

Fourier–transform infrared spectroscopic characterization of naturally occurring glassy fulgurites

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MS received 7 August 2007

Abstract. We report here for the first time the spectroscopic characterization of natural fulgurites of Garuamukh. On April 22, 2005 at 04:00 local time, large amounts of black-brown colour of colloidal solution came out from below the earth's surface at Garuamukh near Nagaon town (latitude 26°20'39"N, longitude 92°41'39"E, Assam, India) with fire and smoke. This colloidal solution got transformed into fulgurites, glassy material, within a few hours. We present here the characterization of the fulgurites by Fourier transform infrared (FTIR) absorption, X-ray diffraction and X-ray fluorescence methods. The amorphous nature of the substance has been confirmed by Fourier transform infrared spectra of the fulgurites, which exhibit prominent absorption band in the region 400–1200 cm⁻¹, the basic component of amorphous silica. The present study might have significant implications in understanding the thermodynamic properties of naturally occurring glasses, which are formed by shock metamorphism.

Keywords. Glasses; infrared spectroscopy; fulgurites.

1. Introduction

Natural glass on Earth occurs due to either meteorites impact or lightning strike. The glass formed as a result of the collision of a meteorite with the Earth's surface is called meteoritic glass or tektite (Carron and Lowman 1961; Essen and Fisher 1986). Glass (a glassy object, to be exact) that is made as a result of a cloud-to-ground lightning discharge is called a fulgurite, from the Latin word 'fulgur' which means lightning. It is worth noting that lechatelierite (natural silica glass) is not present in obsidian, a glass-like material associated with volcanic activity. On the other hand, lightning strikes on sandy soil may produce fulgurites (Yavuz and Can 1999). Such a silica-based natural glass has also been produced at the nuclear explosion sites. The mineralogical composition (lechatelierite, cristobalite, chalcedony, opal) of fulgurites is related to the palaeo-environmental conditions of the semi-arid regions and to the melting conditions during the fulgurite forming lightning strike to the ground (Sponholz 2004). Fulgurites are also very resistant to weathering and hence the study of properties of fulgurites may be helpful in understanding the ultra-high temperature natural phenomena during lightning (Clocchiatti 1990).

There are two major types of fulgurites: sand fulgurites and rock fulgurites. Sand fulgurites are usually hollow,

glass-lined tubes with sand adhering to the outside. Rock fulgurites are formed when lightning strikes the bare surface of rocks. Rock fulgurites are relatively low in silica and exhibit a wide variety of colours, depending on the composition of the host rock. Each cloud-to-ground lightning involves energy of about 10⁹–10¹⁰ Joules. The peak temperature of lightning channel is in the order of 30,000 K, which is five times higher than the surface temperature of the Sun. The process of lightning strike in rock and sand is chemically similar to the micrometeorite impacts (Sheffer *et al* 2006). In both cases there is a rapid rise of temperature followed by a rapid cooling. The peak temperature of lightning is in between 1900 and 2300 K depending on moisture content, which is higher than the melting point of silica. Since all rocks and soil contain silica, so at this high temperature silica melts and passes through a relatively rapid cooling which causes the glass to solidify. Jayakaran (1998) reported the occurrence of fulgurites in Udhiyur, Tamil Nadu, in a short note. However, there are no previous reports on any physical properties studies on Indian fulgurites.

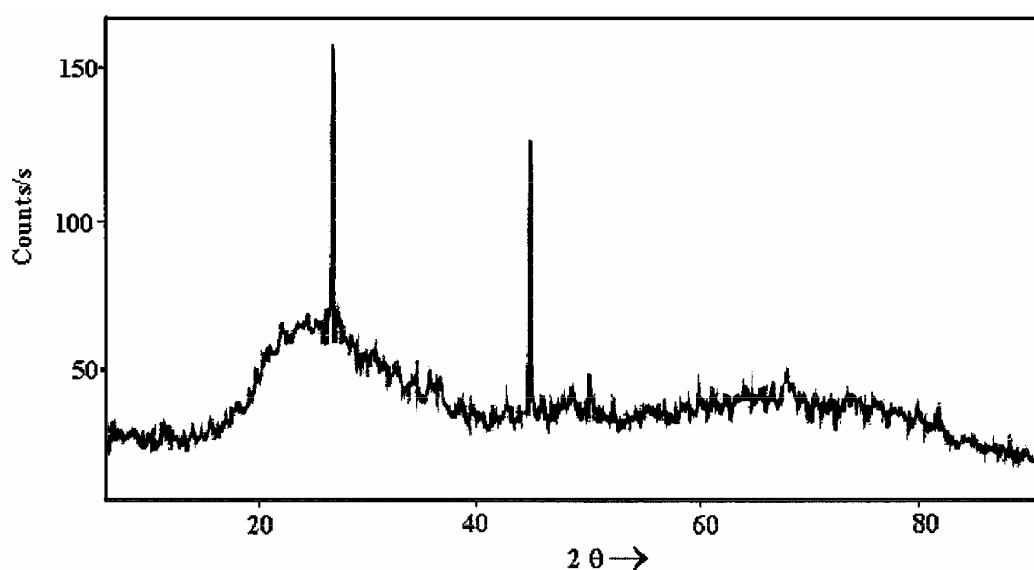
On April 22, 2005 at 04:00 local time, large amounts of black-brown fulgurites were formed at Garuamukh near Nagaon town (latitude 26°20'39"N, longitude 92°41'39"E, Assam, India). The melt formed on the earth's surface with fire and foul odour smoke and the upper part of it gradually solidified. The solid material has been found to have a temperature of about 350 K even after a lapse of two days after occurrence of the event whereas the room

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Table 1. Comparison of chemical compositions of the Garuamukh fulgurites with other fulgurites.

	Garuamukh (G-01)	Garuamukh (G-02)	Garuamukh (G-03)	Germany	New Jersey	Illinois	Holland
SiO ₂	97.5	96.8	97.2	93.8	99.0	91.66	90.2
Fe ₂ O ₃	0.6	0.8	0.7	—	0.3	—	0.7
Al ₂ O ₃	1.4	2.0	1.6	3.8	0.7	6.69	0.9
TiO ₂	0.5	0.3	0.6	—	—	—	—
CaO	—	—	—	0.6	—	0.38	0.1
MgO	—	—	—	—	—	0.12	0.5
Na ₂ O	—	—	—	—	—	0.77	0.6
K ₂ O	—	—	—	—	—	0.73	0.5

Note: The data for Germany, New Jersey, Illinois and Holland are taken from Frondel (1962).

**Figure 1.** X-ray diffraction pattern of the Garuamukh fulgurites sample.

temperature during that period was 300 ± 5 K. The aim of this study is to analyse FTIR spectra of the sample with reference to 10 μm and 20 μm bands, because these absorption bands at middle infrared wavelengths detected the valence vibrations or deformation vibration of SiO₄ tetrahedrons in silicate. The spectral characteristics of the fulgurites would be helpful in determining the peak shock temperature by identifying high-temperature phase of silica. The present study describes, for the first time, the FT-IR spectroscopic characterization of the fulgurites found at Garuamukh.

2. Experimental

The glassy nature of the samples were confirmed by powder X-ray diffraction (XRD) analysis, by using the Philips PW 3710 XRD system which was operated at 40 KV and 45 mA, with a CuK α ($\lambda = 1.54$ Å) radiation and a graphite monochromator. The composition of the fulgurites was determined by using a Philips X-ray fluorescence (XRF) machine at the National Geophysical Research Institute,

Hyderabad, India. In X-ray fluorescence method, typical uncertainty involved in oxide analyses was about 0.01 wt%. One part of the sample was crushed into fine powder for analysis. The powdered sample was homogenized in spectroscopic grade KBr (1 : 20) in an agate mortar and pressed into 3 mm pellets with a hand press. We tried to minimize the grinding time to avoid the deformation of the crystal structure, the ion exchange and the water absorption from atmosphere. The infrared spectra was acquired using Perkin-Elmer system 2000 FTIR spectrophotometer at Guwahati University, Guwahati, India, with helium-neon as the reference, at a resolution of 4 cm⁻¹. The spectra were taken in the region 400–4000 cm⁻¹. The room temperature was 30°C during the experiment.

3. Results and discussion

Sand fulgurites are usually created when lightning strikes the Earth and locally melts quartz sand, and the sand is instantly heated up to ultra high-temperatures (air temperatures may temporarily reach 10,000–30,000° Celcius)

and fulgurites can then form, tracing the path the lightning took, generally decreasing in diameter and sometimes branching as they descended. Fulgurites often take the form of tubes, sometimes exceeding 30 mm or more in diameter, and are known to exceed 8 meters in length (although this great length makes their recovery as a whole impossible as they are extremely fragile). The outer surfaces are often rough with adhering, unfused quartz sand grains. If they are tubular, the inner surfaces are usually smooth and glassy. Because of the rare occurrence, typical fulgurites cost from 50–150 US dollars. The XRF results show the major component of the sample to be SiO₂. The results are compared with that of the previous work on fulgurites found elsewhere in similar geological settings (Fron del 1962). Table 1 shows the chemical composi-

tions of the natural fulgurites sample from Garuamukh and their comparison with earlier data on fulgurites produced by lightning. The absence of diffraction peaks in the broad pattern indicates that quartz is amorphous or glassy. The spectrum shows a slope of peak around 23° corresponding to the amorphous matrix of SiO₂. The overall pattern is that of amorphous silica. The sharp peaks observed in XRD (figure 1) are due to the presence of crystalline quartz as impurities.

The FTIR spectrum reveals a few absorption bands. The groups of bands in the region 400–700 cm⁻¹ and 800–1175 cm⁻¹ are assigned as 20 μm and 10 μm, respectively. In the Si–O stretching vibration region (800–1175 cm⁻¹), the bands at 787, 952, 1069, 1170 cm⁻¹ are identical to the bands at 800, 958, 1088 cm⁻¹ due to amorphous silica (Ojama 2003). The 10 μm and 20 μm bands of Garuamukh fulgurites and the amorphous silica is shown in figure 2. It is seen that the characteristic frequencies slightly differ but the relative intensities vary in both silicates. Amorphous silica exhibited a relatively strong peak at 800 cm⁻¹ and it can be distinguished from the band of crystalline silicate (Ojama 2003).

The structure of most SiO₂ polymorphous, both crystalline and amorphous, is based on tetrahedral unit of silicon coordinated to four oxygen atoms. Amorphous silica is one of the polymorphous of silica and at high temperature it can easily transform from quartz. In the Si–O–Si bending vibration region (400–700 cm⁻¹) of quartz, the band at 695 cm⁻¹ is determinative whether it is crystalline or amorphous (Parthasarathy *et al* 2001). In the amorphous state this band will be missing. In the fulgurites sample, we did not get 695 cm⁻¹ peak which indicates that the silica mineral in this sample is in amorphous form. The absorption band at 695 cm⁻¹ is due to the vibrations in octahedral site symmetry and at 780 cm⁻¹, it is due to the vibration in tetrahedral site symmetry (Schneider 1974; Parthasarathy *et al* 2001). The tetrahedral symmetry is stronger than that of octahedral symmetry. Therefore, for any structural change, the damage occurs first in octahedral then in tetrahedral symmetry. When the temperature

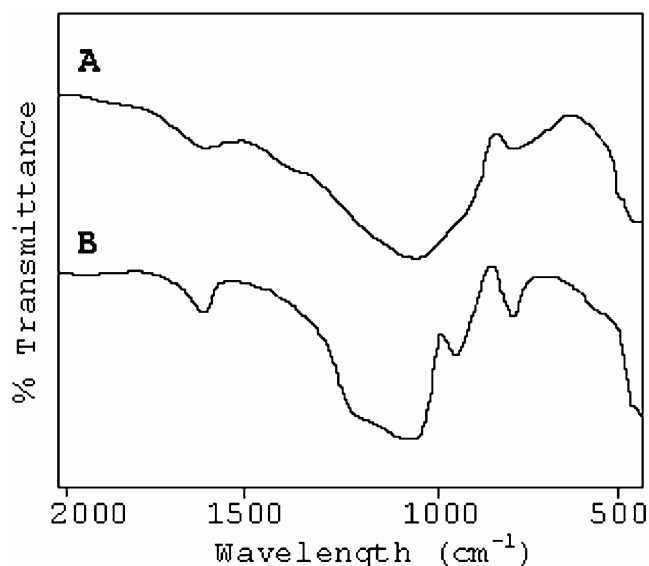


Figure 2. Comparison of FT-IR spectra of the natural fulgurites sample (A) and the spectra of the amorphous silica (B) (Ojama 2003) in the 20 μm (500 cm⁻¹) and 10 μm (1000 cm⁻¹) regions.

Table 2. The observed absorption frequencies (cm⁻¹) of Fourier transform infrared spectra of the natural fulgurites and the assignments.

Wave number (cm ⁻¹)	Assignments
459	Si–O asymmetrical bending vibration
787	Si–O symmetrical stretching vibration
952	Si–O stretching vibration
1069	Si–O asymmetrical stretching vibration
1170	Si–O asymmetrical stretching vibration
1392–1476	CO ₃ ²⁻ stretching
1508–1560	CO ₃ ²⁻ symmetric stretch (ν ₃)
1635	OH bending vibration
1684–1720	CO ₃ ²⁻ symmetric stretch (ν ₃)
2868–2969	C–H stretching vibration (organic contaminants)
3452	OH stretching vibration

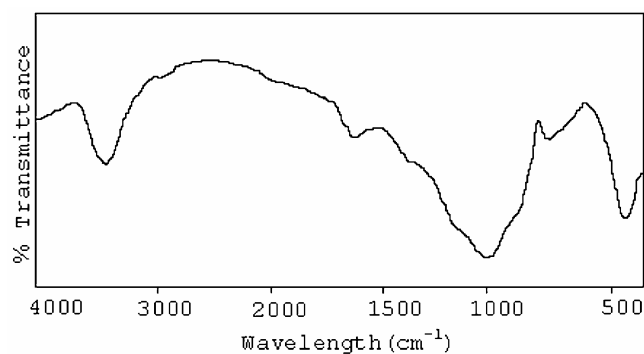


Figure 3. The IR spectra of the natural fulgurites sample from Garuamukh, Assam (India) in between 400 and 4000 cm⁻¹.

generally quenched so rapidly to 600–700°C, the SiO₄ tetrahedral could not be ordered to crystalline state and were preserved in an amorphous silicate phase.

The transmission FTIR spectrum of the fulgurites sample is shown in figure 2. The frequencies of IR bands and the possible assignments are listed in table 2. In the 20 μm region only one band is found at 459 cm⁻¹ corresponding to the Si–O asymmetrical mode of vibration. The carbonate structure contains isolated CO₃²⁻ group with a doubly degenerate symmetric stretch (ν₃) at the region 1508–1560 cm⁻¹ (Parthasarathy et al 2002). The IR bands at 1684–1720 cm⁻¹ could be assigned to the bending vibration of H–O–H dissolved volatile species. The bands at 2868–2969 cm⁻¹ could be assigned to stretching vibration of C–H band which may be introduced during sample handling or some hydrocarbon present in the soil contaminant. The bands at 1392–1476 cm⁻¹ is due to the Na–non-bridging oxygen–carbonate ion stretching vibration (Na–NBO–CO₃) (King et al 2004). The speciation of water in silicate glass formed by rapid quenching from melt equilibrated at high temperature reflect the nature of the melt, so it is important to note that the molecular water and hydroxyl group coexist in rapidly quenched glass (Stopler 1982). The absorption bands at 3452 cm⁻¹ and 1635 cm⁻¹ arise due to adsorbed water molecule commonly observed in natural silica (Parthasarathy et al 2001).

4. Conclusions

The present investigation of the Assam fulgurites represents the first FTIR spectroscopic study on any Indian fulgurites till date. The characteristic features of amorphous silica with some other trace minerals were identified by FT–IR spectroscopic method. In the silica, structural change is due to the coordination change. The amorphous phase due to the effect of tetrahedron and octahedron can be observed in the infrared data. While this transformation occurs, the materials pass through intermediate state. The XRF results show the major component of the sample to

be SiO₂. The broad Bragg peaks observed in X-ray diffraction studies reveal that the sample could be nanocrystalline quartz. The temperature required for the formation of octahedral symmetry in glassy fulgurites is found to be much lower than that of crystalline samples. The present characterization study of fulgurites could be useful in understanding the short-range order in fulgurites produced by shock metamorphism.

Acknowledgements

We thank Directors of NGRI and IICT, for providing the analytical facilities. We also thank Prof. A J Choudhury, Gauhati University and N K Gogoi, NGRI, for useful discussions. One of us (GP) is thankful to ISRO, Department of Space, Government of India, for financial support under PLANEX program.

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