57    | 7.4  | 7.7  | 10.2  | 1.8  | 3200 |
| RS Per  | 1.4      | 0.12    | 1.3  | 2.2  | 4.0   | 1.1  | 2000 |
| $\mu$ Cep | 2.3     | 0.083   | 1.3  | 0.84 | 9.1   | 1.03 | 5000 |

Note. $M_{\text{dust}}$ is the mass-loss rate of the dust species in units of $10^{-7} M_\odot$ yr$^{-1}$. $f$ is the estimated fraction of the key element for dust formation (Si for silicates, Al for corundum, Fe for iron) that is condensed into dust.

which we have to interpolate sufficiently well. It appears desirable, however, to also determine optical data for iron contents intermediate between that of our four samples. This would enable a more accurate determination of the iron content from our admittedly rather coarse grid.

A fit of the spectra with the iron-free silicate Si-film1 and also with the iron-free silicate of Jäger et al. (2003) was not possible. It remains to check whether this is a peculiarity of our selected sample or if this looks different when more objects are studied.

Table 6 shows the dust masses required for a best fit in the range from the inner edge $R_i$ where a dust species condenses to the outer radius $R_o$ at $10^5 R_o$ assumed in the model calculation. It would be more instructive to convert this into a dust mass-loss rate or into the fraction of the dust-forming elements condensed into dust. Unfortunately, this requires knowledge of the velocity structure of the stellar wind. The assumed variation $\propto r^{-2}$ of the density for the model calculation requires a constant velocity, which is not realistic since the radiation pressure on dust increasingly accelerates the outflow with progressing dust condensation. The simplification of a constant velocity is acceptable to calculate the dust mass in optically thin shells, but it may be a problem when we determine dust mass-loss rates. This is particularly a problem for the radius range where corundum but no other dust species exists, because in this range the velocity may be significantly lower than in the range where the dominant dust species exist, i.e., silicates and possibly iron, and where they accelerate the dusty gas. We cannot simply use the observed outflow velocity as listed in Table 5 either because this refers to the asymptotic value of the velocity at large distances. In order to give a crude estimate despite the uncertainty of this approach, we assume an average velocity in the dust condensation zone of $v = 10 \text{ km s}^{-1}$ for all stars and species (typically, one half of the final velocity) and calculate a dust mass-loss rate from $M_{\text{dust}} = M_{\text{dust}} v/(R_o - R_i)$. The result is shown in Table 7. This can be compared to the gas mass-loss rate, which shows that as expected, the dust mass-loss rate is a fraction of about $10^{-2}$ to $10^{-3}$ of the gas mass-loss rate. The accuracy of the estimated dust mass-loss rate is low, however, because the value of $M_{\text{gas}}$ is only known for $\mu$ Cep with some accuracy; in the other cases, the values are only rough estimates.

We can even proceed and calculate from $f = M_{\text{dust}}/(A \epsilon M_{\text{gas}})$ a condensation fraction $f$ of the key elements (Si for silicates, Al for corundum, Fe for iron) for condensation into dust, where $A$ is the atomic weight of the chemical formula unit of the solid and $\epsilon$ is the element abundance of the key element. The results are also shown in Table 7. In principle, the fraction $f$ should satisfy $f < 1$. This is satisfied for $\mu$ Cep, where the value of $M_{\text{gas}}$ is accurately known. In the other cases, we partly obtain distinctly higher values. For corundum dust, this may result from a lower-than-assumed value of $v$ in the inner range of the dust shell where only corundum dust exists, as mentioned above. For iron, it may result from the fact that we used optical data for pure iron, while iron in space is always a nickel-iron alloy that may have different extinction properties. Finally, the estimated dust mass-loss rates as derived by Mauron & Josselin (2011) from the formula of Jura & Kleinmann (1990) may be systematically too low. A more accurate modeling of the dust shell considering the growth of grains and the outflow dynamics is required to determine the condensation degrees for the dust species.

6. Concluding Remarks

This paper studied the optical properties of iron-bearing amorphous silicates with oxygen-to-silicon ratios deviating from the stoichiometry of the usually considered silicates with olivine- and pyroxene-like compositions. We showed that for the four selected supergiants we used as test objects, the observed mid-infrared emission as determined by ISO may be well explained with the presence of this type of material.

By the method of vapor deposition on a cold substrate, we produced thin films of truly amorphous silicates with different iron and magnesium contents and non-standard oxygen-to-silicon ratios that were within the range of values observed for presolar grains. The high degree of homogeneity and uniform thickness of the produced films achieved by our experimental method allowed an accurate determination of the optical constants of the material. We reported here on our results for four amorphous magnesium-iron silicates with non-standard stoichiometric composition: for the two end-member compositions of pure magnesium silicate and pure iron silicate, and for two intermediate values of the iron contents with magnesium-rich and iron-rich composition.

We determined new optical constants for the four materials by IR spectroscopic transmittance measurements and by ellipsometry. From the combined data, a model dielectric function was constructed that can be used to analyze circumstellar emission spectra.

The new data were applied to a sample of four selected supergiants that are optically thin at $\lambda = 10 \mu$m, but show substantial infrared excess emission. We aimed to determine how well we can fit observed ISO-spectra for these stars with synthetic spectra calculated for emission from a circumstellar dust shell enshrouding these stars. Since real stars generally seem to also form aluminium oxide dust when they form silicate dust, we included this dust in our model calculation. We also included a separate iron dust component, because this dust also seems to be present. The dust mass of each species and the temperature at the inner edge of the respective dust shell were determined from an automated fit between the synthetic spectrum from the radiative transfer model and the observations. To obtain a good fit, we interpolated with respect to the Fe/(Mg+Fe) ratio between the four data sets. We found that

1. it is possible to obtain a good fit between model and observation with the type of amorphous silicate with non-standard stoichiometry studied in this paper;
2. a good fit requires a significant iron content of the silicate material; and
3. the 10 and 18 μm features can be fit simultaneously with our non-stoichiometric amorphous iron-bearing silicates.

Although the obtained fits are not perfect, they are so close that the remaining deviations appear to be more likely due to shortcomings in the modeling (e.g., the assumption of CDE) than to not completely realistic optical constants. In particular, it is not necessary to invoke additional dust species to reproduce the peak wavelengths and strengths of the two broad 10 and 18 μm amorphous silicate features.

Metallic iron dust particles also seem to be formed in the outflow, which form separate particles not in physical contact with the silicate dust grains. They are required to explain the observed mid-infrared excess between λ = 5.5 μm and λ = 8 μm, but a reasonable fit for the spectral region λ > 9 μm dominated by the silicate emission can be obtained without such a component when we leave the question on the origin of the flux excess at λ < 8 μm open.

For a future analysis of much broader samples of stars, it would be desirable to have the optical data for a much finer grid of Fe/(Mg+Fe) ratios available. The corresponding thin films are already produced and the raw data have already been acquired for this.

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**Software:** SCOUT (Theiss 2011), PIKAIA (Charbonneau 1995).

**Appendix**

**Fitting Synthetic Spectra**

**A.1. Model Assumptions**

The synthetic spectrum of a dust shell is calculated by taking advantage of the assumption of an optically thin dust shell. This allows a very rapid calculation of a model spectrum, and this in turn enables creating large sets of such models to obtain optimized fits between model spectra and observations. The model is calculated as follows.

1. For the emission from the central star, we assume a blackbody spectral energy distribution with effective temperature \( T_{eff} \). Alternatively, a read-in spectral energy distribution can be used.

2. The dust temperature \( T_d \) is determined from radiative equilibrium between absorption and emission of a dust grain

\[
\int_0^\infty \kappa_{\nu}^{(abs)} B_{\nu}(T_{d}) W(\nu) e^{-\tau_{\nu}} d\nu = \int_0^\infty \kappa_{\nu}^{(abs)} B_{\nu}(T_{eff}) W(\nu) d\nu,
\]

where \( B_{\nu} \) is the Kirchhoff–Planck function, \( \kappa_{\nu}^{(abs)} \) is the mass-absorption coefficient of the dust material, and \( W(\nu) \) is the geometric dilution factor of the stellar radiation field

\[
W = \frac{1}{2} \left( 1 - \sqrt{1 - \frac{R_s^2}{r^2}} \right),
\]

where \( R_s \) is the stellar radius. Each dust species has its own dust temperature \( T_d \). The quantity

\[
\tau_{\nu} = \sum_j \int_{R_s}^r \varrho_j \left( \kappa_{\nu}^{(abs)} + \kappa_{\nu}^{(scat)} \right) d\nu
\]

is the optical depth between the stellar surface and the radial distance \( r \) of the dust grain from the stellar center. The density \( \varrho_j \) is the mass density of the dust species \( j \), and the summation is over all dust species. Our assumption of an optical thin dust shell mainly refers to the mid- to FIR wavelength for which we compare the emission from the dust shell with observations. The heating of the dust grains is due to absorption of stellar radiation which peaks around 1...1.5 μm. Since the extinction by dust grains strongly increases from the near-infrared to the ultraviolet, the dust shell may be optically thin in the mid- to FIR wavelength even if its optically thickness is not small in the optical spectral region. For this reason, we retain the factor \( \exp(-\tau_{\nu}) \) despite our assumption of an optically thin dust shell.

3. For each dust species it is assumed that the dust is spherically symmetrically distributed around a central star and extends from some inner radius \( R_i \) to an outer radius \( R_o \). The radial distribution of the dust density \( \varrho \) is assumed to follow a power law \( r^{-p} \), where \( p \) is generally assumed to equal \( p = 2 \), which corresponds to a stellar wind with constant outflow velocity. The inner radius, \( R_i \), is determined such that the dust temperature of the species takes a prescribed value \( T_c \) at this radius. The outer radius, \( R_o \), is prescribed.

4. The observed spectral energy flux from the object observed at Earth is

\[
F_{\nu} = e^{-\tau_{\nu}^{ISM}} \frac{4\pi}{D^2} \left\{ \frac{1}{4} B_{\nu}(T_{eff}) e^{-\tau_{\nu}} R_s^2 \right. \\
+ \sum_j \int_{R_i}^{R_o} B_{\nu}(T_d) \varrho_j \kappa_{\nu}^{(abs)} r^2 \, dr \left. \right\},
\]

where \( D \) is the distance of the object from Earth and \( \tau_{\nu}^{ISM} \) the optical depth of the ISM along the sightline. The first term in curly brackets is the contribution from the star and the second term is the contribution of the dust shell.

For optically thin dust shells, the dust temperature distribution calculated from Equation (7) is spherically symmetric even if the dust distribution is not. Therefore we introduced in the emission term spherical coordinates. More generally, the corresponding integral is a volume integral

\[
\int B_{\nu}(T_{d}) \varrho_j \kappa_{\nu}^{(abs)} \, dV,
\]

where we may decompose the integration domain into spherical shells and perform the angular integrations over each shell separately. Then we can write the volume integral equally well in terms of the average mass densities of the shells. Hence, we have to interpret \( \varrho \) in Equation (10) as the mass density averaged over
concentric shells around the star. In this sense, Equation (10) also holds when the real dust distribution is not strictly spherically symmetric.

5. The model allows us to consider an arbitrary number of dust species. The mass absorption and scattering coefficients are calculated from the complex index of refraction. For inhomogeneously composed particles, an effective complex index of refraction according to the Bruggeman mixing rule (cf. Berryman 1995) can be calculated. The calculation can be made for either spherical particles (Mie theory) or for small ellipsoidal particles (Bohren & Huffman 1983) with a numerically specified distribution of axis ratios and radii, for a continuous distribution of ellipsoids (CDE, see Bohren & Huffman 1983), or for small cubes (Fuchs 1975).

A.2. Model Parameter

In order to calculate a model for the spectral energy distribution of a given object with observed infrared spectrum, we have to specify the luminosity $L$ and effective temperature $T_{\text{eff}}$ of the star. The stellar radius follows from the standard relation $4\pi R_\star^2 \sigma T^{4}_{\text{eff}} = L$. Furthermore, we have to specify the dust species considered in the model, the corresponding optical properties, and the particle shape and size distribution. For all dust species, $\kappa^{\text{abs}}_\nu$ is calculated at the specified wavelength grid. For the dust distributions of all species $j$, we fix the power $p$, the outer radius of the dust shell, $R_o$, and the total dust masses, $M_j$, and condensation temperatures, $T_{j,c}$, of the dust species.

A.3. Model Calculation

For a given set of parameters, the radial variation of dust temperature for each species is calculated according to Equation (7) for a small set of assumed values for $R_o$, and the value of $R_o$ corresponding to the specified value of $T_{j,c}$ is determined by backward interpolation. Then the dust temperatures for $r > R_o$ are calculated, and the spectral energy distribution is calculated according to Equation (10).

A.4. Optimization

For given dust properties, a model depends on the two parameters $L$ and $T_{\text{eff}}$ and on the $2J$ parameters $M_j$ and $T_{j,c}$, where $J$ is the number of dust species. The parameters $L$ and $T_{\text{eff}}$ are derived from astronomical observations and are given quantities for an object. The parameters $M_j$ and $T_{j,c}$ of the dust shell are unknown and have to be determined by fitting the observed spectrum with the model spectrum.

The goodness-of-fit between the synthetic and the observed spectrum is checked by calculating the quality function

$$\chi^2 = \sum_i \left( \frac{N_i^{\text{obs}} - N_i^{\text{calc}}}{N_i^{\text{calc}}} \right)^2. \quad (11)$$

To calculate $\chi^2$, not all frequency points used to calculate the spectrum are taken into account, but only those where no strong molecular features from the underlying star are seen in the observed spectrum. The quantity $N_i$ is a normalization factor that accounts for the circumstance that the distance $D$ is usually not accurately known, such that to enable a comparison of the two spectra, we have to apply a shift to one of them to place them on top of each other. This factor is determined such as to minimize $\chi^2$ as the solution of

$$\frac{\partial \chi^2}{\partial N} = 0 \quad (12)$$

for $N$. The value of $\chi^2$ calculated with this normalization is taken as the quality function. Then we vary the $2J$ parameter dust masses $M_j$ and condensation temperatures $T_{j,c}$ and search for the parameter combination for which $\chi^2$ takes the lowest value. This parameter set is then considered as the best-fit model for the dust shell.

Such nonlinear minimization problems are notoriously difficult to solve. Here the minimization of $\chi^2$ was made by applying a genetic algorithm that usually allows an efficient minimum search even if many parameters are involved. We used the special variant of such an algorithm described in Charbonneau (1995) because this worked quite well in other projects where we used this method.

The genetic algorithm operates with discrete values of the model parameters. The optimized parameter set resulting from this method is therefore slightly off from the true minimum. Instead of improving the accuracy of the genetic algorithm by using a finer resolution of the variable space, we perform a final refinement step by minimization with a gradient method. This converges rapidly because we start already from a position in variable space that is very close to the searched-for minimum.

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