Spectroscopic studies of ruby and pink sapphire samples

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Abstract

X-ray fluorescent spectrometry and UV-vis spectroscopy are advanced techniques that can be used to characterize gem materials. Transition metal defects are causes of colors in corundum. Fe and Ti are the causes of the blue color in blue sapphire while Cr is the cause of the colors in ruby and pink sapphire. In this work, we investigated the differentiation between ruby and pink sapphire samples. The amount of Cr, Ti, Fe and V were analyzed by x-ray fluorescent spectrometry. The concentrations of the defects were calibrated using NIST 610 standard reference material (SRM) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The optical characteristics were analyzed by the UV-vis spectroscopic technique.

Materials and Methods

Figure 1. Varieties of sapphire samples chosen for the experiment. The samples were labeled PS for natural sapphires and SPS for synthetic sapphires.

Table 1. The amounts of Cr, Ti, Fe and V elements in samples, as determined by x-ray fluorescence. Relative standard uncertainties of concentration were 14%, 45%, 37% and 23% for Ti, Cr, Fe and V respectively.

Samples	Concentration (mg kg^{-1})			
	Cr	Ti	Fe	V
PS-1	38.5	270.4	560.2	14.7
PS-2	54.6	268.2	868.1	2.4
PS-3	95.6	1383.8	814.4	28.0
PS-4	48.4	233.3	553.4	2.2
PS-5	63.1	3092.7	1020.4	137.4
PS-6	60.5	320.8	912.3	30.1
PS-7	178.3	973.3	2648.3	86.2
PS-8	222.0	652.1	2752.8	29.5
PS-9	208.1	86.9	5755.6	96.4
PS-10	151.7	71.2	407.0	2.5
PS-11	157.7	28.1	400.7	0.6
PS-12	188.6	76.8	353.1	6.3
PS-13	383.7	14.4	126.0	112.7
SPS-1	77.1	107.5	14.0	3.7
SPS-2	101.3	35.3	15.3	3.8

Results and Discussion

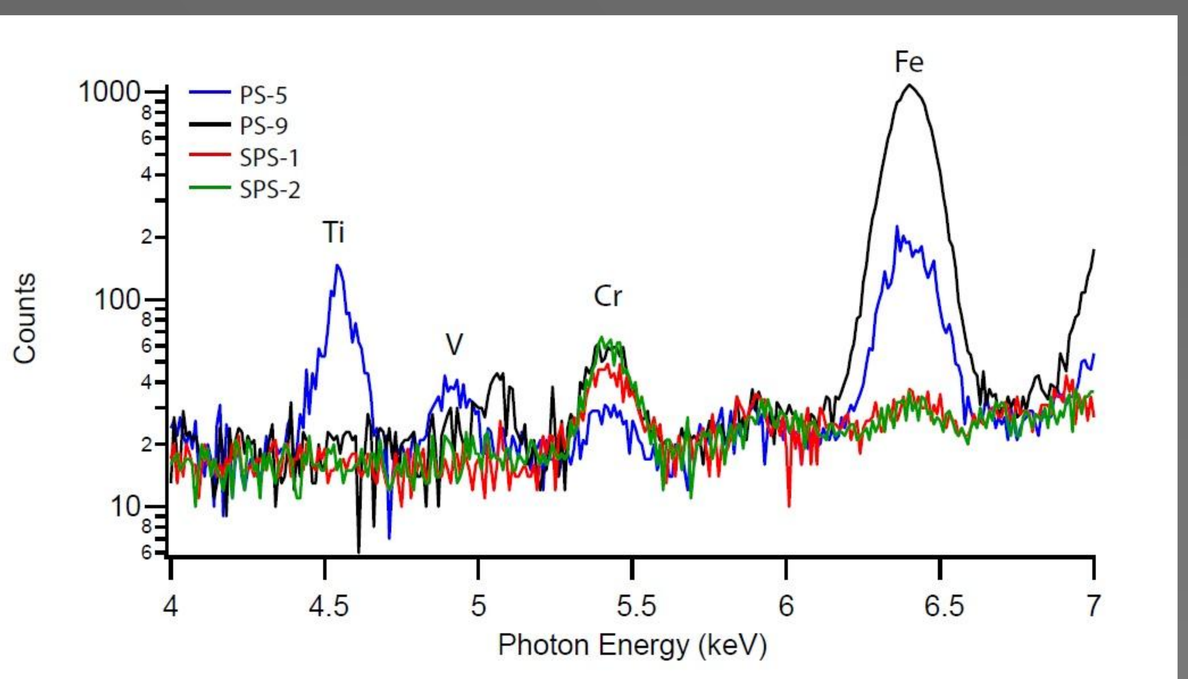

Figure 2. XRF spectra of sapphire samples using 40.0 keV x-ray excited energy.

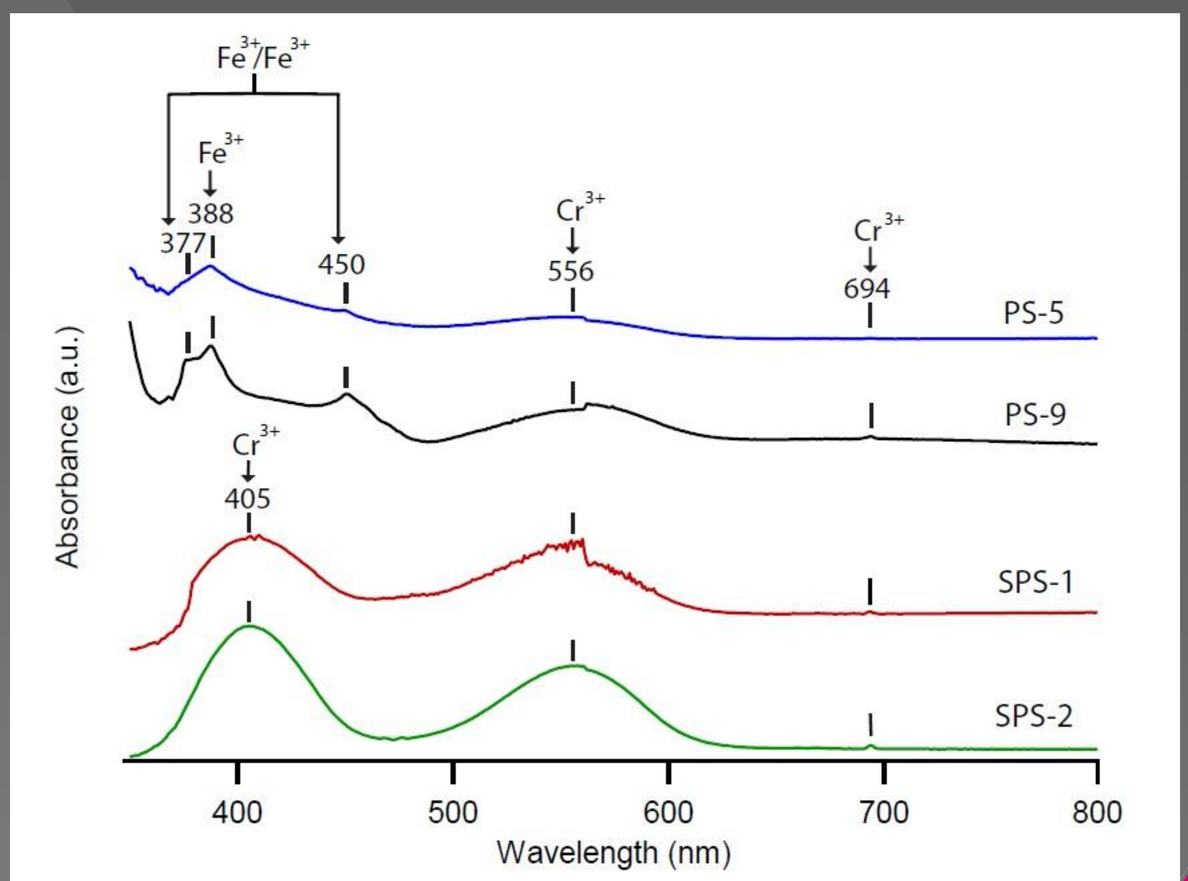

Figure 3. UV-vis absorption spectra of corundum samples show peaks of Cr^{3+}, Fe^{3+}, Fe^{3+}/ Fe^{3+}.

The x-ray fluorescent exited energy of Rh was 40 keV. The selected XRF spectra of the sapphire samples with the peaks of Ti, Cr, Fe and V are shown in figure 2. The contents of the elements can be calculated using the area under the curves evaluated by PyMca software [1, 2]. The concentration of the transition metal element is given by

$$C_{\mathrm{i}} = \left[\frac{A_{\mathrm{r}}}{A_{\mathrm{nr}}} \times LAICPMS\right]\frac{A_{\mathrm{i}}}{A_{\mathrm{n}}}$$

where

A_{r} is the fitted area of transition metal elements of the referent sample

A_{nr} is the normalized fitted area of the referent sample

LAICPMS is the contents of the elements obtained from the SRM and LA-ICP-MS

A_{i} is the fitted area of the i^{th} transition metal element of the sample

A_{n} is the normalized fitted area of the sample

Conclusion

Fifteen sapphire samples with different origin including natural and synthetic sapphires collected to study the cause of the colors for differentiation between the pink sapphires and the ruby samples. Cr was the cause of the pink-red color. The concentration of Cr could not classify the pink sapphire and ruby samples. We suggest the UV-vis spectroscopic method to differentiate between pink sapphires and ruby.

References

[1] Solé, V.A., E. Papillon, M. Cotte, Ph. Walter and J. Susini. 2007. A multiplatform code for the analysis of energy-dispersive X-ray fluorescence spectra. Spectrochimica Acta Part B. 62: 63-68.

[2] Wongrawang, P., N Monarumit, N Thammajak, P Wathanakul and W Wongkokua. 2016. Oxidation states of Fe and Ti in blue sapphire. Materials Research Express. 3, 026201.