Phase Composition and Microstructure of UHPHT Vein Glass from Giant Diamondiferous Kara Impact Crater by Raman Mapping

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Abstract. 2D and 3D Raman mapping allows to observe "in situ" distribution of phases and relationship of minerals in rock samples, different mineral aggregates, mineral inclusions within crystals and other quantitative spectroscopic studies of mineral substances and materials. The method is realized in accumulating and processing of big data array of Raman spectra (RS) from selected areas of a studied sample with subsequent visualization in XY plane at 2D mapping or in the form of 3D experimental models with XYZ coordinates in a case of 3D Raman mapping. During the mapping different analytical data can be visualized as maps such as spatial distribution of mineral phases, degrees of their crystallinity, orientation of crystallites and their size, residual tension in minerals and inclusions and many other parameters. As 3D Raman mapping demands higher requirements to quality of samples, takes significantly long time expenditure and big data for processing, 2D Raman mapping looks to be the most effective for different mineralogical applications. In this work we demonstrate advantages of 2D Raman mapping on the example of studying of the impact ultrahigh-pressure high-temperature (UHPHT) vein glasses with melt-crystallized ultrahigh-pressure silica phase – coesite, for the first time found within diamondiferous impactites of the giant Kara meteorite crater. The mapping was produced with processing of typical spectra ranges of recognized mineral phases met in analyzed areas. As a result of the conducted studies it has been established what according to spectroscopic data coesite hangs to central parts of UHPHT silica glass located in general matrix of aluminosilicate glass. The sites of silicate glass are characterized by fully amorphous state that is obviously shown in its typical ranges. The areas with a high luminescence correspond to inclusions of smectite micro-drops in UHPHT silica glass isolations that has been confirmed with the accompanying study with use of electron probe microanalysis (EPMA), energy dispersive spectroscopy (EDS) and electron diffraction (ED). The used 2D Raman mapping to the impact vein glasses of the Kara meteorite crater allowed to reveal distribution of mineral phases in UHPHT glass, showing distribution of amorphous and crystalline phases that is undoubted advantage of the Raman spectroscopy. In full text of the paper technical features of Raman 2D mapping are shown that can be useful for similar mineral objects and materials with complex phase structure and different degree of ordering.
1. Introduction
The Raman scattering (Raman effect) for the first time was observed in 1928 by G.S. Landsberg and L.I. Mandelstam [1] and detected in liquids by C.V. Raman [2]. At present Raman spectroscopy is a very important tool for materials characterization. Despite of broad development of various methods of solids analysis the Raman spectroscopy has a number of the advantages allowing it to remain the indisputable leader in the field of mineral substance studies [3]. First of all, this method is nondestructive, that is especially important for studies of rare, value and museum specimens. Also, the method usually does not require any specific preparation or a minimum sample preparation may be required. Raman spectroscopy is widely used for mineral substance of meteorites, space particles and planetary studies [5-7].

One of the most progressing techniques of Raman spectroscopy is mapping, being a powerful method for mineralogy and petrography applications. The micrometer-size spatial resolution of the laser beam allows phase identification of very small portions of mineral substance recognised on the physical limit of optical microscopy resolution. Modern methods of Raman data evaluation allow provide processing for analysis of structural or compositional properties of individual crystalline and non-crystalline phases, vastly improving the whole complex of the standard analytical possibilities of mineral substance studies. Probably in the coming future Raman mapping is expected to be quite widely used procedure at Raman studies for multiphase mineral aggregates and structurally inhomogeneous mineral substances. Additionally to standard phase analysis Raman spectroscopy allow to investigate level of crystallinity, strain defects, level of compressing and so on [8-11]. Thus, it is one of the most useful instruments for materials diagnostics and characterisation.

At present the method of two-dimensional (2D) Raman mapping or mapping in the XY plane allowing to observe “in situ” distribution and relationship of mineral phases and other spectroscopic parameters in the studied sample [3] looks especially perspective. The method requires big data of Raman spectra for a selected area of the studied sample with the subsequent data visualization in the form of a colour images of spatial distribution of mineral phases, allowing to analyze features of morphology, grain sizes and relationship of minerals, degrees of their crystallinity, orientation of crystallites and their size, as well as other different structural parameters, such as residual tension in minerals, quantitative ratios of the analyzed spectral elements and many others. More exotic use can be connected with collecting luminescence signal which can be applied detection of some phases. Some experimental results in Raman mapping for mineral substances and rocks were described in [3, 8, 9, 12].

Here we present for the first time the Raman mapping application for multi-component UHPHT impact glasses with coesite being inhomogeneous tight aggregates of phases with different level of crystallinity [13-16].

2. Materials and methods
The material was sampled in 2015 at the Kara astrobleme (Pay-Hoy ridge, Russia). The ultrahigh pressure high temperature (UHPHT) impact glasses of the vein type were described in natural outcrops [13-15]. The preliminary detailed studies of the UHPHT impact glasses were provided by a complex of mineralogical studies in the Center of Collective Use “Geonauka” at the Institute of Geology of Komi Scientific Center UB RAS (Syktyvkar, Russia) including Raman spectroscopy, scanning electron microscopy (SEM), electron microprobe analysis (EMPA), X-Ray diffraction (XRD), atomic-force microscopy, thermal analysis, fluid chromatography, chemical analysis; at the National Research Center «Kurchatov Institute» (Moscow, Russia) high resolution transmission electron microscopy (HRTEM) was produced [13-16].
The Raman studies were conducted at the Center for collective use “Geonauka” (IG Komi SC UB RAS, Syktyvkar, Russia). The spectral data were registered with use a Raman spectrometer LabRam HR 800 (Horiba, Jobin Ivon) in the mode of two-dimensional Raman mapping for XY axes.

For deep study of the natural UHPHT impact glasses by Raman mapping we prepared double-side polished petrographic thin sections without covered glass.

The He-Ne laser ($\lambda = 633$ nm) was used for Raman scattering excitation with the power of 20 mW, in the 100–4000 cm$^{-1}$ range using a spectrometer grating of 600g/mm, with a confocal hole size of 300 $\mu$m and a slit of 100 $\mu$m. The long-distance objective $\times 50$ was used for laser spot focusing with a local size on a sample about 1.5 $\mu$m$^2$, touching the specimen square analysis about 5 $\mu$m$^2$. A signal accumulation time was 3 seconds with 1 cycle in the spectral range 100–1100 cm$^{-1}$. The system was equipped with an Olympus BX41 optical microscope and a Si-based CCD detector. For the spectral data processing LabSpec 5.39 software was used.

The characterised spectra of individual phases present within the aggregates (Table) were used for the Raman maps processing. The mapping was provided by the net 50×50 points with a step about 1.6-1.8 $\mu$m within the selected area of the specimen (80×90 $\mu$m$^2$). In total the massif of about 2500 points has been received during 2.5 hours. After the data accumulation the spectra were processed for deleting of cosmic rays and base noise through the 3rd degree polynomial function.

3. Results

During the complex of mineralogical studies of the UHPHT impact glasses of vein type [13-16] we have found their multi-component composition with presence of coesite crystals. The vein glasses are inhomogeneous tight aggregates of phases with different chemical composition and level of crystallinity that is evidently seen on the SEM images and elemental mapping (Figure 1) and at high resolution TEM data [15]. The UHPHT vein glass consists of aluminosilicate general amorphous glass with augite microcrystallites. The host matrix keeps inside UHPHT silica drops of glass with coesite (Figure 1).

After the detailed SEM, elemental mapping studies and individual Raman spectra studies we have selected regions with silica drops for detail phase analysis. Using typical spectra of the individual optically recognised phases (Figure 2, right column, table) we have processed the individual maps for different phases (Figure 2, left column). The resulted Raman mapping data allowed recognize spatial phase’s resolution within the analyzed area (Figure 3, 4).

The received data (Figure 3, 4) demonstrate that within the silica drops coesite crystals are set close to the central parts of the silica UHPHT isolations. At the same time we observe a presence of regions with high luminescence belonging to smectite phase, crystallized from impact melt [15]. The tight spatial co-existence of smectite and coesite crystals allow conclude that the smectite was formed under UHPHT conditions.
Figure 1. Elemental mapping of a drop of UHPHT silica glass with coesite within aluminosilicate general amorphous glass with augite microcrystallites, secondary electrons mode: a – SEM image for elemental mapping region, b – combined SEM/multi-elemental map, c – individual elements maps for the selected area
Figure 2. Raman phase maps with corresponding Raman spectrum, right column – individual phases spectra (basic for mapping), left column – corresponding individual phases Raman maps (from top to bottom): coesite, silica glass, aluminosilicate glass, luminescence region (belonging to smectite [15]).
Table 1. Spectroscopic data description for typical spectra used for Raman mapping of the UHPHT impact glass

| Mineral                              | Band position, cm\(^{-1}\) | FWHM*, cm\(^{-1}\) | Area, % |
|--------------------------------------|----------------------------|--------------------|---------|
| Coesite                              | 115                        | 8                  | 3       |
|                                      | 176                        | 7                  | 4       |
|                                      | 271                        | 7                  | 3       |
|                                      | 427                        | 5                  | 1       |
|                                      | 521                        | 7                  | 1       |
| Silica glass                         | 364                        | 153                | 56      |
|                                      | 462                        | 98                 | 31      |
|                                      | 677                        | 51                 | 2       |
|                                      | 800                        | 57                 | 6       |
|                                      | 994                        | 100                | 5       |
| Enstatite (+host aluminosilicate glass) | 139                       | 97                 | 8       |
|                                      | 345                        | 51                 | 11      |
|                                      | 399                        | 35                 | 6       |
|                                      | 513 (glass)                | 136                | 35      |
|                                      | 681                        | 60                 | 23      |
|                                      | 929                        | 79                 | 4       |
|                                      | 1011                       | 47                 | 13      |

* FWHM — full bandwidth at half maximum; Area, % — relative integrated intensity of the band (the ratio of the band area to the sum of all areas of the bands of the spectrum)

Figure 3. Multi-phase Raman map, corresponding to the data from the Figure 2: red – coesite, green – silica glass, purple – aluminosilicate glass, blue – regions with high luminescence
Figure 4. Resulted Raman mapping in combined optical image in transparent non-polarised visible light: a – optical image with the selected area for mapping; b – combined optical image with individual phases by Raman data (mineral phases correspond to Figure 3).

4. Discussion
According to the provided Raman mapping the specific phase distribution within UHPHT impact vein glasses has been analyzed pointing to central position of the coesite crystals aggregation within silica melt located in general matrix of aluminosilicate matrix. The silicate glass within the drops are characterized by totally amorphous state, no any quartz presence has been. In combination to our previous HRTEM data [15] areas with a high luminescence correspond to inclusions of smectite micro-drops within UHPHT silica glass isolations that has been confirmed with the accompanying study [13-15] with use of electron probe microanalysis, energy dispersive spectroscopy, high resolution transmission electron microscopy and electron diffraction.

5. Conclusion
For the studied UHPHT impact glasses by 2D Raman mapping the unusual UHP mineral association was established presented by unusual tight coesite-smectite co-existence within pure amorphous silica glass. The presented 2D Raman data demonstrate that Raman mapping is provide very important additional information to the standard complex of the other methods and can be useful for analyzing of complicated aggregates consisting of amorphous and crystalline phases that is undoubted advantage of the Raman spectroscopy that can be applied either for other natural objects or materials with complex phase structure and different degree of ordering.

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