

Synthesis of GEMS analogue particles by condensation experiments in the system of Fe-Mg-Si-O-S

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Amorphous silicate particles called GEMS (glass with embedded metal and sulfides) are found in cometary dust particles [1,2]. GEMS is submicron-sized (100-500 nm) particle composed of amorphous silicate and nanometer-sized (10-20 nm) Fe-Ni and Fe sulfides. Metals are typically present inside of an amorphous silicate grain while sulfides on its surface [1,3]. GEMS are considered to be one of the most primitive materials in the solar system and understanding its origin is important to clarify the origin of the solar system materials. However, the origin of GEMS is still in controversy; (1) GEMS formed by non-equilibrium condensation from protoplanetary disk gas in the solar system [1] and (2) GEMS was formed by irradiation of charged particles to interstellar crystalline grains [2]. Condensation experiments based on (1) have been performed so far to reproduce GEMS analogue particles [3,4]. However, the experiments were made using sulfur-free systems, and it is unclear whether or not GEMS analogue particles can be really synthesized when sulfur is added. In this study, condensation experiments using a sulfur-bearing system were performed systematically by changing redox conditions to understand the origin of GEMS.

In the present experiments, induction thermal plasma (ITP) system (JEOL: TP-40020NPS) was used to produce GEMS-like materials by condensation as in the previous experiments [3,4]. A schematic illustration of the ITP system is shown in Figure 1. The ITP system generates high temperatures ($\sim 10^4$ K) flame for vaporizing starting materials and high cooling rates ($10^4 \sim 10^5$ K/s) for rapid condensation to nanomaterials from the vapor. Run products are collected in the bottom of a chamber. Powders materials of SiO₂, Si, MgO, Fe and FeS₂ powders were mixed with the GEMS mean composition (Mg:Fe:Si:S = 0.7:0.6:1:0.3 in mol. ratio) and were used as starting materials. The mixing ratio of Si and SiO₂ was changed to obtain different redox conditions; SiO₂/(Si+SiO₂) = 1 (ITP-100), 0.95 (ITP-95), 0.85 (ITP-85), 0.75 (ITP-75), 0.5 (ITP-50). Detailed operating conditions in the ITP system are shown in Table 1. Run products were characterized using powder X-ray diffraction (XRD: SmartLab, Rigaku), Fourier transform infrared spectrometry (FT-IR: MFT-680, JASCO), scanning electron microscopy (SEM/EDS: JSM-7001F, JEOL), (scanning) transmission electron microscopy ((S)TEM/EDS: JEM-2100F, JEOL).

SEM observation shows that the run products are mainly composed of condensed nanomaterials but some evaporation residues are also present. The evaporation residues were detected as well as the condensation products by XRD and FT-IR. In contrast, the condensed nanomaterials were easily recognized by TEM. The results based on the TEM/EDS analysis are summarized in Table 2. In the most oxidized run (ITP-100), submicron-sized amorphous silicates with only iron sulfides (troilite) were observed. In moderate redox conditions (ITP-95, 85, 75), submicron-sized particles

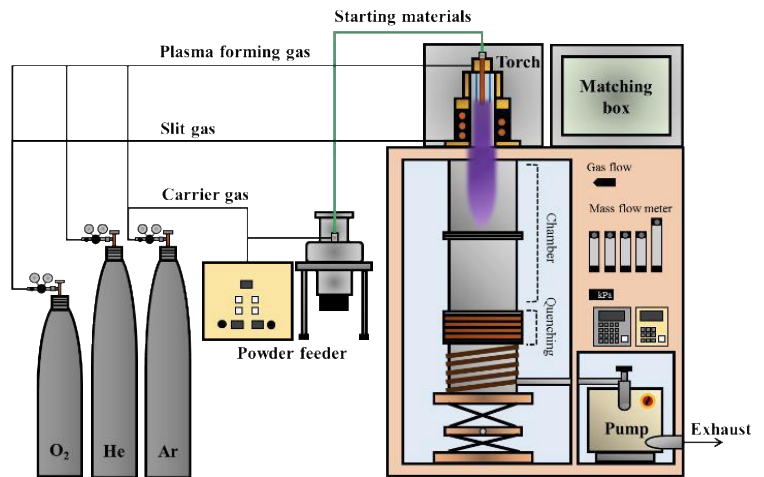


Figure 1. Schematic illustration of ITP system[4].

Table 1. Operation conditions in ITP system.

Run name	ITP-100	ITP-95	ITP-85	ITP-75	ITP-50
Starting material					
SiO ₂	1	0.95	0.85	0.75	0.5
Si	0	0.05	0.15	0.25	0.5
MgO	0.7				
Fe	0.45				
FeS ₂	0.15				
Plasma condition					
Plasma forming gas	Ar 30 L/min + He 3 L/min				
Carrier gas	Ar 3 L/min				
Pressure	70 kPa				
Power supply	6 kW				

composed of amorphous silicate containing metallic iron and iron sulfide were observed. Sulfide particles in ITP-85 and 75 were attached with metallic iron particles while those in ITP-95 were not attached to metallic iron and present separately (Figure 2). In the most reduced condition (ITP-50), amorphous silicate particles containing iron silicide (Fe_3Si) were formed. However, the presence of iron sulfide was unclear in this run. The chemical compositions of amorphous silicates were analyzed using STEM/EDS. The amorphous silicates in ITP-100 and 95 were relatively Fe-rich (probably as FeO) compared to the other run products. Some amounts of sulfur were present ($\text{S}/(\text{Fe}+\text{Mg}) \sim 0.1$) in all the run products irrespective of the redox conditions. Most of amorphous silicate particles have Mg-rich and Si-rich regions. This indicates that amorphous silicate condensed as melts from gas and separation into two liquids, Mg- and Si-rich, occurred at low temperatures.

Spherical sub-micron particles of amorphous silicates having Fe-bearing nanoparticles produced in the present experiments are similar to the texture of the previous experiments without sulfur [3,4] and also of GEMS. In particular, the run products ITP-95, where metallic iron and iron sulfide nanoparticles are separately present (Fig. 2), are very close to GEMS (Table 2). However, the chemical compositions of the amorphous silicates seem to be slightly richer in Fe than those of GEMS. Probably, run condition between ITP-95 and ITP-85 is the most suitable one to reproduce GEMS. The present results strongly suggest that the condition for GEMS formation is limited to a narrow redox condition. GEMS-like materials are also observed in the matrix of primitive carbonaceous chondrites such as Paris meteorite [5]. The amorphous silicates in these GEMS-like materials are FeO-rich and only iron sulfides are present as nanoinclusions. These features are similar to the run product of ITP-100. It has been considered that GEMS-like materials were formed by aqueous alteration of GEMS. However, the present experiments indicate different origin for GEMS-like materials, where they were formed by direct condensation from nebular gas under slightly more oxidized conditions than GEMS.

Table 2. TEM /EDS results of the present experiments. The features of GEMS are also shown for comparison.

Run name		ITP-100	ITP-95	ITP-85	ITP-75	ITP-50	GEMS
Fe (metal)		-	○ (~10 nm)	○ (10~30 nm)	○ (10~30 nm)	-	○ (~10 nm)
FeS (troilite)		○ (30~50 nm)	○ (30~50 nm)	○ (10~30 nm)	○ (10~30 nm)	△	○ (30~50 nm)
Relation between Fe and FeS		only FeS	separated	attached	attached	-	separated
Iron-silicide (Fe_3Si)		-	-	-	-	○	-
Size and composition of amorphous silicate	size	50~100 nm	50~100 nm	50~100 nm	50~100 nm	50~100 nm	100~500 nm
	S	○	○	○	○	○	×
	FeO	rich	rich	poor	poor	poor	poor

○ present, △ unclear, - absent

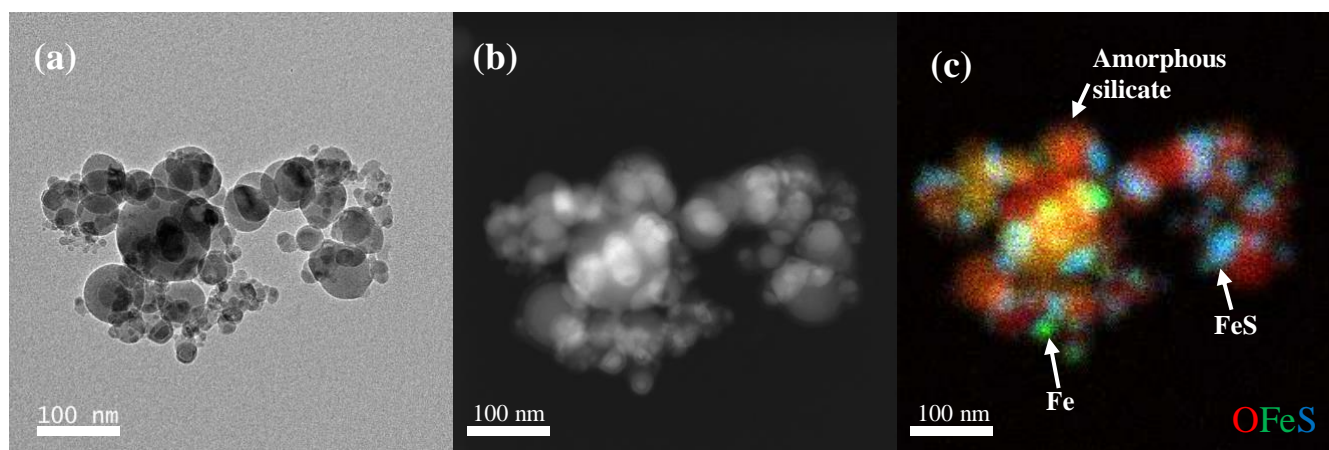


Figure 2. Run products of ITP-95. (a) TEM image. (b) STEM-HAADF* image. (c) Elemental map image.

*HAADF (High Angle Annular Dark Field) : The brightness depends on Z-number.

References

- [1] L. P. Keller and S. Messenger (2011) GCA, 75, 5336-5365. [2] J. P. Bradley et al. (2004) ApJ, 17, 650-655. [3] J. Matsuno (2015) Ph.D. thesis, Kyoto University. [4] T. H. Kim, et al. (2017) ISPC, 23, P2-33-7. [5] H. Leroux et al. (2015) GCA, 170, 247-265