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Application News

No. X276

X-Ray Analysis

Analysis of Precious Stones by EDX-8100:

Differentiation of Natural Stones/Synthetic Stones, Determination of Geographic Origin of Natural Stones

Various instruments are used in appraisals of precious stones, including not only general gemstone appraisal tools such as the stereoscopic microscope, but also various analytical instruments (1).

For example, the Fourier transform infrared spectrophotometer (FT-IR) is used to determine whether heat treatment/resin impregnated treatment have been applied or not, and the UV-Vis spectrophotometer (UV-Vis) is used to judge the presence or absence of coloring treatment.

The energy dispersive X-ray fluorescence spectroscope (EDXRF) is also a necessary and indispensable instrument that enables quick, nondestructive composition analysis. For example, EDXRF can clearly detect the lead used in lead glass-filling treatment of gemstones.

Here, a Shimadzu EDX-8100 was used in a composition analysis of rubies, emeralds, and Paraiba tourmalines, which are commonly seen gemstones and strongly loved by many people, and effective results for distinguishing natural stones and synthetic stones and identifying the geographic origin of natural stones were obtained.

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Samples

The precious stones (natural and synthetic stones) and rough gemstones shown below were used.

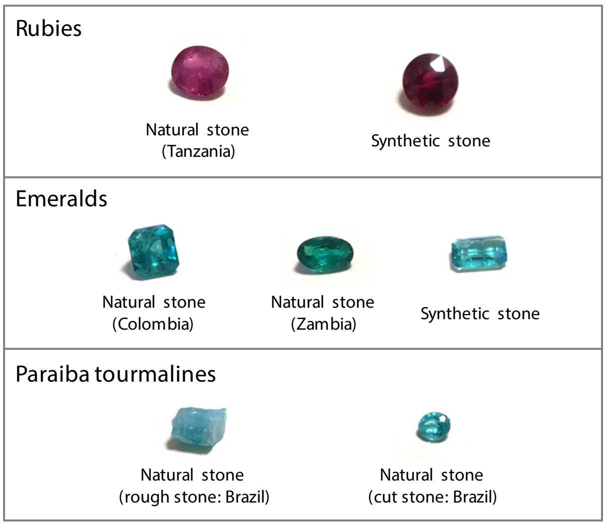


Fig. 1 Types and Origins of Precious Stones and Gemstones

Elements

$_{11}$Na - $_{92}$U

Sample Preparation

Samples were set to enable direct X-ray irradiation and measured.

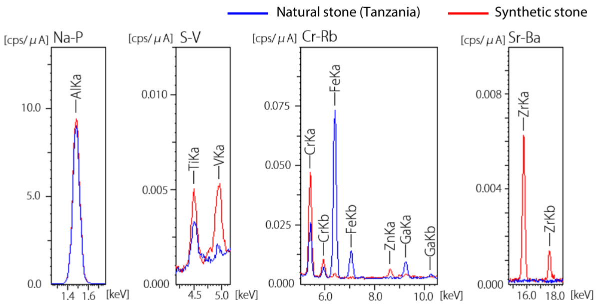
Ruby

1. Measurement results

Fig. 2 shows the qualitative analysis and quantitative analysis results for the natural stone (mined from Tanzania) and the synthetic stone.

2. Differences between natural stone and synthetic stone

A trace amount of gallium was not detected in the synthetic stone, and in comparison with the natural stone (Tanzania), the synthetic stone had a high content of chromium. As one example, natural stones and synthetic stones can be distinguished by this kind of difference. However, elements originating from a catalyst may also be detected in synthetic stones in some cases.



[wt%]

Element	Composition	Natural stone (Tanzania)	Synthetic stone
Aluminum	Al_2O_3	99.395	99.439
Titanium	TiO_2	0.018	0.025
Vanadium	V_2O_5	0.003	0.017
Chromium	Cr_2O_3	0.255	0.477
Iron	Fe_2O_3	0.324	0.009
Gallium	Ga_2O_3	0.005	—
Zirconium	ZrO_2	—	0.035

Fig. 2 Results of Qualitative Analysis/ Quantitative Analysis of Rubies

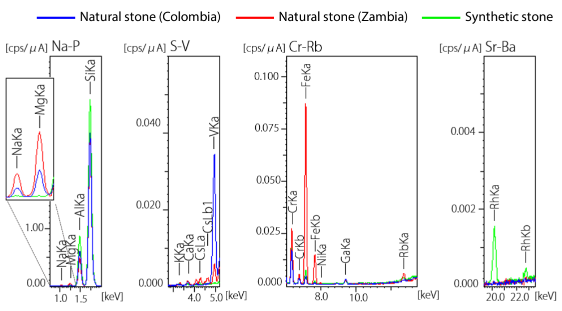
Emerald

1. Measurement results

Fig. 3 shows the qualitative analysis and quantitative analysis results for the two types of natural stones (mined from Colombia and Zambia) and the synthetic stone.

2. Identification of natural or synthetic stone

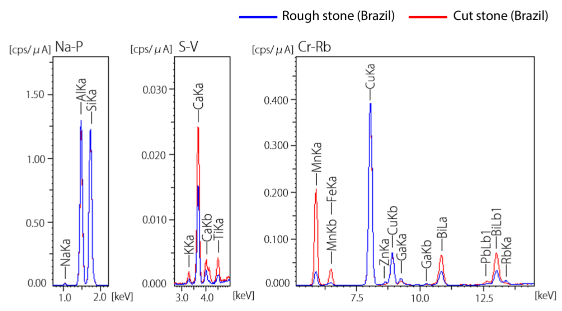
Chromium, iron, and vanadium are elements that give emeralds their color, and the hues of stones changes depending on the contents of the respective elements. In the results in Fig. 3, the Zambian stone has high contents of chromium and iron and a low content of vanadium in comparison with the Colombian stone. Comparatively large amounts of sodium, magnesium, and potassium and trace amounts of rubidium and cesium were also detected in the Zambian stone, providing one indicator for distinguishing this stone from the Colombian stone. Although the price of emeralds is mainly determined by their transparency, hue, and depth of color (color strength), the geographic origin is also a factor in the price. As distinctive features of the respective geographic origin, Colombian emeralds display a bright green color, while Zambian stones are characterized by high transparency, and the price of Colombian stones is generally higher. Since it is difficult to distinguish deep green Zambia emeralds from Colombian emeralds, elemental analysis is used as a technique for determining the geographic origin. The synthetic stone was identified based on detection of rhodium, which was estimated to originate from a catalyst, and the absence of sodium and magnesium in the detection results.



[wt%]

Element	Composition	Natural stone (Colombia)	Natural stone (Zambia)	Synthetic stone
Sodium	Na_2O	0.879	2.335	—
Magnesium	MgO	0.954	2.518	—
Aluminum	Al_2O_3	18.033	15.028	21.252
Silicon	SiO_2	79.021	77.925	78.098
Potassium	K_2O	—	0.031	—
Calcium	CaO	0.031	0.037	—
Vanadium	V_2O_5	0.518	0.069	—
Chromium	Cr_2O_3	0.506	0.829	0.560
Iron	Fe_2O_3	0.051	1.136	0.075
Gallium	Ga_2O_3	0.006	0.005	0.003
Rubidium	Rb_2O	—	0.002	—
Cesium	Cs_2O	—	0.084	—
Rhodium	Rh_2O_3	—	—	0.012

Fig. 3 Results of Qualitative Analysis/ Quantitative Analysis of Emeralds



[wt%]

Element	Composition	Rough stone (Brazil)	Cut stone (Brazil)
Sodium	Na_2O	2.235	2.894
Aluminum	Al_2O_3	45.291	42.494
Silicon	SiO_2	49.379	47.285
Potassium	K_2O	0.040	0.092
Calcium	CaO	0.516	0.822
Titanium	TiO_2	0.027	0.074
Manganese	MnO	0.561	4.021
Iron	Fe_2O_3	0.032	—
Copper	CuO	1.767	2.054
Zinc	ZnO	0.017	—
Gallium	Ga_2O_3	0.043	0.027
Rubidium	Rb_2O	0.006	—
Lead	PbO	—	0.021
Bismuth	Bi_2O_3	0.087	0.217

Fig. 4 Results of Qualitative Analysis/ Quantitative Analysis of Paraiba Tourmaline

Paraiba Tourmaline

1. Measurement results

Fig. 4 shows the qualitative analysis and quantitative analysis results for the rough gemstone and the cut stone (both produced in Brazil).

2. Geographic origin

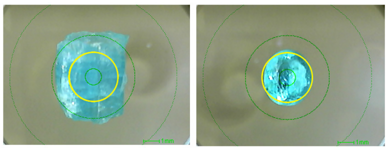
From the results in Fig. 4, the main components are oxides of aluminum and silicon, and the samples also contain manganese and copper, indicating that both samples are natural Paraiba tourmalines. Although Paraiba tourmaline is produced in three areas (Brazil, Nigeria, and Mozambique), these stones are estimated to be of Brazilian origin because their copper contents exceed 0.6 w% (CuO). A detailed analysis was also conducted using LA-ICP-MS (2).

3. Hue

The results in Fig. 4 showed that the cut stone had a high manganese content of 4 wt% (MnO) in comparison with the 0.5 wt% (MnO) content of the rough stone. Stones generally have a strong green hue if the Mn content is high, but the hues of both stones appeared to be the same neon blue when examined with the naked eye (Fig. 5). Therefore, the samples were observed with an OLS5000 3D measuring laser microscope, as shown in Fig. 6. Green areas were observed in the interior, and these are thought to be a factor in the high content of Mn.

Table 1 Measurement Conditions

Instrument	: EDX-8100 (EDX-8000)
Elements	: Na - U
Analysis group	: Qualitative analysis and quantitative analysis
Detector	: SDD
X-ray tube	: Rh target
Tube voltage	: 15 [kV] (Na-V), 50 [kV] (Cr-U)
Tube current	: Auto [μA]
Collimator	: 3 [mm φ]
Primary filter, channel	: Non [Na-P], #1 [Sr-Ba], #2 [S-V], #4 [Cr-Rb]
Atmosphere	: Vacuum
Integral time	: 50 [s] × 4 Ch
Dead time	: Maximum 30 [%]



Rough stone (Brazil) Cut stone (Brazil)

Fig. 5 Observation Images of EDX Samples (◯: X-Ray Irradiation Range 3 mm φ)

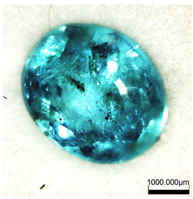


Fig. 6 Observation Image of Cut Stone (OLS5000)

Conclusion

As demonstrated by these results, Identification of natural stone or synthetic stone and determination of the geographic origin of natural stones can be roughly estimated from the types of elements, differences in their contents, and trace detection. In comparison with measurements using only EDX, higher accuracy can be expected in appraisals of gemstones by using EDX measurement in combination with other analytical instruments (FT-IR, UV-Vis) (3).

<References>
(1) Dr. Ahmadjan Abduriyim: The Science of Gemstones, ARK PUBLISHING INC.
(2) Ahmadjan Abduriyim, Hiroshi Kitawaki, Masashi Furuya, and Dietmar Schwarz: "Paraiba"-Type Copper Bearing Tourmaline from Brazil, Nigeria, and Mozambique: Chemical Fingerprinting by LA-ICP-MS
(3) Ahmadjan Abduriyim and Hiroshi Kitawaki: Applications of Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to Gemology

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