Low-temperature crystallization of MgSiO$_3$ glasses under electron irradiation: Possible implications for silicate dust evolution in circumstellar environments

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Abstract—Synthetic MgSiO$_3$ glasses were irradiated at room temperature by 300 keV electrons in a transmission electron microscope (TEM). One of the samples had been previously irradiated by 50 keV He$^+$ ions. Electron irradiation induces the nucleation and growth of randomly oriented nanometer-sized crystallites. The crystallites first consist of MgO and subsequently of forsterite (Mg$_2$SiO$_4$). Both are seen to form within an amorphous SiO$_2$ matrix. The rate of crystallization of the samples has been monitored by conventional TEM imaging and electron diffraction. The sample that had been pre-irradiated with He$^+$ ions is found to transform faster than the as-quenched glass. The crystallization of metastable MgSiO$_3$ glasses is explained by ionizing radiation-induced elemental diffusion that allows the reorganization of matter into a more favourable thermodynamic state. These results show that ionizing radiation interactions could account for crystal formation as observed in infrared spectroscopy in some young stellar environments.

INTRODUCTION

The results obtained with the short wavelength spectrometer (SWS) on board the infrared space observatory (ISO) have allowed some important progress in our understanding of the silicate lifecycle. Before ISO, it was thought that all silicate dust in space was amorphous. This silicate dust was then identified only by the two bands at ~9.7 and 18 µm, due to the stretching and bending modes of the Si–O bonds in silicates, respectively. The broadness of these bands and the absence of structure in them reveal an amorphous state of their carriers. Thanks to ISO SWS spectroscopy, magnesium-rich crystalline silicates (mostly forsterite) have been discovered in some circumstellar dust shells, in disks around evolved stars (e.g., Waters et al., 1996; Molster et al., 1999), in protoplanetary accretion disks around young stars (Waalkens et al., 1996, 1998; Malfait et al., 1998) and in comets (Crovisier et al., 1997) via the detection in the infrared spectra of these objects of new emission features at wavelengths above 20 µm. These emission features are due to the lattice vibrations of crystalline silicates. However, silicates in the interstellar medium are still observed to be amorphous (e.g., Li and Draine, 2001) and no crystalline silicates have been detected yet in the interstellar medium, as well as in molecular clouds around early protostars where "aged" silicates are supposed to be located (Demyk et al., 1999). Silicate grains are formed in the circumstellar shells around evolved stars (AGB stars) and are then injected into the ambient interstellar medium through the effects of the stellar winds of these stars. During the collapse of molecular clouds leading to the formation of new stars, these interstellar dust grains will eventually be incorporated into the regions around young stars in the form of shells, disks and eventually comets as the young stars evolve. The ISO results thus raise several important and fundamental questions concerning the lifecycle of the silicate dust.

The fact that part of the silicates produced around evolved stars are crystalline but that no crystalline silicates have yet been detected in the interstellar medium raises the question of the structural evolution of this crystalline dust during its life. The problem of the crystalline–amorphous silicate transition in the interstellar medium has also been studied and discussed by Demyk et al. (2001) and Carrez et al. (2002). They proposed that in the interstellar medium, the dust is modified by interaction with ions accelerated by the propagation of shock waves resulting from supernovae explosions. They performed laboratory experiments on silicate dust analogues and showed that ion bombardment of the grains indeed induces an
amorphization of crystalline silicates and could well explain the absence of crystalline silicates in the interstellar medium. Energetic particles could also account for dust modification in the interstellar medium (e.g., Kratschmer and Huffman, 1979).

The occurrence of crystalline silicates in the dust shells of evolved star raises important questions about dust formation. Is the dust formed in the crystalline or amorphous state? In the latter case what mechanism can lead to its crystallization? This problem has been tackled in several studies. For example, Sogawa and Kozasa (1999) proposed that the formation of crystalline silicates occurs, depending on the mass loss rate of the stars, for heterogeneous grains composed of an aluminium oxide core and a silicate mantle. From a study of the ISO spectra of several evolved stars, Molster et al. (1999) found that the silicate dust in the disks surrounding binary red-giant stars is crystalline whereas in a previous stage of their evolution it is thought that the dust was formed in the amorphous state in the outer part of the dusty shell. This suggests that the amorphous dust grains may have been crystallized in the disks. However, the associated temperatures seem to be too low to induce thermal crystallization and they thus suggest a low-temperature process, which has yet to be identified, might have occurred. Since the amorphous-crystalline transition requires atomic diffusion, this must involve a process in which the atoms have to overcome an energy barrier to change their position and to create a crystalline structure. In addition to direct heating, a process which is thermodynamically equilibrated, another process that can induce atomic diffusion in matter is irradiation, as previously suggested by Molster et al. (1999). In the latter case, the process is out of equilibrium and cannot be characterized by an activation energy.

The presence of magnesium-rich crystalline silicates around young stars (accretion disks, protoplanetary disks and comets), in contrast to the amorphous dust in the interstellar medium and around class O protostars, suggests that the interstellar dust has been crystallized during the early phases of stellar evolution. The simplest process for this crystallization would be the thermal annealing of the amorphous dust near the stars. Following this scheme, the presence of crystalline silicates in comets would indicate that some of the refractory materials were formed much closer to the Sun that previously thought. This model implies annealing, radial mass transport and mixing from the inner region to the outer region (Shu et al., 1996; Nuth et al., 2000; Gail, 2001; Bockelée-Morvan et al., 2002). An alternative possibility to explain the presence of crystalline dust in comets has recently been proposed which does not invoke mass transport and mixing in the nebula. Harker and Desch, (2002) proposed that, depending on the grain size and the gas density, dust grains could be heated in nebular shocks at 10 AU to temperatures high enough to crystallize the grains. In recent years, several laboratory experiments have been carried out to determine the crystallization temperature of amorphous silicates (e.g., Rietmeijer et al., 1986, 2002; Hallenbeck et al., 1998; Fabian et al., 2000; Brucatto et al., 1999, Thompson and Tang, 2001). These different studies show that, depending on the evolutionary timescale of these objects, the crystallization of silicate dust requires temperatures typically higher than 800–1000 K. It is not yet clear whether these temperatures can be reached. Since young stars are believed to be very active, as shown by the emission of energetic particles, flare sequences and x-rays (e.g., Shu et al., 1996; Feigelson and Montmerle, 1999; Feigelson et al., 2002), the irradiation of the dust by ionizing radiation could also play a role in explaining the presence of crystalline dust around young stars and in comets.

The aim of this paper is to examine the role of ionizing radiation on the crystallization behaviour of a magnesium silicate glass. For this preliminary study, ionizing irradiation conditions have been simulated in situ in a transmission electron microscope (TEM) on thin films of amorphous MgSiO$_3$. One of the samples has been pre-irradiated with He$^+$ ions (50 keV) in order to test the influence of a residence time in the interstellar medium on further phase transformations under ionizing radiation.

**EXPERIMENTAL PROCEDURE**

**Samples and Sample Preparation**

The MgSiO$_3$ glass was prepared by mixing in equal molar ratio powders of SiO$_2$ and MgO oxides. The powders were melted at 1750 °C and quenched at high cooling rate. Two samples were thinned using classical TEM preparation methods for oxides (i.e., ion thinned by low (14°) angle of incidence Ar$^+$ bombardment at 5 kV). Because of the low incident angle and the low acceleration tension, this ion milling affects the sample structure only for 1–2 nm thick. After this preparation, the samples are bevel-shaped and the thinnest areas are typically a few tens of nanometers thick. Under these conditions, the samples have a high surface to volume ratio, similar to that expected for the dust in the interstellar medium.

**Helium Pre-Irradiation**

In order to simulate a residence time within the interstellar medium, one of the ultra-thin samples was irradiated at room temperature with He$^+$ ions accelerated to 50 keV at the Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse (CSNSM) facility in Orsay. The irradiation was performed at room temperature under vacuum ($10^{-7}$ mbar). The fluence was 10$^{18}$ He$^+$/cm$^2$, obtained with a current beam of 9 $\mu$A/cm$^2$, with a scanning mode in order to prevent the heating of the sample.

**Ionizing Irradiation and Transmission Electron Microscope Characterisation**

In order to simulate ionizing radiations that could occur in stellar environments, we used the electrons of a TEM. The
The geometric configuration of the irradiation is shown in Fig. 1. The TEM used for irradiation and observation of the microstructural evolution was a Philips CM30 (University of Lille), operating with an acceleration voltage of 300 kV. The experiments were performed at room temperature. The beam current was estimated by measuring the screen current density (taking into account the backscattered electron correction factor) through the hole in the sample, before and after each irradiation experiment. The electron fluence rate has been obtained by dividing the beam current by the surface of the irradiated area on the sample. The diameter of the irradiated area (focused electron beam) was on the order of a micrometer, and the electron fluence rate was between $10^{14}$ and $10^{16}$ electrons/(cm$^2$ s). Under these experimental conditions, beam heating is not significant (see Meldrum et al., 1997 or Carrez et al., 2001 for more details on this topic). The microstructural evolution and the kinetics of the transformation were followed with conventional imaging (bright-field mode) and selected area electron diffraction (SAED). During these microstructural characterizations, the electron beam was defocused in order to minimize irradiation as soon as possible.

**RESULTS**

**Electron Irradiation of the As-Quenched MgSiO$_3$ Glass**

Before electron irradiation, the samples display diffuse halos in the SAED mode (Fig. 2a); these halos are characteristic of an amorphous material. No particular structure is observed in the glass (Fig. 3a). The samples were irradiated using a 300 keV electron beam at room temperature. The fluence used was typically on the order of $10^{18}$ electrons/cm$^2$ for the study of the microstructural development. Focusing the electron beam induced rapid microstructural change of the initial glass.

**Fig. 2.** (a) Selected area electron diffraction of the starting materials. The diffuse halos are characteristic of an amorphous material. (b) After a fluence of $3.10^{17}$ electrons/cm$^2$, crystallization takes place in the sample as revealed by the appearance of rings that correspond to periclase. (c) After a fluence of $5.10^{18}$ electrons/cm$^2$, the MgO rings disappear and new rings appear; the new rings correspond to forsterite.
structure. Above a fluence of \(\approx 5 \times 10^{16}\) electrons/cm\(^2\), a structure begins to appear in the amorphous phase (Fig. 3b). Nanosized domains are visible on the images. The domains sizes are found to increase with the electron fluence (Fig. 3c; see also Fig. 4). Despite the appearance of some structure, the material is still amorphous, at least for a fluence below \(\approx 3 \times 10^{17}\) electrons/cm\(^2\) as revealed by the diffuse halos present in the diffraction patterns.

Above a fluence of \(\approx 3 \times 10^{17}\) electrons/cm\(^2\), the material crystallizes. Small crystallites with random orientation appear as revealed by rings in the diffraction patterns. At the beginning the rings are broad because of the very small size of the crystallites (Fig. 2b). With increasing electron fluence the rings progressively sharpen indicating the growth of the initial nuclei. We also observe an evolution of the newly-formed crystallites. The first rings correspond to strong reflections with \(d\)-spacings of 0.212, 0.152 and 0.121 nm and can be assigned to periclase, MgO. These crystallites are embedded in an amorphous matrix (presumably SiO\(_2\)-rich) as revealed by the diffuse halos which are superimposed on the MgO rings. For a higher fluence, typically \(\approx 5 \times 10^{18}\) electrons/cm\(^2\), new rings appear while the MgO rings progressively disappear. These new rings have been attributed to forsterite, with the strongest reflections corresponding to \(d\)-spacings of 0.396, 0.283 and 0.276 Å (Fig. 2c). Once again, the diffuse halos, coming from an amorphous material, are still observed indicating that crystallization is not complete. The kinetics of crystallization increases with the electron fluence rate. However, the phase transformations occur at the same fluence, that is, \(\approx 3 \times 10^{17}\) electrons/cm\(^2\) for the formation of MgO and \(\approx 5 \times 10^{18}\) electrons/cm\(^2\) for the formation of forsterite, within the fluence rate range of \(3 \times 10^{14}\) to \(5 \times 10^{15}\) electrons/(cm\(^2\) s). The domain sizes continue to increase during MgO and forsterite formation. Its coarsening is proportional to \(t^{1/3}\) (or \(\text{fluence}^{1/2}\)). This kinetic behaviour, very common for a wide range of phase transformations in materials, is characteristic of a diffusion controlled process (e.g., Porter and Easterling, 1992).

**Fig. 3.** Structural evolution of the glass with increasing fluence (TEM bright fields). (a) View of the sample before irradiation. No particular texture is visible. (b) Same sample after a fluence of \(3 \times 10^{16}\) electron/cm\(^2\). A texture is appearing. (c) Same sample fluence of \(7 \times 10^{17}\) electron/cm\(^2\). The structure develops with irradiation time.

**Fig. 4.** Domain size evolution as a function of the electron fluence. The two curves allow a comparison of the kinetic evolution of the pre-irradiated sample and the as-quenched sample. Domain size coarsening is proportional to \(t^{1/3}\) (fluence\(^{1/2}\)).

**Transmission Electron Microscope Characterization of the Sample Pre-Irradiated with 50 keV Helium and Electron Irradiation**

The sample pre-irradiated with He\(^+\) ions is amorphous, as indicated by the absence of electron diffraction spots characteristic of a crystalline phase in the electron diffraction
patterns. Numerous spherical bubbles are visible (Fig. 5) with sizes ranging from 10 to 150 nm. They are presumably He bubbles. The bubbles are not present in the thinnest areas of the sample. The sample shows a rim free of bubbles, running parallel to the thin edge of the TEM foil. Indeed, for these areas, the sample is transparent for the He⁺ ions accelerated at 50 kV. Using the Monte Carlo TRIM calculation codes (TRansport and Range of Ions in Matter; Ziegler et al., 1996) we have calculated that the average He⁺ ions implantation thickness is ~450 nm. As a consequence, only ~1% of the incident ions are trapped in a 100 nm thick sample. This explains why the bubble density is so low in the thinnest areas.

The pre-irradiated glass was subjected to the same electron-irradiation conditions as above. It is found to undergo the same phase transformations, with the same succession of events. However, the two glasses differ in the kinetics of the reaction. The pre-irradiated sample is more sensitive to the electron beam. The domain size is found to increase 5 to 10× faster (Fig. 4). The appearance of periclase and forsterite occur at ~2.10¹⁷ and 10¹⁸ electrons/cm², respectively. In addition to this differential kinetic behaviour, we also observed an evolution of the He bubbles implanted in the pre-irradiated sample. They tend to disappear under the electron beam (Fig. 6), showing that He diffusion occurred, at least, in the sample during electron irradiation. He loss resulting from electron beam damage was also observed in silicates from He-rich interplanetary dust particles (IDPs) (Brownlee et al., 1998).

DISCUSSION

Crystallization of the MgSiO₃ Glass Under Electron Irradiation

It is well known that ionizing transfer in material can induce microstructural changes in oxides (e.g., Devanathan et al., 1998). The interaction of the incident electrons with atoms in the solid causes the ejection of secondary electrons of the inner K and L shells of the atom target. This process is widely similar to photo-ionization produced by x-rays but the ionization cross-section is different (higher in the case of electron irradiation). The primary effect is the creation of electron-hole pairs, also evidenced by changes of charge state of the species. Since oxides are insulating materials, electron recombination is difficult and can lead to bond breaking. This process is often referred to as radiolysis. The formation of new bonds involve the rearrangement of unstable bonds into a more favourable position or bond orientation, which can lead, after repeated changes, to a modification of the initial structure of the material. In addition, the ionized elements are found to be in an unusual charge and state energy that can promote their migration by Coulombian repulsion. As a consequence, ionizing radiation can enhance the mobility of atoms. This elemental mobility can promote phase changes (e.g., Hobbs, 1979; Cazaux, 1995). Changes in silicates (crystalline or amorphous) have already
been observed under ionizing radiation. The changes involved the breaking of the Si–O–Si bonds (e.g., Carrez et al., 2001), modification of the Si–O–Si angle (e.g., Boizot et al., 1999), and enhanced atomic diffusion and phase transformation (e.g., Hobbs, 1979; Carrez et al., 2001), including recrystallization of amorphous material (e.g., Meldrum et al., 1997).

In MgSiO₃ glass, electron irradiation-induced modifications occur in three stages. First, the glass evolves as revealed by the nanosized domains that appear in the TEM images. At this stage there is no nucleation of any crystalline material. Indeed, the corresponding diffraction patterns reveal that the material is still amorphous. The absence of a crystalline phase shows that the domains are formed by spinodal decomposition, which is a process analogous to a phase de-mixing in liquids. It corresponds to the formation of SiO₂-rich (MgO-poor) domains and SiO₂-poor (MgO-rich) domains. This phase transformation indicates that SiO₂ and MgO are not miscible in the proportion of 50–50 mol% under our experimental conditions. This oxide separation is not surprising since the SiO₂–MgO phase diagram displays a liquid immiscibility at high temperature within the composition range of interest (Dalton and Presnall, 1997). If we extrapolate the immiscibility curves at low temperature (this hypothesis is valid since a glass is structurally very similar to a liquid), the 50–50 mol% composition is included in the immiscibility domain. The glass is thus thermodynamically unstable and tends to decompose into MgO- and SiO₂-rich domains if diffusion occurs. Here the diffusion is not thermally activated but is enhanced by ionizing events. During the first stage of phase transformation (during the spinodal decomposition) no nucleation process is necessary. A composition wave develops with time.

The second stage is the formation of nanosized MgO crystallites. They appear above a fluence of ~3.10¹⁷ electrons/cm². They might occur in the MgO-rich domains of the spinodal decomposition when a critical composition is reached. The MgO crystallites precede the formation of forsterite. The reason for this sequence is probably a kinetic effect. Indeed, it is relatively easy to build a periclase lattice, while the formation of forsterite involves the creation of a more complex structure that probably requires more time. The nucleation and growth processes are also activated by the radiation-enhanced diffusion as a result of ionization processes as well as a thermodynamic driving force for crystallization since crystals have a more favourable free enthalpy than glasses. The crystallites are not MgSiO₃ (enstatite) but forsterite, although the starting material has the enstatite composition. The formation of forsterite (rather than enstatite) is due to the formation of SiO₂ and MgO-rich domains during the spinodal decomposition, a favourable configuration to form MgO-rich crystals.

Influence of Helium Pre-Irradiation

The He⁺ pre-irradiated sample displays the same structural evolution as the as-quenched glass. The modification sequence is first a spinodal decomposition, then the formation of MgO crystallites and finally the formation of forsterite crystallites. However, the kinetics of phase transformation strongly differs. This glass is found to transform about 5 to 10× faster than the as-quenched glass. Obviously, the pre-irradiation state of the glass influences the crystallization behaviour under ionizing radiation. Two explanations can be invoked to explain the differential behaviour. First, the glass structure of the two samples is different. The pre-irradiated sample contains defects formed during the He⁺ irradiation. Its reactivity is thus enhanced by the presence of these defects. Second, the pre-irradiated sample contains He bubbles that can act as preferential sites for the nucleation of a new phase due to the presence of the extra surfaces which can contribute their surface energy to the transformations. Note that such He bubbles have been also observed in silicates in some IDPs (Brownlee et al., 1998). Residence time in the interstellar medium might thus significantly affects the structure of the glass and consequently its crystallization aptitude.

**Astrophysical Implications**

Young stellar objects (YSOs) are known to undergo active and frequent flaring events (e.g., Feigelson and Montmerle, 1999) in which electrons (and protons) are accelerated to million electronvolts energies. The spiralling of these electrons around the magnetic field lines is revealed by their gyrosynchrotron radio emission. These flares are of the order of daily events arising from magnetic re-connection at the YSO surface and in its interaction with the surrounding disc. The proton, and hence the electron, fluence is thought to be of the order of 10⁷ protons/cm² and to endure for several million years (Feigelson et al., 2002). Thus, the total electron fluence in these objects is likely to be of the order of 10²⁰ electrons/cm².

Our experiments using 0.3 MeV electrons are therefore directly relevant to the irradiation of dust in YSO environments. The required electron fluences for the formation of crystallites of MgO (a few 10¹⁷ electron/cm²) and of forsterite (1–5.10¹⁸ electron/cm²) are much lower than the likely available fluence over the lifetime of the YSO phase (10²⁰ electrons/cm²). Thus, in order to crystallize preexisting interstellar medium grains in these environments it is only necessary that they are exposed to a small fraction (of the order of 1%) of the likely total fluence available in these objects during their active flaring stages. This would therefore seem to imply that extensive radial transport and mixing of the circumstellar material in YSO environments is indeed necessary in order to limit the dust exposure to the effects of flaring events close to the star. This must also be the case if a significant and observable fraction of the total dust mass is to be processed (crystallized) in this way.

The electron irradiation of dust in YSO environments could therefore explain the origin of the crystalline silicates around young stars and also in comets in the solar system. In the case of the crystalline silicates seen in comets (Crovisier et al., 1997;
Harker et al., 1999) this low-temperature processing of the material could explain how the silicates were partially crystallized to forsterite (rather than enstatite, as is the case for supernova shock processing) and also explain why they can be associated with volatile icy components. Indeed, if the pre-irradiation of silicates in the interstellar medium, due to the effects of supernovae shock-wave ion implantation, is as important as expected, then amorphous interstellar silicates may be rather susceptible to this low-temperature crystallization process. This effect could favor the amount of crystalline silicates in circumstellar disks.

CONCLUSION

Young stars are believed to be very active, implying a strong interaction between the dust and radiation. The aim of this study was to test the influence of ionizing radiation on the structural evolution of a magnesium silicate glass. The radiation source was the 300 keV electrons of a TEM. We have shown that electron irradiation induces crystallization of MgSiO3 glass. Phase transformations occur in three stages. The glass first undergoes a spinodal decomposition in which nanosized SiO2-rich and SiO2-poor domains form. Second, MgO crystallites are formed, followed by the formation of forsterite crystallites. Both stages require elemental diffusion which is enabled by the effects of the irradiation. Ionizing radiation is thus a possible cause of low-temperature crystallization of silicates in disks surrounding young stars and could also explain the simultaneous occurrence of crystalline forsterite and volatile ices in solar system comets.

We have shown that the structure of the glass before irradiation strongly influences the crystallization kinetics. In particular, we find that a glass pre-irradiated with 50 keV He+ ions (in order to simulate a residence time in the interstellar medium) crystallizes more rapidly than a non-irradiated glass. The silicate structural evolution in the interstellar medium thus modifies the silicates aptitude to react into circumstellar environments.

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