

Developing Glassy Magnets from simulated Composition of Moon/Mars Regolith for Exploration Applications

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ABSTRACT

The feasibility of preparing glasses and developing glass-ceramic materials that display magnetic characteristics using the simulated compositions of Lunar and Martian regoliths have been demonstrated. The reported results are preliminary at this time, and are part of a larger on-going research activity at the NASA Marshall Space Flight Center (MSFC) with an overall goal aimed at (i) developing glass, ceramic and glass-ceramic type materials from the Lunar and Martian soil compositions in their respective simulated atmospheric conditions, (ii) exploring the potential application areas of these materials through extensive materials characterization, and (iii) further improving the related materials properties through a variation of the processing methods. This research activity is an important component of NASA's current space exploration program, which encourages feasibility studies for materials development using in situ resources on planetary bodies to meet the technological and scientific needs of future human habitats on these extra terrestrial outposts. This paper presents an overview of this on-going work at NASA (MSFC) and reports on a few selected results obtained to date.

INTRODUCTION

The long-term space exploration goals of NASA include developing human habitats and conducting scientific investigations on planetary bodies, especially on Moon and Mars. In-situ resource processing and utilization on planetary bodies, therefore, is recognized as an important and integral part of NASA's space exploration program [1], since it can minimize (or eliminate) the level of up-mass (transporting materials from earth to the planetary bodies) and, hence, can substantially reduce the overall work-load and costs of exploration missions. Within this scope and context, a general effort aimed primarily at developing glass, glass-ceramic, or traditional ceramic type materials using Lunar and Martian soil simulants, and exploring various applications of these materials for planetary surface operations has been undertaken at NASA MSFC.

Glass and ceramic materials have been playing important roles in the progress of human civilization since the ancient times with their range of applications expanding almost everyday. Examples of applications of these materials range from common, every day use of structural materials (building and sealing, composites, containers, automotive components, substrate materials for solar cell and electronic applications, etc.) to such sophisticated applications as optical including laser devices, glass fibers for communications, photonic devices (e.g., optical switching), gas sensors, bio-materials, numerous electronic ceramics (capacitor, magnet, semi-

conductor), rocket nozzles, heat resistant ceramic tiles for space vehicles, and many more. Specific applications of a material are controlled primarily by the composition and processing methods or conditions. The major objective of our on-going research at MSFC is to investigate what types of glass and ceramic materials can be developed from Lunar and Martian soil compositions while concurrently exploring the potential application areas of these materials through extensive materials characterization. We also plan on further improving the related materials properties through a variation of the processing methods and conditions.

The major components present in the soils of Moon and Mars include SiO_2 , Al_2O_3 , FeO (moon) and Fe_2O_3 along with minor amounts of CaO , MgO , TiO_2 , and a few other constituents, see Table 1 for the compositions of Lunar and Martian soils. A phase diagram for the system SiO_2 - Al_2O_3 - FeO - Fe_2O_3 that provides useful information on the compatibility and equilibrium melting relations of the various phase assemblages occurring in this system is available [2]. The existing phase diagram [2] strongly suggests the possibility of producing several ceramic-based products that can be used as structural and magnetic materials from the compositions of both Lunar and Martian soils. For example, the possibility exists for producing Al_2O_3 or mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)-based ceramics, which possess high mechanical strength and are extensively used as structural materials. Producing anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) type ceramics, which possess a very low dielectric constant and are useful as substrate materials for solar cell and electronic applications, is another possibility. In addition, these compositions appear to have a high potential for developing aluminosilicate-based materials for thermal barrier coatings. The presence of a large phase field area for the Fe-based spinel in the phase diagram [2] suggests the possibility for producing magnetic ceramics or glass-ceramics.

Table 1. Simulated compositions of Martian and Lunar (JSC-1) soils

Oxide	Mars 1 (wt%)	Mars 2 (wt%)	Lunar soil (JSC-1)
SiO_2	43.2	48.6	47.7
Al_2O_3	23.2	8.2	15.0
TiO_2	3.8	0.9	1.6
Fe_2O_3	15.6	19.8	3.4
FeO	-	-	7.4
MnO	0.3	-	0.2
CaO	6.2	6.4	10.4
MgO	3.4	7.1	9.0
K_2O	0.6	0.2	0.8
Na_2O	2.4	0.8	2.7
P_2O_5	0.9	-	0.7
SO_3	-	7.3	-
Cl	-	0.7	-
Others	-	-	1.1
Total	100.0	100.0	100.0

The different glass and ceramic-based materials that can be developed from the lunar or Martian soil and their full application potentials, which are completely unknown at this time, are the long-term objectives of this research. The results of this research will provide the knowledge base and information to prepare materials using resources on Moon or Mars for use in future habitats on these planets in technological as well as scientific applications so “as to support

sustained human space exploration to Mars and other destinations” [1]. Potential presently identified application areas with a high probability of success are:

1. Structural materials: Brick; Glass fiber reinforced composite; Glass as cement; Alumina or aluminosilicate-based high strength composites.
2. Durable glass/glass-ceramic matrix for immobilizing nuclear wastes.
3. Heat resistant coating/thermal insulator.
4. Ceramic/glass-ceramic magnets.
5. Substrate materials for silicon solar cells and other electronic applications.
6. IR, UV windows or blockers for instrumentation, etc.

The present paper reports preliminary results on a few selected properties with special emphasis on the magnetic properties of glasses prepared using Lunar and Martian simulants. Magnetic materials, depending upon the type of magnetism, have a variety of applications. For example, soft magnets, which can be easily magnetized and demagnetized, are used in high frequency applications and electrical transformers. Hard magnets are difficult to demagnetize, making them suitable for devices requiring a constant magnetic field, such as motors and generators. Semi-hard magnets, incorporating qualities of both hard and soft magnets, are ideal for use in magnetic recording media.

Magnetic glasses can be used in applications such as electroforming and heat generation. Electro forming is a process of fabricating a metal part by electro deposition in a plating bath over a base form or mandrel, which is subsequently removed. Significant improvements of many physical and mechanical properties can be achieved by incorporating ceramic particles into the metal matrix. For example, in comparison to conventionally electrodeposited nickel (already superior to wrought iron), magnetically oriented Metal Matrix Composites (MMCs) have a ten fold improvement in wear resistance, a five fold improvement in the hardness, a three fold strength augmentation and friction reduction by 50% [3]. Products such as aircraft components, heat shields, maneuvering thrusters for satellites, waveguides, rocket engine combustion chambers and nozzles can be manufactured using electro forming. For space transportation, MMCs are attractive due to significant improvements in high temperature mechanical properties and corrosion resistance. Using a proprietary method, MSFC has developed a nickel coating technique for ceramic nano-particles and used these to produce MMC components. The use of a magnetic field, by making the mandrel or base form magnetic using magnetic glass, allows the precise orientation control of these fibers that give the manufactured component improved mechanical characteristics. Although not reported in this paper, one of our major objectives is to identify the type of magnetism that is developed in the glasses prepared from Lunar and Martian simulants, and explore their appropriate application fields.

REGOLITHS AND SIMULANTS

Mars Regolith Overview

Mars has come into keen focus in NASA’s exploration goal in recent years. The prospect of finding water in the polar regions and the promise of the existence of primitive life forms [4] has fueled this curiosity and essentially made Mars as the next exploration destination for NASA. Through the Viking missions carried out in the 1970s and the more recent Pathfinder lander mission, considerable information has been collected regarding the composition of the Martian

regolith and its properties. Testing of Martian meteorites has also served to corroborate some of these findings. Manned exploration of Mars presents several challenges in the materials area and Martian regolith is the starting point for in situ processing. For magnetic studies of soil, one is usually concerned with ferrimagnetic materials (such as magnetite, Fe_3O_4 and maghemite, $\gamma\text{-Fe}_2\text{O}_3$) and anti-ferrimagnetic phases (hematite, Fe_2O_3 and pyrrhotite, $\text{Fe}_{(1-x)}\text{S}$, $x = 0-0.2$). The contribution of paramagnetic materials such as clays, pyroxenes (XYZ_2O_6 , X: divalent metal, Y: trivalent metal and Z= Si or Fe^{3+} or Al^{3+}) can also be important if they are in abundance. The Mars exploration missions have confirmed a strong magnetic component of the soil [5-8]. Optical and magnetic properties of in situ analyzed Mars dust samples have tentatively identified the magnetic phase to be maghemite present as a cement on silicate agglomerates [7]. Contributions to the magnetic properties from titanium inter-metallics such as titanomagnetite or titanomaghemite derived from bedrock are also important [5,9,10]. Magnetic studies of Martian meteorites support the latter hypothesis since the remnant magnetization measured in the samples seems to suggest magnetic contributions from two minerals with differing Curie temperatures [11].

Lunar Regolith Overview

Numerous studies have been undertaken in the areas of microgravity and lunar materials processing to support extended duration space missions as well as for establishing a permanent base on the Moon. See for instance a couple of proceedings dedicated to this subject and the references therein. [12,13]. Various topics such as development of structural elements, habitats, glass, silicon-based solar cells, radiation shielding components, as well as ore purification and metal extraction techniques from lunar regolith are discussed. The general conclusion is that on the lunar surface, abundant materials exist which can be used to produce structural materials including glass [14-16]. On site or in situ manufacture of glass looks promising not only because of the ease of manufacture but also because of its wide applicability [17]. Preliminary tests using lunar soil simulants [18] have also shown that glass fibers can also be produced in short lengths but the soil is unsuitable for the production of continuous glass fibers. The main reasons are problems with recrystallization near the melting point and a narrow viscosity range from which fibers can be pulled. Doping the soil with boric oxide, which extends the viscosity range for pulling fibers and suppresses recrystallization seems to alleviate the problems with continuous fiber pulling [18].

Other aspects of materials processing such as ore purification, metal extraction from ore, and metal casting operations have also been studied [19,20]. Important technical issues are related to the reduced gravity-level, the low temperature environment, and the absence of a substantial atmosphere on a planetary base that will affect the speed at which the liquid metal flows into moulds and the speed at which the metal cools, changing the size of the crystal structure and therefore the properties of the metal [20].

PRELIMINARY WORK AND RESULTS

Glass Preparation

As of this time, two simplified compositions that simulate the composition of the Martian soil as reported in ref. [21] were designed and prepared, see Table 1 for the simulated

compositions in wt% that have been used in the present investigation. The composition for Mars 1 is basically the same as that for volatile-free, normalized composition for JSC Mars-1 as determined by x-ray fluorescence analysis (XRF) [21]. The Mars 2 composition in Table 1 was designed from the composition determined by XRF for the sample from Viking mission (Lander 1 site) [21,22]. The Viking sample contained about 11 wt% of several volatile components, the exact nature (carbonates, hydroxides, etc.) of which is not clearly known. In designing the simulated Mars 2 (Table 1) composition, the wt% content of each oxide component was proportionally increased so as to balance a total of 11 wt%, which was lost on ignition. The composition of a type of volcanic dust in Hawaii is reported [21,22] to be very close to that of Mars 1 (Table 1), but contains a large amount of volatile components. This volcanic dust, which is now available through the Office of the Curator, Johnson Space Flight Center, will also be used in future work.

The composition of the lunar regolith (JSC-1) in Table 1 was developed under the auspices of NASA Johnson Space Center from a volcanic ash deposit located in the San Francisco volcano field near Flagstaff, AZ. This ash, which was erupted from vents related to Merriam Crater (35°20' N, 111°17' W), was mined, processed (crushing, grinding, mixing, sieving), and stored for future use. The JSC-1 composition resembles closely to that of the Lunar soil retrieved by Apollo 14 mission, Lunar soil 14163 [23].

The appropriate amounts of raw materials that produce 50g of glass for each composition (Table 1) were mixed in a sealed plastic container for sufficient time to produce a homogeneous mixture. Then the mixture was put in a platinum crucible and melted in air at 1500°C for 6 hours in an electric furnace. The melt was stirred 3 to 4 times with a fused silica rod (melting temperature 1710°C) over a period of 1 hour to ensure chemical homogeneity. Most of the melt was poured onto a steel plate and cooled to room temperature in air without annealing. A small portion (a few grams) of the melt was also poured into steel molds to form rectangular bars for dissolution rate (chemical durability) measurements in water. These bars were annealed at 600 °C for approximately 4 hours and slowly cooled overnight in the annealing furnace back to room temperature (by turning off the power to the annealing furnace).

Table 2: Selected properties for the Lunar and Martian glasses

Glass ID	Glass Properties			
	T _g (°C) ±3	T _c (°C) ±3	Density (g/cm ³) ±0.02	D _R (g/cm ² .min)
Lunar, JSC-1	680	750 - 820	2.91±0.02	2.1E-08
Mars 1	710	750 - 1140	2.84±0.02	5.1E-09
Mars 2	640	660 - 790	2.83±0.02	1.0E-08

Physical Properties

The as-made glasses were opaque to visible light, and almost black in color, which was expected due to the presence of considerable amounts of iron oxide in both compositions. However, powder X-ray diffraction analysis (Figure 1A) and optical microscopy did not reveal

any crystalline phase in any of the quenched samples, suggesting that all the melts (Mars 1 & 2, and Lunar JSC-1) vitrify easily on cooling to form glass. The density as measured by Archimedes' method with kerosene as the immersion liquid was comparable for the Lunar and Mars glasses, Table 2, the density for the Lunar glass being slightly higher. However, the densities for the Lunar and Mars glasses are considerably higher than that of the commercial window (soda-lime-silica) or laboratory-ware (borosilicate) glasses, which range between 2.34 and 2.42 g/cm³.

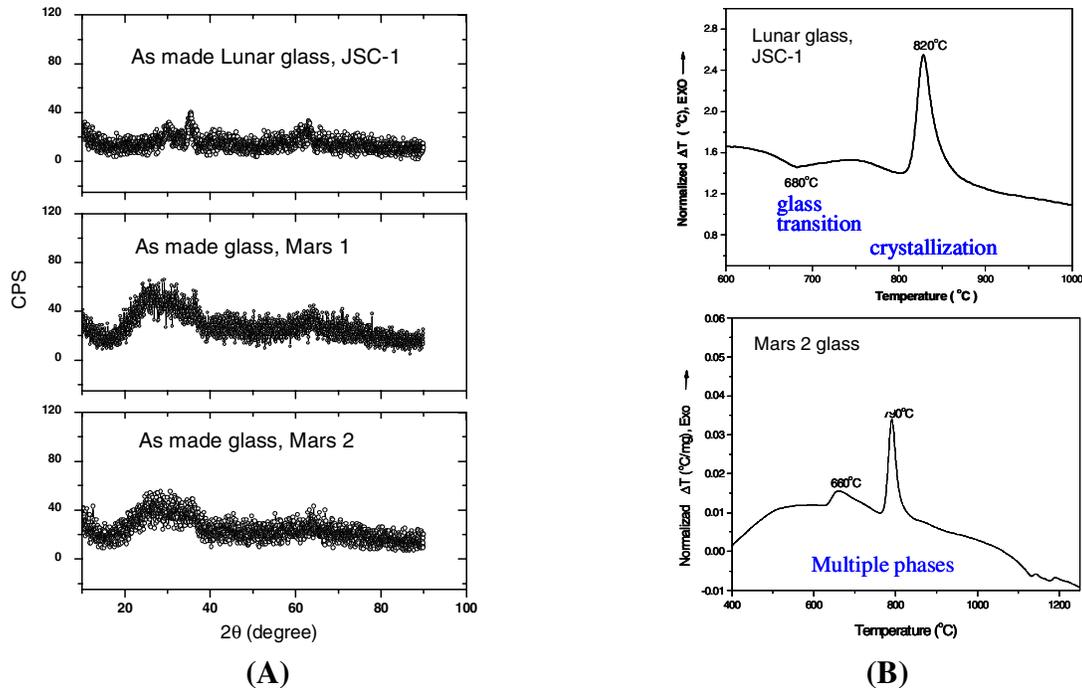


Figure 1. (A) X-ray diffraction patterns for as-quenched glasses produced from simulated lunar and Martian regolith; (B) Differential Thermal Analysis (DTA) curves for lunar and Martian stimulant glasses.

Fig. 1B shows the typical DTA thermograms for the as-made Lunar and Mars 2 glasses obtained at a heating rate of 10°C/min. The glass transition (T_g) and crystallization (T_c) temperatures as obtained from DTA for these glasses are given in Table 2. As shown in Table 2, the working temperature window, $T_c - T_g$, is much larger for the Lunar glass than that for the Martian glasses, which suggests that drawing glass fibers will be easier from the Lunar melt. Also, the values of T_g and T_c for these glasses are considered high compared to conventional alkali-silicate or alkaline earth-silicate glasses, which make these glasses especially suitable for high temperature applications. The DTA for the Mars glasses shows multiple crystallization (exothermic) peaks indicating crystallization of more than one phase from these glasses.

Chemical Durability

The chemical durability of the glasses was measured from their dissolution rate in deionized water (DIW) at 90°C. The dissolution rate (DR) was calculated from the measured weight loss (ΔW) using the equation:

$$D_R = \frac{\Delta W \text{ (g)}}{A \text{ (cm}^2\text{)} \times t \text{ (min)}} \quad (1)$$

where A is the surface area (cm^2) of the specimen and t is the time (min) that the specimen was immersed in the test solution at 90°C. The weight loss (ΔW) is $W_i - W_t$, where W_i is the initial weight and W_t is the weight of the same specimen after time t , in DIW at 90°C. The DR values for the Lunar and Mars glasses range between 5.1×10^{-9} and 1.0×10^{-8} $\text{g/cm}^2/\text{min}$, see Table 2, and these values are comparable or smaller (better) than that of the environmental assessment glasses (borosilicate type) used as standards by the Department of Energy, DoE [24]. In other words, both the Lunar and Mars glasses are extremely chemically durable in water.

Magnetic Properties

In an effort to characterize the magnetic properties of the Mars glasses, a series of tests were performed. Preliminary tests indicated that the glasses were attracted to a magnet, and also had a small amount of residual magnetism. They were opaque (almost black in color). As the first step, a sample of Mars 1 glass ($\sim 1\text{mm}^2 \times 5\text{mm}$ length) was machined, weighed and its hysteresis curve was measured using a Vibration Sample Magnetometer (VSM), Fig. 2A. Next, the sample was heated in a small furnace (designed and built in-house) in a graphite crucible at 800°C in flowing Argon gas for 3 hours in the presence of a uniform, transverse (transverse to the 5mm length of the sample) magnetic field of 0.37 Tesla. The heat treated sample showed reddening on the outside surface and displayed substantially increased residual magnetism as analyzed in the VSM, Fig 2B. The magnetic property measurements for other glasses reported in this paper are continuing.

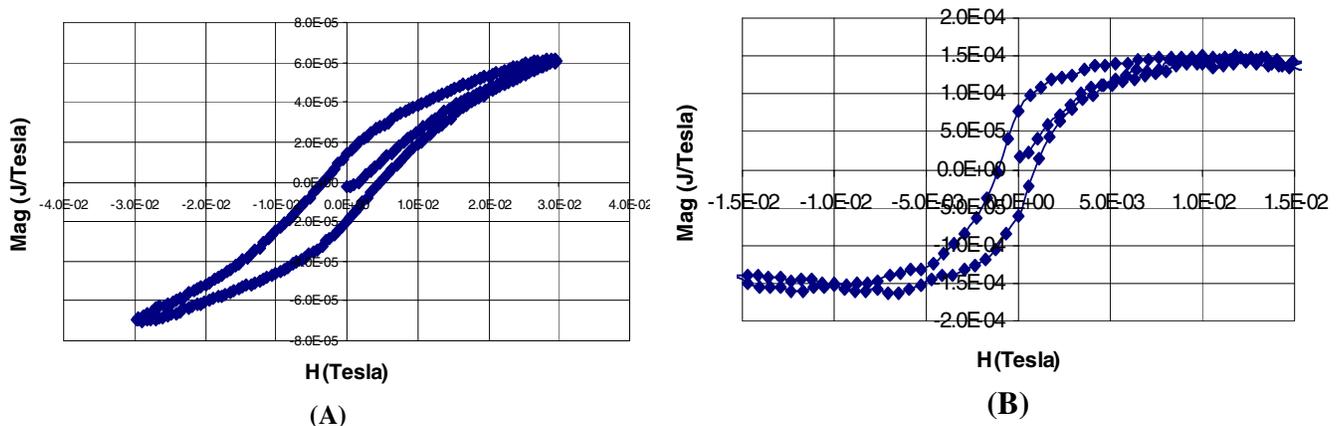


Figure 2. Hysteresis curves for Mars 1 glass; (A) as made glass; (B) heat treated in a magnetic field. Measurements are at room temperature.

The data clearly show that some chemical change occurred during the heat treatment (color change) and that both the glasses, as-made and heat treated have useful magnetic properties. Although no orientation effects of the magnetic field were considered, the data show:

- Both glass samples are primarily soft magnets and display ferromagnetic behavior (hysteresis, saturation, etc.)
- The heat treated glass has improved saturation magnetism (order of magnitude increase), retentivity (factor of 6 increase) and susceptibility (order of magnitude increase) compared to the as-made glass
- The as-made sample has higher coercivity (~50% that of Nickel standard) than the heat treated sample
- Both samples have similar energy density (enclosed area).

Mössbauer Spectra

Mössbauer spectra for a few as-made and heat treated glasses were obtained in order to know the valence state of iron ions (Fe^{2+} and Fe^{3+}) and their concentration in the samples. These spectra were obtained at room temperature on a constant acceleration spectrometer (ASA600) that utilized a 50 mCi rhodium matrix cobalt-57 source using 200 mesh powdered samples. The spectrometer was calibrated at room temperature with an α -iron foil and the line width of the α -iron spectrum was 0.27 mm/s. Each spectrum was fitted with eight broadened paramagnetic Lorentzian doublets. Details of this fitting procedure are given elsewhere [25].

Typical Mössbauer spectra for the as-made Mars 1 glass and for the same glass heat treated at 760°C and 1140°C for 2 h in air are shown in Fig. 3. The as-made glass is shown to contain a noticeable amount of Fe^{2+} ions along with Fe^{3+} ions. The amount of Fe^{2+} ions decreased as the glass was heated at progressively higher temperatures. A magnetic phase appeared when the glass was heated at 1140°C. The amount of the magnetic phase estimated from the Mössbauer spectra is given in Table 3 for the Mars 1 and Mars 2 glasses as function of heat treatment temperature. Table 3 shows that Mars 2 composition should have better magnetic properties than the Mars 1 composition. The exact nature of this magnetic phase is not known at this time, and is one of the important issues of our on-going investigations.

Table 3: Wt% magnetic phase as calculated from Mössbauer spectra in Mars 1 and Mars 2 simulated glasses.

Sample ID	Heat-treatment Temp/Time	Wt% Magnetic Phase
Mars 1	As-made	0
Mars 1	760°C/2h	0
Mars 1	1140°C/2h	27
Mars 2	As-made	35
Mars 2	660°C/2h	35
Mars 2	790°C/2h	74

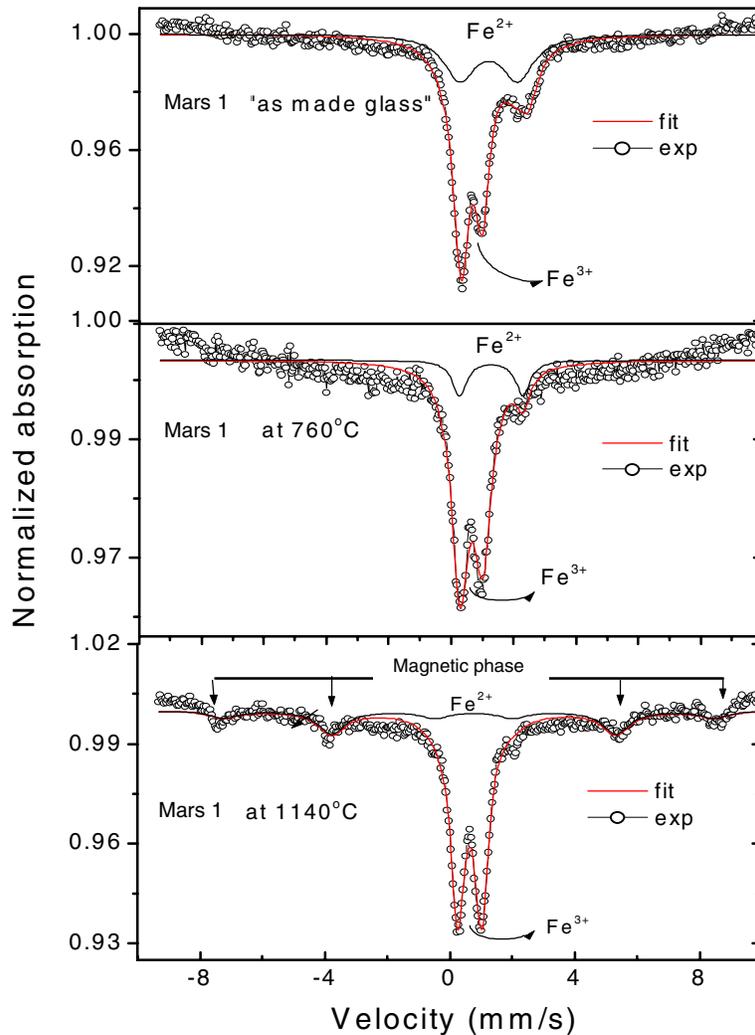


Figure 3. Mössbauer Spectra for as made and heat treated Mars 1 glasses.

CONCLUSIONS

This preliminary investigation demonstrates that glass and ceramic-based materials can be fabricated from both Lunar and Martian regoliths. The full application potentials of these materials are yet to be investigated and are the subjects of an on-going research at NASA MSFC. However, investigations conducted up to this time show that glasses prepared from Martian soil simulants are highly promising for use as magnetic materials. The chemical compositions of the Lunar and Martian soils are very interesting and offer the possibility of fabricating a variety of glass and ceramic-based materials that may have a wide range of applications. The on-going research at NASA MSFC is aimed at identifying the various application areas of these materials by extensive property evaluation and characterization, and optimizing the properties of interest through a variation in the processing methods and conditions. At the conclusion of the work, it is believed that well-defined materials processing methods could be developed that could be used to prepare materials for use on Moon or Mars using in-situ resources.

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