Laboratory Astrophysics: from Observations to Interpretation
Proceedings IAU Symposium No. 350, 2019
F. Salama & H. Linnartz, eds.
doi:10.1017/S1743921319009360

Crystallisation of amorphous Mg-Fe silicates produced from microwave-dried sol-gels

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Abstract. Amorphous Mg-Fe silicates are produced from microwave-dried sol-gels and their thermal crystallisation is studied via *in situ* synchrotron X-ray powder diffraction. Mg-pyroxene crystallised to forsterite, enstatite and cristobalite. The inclusion of 10% Fe formed only forsterite at much higher temperature, while pure Mg-olivine crystallised at a lower temperature than Mg-pyroxene. Cristobalite is observed as a high-temperature crystallite in the pure-Mg compositions. Crystallisation activation energies are derived and discussed in relation to protoplanetary disks.

Keywords. methods: laboratory, planetary systems: protoplanetary disks, ISM: dust, comets: general, infrared: general, X-rays: general

1. Introduction

Laboratory experiments using analogues allow cosmic dust properties to be systematically explored. Sol-gel reactions represent a highly reproducible means of synthesising amorphous silicates. However, incorporating Fe is problematic due to the formation of unwanted crystalline oxide phases. Previously, we overcame this by drying gels under vacuum for >24 hrs (Thompson *et al.* 2016). Recently we have shown that fast drying in air (∼10 min) can be achieved using microwaves to produce amorphous Mg-Fe-silicates (Thompson *et al.* 2019). Since the microwave field interacts with charge carriers in the material, heating is instantaneous and volumetric, with no long-tail, cool-down sintering or Fe oxidation. The crystallisation by thermal annealing of these silicates is investigated in relation to crystalline dust in protoplanetary disks (PPD).

2. Experimental

Amorphous (a:) silicates are produced by drying sol-gels created by mixing metal salt solutions: $Na_2SiO_3 + MgCl_2$ for pyroxene (a:$MgSiO_3$) and $Na_4SiO_4 + 2MgCl_2$ for olivine (a:Mg_2SiO_4). Fe is incorporated by adding $Fe(II)(NH_4)_2(SO_4)_2$ in ratio with $MgCl_2$ to give the required Mg:Fe. To dry by microwave, the gels, spread on a watch glass, were exposed to 900 W microwaves in a domestic oven, in successive 1 minute bursts, until dry (typically 10 bursts; Thompson *et al.* 2019) and characterised (Fig. 1) by FTIR and synchrotron X-ray powder diffraction (XRD). Samples in 0.7 mm internal diameter quartz capillaries were then heated using a hot air blower (5°C steps from 200°C to 995°C, 12°C min^{-1} ramp rate, 1 min equilibration time per step) and their *in situ* structural evolution monitored by fast XRD (2 s exposure per temperature step, 15 keV X-rays). From these data, the crystallisation temperatures, T_c, of the mineral phases forsterite (Mg_2SiO_4), enstatite ($MgSiO_3$) and cristobalite (high-temperature SiO_2 phase) were determined, along with their respective activation energies E/k.

Table 1. Measured crystallisation temperatures, identified phases and activation energies.

Composition	Phase	T_c [°C]	Crystallinity	E/k [K][3]	T_m [°C][4]
a:Mg_2SiO_4	forsterite	495	57%	30,000	205
	cristobalite	895		46,100	465
a:$MgSiO_3$	forsterite	740	42%	39,900	365
	enstatite	735		39,600	365
	cristobalite	765		41,400	390
a:$Mg_{0.9}Fe_{0.1}SiO_3$	forsterite	890	2%	46,000	460

Notes: [1]Confirmed by ICDD PDF4$^+$ XRD database search-match and whole-pattern Pawley fitting. [2]Contribution of all phases to XRD patterns measured at maximum annealing temperature (995°C). [3]Obtained from time and temperature, T_c, at which peaks from each crystalline phase become visible in XRD patterns. [4]Minimum in-disk temperatures required for crystallisation within typical 3 Myr PPD lifetime.

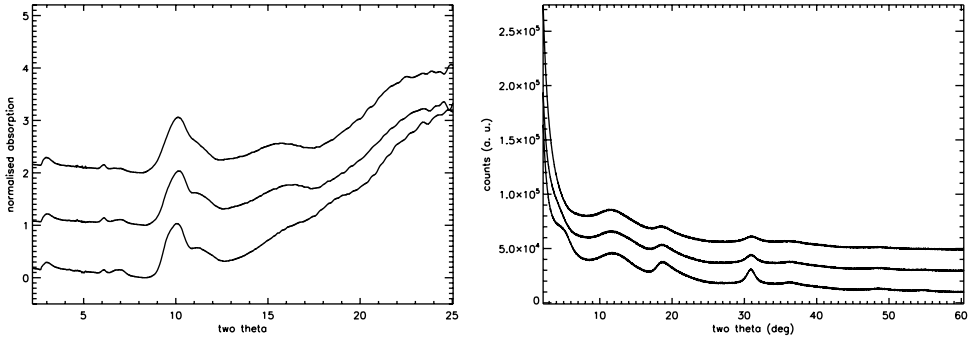

Figure 1. IR spectra normalised to 10 μm peak (left) and XRD patterns (right) for microwave-dried a:Mg_2SiO_4, a:$MgSiO_3$ and a:$Mg_{0.9}Fe_{0.1}SiO_3$ (bottom to top).

3. Results

Table 1 summarises the results. All the silicates retain significant amorphous components, while Fe increases T_c and retains greater amorphicity, with forsterite observed only as a minor phase. For a:$MgSiO_3$ forsterite and enstatite form, while cristobalite is only observed in the Fe-free silicates. However, PPD grains experience lower temperatures for very long periods and E/k constrains the minimum temperatures, T_m, needed to crystallise grains within a typical 3 Myr PPD lifetime, τ ($=\nu^{-1}\exp^{E/kT_m}$; $\nu \sim 2\times10^{13}$ s^{-1}, the mean lattice vibrational frequency). The T_m are shown in Table 1. Forsterite formation from a:Mg_2SiO_4 is consistent with observations of a 69 μm Fe-poor olivine feature from warm dust (∼230°C to -170°C) typically ∼3 to ∼few×10 AU from the star (Sturm *et al.* 2013) and which therefore likely crystallised *in situ*. SiO_2 is observed in the cool components of PPD and associated with olivine in STARDUST samples, suggesting a possible link between PPD mineralogies and the early solar system (Roskosz & Leroux 2015) and potentially diagnostic of Mg-rich mineralogies.

References

Roskosz, M. & Leroux, H. 2015, *ApJ*, 801, L7

Sturm, B., Bouwman, J., Henning, Th., & 13 others 2013, *A&A*, 553, A5

Thompson, S. P., Demyk, K., Day, S. J., Evans, A., Leroux, H., Depecker, C., Parker, J. E., Connor, L., Wilhelm, W., & Cibin, G. 2016, *J. Non-Cryst. Solids*, 447, 255

Thompson, S. P., Herlihy, A., Murray, C. A. M., Baker, A. R., Day, S. J., Smith, A. J., & Snow, T. 2019, *A&A*, 624, A136

https://doi.org/10.1017/S1743921319009360 Published online by Cambridge University Press