Crystals in the 19th Century Glass Beads

I. F. Kadikova[1], T. V. Yuryeva[1], E. A. Morozova[1, 2], I. A. Grigorieva[3], M. V. Lukashova[4], I. B. Afanasyev[5], and V. A. Yuryev[6]

[1] *The State Research Institute for Restoration, Bldg 1, 44 Gastello Street, Moscow 107114, Russia*

[2] *N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky Avenue, Moscow, 119071, Russia*

[3] *The State Hermitage Museum, 34 Dvortsovaya emb., Saint-Petersburg, 190000, Russia*

[4] *TESCAN Ltd., 11 Grazhdansky Avenue, Saint-Petersburg 195220, Russia*

[5] *The Russian Federal Center of Forensic Science of the Ministry of Justice, Bldg. 2, 13 Khokhlovskiy Sidestreet, Moscow 109028, Russia*

[6] *A. M. Prokhorov General Physics Institute of the Russian Academy of Sciences, 38 Vavilov Street, Moscow 119991, Russia*

Introduction

Glass is one of the most important and mysterious materials in human history. From ancient times to the modern era, it played an essential role in culture. However, only in the middle of the 18th century the real flourishing of beadwork art took place. Although this period was rather short and lasted only until the end of the 19th century, a lot of artworks were created. At that period the craft was extremely fashionable and popular in Europe, in the North America, in Russia, etc. Therefore, objects made of historical art glass surround people in museums, churches, and sometimes even on the streets of cities (*Fig. 1a*).

Probably, glass seed beads is the most numerous group of glass historical glass, as they were used, for example, to decorate clothing, religious objects and functional tools, and served as an important good for global trade. Therefore, the conservation state of items made of glass beads is an actual problem for curators and conservators. Glass, as well known, is often an unstable material, so a number of internal (e.g., the glass composition) and external factors, such as temperature, humidity and other storage conditions, affect chemical and physical processes in glass and on the glass surface.

Some types of historical beads dated 19th century are subjected to more intense destruction than others. For example, translucent turquoise lead-potassium ones change their colour to greenish and yellowish; a large net of cracks is observed on the turquoise, transparent, red, peach and some other types of glass beads (*Fig. 1b-e*). As a result, the beads become very fragile and could not be restored and returned to their places on the embroidered issues.

The cracks are the result of removal of internal stresses in glass that arise during the production of beads (cutting the glass tubes, tumbling and cooling). Also, the probable causes of internal stresses can be crystals, that were found in the glass beads, both subjected to corrosion and well-preserved.

Figure 1. Embroidered issues from the Russian museum collections: (a) *Glass Beaded Passion, or Three Centuries of Beads in Russian Art* exhibition, the Ostankino museum-estate; (b – d) the fragments of embroiders where corroded glass beads are observed (rows show examples of destructed historic turquoise beads, some of them are replaced by larger modern blue transparent beads); (e) corroded and mechanically damaged turquoise glass beads from museum exhibits of the 19th century obtained during its restoration.

Techniques and Equipment

A complex of analytical methods was used to examine the samples of glass beads of different colours and states of preservation. Elemental compositions of all samples were analysed by M4 TORNADO X-ray fluorescence (XRF) microspectrometer (Bruker) and MIRA 3 LMU scanning electron microscope (SEM) (Tescan) with INCA-450 energy dispersive X-ray (EDX) spectrometer (Oxford Instruments). For the direct phase analysis of crystallites in glass, the Nordlys II S electron backscatter diffraction (EBSD) detector (Oxford Instruments) was used (*Fig. 3*).

Results and Discussion

Numerous crystals with sizes ranging from several hundred nm to several µm were found in the turquoise glass beads. They tend to form large clusters through which cracks often pass (*Fig. 2c, d*). These crystallites were identified as orthorhombic $KSbOSiO_4$ (KSS) (*Fig. 3a*). Probably, the crystals were formed during the melting process at a high temperature (more than 1200 °C).

Yellow glass beads also contain micro-inclusions, however, they are not subjected to destruction. Their stability can be explained by smaller crystallite size (no more than ~0.4 µm) and the fact that they do not form large clusters. We identified them as crystals of cubic lead antimonate ($Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$) (*Fig. 3b*) - a type of Naples yellow, modified by iron atoms.

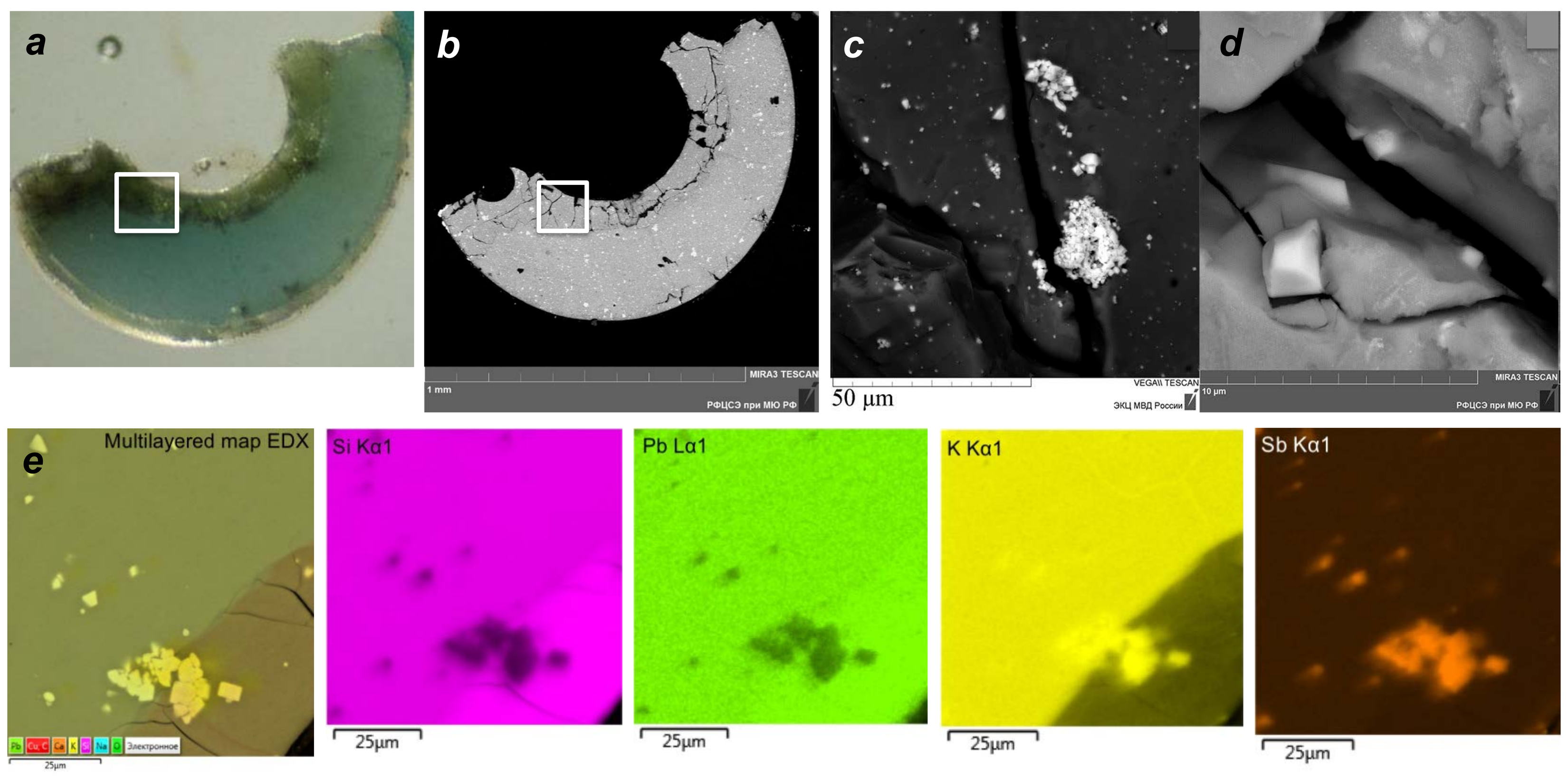

Figure 2. The cross-section of the turquoise glass bead: (a) image in polarized light and (b) SEM image; (c, d) SEM images of clusters and large individual KSS crystals in glass; (e) elemental mapping of the part of the cross-section.

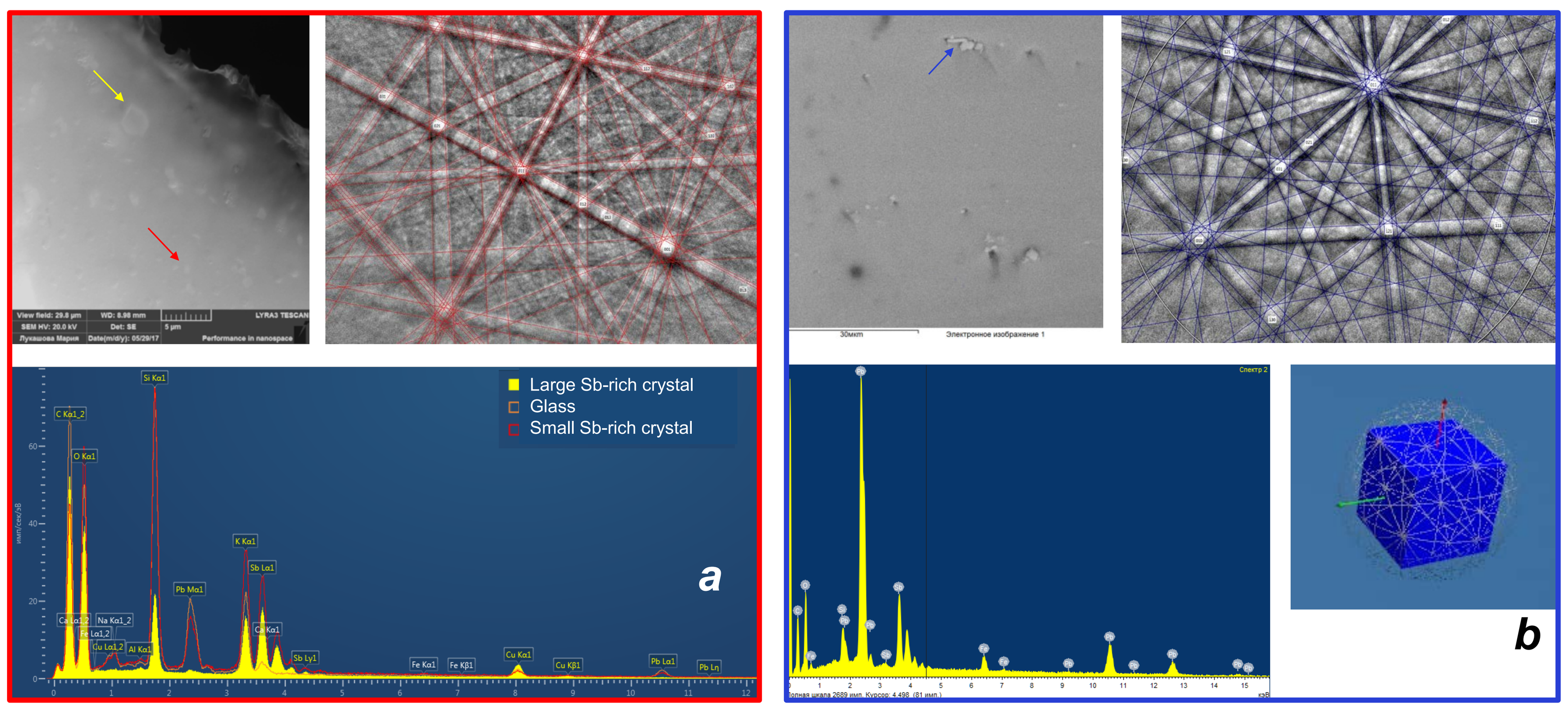

Figure 3. A study of the structure of Sb-rich crystals (pointed with arrows on SEM images) in (a) turquoise and (b) yellow glass beads. EBSD patterns obtained from the precipitates in thin foils make it possible to unambiguously identify them as orthorhombic $KSbOSiO_4$ and cubic $Pb_2Fe_{0.5}Sb_{1.5}O_{6.5}$ [1].

In the red glass beads, hexagonal CdZnSSe crystallites (~1 µm) of chromophore (colloidal staining of glass) were found (*Fig. 4a-c*). In the opal faceted beads, cubic $NaSbO_3$ crystals with sizes ranging from several hundred nm to several µm were found (*Fig. 4d-f*). Two-colored types of beads are, as a rule, stable. Hexagonal crystallites $Ca_2Pb_3(AsO_4)_3Cl$, ~200 - 300 nm in size, in white-red beads (*Fig. 4g-i*) and crystallites ~100 - 200 nm in white-green beads were found in the white layers. In our opinion, they didn't cause cracks formation and glass destruction due to the small size of the crystals.

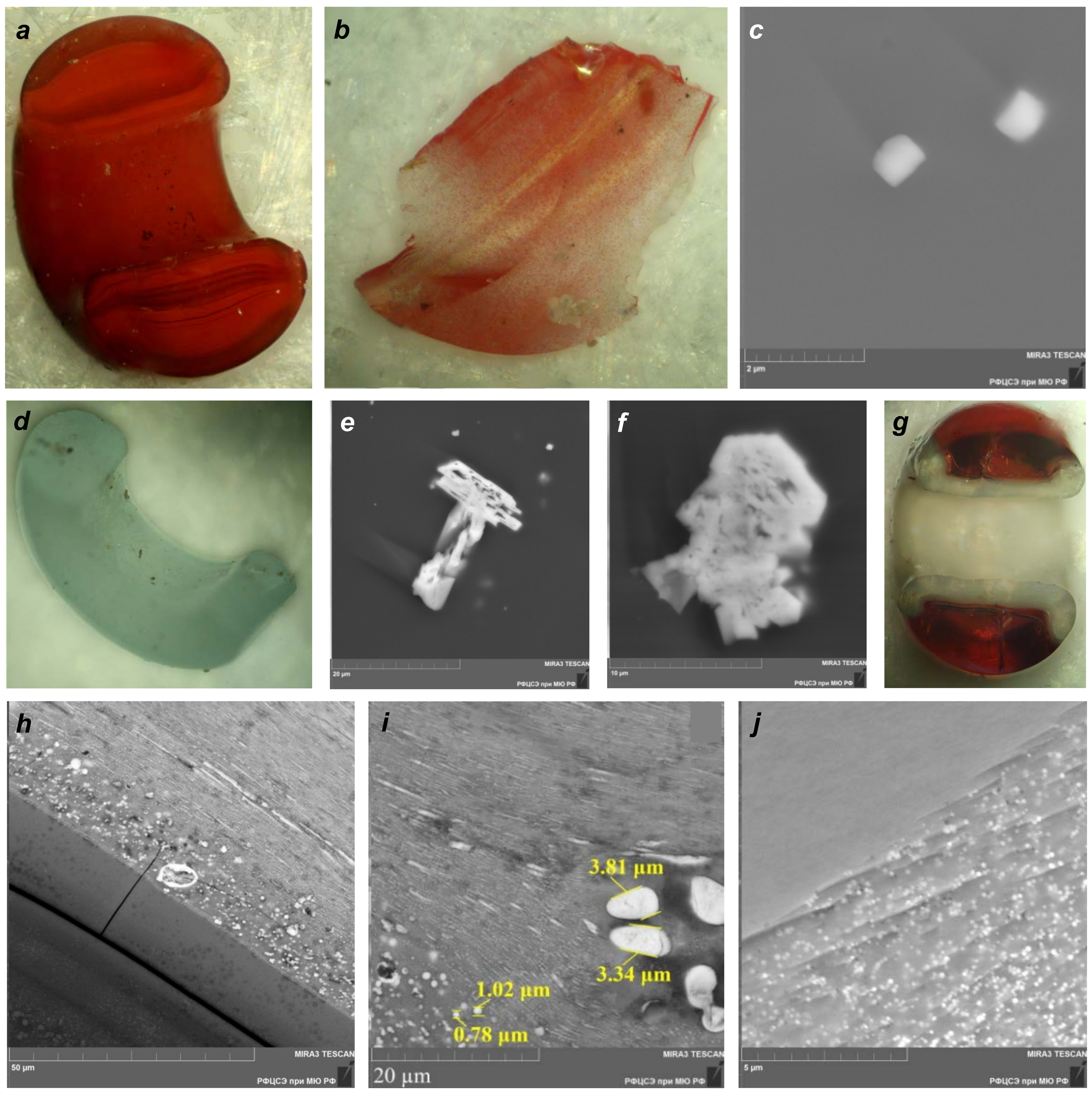

Figure 4. SEM image of individual hexagonal crystals CdZnSSe (c) in the red opaque glass bead (a, b); SEM images of cubic $NaSbO_3$ crystals (e, f) in the samples of opal faceted glass bead (d); SEM images of hexagonal $Ca_2Pb_3(AsO_4)_3Cl$ crystals (h, i) in a white opaque layer in the two-layers red-white glass bead (g); crystallites in a white layer of the white-green glass bead (j).

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References

1. T.V. Yuryeva, E.A. Morozova, I.F. Kadikova, O.V. Uvarov, I.B. Afanasyev, A.D. Yapryntsev, M.V. Lukashova, S.A. Malykhin, I.A. Grigorieva, V.A. Yuryev, "Microcrystals of antimony compounds in lead-potassium and lead glass and their effect on glass corrosion: a study of historical glass beads using electron microscopy," J. Mater. Sci. 53 (15), 10692–10717 (2018).