Crystalline Silicates [*]

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Abstract. One of the big surprises of the Infrared Space Observatory (ISO) has been the discovery of crystalline silicates outside our own Solar system. It was generally assumed before that all cosmic silicates in space were of amorphous structure. Thanks to ISO we know now that crystalline silicates are ubiquitous in the Galaxy (except for the diffuse ISM) and sometimes even in very large quantities ($>$ 50% of the small dust particles). The evolution of the crystalline silicates is still not completely clarified, but the combination of theoretical modelling and observations have already shed light on their life-cycle. The absence of crystalline silicates in the diffuse ISM provides us with information about the dust amorphization rate in the ISM.

Keywords: crystalline silicates, infrared astronomy

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1. Introduction

Before ISO (Kessler et al., 1996; Kessler et al., 2003) opened the mid- and far-infrared range for high-resolution spectroscopy, it was generally assumed that cosmic dust silicates were of amorphous structure. The crystalline silicates, the highly ordered counterparts of the amorphous silicates, were only known to be present on earth, in the solar system in comets (Hanner et al., 1994; Hanner, 1996), Interplanetary Dust Particles (IDPs) (MacKinnon and Rietmeijer, 1987; Bradley et al., 1992) and in the dust disk of β-Pictoris (Knacke et al., 1993; Fajardo-Acosta and Knacke, 1995), also a crystalline olivine feature was reported in the polarized 10 μm spectrum of AFGL2591 (Aitken et al., 1988). Apart from the crystalline silicates in the IDP's, that were found with the aid of transmission electron microscopy and only later confirmed by infrared spectroscopy (Bradley et al., 1992), in all other cases the crystalline silicate features were found by infrared spectro(polari)metry around 10 μm.

With the present day knowledge it is relatively easy to understand why crystalline silicates were only discovered to be ubiquitous after ISO was

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operational. Before ISO was launched the primary MIR/FIR window for observations was around 10 μm. And although the crystalline silicates do have strong features in this area, they are in general overwhelmed by emission from the much more abundant and warmer amorphous silicates. Furthermore, most of the crystalline silicates have a (relatively) low temperature ($<$ 150K), which suppresses the intrinsically strong crystalline silicate features in the 10-micron region. Thanks to the extended wavelength range (up to 200 μm) of the spectrographs on board ISO, the composition of the cold ($<$ 150K) dust, which has the top of its SED at wavelengths above 15 micron, could be studied in detail for the first time. With ISO, crystalline silicates have been found around young stars (Waelkens et al., 1996), comets (Crovisier et al., 1997), and evolved stars (Waters et al., 1996), but not convincingly so in the interstellar medium. The presence of the crystalline silicates in the different galactic environments will be discussed in Section 2. The properties of the crystalline silicates will be discussed in Section 3. In Section 4 we will discuss the crystalline silicate (trans-)formation and destruction processes based on the ISO (and other astronomical) observations in comparison with laboratory measurements.

2. The ubiquitous presence of crystalline silicates

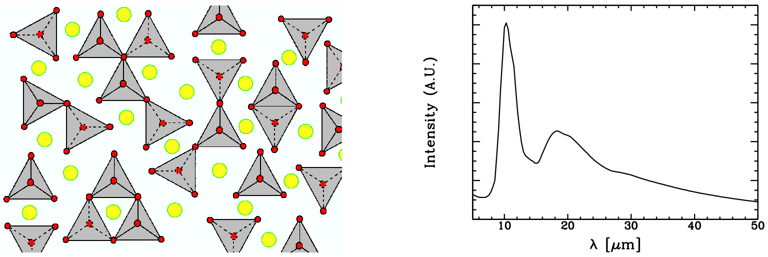
2.1. WHAT ARE SILICATES?

Silicates are the most common form of minerals in the solar system, and probably also beyond. Chemically, they consist of silica tetrahedras (SiO_4) which are combined with metal cations, such as $Mg2+$ or Fe^{2+} in a lattice structure. In ordered (crystalline) lattice structures, the tetrahedras can share their oxygen atoms with other tetrahedras to form different types of silicates: olivines: $(Mg,Fe,..)_2SiO_4$, pyroxenes: $(Mg,Fe,..)SiO_3$ or quartz: SiO_2. In case of unordered (amorphous) structures, the number of shared oxygen-atoms may vary for each silica-anion (see Figure 1). The reader is referred to for instance Klein & Hurlbut (1993) for more background reading on mineralogy.

Spectroscopically, all silicates, amorphous and crystalline alike, will show resonances around 10 and 20 μm in the mid-infrared, due to the Si-O stretching and the O-Si-O bending mode arising from the silica-tetrahedras. Alignment of the tetrahedras may cause sharp peaked resonances, whereas amorphous silicates will show a broad feature which can be seen as a blend of such sharp resonances. Crystalline silicates can also be distinguished from amorphous silicates due to the presence of lattice modes at $\lambda \gtrsim 25$ μm, see Figure 1.

The formation temperature determines whether a silicate grain becomes crystalline or amorphous. If silicates are formed above the glass temperature

Amorphous structure



Crystalline structure

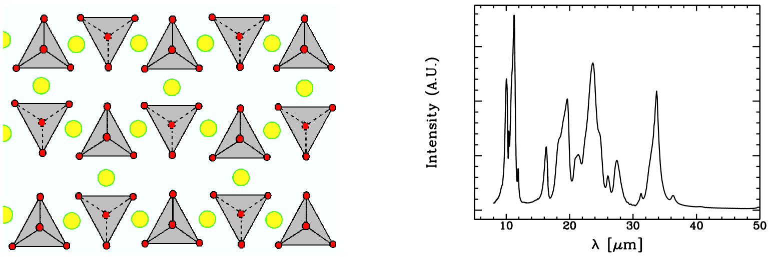


Figure 1. A possible atomic structure of a disordered (or amorphous) silicate and that of an ordered (or crystalline) silicate together with their typical infrared emission spectra. The tetrahedras are 4 oxygen atoms around a silicon atom and the big circles are metal atoms. Note the many sharp features in the crystalline silicate spectrum and the 2 broad bumps at 10 and 20 μm for the amorphous silicate spectrum.

($T_{\rm glass}$), then there is enough mobility in the silicate to from the crystalline, energetically most favourable, lattice structure. However, when the silicates condense at lower temperatures, such mobility is not present, and the grain solidifies in amorphous form. Amorphous grains can become crystalline by annealing (crystallization through heating) or vaporization and recondensation above the glass temperature. Hence, the presence of crystalline silicates traces the occurrence of high-energy processes. On the other hand, damage caused by cosmic ray hits or grain-grain collisions can amorphitize silicates.

2.2. OBSERVATIONAL INVENTORY

Crystalline silicates have been found around evolved stars with an oxygen-rich dusty outflow: AGB-stars, post-AGB stars and Planetary Nebulae (Wa-

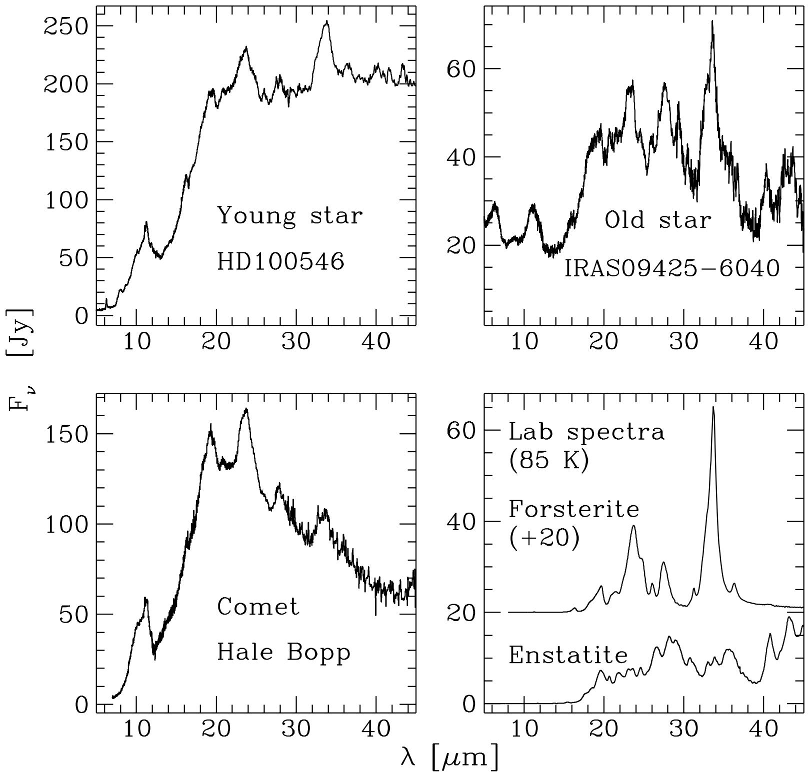


Figure 2. Crystalline silicates are detected in many different environments. These environments include young stars such as HD 100546 (upper left), evolved stars such as IRAS 09425-6040 (upper right) and also comet Hale-Bopp (lower left). A featureless dust continuum has been subtracted from the spectra to enhance the appearance of the crystalline silicates. For reference, laboratory spectra of the crystalline silicates enstatite and forsterite, multiplied with 85 K blackbodies, are shown in the lower right panel.

ters et al., 1996; Sylvester et al., 1999; Molster et al., 2001a; Molster et al., 2002b). Surprisingly however, there are also several examples of crystalline silicates being present around stars with a carbon-rich chemistry (e.g. Waters et al., 1998; Molster et al., 2001b). It is expected that in such cases, the crystalline silicates originate from (a) previous mass-loss episode(s), when the mantle of the star was still oxygen-rich.

The fraction of silicates that is in crystalline form is modest; using full radiative transfer calculations it is found that the typical abundance of crystalline silicates in the winds of low mass post-MS stars is of the order of 10% or less of the total silicate mass (Kemper et al., 2001). It should be noted that this number does depend on the laboratory spectra used. Using different sets of laboratory data, can make a difference in the abundance sometimes up to a factor 2. A simple model fit to the spectra reveals that enstatite is about 3 times as abundant as forsterite in these outflows (Molster et al., 2002c). The above mentioned values for the abundances are only derived for stars with a relatively high mass loss rate ($\dot{M} \gtrsim 10^{-5}\ M_\odot\ \mathrm{yr}^{-1}$). To date, there is no evidence for the presence of crystalline silicates around low mass-loss-rate AGB stars ($\dot{M} \lesssim 10^{-6}\ M_\odot\ \mathrm{yr}^{-1}$; (Waters et al., 1996; Cami et al., 1997; Sylvester et al., 1999)). It is well possible that this is a temperature effect. Kemper et al. (2001) show that the temperature difference between the crystalline and amorphous silicates will cause the emission from the crystalline silicates to be overwhelmed by the warm amorphous silicates in the optically thin dust shell around low mass-loss-rate stars. This temperature difference is caused by the difference in optical properties (see also Section 3).

Although most post-main-sequence stars have modest degrees of crystallinity, in some peculiar objects, likely as a result of binary interaction, the crystalline silicate abundance can be very high, up to 75% of the small grains (Molster et al., 2001b).

Despite the deposition of crystalline silicates into the interstellar medium, we do not have strong evidence for the presence of crystalline silicates in this environment. From the absorption profile in the direction of the galactic center an upper limit of about 0.2 ± 0.2% for the degree in crystallinity of silicates in the diffuse interstellar medium has been derived (Kemper et al., 2004). Crystalline silicates are suggested to be present in the dense ISM in Carina, by the detection of the 65 μm band ascribed to diopside ($CaMgSiO_3$; Onaka and Okada, 2003), although the intrinsically strong mid-infrared features are not detected. Cesarsky et al. (2000) suggest that several emission bands in the ISO spectra of the Orion bar may be due to crystalline silicates. We note however that the peak position, shape and width of the bands seen in Orion differ from those of crystalline silicates in other environments. Re-analysis of the ISO spectrum of this line-of-sight shows that there is no evidence for crystalline silicates in the Orion Bar (Kemper et al., *priv. comm.*).

The ISO data show that the abundance of crystalline silicates in Young Stellar Objects (YSOs) is higher than the upper limits that are established for the interstellar medium. The first Herbig Ae/Be star observed by ISO-SWS, HD 100546, shows a remarkably rich crystalline silicate spectrum (Waelkens et al., 1996; Malfait et al., 1998). A thorough analysis of the infrared spectrum of this star indicates that the crystalline silicates dominate in the 100-200 K temperature range (Bouwman et al., 2003). In this temperature range the crystalline silicates are the dominant small dust grains, even more abundant than the small amorphous silicates. As it later turned out, this star does not have a typical dust composition. Most other young stars show much more modest crystalline silicate abundances (Meeus et al., 2001), but still higher than the ISM. The relatively high abundance of crystalline silicates in the circumstellar dust shells and disks around young stars compared to the interstellar medium points to an in situ formation mechanism.

For most comets only ground-based spectra of the 10 micron region are available. This limits the determination of dust abundances. These abundances are very sensitive to the temperature of the different dust components, which is very difficult to determine from a small wavelength range (8-13 μm). Fortunately, while ISO was operational the comet Hale-Bopp passed by. The long wavelength coverage of ISO made it possible to constrain the temperature distribution of the individual dust components much better than before. Several authors have tried to determine the crystallinity of the silicates in Hale-Bopp (Wooden et al., 1999; Brucato et al., 1999; Bouwman et al., 2003). Depending on additional grain properties, such as grain size, shape and whether the grains are thermal contact with each other, the derived degree of crystallinity of the silicates ranges between more than 90% (Wooden et al., 1999) and about 7% (Bouwman et al., 2003) of the total dust mass. Recent work by Min et al. (*priv.comm.*) suggests that the crystallinity of the silicates in Hale-Bopp may be even lower. This illustrates the still remaining difficulty in determing the dust composition. The main differences come from the use of different laboratory spectra with different Fe contents for the silicates and different grain size and shape distributions. A high resolution high S/N spectrum of the dust features might help to determine the composition and even the average shape of the dust grains in future comets (see also Section 3), but the abundance of the crystalline silicates in this comet will remain uncertain.

An interesting correlation has been found between the abundance of the crystalline silicates and the geometry of the dust distribution around a star. Figure 3 shows the correlation between the strength of the 33.6 micron feature (attributed to forsterite) and the IRAS 60μm/mm flux ratio in post-MS stars. The first value gives an indication of the abundance ratio between amorphous and crystalline silicates in the dust, while the second ratio gives an indication of the average grain size. It is interesting to note that those sources which seem to have a large abundance of crystalline silicates, also show evidence for the presence of a disk-like structure and for grain coagulation (Molster et al., 1999b). Note that the opposite is not true, if stars do have a disk (and large grains) it does not automatically imply that they have a high fraction of crystalline silicates. A similar correlation between degree of crystallinity and grain size is seen in the disks around pre-MS stars (see Figure 4) (Bouwman et al., 2001). The origin of this correlation remains unclear. Whether the crystallization of amorphous silicates is related to grain coagulation, or that we are simply dealing with two different processes, which both require long timescales has not yet been established (see also Section 4).

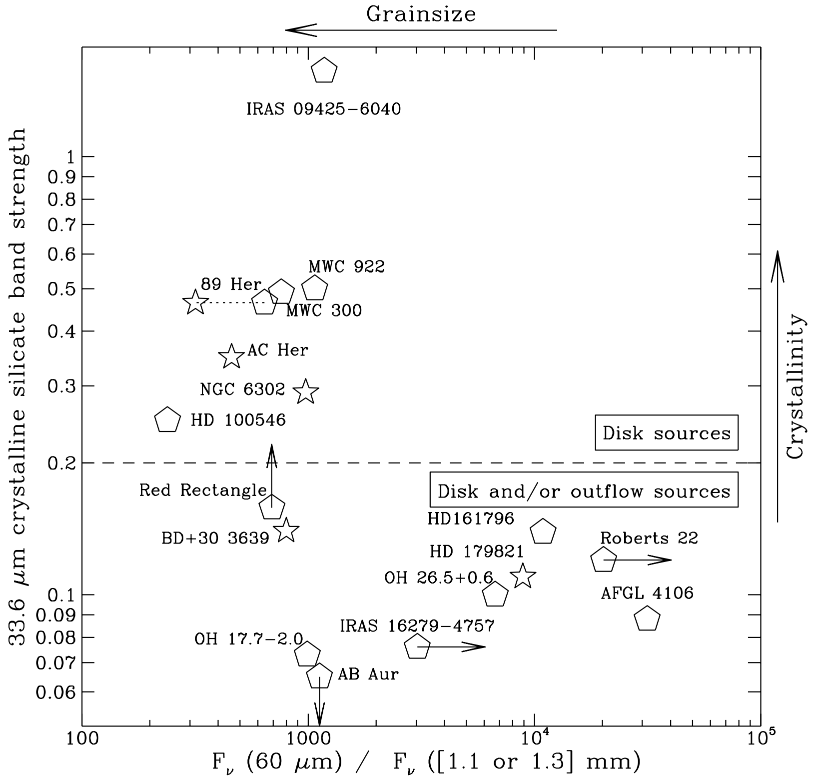


Figure 3. Correlation between the IRAS 60 μm over 1.1 mm (stars) or 1.3 mm (pentagons) flux ratio and crystalline silicate band strength, measured from the crystalline forsterite band at 33.6 μm ($[F_{33.6\ \mu\mathrm{m\ peak}} - F_{\mathrm{cont}}]/F_{\mathrm{cont}}$). The selected sources have dust colour temperatures above $\approx$ 100 K, so that the Planck function peaks at wavelengths shorter than 60 μm. The emptiness of the upper right corner of this diagram is an indication that the presence of highly crystalline dust is correlated with disks and grain-growth. All stars above the line $(F_{33.6\ \mu\mathrm{m\ peak}} - F_{\mathrm{cont}})/F_{\mathrm{cont}} = 0.2$ have relatively small 60 μm over mm-flux ratios and have indications for the presence of a disk (e.g. by direct imaging and/or the spectral energy distribution). The stars below this line are predominantly normal outflow sources, without any evidence for a disk, although exceptions exist (e.g. Roberts 22). NGC 6302 and BD+30 3639 have been shifted by a factor 2 along the x-axis since it is estimated that only half of the mm continuum flux is due to dust emission while the other half is due to free-free emission. Figure taken from Molster et al., 1999b.

3. The properties of crystalline silicates

The sharp infrared features (see e.g. Jäger et al., 1998 for an assignment of the bands of forsterite and enstatite) of the crystalline silicates allow a quite accurate identification of the crystalline materials. The two most abundant crystalline silicates that have been found are forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$, which can have a monoclinic and orthorhombic crys-

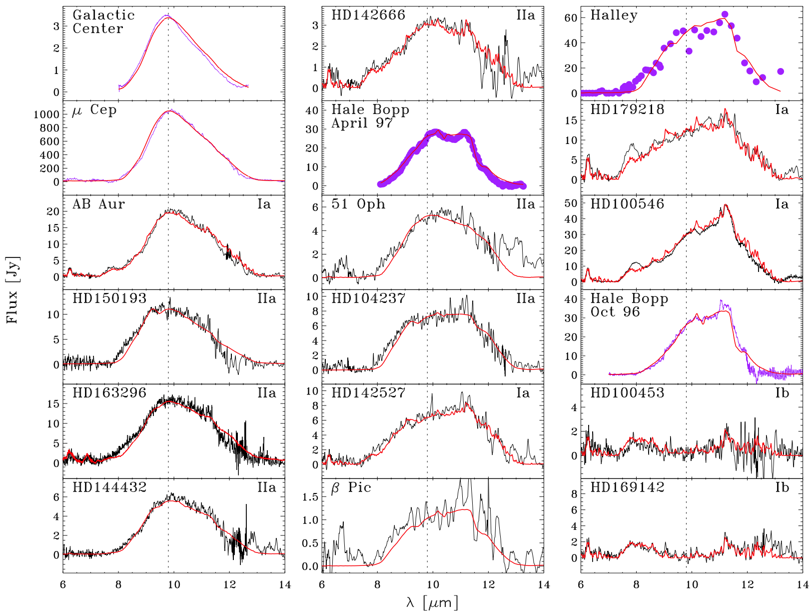


Figure 4. Dust processing in planet forming systems. The panels show ISO-SWS continuum subtracted spectra of the 10 micron regions, ordered by peak position, the first spectrum (of the ISM) shows the bluest feature. A model fit to each spectrum is included in the plot. The model includes grain growth, which is reflected in the width of the feature, and the shift towards longer wavelengths, as well as crystallization with the appearance of the 11.3 μm feature. From this plot it becomes clear that there is a correlation between grain growth and crystallinity in the various phases of planet formation. Relatively young and unprocessed silicates are seen in the top first few spectra (including the spectra of the diffuse ISM and a red giant, μ Cep) whereas the more evolved planetary systems are found further down in the sequence. Figure adopted from (Bouwman et al., 2001).

tallographic structure, called respectively clino and ortho-enstatite). As an example, a fit to the continuum subtracted spectrum of MWC922 with only these two species is shown in Figure 5.

The high resolution spectroscopy of ISO-SWS ((de Graauw et al., 1996; Leech et al., 2003) and LWS (Clegg et al., 1996; Gry et al., 2003) made it not only possible to determine the type of crystalline silicates, it also made it possible for some stars to determine their exact mineralogical composition of some circumstellar dust components. The presence of Fe^{2+} in crystalline silicates not only changes the opacity, it also reduces the strength and increases the wavelength of the crystalline silicate features significantly (see e.g. Jäger et al., 1998). As long as the amount of Fe^{2+} in the crystal is not too high, a first order estimate is that all the crystalline silicate features are (much) stronger than the continuum. The subtraction of a continuum (caused by other

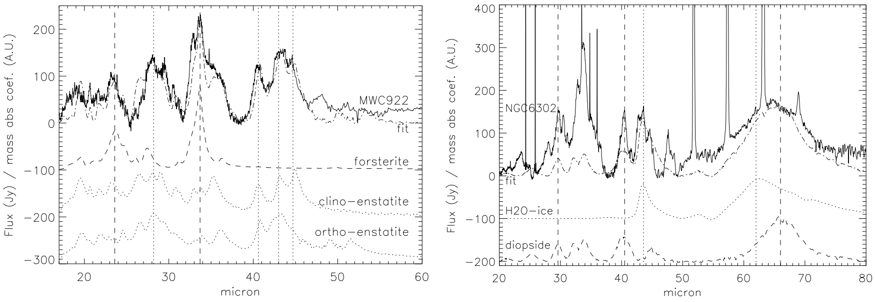


Figure 5. Left: The continuum subtracted spectrum of MWC922 (solid line; Molster et al., 2002b), compared with the calculated emission spectrum of forsterite (at 90 K; dashed line), and clino and ortho-enstatite (at 100 K; dotted line). The temperatures have been derived by fitting the continuum subtracted spectrum with only forsterite and enstatite, 50% ortho and 50% clino enstatite (Molster et al., 2002c). The fit is shown as the dashed-dotted line. The vertical lines denote the diagnostic features of forsterite (dashed lines) and enstatite (dotted lines).
Right: The continuum subtracted spectrum of NGC6302 (solid line; Molster et al., 2002b), compared with the calculated (using optical constants derived from laboratory experiments) emission spectrum of diopside (at 70 K; dashed line), and crystalline water ice (at 40 K; dotted line). The temperature of diopside is chosen the same as the temperature found for the other pyroxenes (Molster et al., 2002c), and water ice has been chosen to fit both the 40 and 60 micron complex. The combined result is shown as the dashed-dotted line. The vertical lines indicate the wavelengths of diagnostic features of diopside (dashed lines) and crystalline water-ice (dotted lines). Note that no effort has been made here to fit the forsterite features at 33 μm and the enstatite feature at 40 μm.

dust components) from the ISO spectra, gives you therefore a reasonable first impression of the crystalline silicates.

In Figure 5 we show two continuum subtracted spectra of observed stars (MWC922, and NGC6302). The diagnostic features are indicated with dashed and dotted lines. Note that the difference between clino- and ortho-enstatite only becomes apparent after 40 μm. A comparison of the strength of the individual features of ortho and clino-enstatite shows that around most stars the abundance is about equal. For some stars, with very high mass loss rates, ortho-enstatite may be more abundant than clino-enstatite (Molster et al., 2002c).

Besides the above mentioned Mg-silicates, there is also evidence for Ca-pyroxenes such as diopside (Koike et al., 2000). In Figure 5, we show the calculated emission spectra of diopside and crystalline water ice. Both have a rather broad feature near the peak of the 60 micron band. However, the observed 60 μm band is broader than the individual H_2O ice and diopside bands, while a sum of both materials gives a satisfactory fit to the 60 micron region (note that the addition of the carbonate dolomite improves the fit even further (Kemper et al., 2002b)). Unfortunately, the low abundance of diopside in combination with blending of the short wavelength diopside bands with those of forsterite and enstatite make it hard to unambiguously identify diopside based on only the shorter wavelength bands. This implies that we can only clearly identify this material in systems which have very cool dust ($T<100$ K), such as OH/IR stars and planetary nebulae.

Another aspect of the chemical composition of the crystalline silicates, in particular the olivines and pyroxenes, is the Fe/Mg ratio in the lattice. The silicate composition can be rather accurately determined because the wavelength and strength of the bands are very sensitive to differences in the Fe/Mg ratio. Laboratory studies show that a simple relation exists between the position of the crystalline silicate bands and the Fe/Mg ratio in the lattice. The peak position shift in the frequency space due to the inclusion of Fe goes roughly linear with the percentage of [FeO] in the silicate (Jäger et al., 1998).

$$100 * x/\Delta\nu \;=\; -1.8 \quad \text{for olivines } (\mathrm{Mg}_{(2-2x)}\mathrm{Fe}_{2x}\mathrm{SiO}_4) \text{ and} \tag{1}$$

$$100 * x/\Delta\nu \;=\; -1.5 \quad \text{for pyroxenes } (\mathrm{Mg}_{(1-x)}\mathrm{Fe}_{x}\mathrm{SiO}_3), \tag{2}$$

with $0 \le x \le 1$ and $\Delta\nu = \nu_x - \nu_0$ where ν_x and ν_0 are respectively the wavenumber of the feature for composition x and $x = 0$. This implies that the shift in the wavelength domain is proportional to λ^2 and therefore clearest at the longest wavelengths. This is the reason why it is very difficult to determine the exact Mg/Fe ratio from observations limited to only the 10 micron region. Forsterite has a weak band at 69 μm. This band is indeed very sensitive to changes in the iron abundance in the crystal (see e.g. Koike et al., 1993; Jäger et al., 1998). Figure 6 shows the evidence for the high Mg/Fe ratio of the crystalline olivines in the outflows of evolved stars. In fact the data is even consistent with the absence of iron in the matrix (i.e. forsterite). From this plot it also becomes clear that the forsterite crystals are very cold. A similar result holds for the pyroxenes based on the 40.5 micron feature. The crystalline olivines and pyroxenes found in the dusty winds of evolved stars invariably show evidence for very Mg-rich crystals (forsterite and enstatite).

The best results in determining the composition of the silicates are achieved for evolved – post-MS – stars, where due to stellar evolution constraints often an oxygen-rich chemistry prevails in the outflow. The determination of the exact composition of the crystalline silicates around young stars is more complicated. Only for the peculiar star HD100546 a 69 micron feature due to forsterite has been found and even that one is rather noisy (Malfait et al., 1998). In all other stars such band has not been found in that wavelength region. This is likely due to a combination of sensitivity, too high dust temperature (a higher temperature creates a broader and weaker feature) and/or too low abundance. In young stars, the characteristic features of crystalline silicates are found at wavelengths below 45 μm, especially in the 10 micron complex region. It cannot be excluded that some Fe is present in the matrix

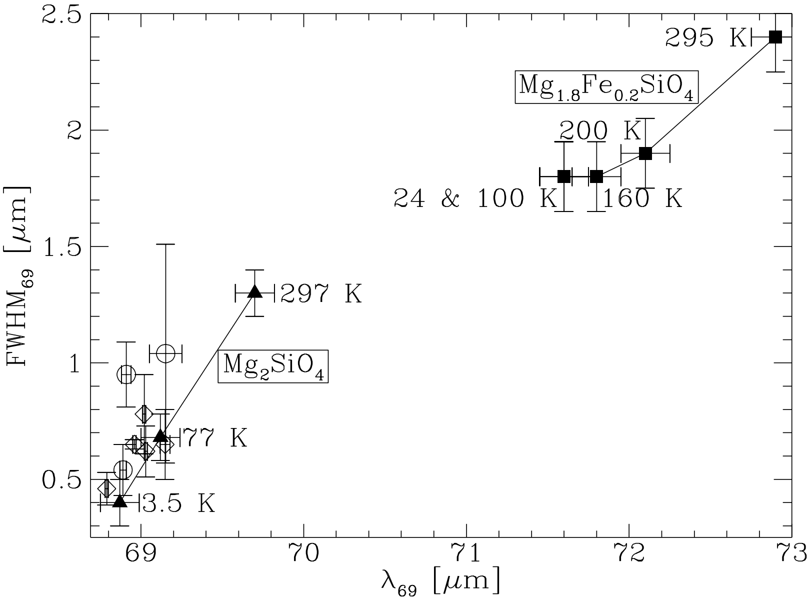


Figure 6. The observed FWHM and peak wavelength of the 69.0 micron feature in the spectra of the dust around stars (open diamonds for the sources with a disk and open circles for the sources without a disk) and in the laboratory at different temperatures (filled triangles - forsterite; Fo_{100} (Bowey et al., 2001), and filled squares - olivine; Fo_{90} (Mennella et al., 1998)). The temperatures are indicated at each point, and within the resolution the 24 K and 100 K for Fo_{90} are similar. Note that the measurements were not corrected for the instrumental FWHM (≈ 0.29, for the ISO observations, and 0.25 and 1.0μm for the laboratory observations of respectively Fo_{100} and Fo_{90}). Figure taken from (Molster et al., 2002c).

and this will also reduce the strength of the feature. Although the position of the features at wavelengths below 45μm seem to indicate that the crystalline silicates in young stars are also relatively Fe-poor.

The large number of bands of the crystalline silicates makes it possible to determine the temperature of the different species of crystalline silicates independent from each other. In general the forsterite and enstatite grains have similar temperatures, but are usually cooler than the amorphous grains (Molster et al., 2002c). This implies that the crystalline and amorphous silicates are not in thermal contact, and either they are spatially distinct, or they have significantly different optical properties. Although it is difficult to exclude the first option, the temperature difference can be explained in a straightforward way if we take into account the differences in the Fe/Mg ratios for the amorphous and crystalline silicates. As shown above, the crystalline silicates are very Fe-poor. In contrast, it has been argued that amorphous silicates contain Fe, either in the matrix or as a metal inclusion (Jones and Merrill, 1976; Ossenkopf et al., 1992; Kemper et al., 2002a). Adding a modest amount of iron already increases the opacity in the near-IR significantly (Dorschner et al., 1995). Radiative transfer modeling shows that, if one assumes that the amorphous silicates have Fe/Mg ≈ 1 and that the crystalline silicates are Fe-free, the temperature differences found are fully explained by the difference in near-IR opacity. Both the amorphous and crystalline silicates can then be co-spatial (see e.g. Molster et al., 1999a; Kemper et al., 2001; Hoogzaad et al., 2002).

4. The evolution of crystalline silicates

Although the crystalline lattice structure is energetically the most favorable state for silicates, the observations show that most of the silicate grains are amorphous or glassy. This requires an explanation. First of all, some threshold energy has to be overcome before an amorphous silicate will crystallize. At temperatures above 1000 K the crystallization takes place on a timescale of seconds to hours, while below 900 K it will take years to more than a Hubble timescale (Hallenbeck et al., 1998). If silicate dust condenses much quicker than the crystallization timescale, it will be amorphous. This implies that if the silicates form or quickly cool off below 900 K, they will remain amorphous. Since the majority of the silicates that forms is amorphous, this may imply a formation below the glass temperature.

An alternative theory assumes that the silicates condense as crystals but their crystal structure will get destroyed in time. Tielens et al. (1997) propose a scenario to explain the difference between crystalline and amorphous silicates by this destruction mechanism. They propose that gas phase Fe diffuses into the Mg-rich crystals around 800 K (which is for all practical purposes below the crystallization temperature) and destroys the crystal structure during its intrusion. In this scenario all grains would form crystalline and only later the bulk would turn amorphous as Fe is adsorbed. Very high spatial resolution far-IR observations of the dust around AGB stars should indicate if there is indeed a rather sudden decrease of the crystalline silicate abundance in the dust shell at a temperature of roughly 800 K.

Finally, the velocity difference between dust and gas particles can be high enough for destruction and sputtering. E.g., for silicate grains the velocity difference with a helium atom should be about 30 km/sec for sputtering, and these velocities are not unlikely (Simis, 2001). Colliding crystalline silicate grains might be heated to high enough temperatures to melt or even evaporate. In the first case, the very quick cooling timescale (depending on the grain size), might result in amorphous silicates. Although it remains difficult to explain the different opacities for amorphous and crystalline silicate grains in this scenario.

4.1. DUST FORMATION IN EVOLVED STARS

There are two main classes of evolved stars that produce significant amounts of dust: i) the evolved low-mass stars, with their slow expanding winds during the AGB phase, and ii) the high-mass stars that go through a red supergiant phase during which they have a stellar wind with properties somewhat similar to those of the low-mass AGB stars. There are also some less common stars may produce dust, such as Luminous Blue Variables, Novae, Supernovae and some pre-main sequence stars. Here we will discuss the dust formation in AGB stars; a similar description holds for the red supergiants.

It is generally believed that the stellar wind from an AGB star increases with time, from $\dot{M} \approx 10^{-7}$ to 10^{-4} $M_\odot$ yr^{-1} (see e.g. Habing, 1996). In M giants with low mass loss rates ($\dot{\mathrm{M}} < 10^{-7}$ $M_\odot$/yr) the dominant dust species that form are simple metal oxides (Cami, 2002; Posch et al., 2002); amorphous silicates are not prominent in the spectra. The low density in the wind likely prevents the formation of relatively complex solids like the silicates, because that requires multiple gas-solid interactions. It is not clear at present whether these simple oxides also form in the innermost regions of AGB winds with higher mass loss rates.

The most abundant dust species in the winds of oxygen-rich stars with intermediate and high mass loss rates are the silicates. The formation of silicates is not well understood. Homogeneous silicate dust formation directly from the gas phase is not possible, it requires first the formation of condensation seeds. It seems reasonable to search for high temperature condensates that can form through homogeneous nucleation that could serve as condensation seeds for other materials. Gail & Sedlmayr (1998) propose that in O-rich winds TiO_2 (rutile) clusters can act as condensation nuclei for silicates. Quantum mechanical calculations seem to confirm this possibility (Jeong et al., 2000). However, no evidence has been found yet for the presence of rutile in the spectra of outflows of evolved stars; probably the low gas-phase abundance of titanium prevents detection.

One of the main discoveries of ISO in the field of solids in space has been the detection of crystalline silicates in the outflows of AGB stars with high mass loss rates. It should be kept in mind that the abundance of crystalline silicates compared to the amorphous silicates is modest, typically 10 to 15 per cent, and only in very special cases the crystalline silicates dominate. Crystalline silicates features are only detected in AGB stars with a fairly high mass loss rate, usually a threshold value of 10^{-5} $M_\odot$ yr^{-1} is observed (Cami et al., 1997; Sylvester et al., 1999). As discussed before it remains unclear whether the lack of crystalline silicate features in the spectra of low mass-loss rate AGB stars indicate that the dust produced by these stars is completely amorphous, or that still a large fraction of crystalline dust can be present, found at lower temperatures than the amorphous silicates (Kemper et al., 2001).

Sogawa and Kozasa (1999) derive that for low mass loss rates ($\dot{M} < 3 \cdot 10^{-5}\ M_{\odot}\ \mathrm{yr}^{-1}$) the growing silicate grains do not heat to high enough temperatures to become crystalline, whereas for higher mass-loss rates, the thermal processing of the grains makes them entirely crystalline. Even though these authors are able to explain a threshold value for the mass-loss rate below which crystalline silicates do not exist, they are unable to provide sufficient explanation for the co-existence of crystalline and amorphous grains in many sources. Dust nucleation theories are now challenged to explain the co-existence and difference in properties of crystalline and amorphous silicates in AGB stars: (i) crystalline silicates are Fe-poor, amorphous ones contain Fe in some form, (ii) crystalline and amorphous silicates have different temperatures and thus are separate populations of grains. ”Partially crystalline” grains do not seem to exist, which can be explained from a thermodynamic point of view: thermal crystallisation timescales are a steep function of temperature, and it requires extreme fine-tuning in the thermal history of a particle to observe it partially crystalline.

As mentioned above, the crystalline olivines and pyroxenes formed in the winds of AGB stars with high mass loss are Fe-free (Molster et al., 2002c). Interestingly, it is also the Fe-free olivines and pyroxenes that are the first silicates that are expected to condense. This will take place at temperatures high enough so they will crystallize very quickly. Thermodynamic calculations show that the Fe-containing silicates will condense at a somewhat lower temperature (Gail and Sedlmayr, 1999), and since there is no evidence for Fe-containing crystalline silicates, they apparently remain amorphous. A possible explanation for this phenomenon is that as soon as some dust forms, radiation pressure will accelerate the dust (and through the drag-force also the gas) and the material will quickly be pushed to cooler regions. So, only the very first condensed silicates, the Fe-free silicates, might have a chance to crystallize, while the later condensed silicates (the Fe-containing silicates) are formed in an environment where the annealing timescale is much longer than the accretion timescale. We should note here that it is not clear that a ferromagnesiosilica will condense at all from the gas-phase. Gas phase condensation experiments of a Fe-Mg-SiO-H_2-O_2 vapor show only condensates of a magnesiosilica and of a ferrosilica composition but not of a ferromagnesiosilica composition (see Figure 7).

While in most cases crystalline silicate dust is only a minor component in circumstellar dust shells, there are some evolved stars with a very high abundance of crystalline silicates. Remarkably, these always have a disk-like dust density distribution (Molster et al., 1999b). Because the temperature in these disks is well below the annealing temperatures of amorphous silicates, Molster et al. (1999b) suggested that a low-temperature crystallization

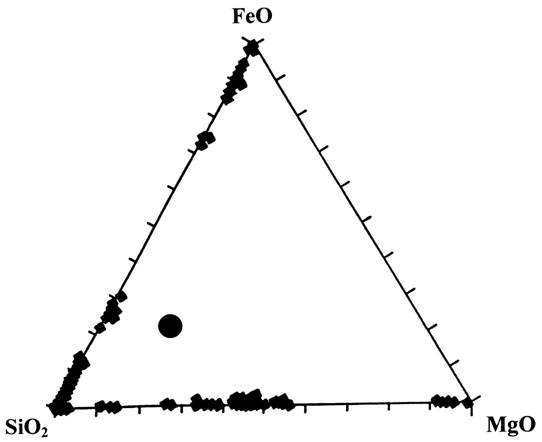


Figure 7. Ternary diagram MgO-FeO-SiO_2 (oxide wt%) with the chemical compositions of gas to solid condensed grains from a Fe-Mg-SiO-H_2-O_2 vapor. The "average bulk solid" composition (the big dot) is roughly the gas phase composition which might have been somewhat less SiO_2-rich. Figure taken from (Rietmeijer et al., 1999).

process is responsible for the higher fraction of crystalline silicates. Several processes were discussed by Molster et al. (1999b), but no conclusive answer could be given. Recently, partial crystallization at room temperature due to electron irradiation has been detected (Figure 8 and (Carrez et al., 2001)). Although these results look promising, there are still open questions. It is not sure that this process can create highly crystalline material in sufficient quantities. Investigations are still necessary to find out whether the particles can become completely crystallized or will simply become partially amorphous and partially crystalline. Note, that electron irradiation only causes local crystallization unlike thermal crystallization, which acts on the whole grain at the same time. Observations indicate that the amorphous and crystalline silicates are two different grain populations which are not in thermal contact (Molster et al., 2002c) and it is unclear that this can be achieved by this process. Finally, the compositional implications (with or without Fe) of this process are also not well studied yet.

4.2. DUST FORMATION IN SUPERNOVAE

Unfortunately, little is known about the dust production rate in supernovae (SNe). Generally, SNe are assumed to produce only modest amounts of dust compared to the dust production by AGB stars. Yet, recent submillimeter continuum observations obtained with SCUBA on the JCMT suggest that a much larger amount of dust may be produced or processed by SNe, up to a fraction of 75 % of the dust injected into the interstellar medium (Dunne et al., 2003). On the other hand, Dwek (2004) argues that if the dust causing

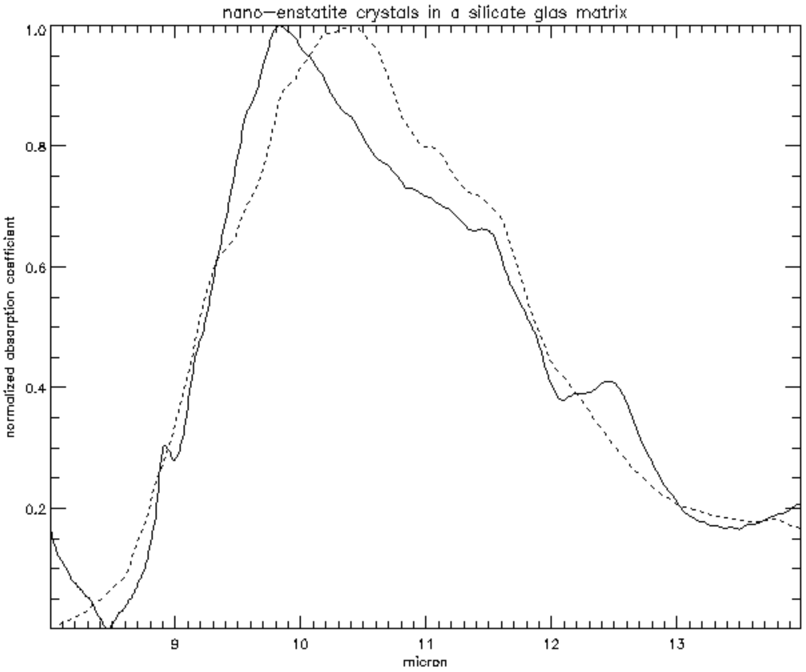


Figure 8. The infrared absorption spectrum of an amorphous silicate smoke before (dashed line) and after (solid line) a 10 minute irradiation by the electron beam of a transmission electron microscope. Note the upcoming of the spectral features.

the submm continuum were present in the form of metallic iron needles, the dust mass reduces to a fraction of the the dust mass derived by Dunne et al. (2003). Hence, determining the composition of dust of supernova origin proves to be of crucial importance. Only few infrared spectra of SN dust ejecta are available and they are not always conclusive. A 22 μm feature is observed in the ISO SWS spectrum of an area centered on a fast moving knot in supernova remnant Cas A. Arendt et al. (1999) identify this dust component as proto-silicates, which appear to have similar properties as amorphous silicates. However, Douvion et al. (2001) reject this identification based on a SWS spectrum taken very close to position N3, which shows much similarities (but is not exactly equal). They fit their spectrum with a mixture of three dust species ($MgSiO_3$, SiO_2 and Al_2O_3) with each having two different temperatures together with some synchrotron emission. The presence of amorphous $MgSiO_3$ was predicted by Kozasa et al. (1991) and fitted the ISOCAM (Cesarsky et al., 1996; Blommaert et al., 2003) spectra reasonably well (Douvion et al., 1999). However, we would like to note that the rather artificial temperatures (all dust species have different temperatures both for the hot and cold phases which are not directly related to opacity differences), the arbitrary dust sizes and the questionable feature identifications, leave some room for alternative interpretations. In addition, the large differences in physical and chemical conditions between AGB winds and SN ejecta make it difficult to assume similarities in the types of dust that may condense in SN ejecta.

4.3. THE PROCESSING OF DUST IN THE ISM

The average lifetime of a silicate dust grain in the ISM is roughly $4 \cdot 10^8$ years, while the replenishment rate of ISM dust is about $2.5 \cdot 10^9$ years (Jones et al., 1996). This means that interstellar dust grains are destroyed and re-formed about six times before finally entering a star forming region to be incorporated into a new generation of stars. Thus, new grains must be formed in the ISM. In addition, silicates may be processed in the diffuse ISM. Below, we discuss dust formation, processing and destruction processes that may occur in the ISM.

The composition of the silicates in the interstellar medium has been subject to several different studies. Based on infrared spectroscopy with SWS and other instruments it is found that the silicates in the ISM are largely amorphous. Olivines are the dominant form, and only some very small fraction may be crystalline (Kemper et al., 2004). Evidence for crystallinity seems to be absent. Some tentative detections of crystalline silicates are reported in the Orion Bar (Cesarsky et al., 2000), and in the Carina star forming region (Onaka and Okada, 2003), although re-analysis of the SWS data of the Orion Bar indicate that there are no detectable features due to crystalline silicates in these spectra. The absorption line-of-sight towards the Galactic Center observed with ISO-SWS, shows that the silicates in the diffuse ISM are completely amorphous (see Figure 9). An upper limit of 0.2% (± 0.2%) can be placed on the degree of crystallinity in the diffuse ISM (Kemper et al., 2004). Using ground-based 10 μm spectroscopy, Bowey & Adamson (2002) argue that a broad feature due to silicates, which appear to be amorphous upon first examination, may in fact be caused by a combination of a large number of different crystalline silicates. Based on only the 10 μm spectroscopy the distinction between purely amorphous silicates and a cocktail of crystalline silicates cannot be easily made, however, all these crystalline silicates will cause sharp resonances in the mid-infrared. The presence of these resonances could be easily checked with ISO-SWS data, and there are not cases known where such resonances exist, while the 10 μm feature appears smooth. Hence, we conclude that the silicates in the ISM are predominantly amorphous. It is evident that, because the silicates around post- and pre-main-sequence stars have a significant degree of crystallinity, while the dust in the ISM is predominantly amorphous, processing of the silicate dust in the ISM plays an important role.

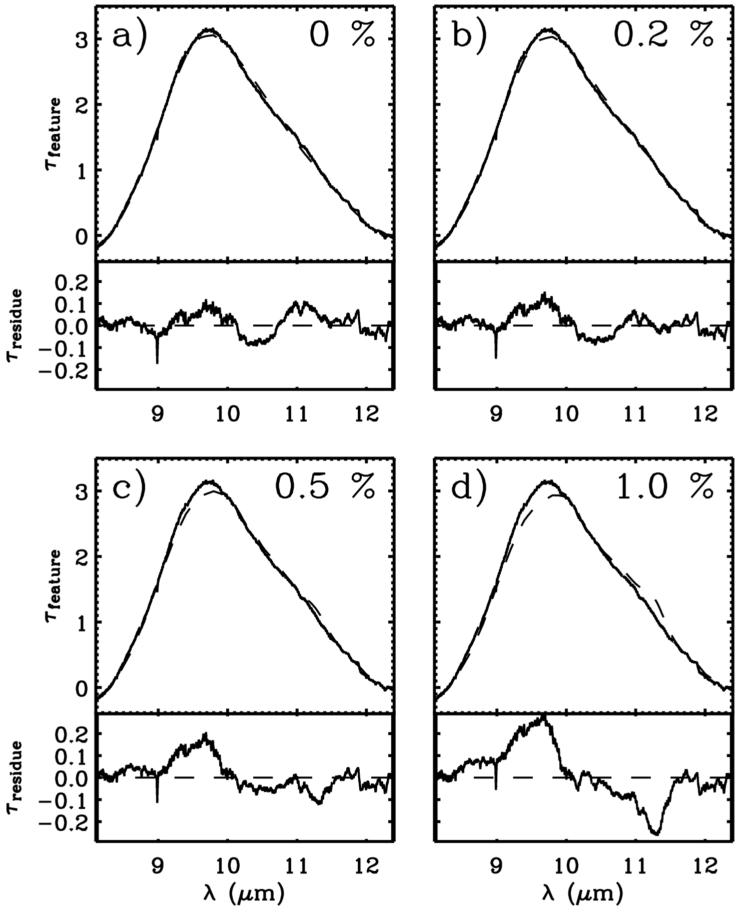


Figure 9. Optical depth in the 10 μm silicate feature observed towards the Galactic Center, with ISO-SWS. The four panels show fits to the feature for 0%, 0.2%, 0.5% and 1.0% respectively of the silicates in the form of crystalline silicates around the line of sight. The bottom part of each of the panel shows the residuals to each fit. The best fit is found for a composition containing 0.2% of the silicates in crystalline form, while 0% and 0.4% mark the limits of acceptable results. Figure adopted from Kemper et al. (2004).

The dust formation process in the ISM is not clear, however it seems inevitable that it takes place in the dark molecular clouds, where high densities prevail. The C/O ratio in the ISM is in general smaller than unity, which normally would result in the formation of oxygen-rich material. However, the conditions for dust formation are totally different. The most important difference between the dust formation process in the interstellar medium and the dust around stars is the temperature and density of the gas. Around stars dust forms at temperature of about 1000 K, while in the ISM dust temperatures between 10 and $\approx$ 100 K are found. These low temperatures are far below the glass temperature, therefore the grains formed in the ISM will be amorphous. This is consistent with the fact that no crystalline silicates have been found in the ISM.

From depletion pattern differences between cool clouds in the Galactic disk and warm clouds in the galactic halo, it seems that the dust that forms in the ISM has an olivine stoichiometric ratio (Jones, 2000). Clearly, this does not imply that they are in fact olivines, let alone crystals.

On the other side of the balance, dust destruction and processing play an important role in the ISM as well. The harsh conditions that prevail in the ISM can result in the destruction or modification of interstellar dust. Interstellar shocks may shatter grains into smaller fragments, thus changing the grain size distribution by producing more small grains, or leading to complete evaporation (Tielens et al., 1994). In addition, the degree of crystallinity goes down in the ISM. We observe these grains in the outflows of evolved stars, but not along lines of sight through the ISM. The exact abundance of the crystalline silicates brought into the ISM by stars is not known yet. This depends on how much cold crystalline silicates are hidden in the warm amorphous silicate profiles, but it is likely in the order of 15% of the silicates (Kemper et al., 2004). But the lack of crystalline silicate features in the ISM, makes it plausible that the crystalline silicates are amorphitized very quickly in the ISM, assuming destruction mechanisms are equally efficient on crystalline and amorphous silicates.

In fact both destruction and amorphization are expected to occur in the ISM. It has been suggested that the amorphization might be explained by lattice defects caused by cosmic ray hits. If the ambient temperature is below the crystallization temperatures there will be not enough internal energy to overcome the threshold energy necessary to fix the defects in the crystal, and an amorphous particle track forms. Not all cosmic rays are useful though, only a select energy range can cause the amorphization of crystalline silicate grains. Day (1977) shows that MeV protons hardly have any influence on the crystalline silicates and electron irradiation might even make grains more crystalline (Carrez et al., 2001).

The stopping power of keV ions in silicate material is high enough to cause significant damage to the lattice structure however. The cosmic flux of such ions is poorly known as only a very small fraction reaches the earth to be measured. The main source of acceleration for these ions are SN shock waves. Laboratory experiments of the irradiation of silicates with keV ions of different nature show that the small crystalline silicates ($\lesssim 1\ \mu$m) are likely to be amorphitized in the ISM (Demyk et al., 2001; Jäger et al., 2003; Brucato et al., 2003). This amorphization process works best on small grains since there is a limited penetration depth, only the first micron will be completely amorphitized. Larger grains might therefore survive complete amorphization, but they will suffer more from sputtering and evaporation in these shocks (Jones et al., 1996). Unfortunately, the cosmic flux of ions in the keV energy range seem to be too small to explain the fast amorphization observed in the diffuse ISM (Kemper et al., 2004), but amorphization by Fe^{2+} ions with keV energies or higher may be feasible on such time scales, due to the larger stopping power (E. Bringa, *priv. comm.*). To summarize, it is expected that the silicate grains, especially the crystalline ones, will not survive a long stay in the ISM: larger grains will be eroded by sputtering and evaporation, while smaller grains may be amorphitized and destroyed completely.

The final structure of silicates exposed to He^{+} irradiation shows some resemblance with the GEMS (Glass with Embedded Metals and Sulphides) in IDPs (Bradley, 1994b; Demyk et al., 2001). In this respect it is also interesting to note that sometimes inside a GEMS a so-called “relict forsterite” grain is found, which shows evidence for heavy irradiation damage, much more than what is expected during their stay in the solar nebula. Furthermore, these irradiation experiments showed that O and Mg are preferentially sputtered away from the first 100nm of the test samples. This might explain the evolution of the amorphous silicate dust which looks more like an amorphous olivine around the evolved stars and more like an amorphous pyroxene around young stars (Demyk et al., 2001). A similar selective sputtering, but then by solar wind irradiation has been observed in solar system material (Bradley, 1994a).

4.4. DUST PROCESSING IN STAR-FORMING REGIONS

Without doubt the solar system is the best evidence available for the dramatic changes in dust composition that occur during star and planet formation. The vast literature on the mineralogy of solar system objects, ranging from planets to IDPs demonstrates that large differences exist between the properties of solids in the solar system and in interstellar space. In recent years it has become evident that these differences also exist for dust in primitive solar system objects such as comets. Clearly, understanding these differences is one of the main challenges of the field of star- and planet formation.

Apart from an increase in average size, infrared spectroscopy has also shown that the composition of dust in proto-planetary disks has changed compared to that in the ISM. Probably the clearest example is the crystallization of the amorphous silicates around Herbig Ae/Be stars. There is no convincing evidence for the presence of crystalline silicates in the ISM. The crystalline silicates found around young stars therefore have to be formed in situ. They will be formed both by gas-phase re-condensation, upon evaporation in the inner solar system, as well as by annealing of amorphous silicates, as is also seen in our own solar system (Molster and Bradley, 2001). Both processes will take place close to the young star. This seems to be supported by the observations. In most of these stars there are indications for the presence of crystalline silicates, but only in the 10 micron region, indicating that the crystalline silicates are indeed hot and close to the star (e.g. Meeus et al., 2001; Bouwman et al., 2001, see also Figure 4). The gas phase condensation process will produce very Fe-poor crystalline silicates, similar to what has been found around evolved stars, while the annealing process will very likely produce Fe-containing crystalline silicates, because the original amorphous silicates are likely to contain iron. Since the amorphous silicates will in general not have the stoichiometric composition of one single mineral (such as forsterite or enstatite), an annealed grain will usually be a grain consisting of two or more different minerals (see e.g. Figure 9 of Rietmeijer et al., 1999). The presence of silica (SiO_2) in the dust emission spectra of young stars supports this scenario. This material is very transparent and will normally be very cold relative to the other minerals. The fact that the silica features in the 10 μm region are detected, indicates that silica is much warmer than expected. It should therefore be in thermal contact with the other minerals, as is expected when it is a product of annealing of amorphous silicates (Bouwman et al., 2001).

Recently, nebular shocks have been suggested as an alternative mechanism to provide the temperatures necessary for annealing of the amorphous silicates in the proto-solar nebula at larger distances (Harker and Desch, 2002). Although, this mechanism fails to explain some of the aspects of the crystalline silicates in the solar system, and will therefore not be applicable to all crystalline silicates found, it cannot be excluded as a competing mechanism. This mechanism might also play a role in the disks around evolved stars.

Unfortunately, the sensitivity of ISO was not high enough to detect crystalline silicate features in the spectra of pre-main-sequence stars of solar mass, and only the much brighter and more massive Herbig AeBe stars are known to have crystalline components based on their ISO spectroscopy. Recent ground based studies however have shown that crystalline silicates are indeed present around T Tau stars, pre-main-sequence stars with a mass comparable to that of the Sun, indicating that processing occurs in these systems as well (Honda et al., 2003; Meeus et al., 2003), a conclusion confirmed by the first results from the Spitzer Space Telescope (Uchida et al., 2004).

A spectacular result of the ISO mission has been the remarkable similarity between the spectral appearance of the solar system comet Hale-Bopp (Crovisier et al., 1997) and that of the Herbig Ae/Be star HD 100546 (Malfait et al., 1998). In both objects the emission bands of crystalline silicates, as usual Fe-poor, stand out (Fig 10). The origin of the high abundance of crystalline silicates in both objects is not clear. In HD 100546 the abundance of forsterite increases with distance from the star (Bouwman et al., 2003), which is not expected in the case of radial mixing of annealed silicates (Nuth et al., 2000; Harker and Desch, 2002; Bockelée-Morvan et al., 2002). Bouwman et

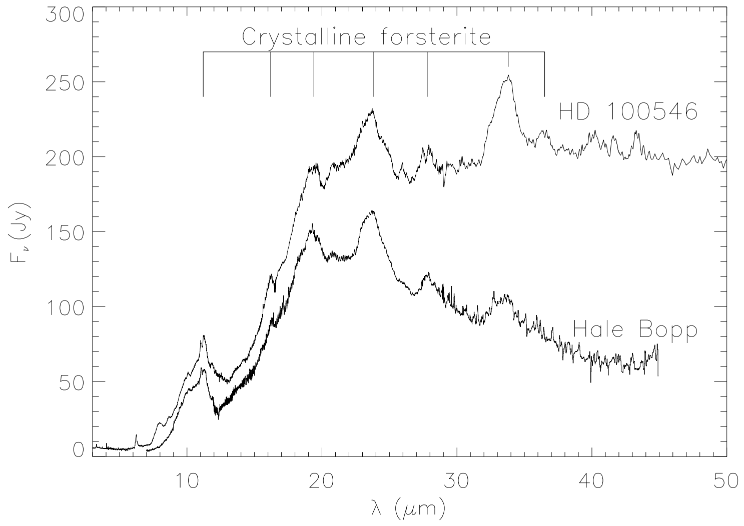


Figure 10. The ISO SWS spectra of Hale-Bopp (Crovisier et al., 1997) and HD100546 (Malfait et al., 1998). The crystalline forsterite features are indicated.

al. (2003) propose a local production of small forsterite grains as a result of the collisional destruction of a large parent body.

Most considerations about the formation of crystalline silicates come from theory. However, also laboratory experiments sometimes shed new light on this subject. There are indications that the width of some features are an indication of the internal structure of a crystal, and therefore of their formation history. Figure 11 shows two laboratory spectra of forsterite: the forsterite sample from Jena has been made from a melt, and is likely polycrystalline, while the sample from Japan is a single crystal. Note the difference in band width between both spectra. It is interesting to compare these band shapes to those of some characteristic bands seen in the spectra of evolved and young stars. The evolved stars, with freshly made stardust, show a band shape which resembles that of the Japan sample, i.e. corresponding to a single crystal. This may be expected, since gas-phase condensation would naturally lead to particles with a single crystal structure. On the other hand, the ISO spectrum of HD 100546 shows a resemblance to that of the polycrystalline sample from Jena. This is an indication that the forsterite in HD100546 has a polycrystalline structure. Both fractionation of a differentiated body (as proposed by Bouwman et al. (2003) for HD100546), as well as annealing of amorphous silicates (as seem to occur around many other young stars) will lead to polycrystalline forsterite and is therefore in agreement with the observations. The signal to noise of the Hale-Bopp spectrum, prevents to draw conclusions

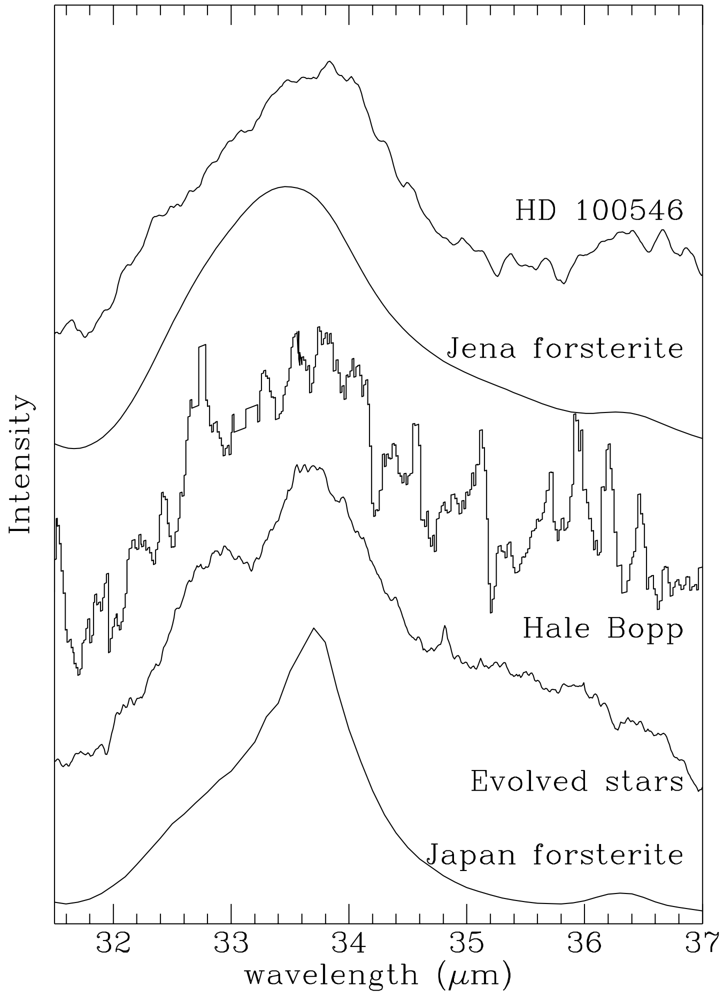


Figure 11. The 33 micron complex of the young star HD100546 (Malfait et al., 1998), the comet Hale-Bopp (Crovisier et al., 1997) and an average of 33 micron complexes of evolved stars with evidence for an excretion disk (Molster et al., 2002a), together with 2 laboratory measurements of forsterite one measured in Jena (Jäger et al., 1998) and one in Japan (Koike et al., 1999). Note the difference in width of the 33.6 micron feature. Figure taken from Molster et al. (2002c).

about the origin of the crystalline silicates in this comet. However, it is important to stress, that there are other effects that can influence the band shape, such as blends with other dust species, and grain size and shape effects.

5. Conclusions and outlook

As often in astronomy, opening a new window to the universe results in a landslide of exciting discoveries, and often in directions that were not really anticipated. ISO is no exception to this: before ISO was launched, it was expected that most discoveries related to dust(formation) would be made in carbon-rich environments. It was thought that the oxygen-rich environments would only show the broad, smooth amorphous silicates. The detection of crystalline silicates in circumstellar environments came therefore as a big surprise.

Of course, the crystalline silicates are just a part of the exciting world of astromineralogy, it includes many more mineral species. This area of research has gained a tremendous momentum with the launch of ISO. The spectral resolution and coverage of this satellite was perfect for the study of dust at infrared wavelengths. ISO went on where IRAS had stopped. The opening of the electromagnetic spectrum beyond 23 μm proved to be very fruitful for astromineralogy. Dust identifications were no longer based on single features, but on complete spectral mapping. It is now even possible to determine for some dust species the exact mineralogical composition, which is a big step forward in the field of astromineralogy.

The ISO discovery of the crystalline silicates triggered many follow-up laboratory studies on silicate formation and processing. These studies indicate that thermal equilibrium calculations cannot explain the diversity and abundances of the amorphous and crystalline silicates. Progress can be made, especially in combination with new laboratory measurements of the infrared properties of dust species. However, the requirements for the cosmic dust analogues, are quite severe (appropriate size, no contaminations and preferably at low temperatures) and these experiments are therefore not easy to perform. Laboratory experiments are an important tool on our path to understand the dusty Universe.

Also radiative transfer models were suddenly confronted with the increase of spectral detail. The infrared spectra are now accurate enough that real dust species can (and should) be incorporated. The adding of more and realistic dust species leads to more complex calculations, but also to a significant increase of our knowledge about the location (and therefore evolution) of the different dust species, a good example is the space distribution of forsterite around HD100546 (Bouwman et al., 2003).

One of the most exciting new venues of dust studies is the possibility to quantitatively compare the dust in our own solar system to that seen in space. Laboratory techniques are becoming increasingly powerful and provide important information about the formation history of solar system and stardust samples.

High spatial resolution observations at infrared wavelengths will allow us to study the (crystalline) silicate formation and growth in red giants and its time dependence, thus putting tight constraints on dust nucleation models. Sensitive spectrometers will allow studies of dust in stars outside our galaxy, giving insight into dust formation in external galaxies with different metallicities.

Observationally, ISO is only the beginning of a development involving new missions such as Spitzer, Herschel, SOFIA and JWST, as well as improved infrared facilities at ground-based observatories such as Subaru and the VLT, which will tremendously increase our knowledge of astromineralogy, and in particular of the mineralogy of proto-planetary systems. We will be able to study the processing of silicates in newly forming planetary systems and compare directly to the history of the formation of our solar system as it is recorded in planets, asteroids and comets. Recent discoveries with Spitzer (see ApJS vol. 154, 2004) show that this telescope is capable of much deeper studies, and will detect weaker crystalline silicate features, in fainter objects. This will be particularly important for the understanding of dust processing in planet forming systems akin the solar system. The higher spatial resolution offered by the state-of-the-art ground based facilities allows for a spectral mapping of circumstellar environments (e.g. van Boekel et al., 2004). Especially with the mid-infrared interferometry available, it will be possible to determine how the degree of crystallinity varies within the circumstellar environment, which will put constraints on the dust processing mechanisms, and help disentangle the physical properties of planet forming systems.

The ISO archive will, however, remain a valuable source of information about astromineralogy in general. This is because the wide spectral coverage of ISO is currently unparalleled. It is precisely this property of ISO, together with its spectral resolution, which made it possible to have so much progress in the field of astromineralogy in general and the field of crystalline silicates in particular.

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