Study of gemmological characteristics and chemical composition of zultanite samples to determine their nature

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Abstract. The article presents the results of gemological examination of inserts into jewellery items marked as “Zultanite” conducted in the research laboratory of Jewelry Design and Technology Department. It was found that this material was not a natural stone zultanite. Therefore, to establish its nature, the chemical composition was determined by non-destructive X-ray spectral fluorescence analysis. The results of the analysis confirmed that these inserts were glass with rare-earth additives (neodymium glass).

1. Introduction
Recently, products with faceted inserts labeled as “zultanite” have appeared on the Russian jewellery market in retail. These inserts have an alexandrite effect - a change in color depending on the light from very light grayish or bright green to light reddish-purple or pink.

In mineralogy, the natural stone zultanite is really known as a mineral of the diaspore group. [1-2]. The word “diaspore” comes from Greek and means “dispersion, fissuring”. This mineral has been known since the beginning of the XIX century [3]; its first finds were found in the Urals. The thin-platy units of the diaspore have long been the subject of research for mineralogist [4-9], but they were of no interest to the jewellery industry, and until the mid-1980s the diaspore was a collection stone. After the discovery of a jewellery green diaspore with alexandrite effect in Turkey in the Anatolian mountains, this stone called zultanite began to be found on the jewellery market [10]. In recent decades, the mining of diaspore has virtually ceased due to the deposit reserve depletion, however, in Russian stores jewellery with zultanite is a real brand.

2. Materials and Methods
In the research laboratory of Jewellery Design and Technologies Department of IRNITU, gemologists have carried out studies of several faceted inserts called zultanite [11]. They have an oval shape and standard sizes of 8x6 mm (Figure 1).

On the laboratory equipment of the department, optical characteristics of the samples were examined using non-destructive gemmological methods [12-16]: optical character (polariscope), refractive index (refractometer), pleochroism (dichroscope), inclusions, internal features (Axio Lab.A1 microscope for laboratory studies, digital stereo microscope Alta CM0745 -T)

Quantitative chemical analysis was carried out by the Center for Collective Use "Geodynamics and Geochronology" of Institute of the Earth's Crust of the SB RAS. The study of the samples was performed by x-ray fluorescence method using a TIGER spectrometer. A qualitative and semi-quantitative analysis of the chemical composition of the samples was carried out using the Best
Detection method with vacuum mode, which is offered by the QUANT EXPRESS software. The analytical lines of chemical elements for this method are graded in the Bruker applied laboratory, and the calibration coefficients are stored directly in the library of lines, and theoretical variables of alpha coefficients are used to correct the matrix effects. On default, QUANT EXPRESS performs measurements in scan mode; this allows checking the superposition of analytical lines with similar excitation energies and to obtain more detailed information about the sample. Semi-quantitative analysis according to OST 41-08-205-04 "Methods of Quantitative Chemical Analysis" refers to the V category of accuracy.

3. Research part
As a result of the gemmological study of the samples, the following data were obtained:
- Optical character is isotropic (polariscope);
- The refractive index is 1.50 (refractometer);
- Pleochroism is absent (dichroscope);
- Inclusions, internal features are absent (microscope, 100-fold magnification) (Figure 2);
- Transparency – transparent;
- Alexandrite effect – a noticeable change in colour from green in daylight to light brown in artificial.

Figure 1. Earrings with sultanite.

Figure 2. Microscope insertion test
The data obtained clearly indicate that the inserts cannot be a natural "zultanite", since they are optically isotropic. However, the range of materials with the effect of colour change is rather limited – among natural stones alexandrite, garnet, corundum have this effect. But the optical character and the refractive index of the inserts (1.50) do not correspond to the optical constants of any of them. After analyzing the gemmological characteristics of the studied inserts, it was assumed that this material is a glass with an alexandrite effect (neodymium glass) (Table 1).

**Table 1.** Comparative analysis of the gemmological characteristics of natural "zultanite" and glass with a change in colour.

| Characteristics          | Diaspore "Zultanite"                           | Glass with Colour Change                              |
|--------------------------|-----------------------------------------------|------------------------------------------------------|
| Optical Character        | Anisotropic                                   | Isotropic                                            |
| Colour                   | Colourless, light yellowish green, light pink, light purple | Yellowish brown, white, light purple, greenish gray |
| Lustre                   | Vitreous, on the cleavage planes it is nacreous | Vitreous                                            |
| Refractive Index          | $n_p=1.730$-$1.752$ $n_m=1.705$-$1.722$ | $n=1.500$-$1.520$                                    |
| Alexandrite Effect       | From very light grayish or green to very light reddish-purple | From purple and violet to blue, from gray to green, from reddish-brown to greenish-yellow |
| Hardness                 | 6-7                                           | 5                                                   |
| Specific Gravity         | 3.3-3.5                                       | 2.4-3                                               |

Neodymium glass (didymium glass, glass chameleon, alexandrite glass, Moser glass, Neophan or neophan glass) is glass that contains neodymium oxide, sometimes a mixture of oxides of other rare earth elements [16-18]. The Alexandrite effect is caused by f-f transitions in the electronic structure of neodymium atom [19–20] and is inherent in glasses with neodymium oxide content of at least 4.3%.

To confirm the nature of this material, additional studies have been conducted, in particular, the chemical composition of the samples by the X-ray fluorescence method using a TIGER spectrometer. The results of the study are shown in Table 2.

**Table 2.** The results of determining the quantitative chemical composition.

| Formula  | Concentration, % |
|----------|------------------|
| Nd$_2$O$_3$ | 35.99            |
| Pr$_6$O$_{11}$ | 23.51          |
| SiO$_2$    | 20.02            |
| Fe$_2$O$_3$ | 4.75             |
| Ba        | 3.64             |
| K$_2$O     | 3.43             |
| As$_2$O$_3$ | 2.69             |
| TiO$_2$    | 2.13             |
| Al$_2$O$_3$ | 1.74             |
| Na$_2$O    | 1.53             |
| MnO       | 0.58             |

4. **Summary and Conclusions**
Thus, as a result of gemmological examination and laboratory research, it was found that the inserts declared on the certificate as “zultanite” are not a natural stone “zultanite”, but they are glass with rare-earth additives (neodymium glass) with alexandrite effect.
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