

Laboratory measurements of the far-infrared to millimeter dust opacity of amorphous Mg/Fe silicates

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Amorphous silicates are expected to be one of the major constituents of dust in the interstellar medium. Laboratory investigations of these compounds are therefore crucial for bettering the understanding of the nature of interstellar dust. For our measurements, we used synthetic analog materials, produced by quenching of melts with well-defined chemical compositions. We performed transmission measurements on a variety of pyroxene-like amorphous silicates with various Mg/Fe-ratios. The wavelength-dependent opacities of these samples in the wavelength range between 50 μm and 1.2 mm and in the temperature range between 300 K and 10 K have been investigated. We observed not only a temperature dependence of the opacities, but also a clear dependence on the iron content. The reason for this behavior lies in the microstructure of amorphous silicates, but is not yet completely explored.

*The Life Cycle of Dust in the Universe: Observations, Theory, and Laboratory Experiments - LCDU 2013,
18-22 November 2013
Taipei, Taiwan*

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1. Introduction

The galactic energy balance is significantly influenced by interstellar dust. It absorbs radiation at ultraviolet and visible wavelengths and re-emits it in the infrared and mm-wave range. At least 30% of the total amount of energy emitted by stars as starlight is absorbed and re-emitted by dust grains in this manner [1]. The low temperature of grains in the interstellar medium leads thereby to emission at long wavelengths.

It has been known for several decades that silicates are a fundamental constituent of interstellar dust [2]. Since their first detection in the late 1960s, the prominent silicate features at 10 μm and 18 μm wavelength have been probed at several surveys. They occur similarly everywhere in the ISM of the Milky Way, independent of the line of sight. Although the observed features differ slightly in their shapes and intensities, depending on the observed region, they are all smooth and very broad. This excludes the presence of a significant amount of crystalline silicates, which would cause sharp and narrow features.

The low temperature optical properties of astronomically relevant silicate dust species at FIR and sub-mm wavelengths have been investigated by several authors in recent years. These investigations dealt mainly with pure magnesium silicates [3, 4], in one case additionally with a pure iron silicate [5]. The influence of a gradual integration of iron has never been studied before. However, all studies revealed a clear temperature dependence of the opacities of silicate grains, particularly of amorphous phases. While focusing on those same phases, we expand the currently available dataset with regard to the influence of the incorporation of Fe atoms into the amorphous network. Our data will be useful for the interpretation of observed spectra from current projects like SOFIA and ALMA, and should contribute to an understanding of observations from the recent space missions *Herschel* and *Spitzer*.

2. Sample preparation and measurement procedure

We synthesized a series of Mg/Fe-glasses with pyroxene-like chemism ($\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_3$). This has been done by quenching of melts using rotating copper rolls [6]. Mixtures of certain amounts of magnesium carbonate (MgCO_3), iron oxalate ($\text{C}_2\text{FeO}_4 \cdot 2\text{H}_2\text{O}$), and silicon dioxide powder (SiO_2) served thereby as precursors for our melts. Since the actual water content of chemicals may change due to surface reactions once they are exposed to air humidity for some time, we frequently checked the water content of our ingredients. Thus, we were able to determine the required mass of precursor material for the different compositions of melts much more precisely and, as a consequence, regulate the chemism of the resulting glasses with a higher accuracy. The glasses were melted at temperatures above 1600°C. The samples, which were placed in a platinum crucible, were removed from the hT-oven at the maximum temperature and immediately poured between two copper rolls, of which one is rotating, driven by an electric engine. The fast cooling preserves the disordered state of the melt and avoids crystallization processes. Unfortunately, it is not possible to completely avoid some early stages of crystallization. The phase content depends on the iron content of the melt. While iron-free MgSiO_3 is almost totally amorphous, a higher iron content tends to result in increased crystallinity. To get appropriate samples it is therefore necessary to remove crystallized areas. The phases are discriminable based on different optically visible characteristics. We separated

amorphous from crystalline phases using a binocular microscope. After removing the crystalline fraction, the remaining glassy fragments were ground to a fine powder. A very small percentage of this powder was embedded into a KBr pellet in order to verify its amorphousness by a MIR absorption measurement.

To measure in the far-infrared region, hot pressed polyethylene pellets with a diameter of 13 mm were used. For measurements in the spectral range between 50 μm and 300 μm we chose a sample to PE ratio of 1:16 with a sample mass of 10 mg. In order to prohibit scattering effects at these relatively short wavelengths we selected grains with a size of 1 μm or less by sedimentation in acetone. For wavelengths above 300 μm we applied pellets with a sample to PE ratio of 8:1 and either 400 mg or 2,4 g (or more) of sample material. The massive pellets deliver the most accurate values at wavelengths around 1 mm but are not measurable below ~ 500 μm because of their high optical depth.

We could obtain glasses in the compositional range between MgSiO_3 and $\text{Mg}_{0,5}\text{Fe}_{0,5}\text{SiO}_3$. We used scanning electron microscopy to check the chemical homogeneity of the samples and electron microprobe analysis to determine their chemical compositions. It turned out that the homogeneity also depends on the iron content. While glasses with a Fe/Mg ratio of 1:3 or lower are absolutely homogeneous, the presence of a higher amount of iron leads to some kind of phase separation into regions with different elemental abundances ($\pm 5\%$ for Si, Fe; less for Mg), spatially separated by a few tens of microns and with smooth transitions from one to another. The separation takes place within the amorphous network and is not accompanied by crystallization. The mean composition of all samples deviates by less than 2 mass-% per element from the respective index values. This deviation is also not exceeded for the homogeneous samples.

For our FIR absorption measurements we used an FTIR spectrometer BRUKER IFS 113v. A LHe continuous flow cryostat, equipped with polyethylene windows, was placed directly into the optical path. For the 1:16 pellets we used a pellet made from pure polyethylene for the reference measurements. This approach is not practicable for the 8:1 pellets because the refractive index of the mixture is completely different from that of pure polyethylene. For that reason, we conducted measurements of the empty beam path as reference and calculated the reflection losses of the samples using effective medium approximations. The spectra obtained from measurements of 8:1 pellets with a sample amount of 400 mg at wavelengths above 250 μm show several fringes at periodic intervals. These fringes are caused by multiple reflections between the surfaces of the pellet. In order to remove these effects we did a least squares fit to the spectrum using a fifth-order polynomial. For all the other measured pellet concentrations and thicknesses interferences caused by reflections do not play an important role.

To adapt our measured absorptivities to those of free-flying single grains, we applied the Bruggeman model to compute theoretical mass absorption coefficients for single grains and agglomerates in a matrix. Thus we could calculate a correction factor, which we used to adapt our data derived from high-concentration pellet measurements. For sample concentrations $< 1/3$ of the total volume, there is no way to compute theoretical absorptivities without assuming a certain grain shape. Therefore, the low-concentration pellet spectra were fitted to those obtained from high-concentration pellets. For a detailed description of the Bruggeman model and its application, we refer to papers by Henning et al. (1995) [7] and Boudet et al. (2005) [4].

3. Results

The wavelength dependent mass absorption coefficient κ of MgSiO_3 glass for temperatures between room temperature and 10 K is shown in Figure 1. To cover the indicated spectral range with the highest possible accuracy, spectra taken from measurements of three pellets have been merged for each temperature. It is evident that a strong temperature dependence of the absorption occurs only at longer wavelengths. The shorter the wavelength, the more the curves of all temperatures converge to one uniform value of κ . Generally, the mass absorption coefficient decreases with increasing wavelength and with decreasing temperature. The appearance of our curves is in good agreement with recent works by Boudet et al. (2005) and Coupeaud et al. (2011) [8]. It has to be mentioned that the absolute κ -values of the latter are in general higher than ours, which may be due to the fact, that their sample material was not a glass, but a sol-gel product. The data from Boudet et al. fits ours almost perfectly, except for the longest wavelengths where our measurements deliver slightly lower values.

The iron containing glasses show similar behavior to MgSiO_3 , only the absolute values of κ are changing according to the incorporated iron fraction. Since the temperature dependence is significant at longer wavelengths, we will focus in the following on the spectral region $\lambda > 0.5$ mm. Comparing our measurements with regard to the iron content, we find that MgSiO_3 , for some reason, is the best absorbing material. The presence of iron seems to lower the absorptivity in general, but apparently without following a constant trend. Room temperature mass absorption coefficients of samples with various iron contents are compared in Figure 2. The spectra are obtained only from measurements of 400 mg pellets and the plotted values at wavelengths close to 1 mm may thus deviate from those of 2,4 g pellets, which are expected to provide more accurate values. Most likely, the actual curves would be located slightly lower than the ones shown. We have to apply the depicted curves until more experimental data of high mass pellets, especially for Fe-rich glasses, are available. However, the plot is totally suitable for demonstrating the basic behavior. Starting from MgSiO_3 , κ decreases with increasing iron content up to the composition $\text{Mg}_{0.7}\text{Fe}_{0.3}\text{SiO}_3$,

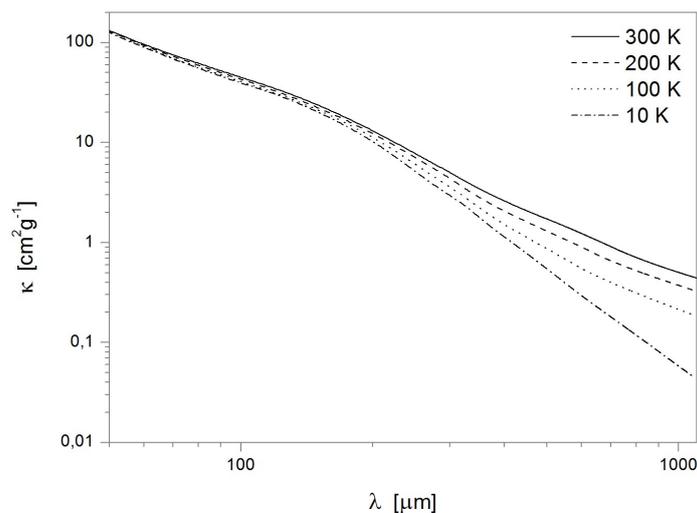


Fig. 1: Mass absorption coefficient for amorphous MgSiO_3 at different temperatures

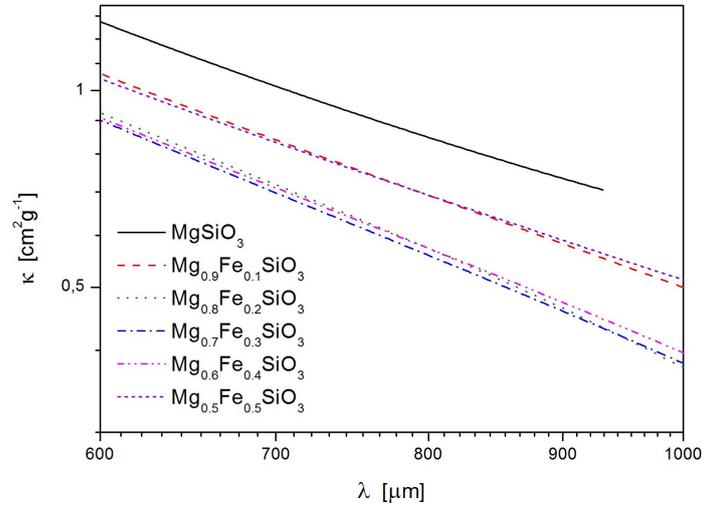


Fig. 2: κ -values at 300 K of amorphous pyroxene-like silicates with variable Mg/Fe-ratio ($\text{Mg}_x\text{Fe}_{1-x}\text{SiO}_3$; solid black: $x = 1$, dashed red: $x = 0.9$, dotted green: $x = 0.8$, dash-dotted blue: $x = 0.7$, dash-double-dotted magenta: $x = 0.6$, short-dashed purple: $x = 0.5$)

which is the weakest absorber of our sample set. By incorporating still more iron in the amorphous network, the absorptivity rises again. We do not believe that this behavior is an intrinsic property of the amorphous silicates. Rather, it is caused either by Fe^{3+} -induced disruptions of the network or by nanoscale iron inclusions like magnetite. Both alternatives are conceivable because the quenching process of our melts cannot be conducted under defined atmospheric conditions. However, detailed investigations on the microstructure of the glasses are necessary to understand the mechanisms governing the observed absorption. We plan to perform several structure elucidating measurements in the near future. The corresponding analytical methods are presented in the last section of this article.

4. Future work

We will continue and complete our measurements at the far infrared range and expand them, especially by reckoning glasses with olivine-like stoichiometry. It is also planned to expand the examined wavelength range towards longer wavelengths. For that purpose, a total power microwave spectrometer, equipped with a closed cycle LHe-cryostat, has already been designed and built (Cologne). First test of the setup have been carried out and went successfully. It is intended to take spectra up to a wavelength of 4 mm.

Furthermore, it will be crucial to conduct a series of microstructural investigations on the glasses. We will apply Mössbauer spectroscopy to determine the ratio of divalent to trivalent iron in our samples, which may have major impact on the absorption properties. By now, one measurement of $\text{Mg}_{0.7}\text{Fe}_{0.3}\text{SiO}_3$ has been carried out and revealed a ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ of almost exactly 1. Of course we will have to obtain values for all our samples, which will be time-consuming because of the required integration time of about one week per measurement. Parallel to this we will apply Raman spectroscopy and high resolution transmission electron microscopy to determine the ratio

of bridging to non-bridging oxygen and to check our samples for inclusions and possible medium-range ordered areas, respectively. If necessary, we will expand the structural investigations to other methods, like NMR spectroscopy, in order to gain a clearer understanding of the possible processes governing the observed optical properties.

5. Acknowledgements

This work is part of the priority program 1573 "The Physics of the Interstellar Medium" of the DFG (Deutsche Forschungsgemeinschaft). We acknowledge the DFG for financial support.

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