Original Study

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Portable XRF: A Tool for the Study of Corundum Gems

Abstract: Origin of gemstones is a key aspect not only in gemological field but also in Cultural Heritage studies, for the correct evaluation of precious artifacts. The studies on gems require the application of non-invasive and non-destructive methods; among them, portable spectroscopic techniques has been demonstrated as powerful tools, providing a fingerprint of gems for origin and provenance determination. In this study, portable XRF spectroscopy has been applied to test the potential of the technique for the origin determination of corundum gems. The obtained results allowed distinguishing natural and synthetic rubies and sapphires.

Keywords: Gems; p-XRF; corundum; natural; synthetic

1 Introduction

The beauty and the intrinsic value of gems has fascinated ancient cultures worldwide since antiquity. Art objects, jewels, statuettes, and religious artefacts have been often adorned by gemstones (Kiefert et al. 2005). Among precious and semi-precious gemstones, minerals no harder than quartz were usually set in prehistoric artifacts (Lu et al. 2005), lapis lazuli and turquoise were widely employed in Egypt (Lo Giudice et al. 2009), several micro- and crypto-crystalline varieties of quartz were engraved to adorn jewels during Hellenistic Age (Barone et al. 2016a), colored precious gems were used during Roman Age (Gliozzo et al. 2011), red garnets, rubies, sapphires, diamonds, but also colored glass, adorned Medieval treasuries (Jehlička et al. 2016; Jeršek & Kramar 2014; Karampelas et al. 2012; Reiche & Lambacher 2004).

The characterization of these archaeological objects often includes the identification of mineralogical identity and the determination of the provenance of gems. In fact, this kind of information can add relevant data to studies regarding the manufacture and trade, as well about the occurrence of recent substitutions, due to the replacement of rare and precious gemstones with less valuable or with synthetic gems.

The unambiguous characterization of gems is not always achievable by naked-eye observations. At the same time, being set on historical valuable objects, gems cannot be removed to avoid irreversible damages. Thanks to recent technique advancements aimed at developing high-resolution mobile equipment for *in-situ* works (Adriaens 2005; Vandenabeele et al. 2014), complementary non-invasive and non-destructive

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methods have emerged as a promising approach for gem characterization. Specifically, the combined use of portable spectroscopic methods, such as Raman spectroscopy and X-ray fluorescence, has demonstrated useful results for routine investigation of gems (Petrovà et al. 2012; Lauwers et al. 2016). Moreover, being non-destructive, and requiring short measurement times and no sample preparation, these techniques have become recently in high demand also in the gemological community (Barone et al. 2015a).

Recent literature has focused on instruments and advanced applications in gems studies. For example, portable Raman spectroscopy has been successfully applied for the mineralogical identification of gems set on jewels preserved in museums (Reiche & Lambacher 2004; Osterrothová et al. 2014; Barone et al. 2015b; Barone et al. 2016a), as well as in the study of loose gems (Barone et al. 2016b; Bersani et al. 2014). However, the value and the importance of a gem goes beyond its mineralogical composition, as origin (natural or synthetic) and geographic or geological source can add extra information in precious artifacts evaluation and characterization (to detect recent substitutions and/or reconstruct specific trading routes). Despite the potential of the method, Raman spectroscopy is not able to distinguish synthetic gems from the natural ones, and genesis (in terms of geological source) and provenance (in terms of geographic locality) can be only hypothesized through the study of the fluid and solid inclusions by micro-Raman equipment (Bersani & Lottici 2010). In this sense, more efficient results can be obtained by analyzing trace-element chemistry. In fact, specific minor and trace element assemblages depend on the origin of the gemstone (Abduriyim, Kitawaki 2006; Rossman 2009). In natural gems, the presence/absence of peculiar elements and their concentration can help to discriminate the geological environment in which they formed, so that the identification of geological deposits and geographical localities can be achieved. Additionally, the trace-element chemistry is able to distinguish natural gems from their synthetic counterparts.

Among gems extensively traded and employed in jewelry assemblages and in historical treasures, rubies and sapphires stand out as desired symbols of beauty and royalty, and they have been often used for adorning crown jewels. Rubies and sapphires are the red and the blue varieties of corundum (aluminum dioxide, Al_2O_3), with their color attributed to the presence of trace elements in the crystal lattice: Cr^{3+} in rubies, and Fe^{2+}-Ti^{4+} pairs in sapphires. Historically, rubies were mainly imported from Mogok, in upper Myanmar (Burma), even if fine quality red corundum were also mined in Thailand, Cambodia, Vietnam, and Afghanistan. Burma, Thailand, Sri Lanka and Kashmir, Cambodia, Vietnam and India are the main sources of sapphires (Hughes 1997; O'Donoghue 2006).

In view of their attractiveness, well-manufactured synthetic and/or treated crystals were increasingly available on the market, especially from the 1900s, even if the first synthesis experiments started already in 1800s. It is not surprising, therefore, the replacement of rubies and sapphires with other more common and less valuable imitations or with synthetic crystals, especially in precious art objects and jewels. From this comes the need to discriminate origin and provenance of corundum gems.

As regards corundum, trace-element chemistry has been proven to be useful to determine provenance and origin of rubies and sapphires (Muhlmeister et al. 1998). Nevertheless, only a few examples of chemical analysis on corundum gems by portable spectrometers are available within the literature (Muhlmeister et al. 1998). Until now, many research projects have applied destructive or micro-destructive analytical methods (e.g. EDXRF, LA-ICP-MS; Joseph et al. 2000; Rankin et al. 2003; Guillong & Günther 2001), not applicable in case of valuable gems mounted in jewels and/or in archaeological and art objects preserved in museums collections.

In this perspective, portable XRF studies are greatly welcomed in order to provide new insights in non-destructive and non-invasive chemical studies of gemstones. The possibility to incorporate high technological instruments into normal studies of gemstones, especially when mounted in objects of art, requires continued researches aimed at obtaining most information from the analysis of gems, namely efficiency and performance of various spectrometers, construction of comprehensive databases, establishment of analytical protocols and best procedures, and use of appropriate standard for calibration.

In this work we demonstrate the utility of trace-element chemistry studies on gems by providing results on rubies and sapphires obtained by using a portable XRF spectrometer. The data demonstrates the potential of p-XRF in corundum gems characterization, especially for the discrimination between natural and synthetic crystals, highlighting the possible limits of the technique and suggesting the use of complementary spectroscopic methods to support the interpretation of chemical data.

2 Materials

Taking advantage from previous studies that allowed to discriminate corundum among numerous and valuable red and blue gems from a private collection by using Raman spectroscopy (Barone et al. 2014; Barone et al. 2016b), the most interesting ones from the gemological point of view, namely ten red and nine blue loose gems, have been selected to be analyzed by portable XRF (Figure 1 and Table 1). In order to work in conditions similar to real cases, we studied samples without tags on origin and provenance, so that the only clues on these aspects come from features such as inclusion, growth lines, and color spots by microscopy observations.

The red corundum gems (labeled as R#) were transparent, characterized by color ranging from pale pink to deep red and exhibiting different weight and shape. Referring to blue corundum (labeled as Z#), they range from 0.930 to 3.40 carats (ct), with color from light blue to blue as well as greenish-blue and purplish-blue, except for Z1 (almost colorless).
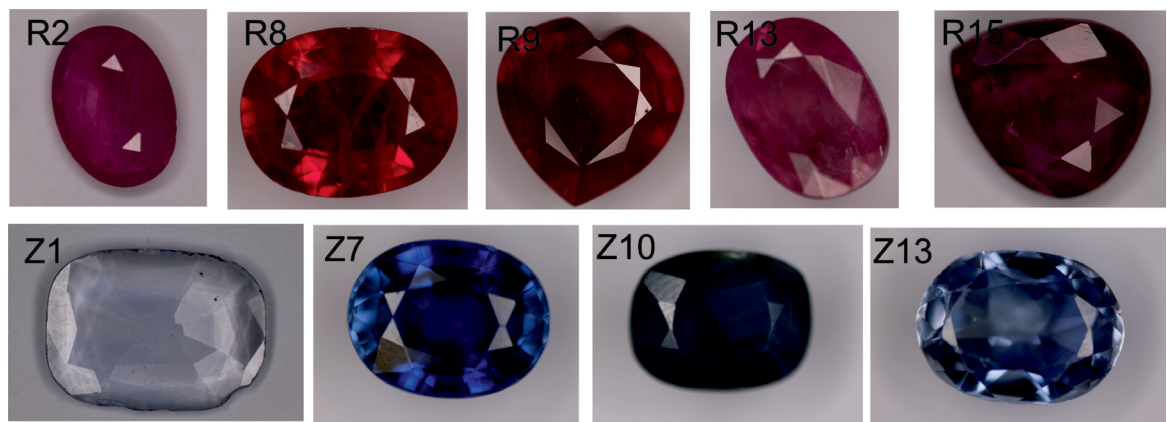

Figure 1. Pictures of some studied gemstones, representative of the analyzed set.

Table 1. List of investigated red (R#) and blue (Z#) corundum varieties, together with information on color, shape and cut, weight and laboratory observations.

Corundum variety	Sample	Color	Weight (Carats)	Shape	Laboratory observation
RED	R2	Pale red	0.65	Oval; pear cut	Fluid feathers and mineral inclusions
	R4	Light red	0.57	Rectangular	Inclusions free
	R5	Light red	1.71	Oval;chabochon	Inclusions free
	R6	Red	2.38	Octagonal	Inclusions free
	R8	Red	3.15	Oval; oval cut	Flakes and streamers
	R9	Deep red	7.97	Heart	Elongate inclusions, orange-red in color
	R10	Red	2.47	Round; brilliant cut	Fluid feathers
	R13	Pale red	1.64	Oval; oval cut	Fluid and mineral inclusions
	R15	Pink/pale red	0.38	Oval; oval cut	Fluid feathers
	R16	Pale red	0.43	Drop; pear cut	Mineral inclusions
BLUE	Z1	Colourless	2.06	Rectangular	Silky net of rutile needles
	Z3	Blue	1.50	Triangular; trilliant cut	Curve growth-lines. Bubble inclusions
	Z4	Blue/Light Blue	2.50	Round; brilliant cut	Inclusions free
	Z5	Blue	1.51	Drop; pear cut	Bubble clouds
	Z7	Blue	3.86	Oval; oval cut	Inclusion free
	Z8	Blue	2.20	Oval; cabochon	Elongated capillary channels; CO_2 gas inclusions
	Z9	Blue	1.91	Oval; oval cut	Parallel growth-lines
	Z10	Blue/Green	3.11	Oval; oval cut	Parallel growth-lines; yellow spot
	Z13	Blue/Purple	3.40	Oval; oval cut	Tadpole-shaped inclusions

3 Method

Portable XRF measurements have been performed on corundum gems by using a Bruker portable XRF spectrometer (Tracer IV-SD). The spectrometer is equipped with an X-ray tube (Rh anode) with a beam collimated at 3mm in diameter. The instrument was set to operate at 40 keV and 17 μA, with an acquisition time of 120s for each analysis.

To perform the quantitative analysis, an aluminum alloy standardized sample has been used for calibration. The limits of detection (LOD) were as follows: Co <1; Cr <1; Cu <1; Fe <1; Mn 1120 ppm; Ni <1; Pb<1; Sn<1; Sr<1; Ti<1; V <1; Zn <1; Zr<1. Ga has not been quantified since it was not present among the elements included in the calibration sample. The concentrations of each element in the sample are expressed as parts per million (ppm).

4 Results and Discussions

The possibility to discriminate natural and synthetic rubies requires the analysis of the entire trace-element assemblage, as a single trace element cannot prove gemstone origin (Muhlmeister et al. 1998). Generally, natural corundum are characterized by a meaningful trace element diversity respect to synthetic ones; additionally, synthetic corundum usually contains the lowest concentrations of Fe, V, Ti, Ga. The percentages of the elements listed above can be used also for separating natural corundum of different origin and provenance.

In Figure 2 (a, b) we report some examples of X-ray spectra acquired on red and blue gems while quantitative data are listed in Table 2. The following elements have been detected in all analyzed rubies: Ti, V, Cr, Mn, Fe, Cu, Zn. Ga was detected only in samples R2, R9, R13, R15, and R16 (a weak peak observed also in R5), while Zr and Pb only in sample R9. In studied sapphires, Ti, V, Fe, Mn, Cu and Zn were detected in all samples, while Ga was present only in Z1, Z5, Z8, Z9, Z10.
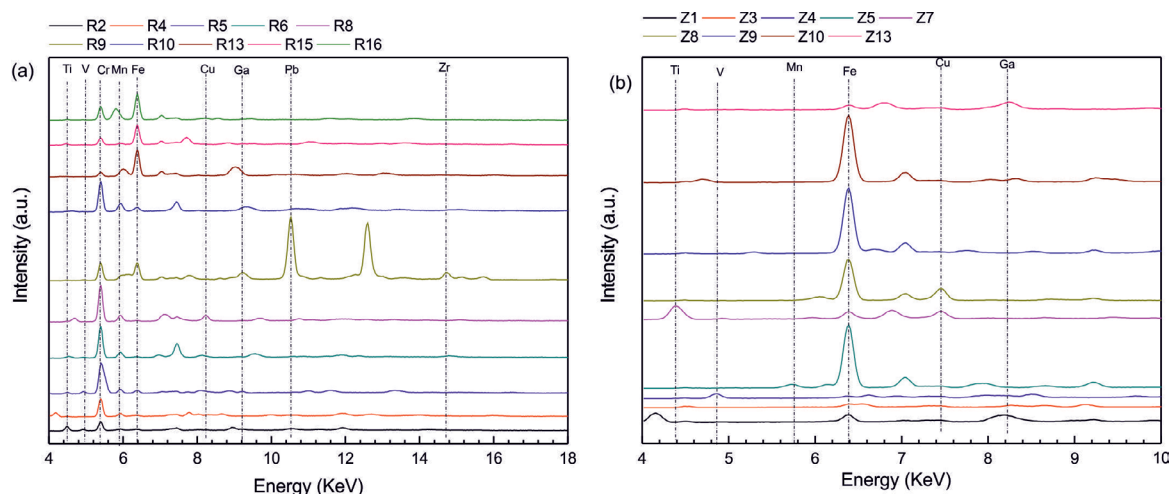

Figure 2. X-ray spectra collected on studied (a) rubies and (b) sapphires.

Regarding rubies, as expected, Cr is the most abundant element, being responsible for the color of this corundum variety. It is interesting to highlight that gems characterized by light red color exhibit levels of Cr< 1000 ppm; therefore, it is possible to conclude that the higher the Cr level is, the stronger is the red hue. Cu, usually considered a proof of synthetic origin even if can be found also in natural rubies within sulfide inclusions, has been detected in all samples with levels ranging from c.a. 150 to c.a. 170 ppm, without concentration differences along the gems. Therefore, it cannot be considered as a discriminating element. According to Muhlmeister et al. (1998), Ga is quite relevant in identifying natural rubies, being usually

absent in synthetic ones; in addition, natural rubies usually exhibit higher content of Ti, V and Fe compared to synthetic gems. Effectively, the elements listed above exhibit a relevant ranging of levels in studied red corundum. More in detail, two different groups can be identified on the basis of V–Ti–Fe percentages (see Figure 3 (a)). The first group (R2, R9, R13, R15 and R16) includes samples characterized by higher level of Fe (> 900 ppm) and Ti (> 40 ppm), with the exception of R2, for which higher Ti (230 ppm) and lower Fe (120 ppm) percentages have been detected. In samples included in the first group, Ga (not quantified in the current study) has also been detected. The second group (R4, R5, R6, R8 and R10) includes samples exhibiting the lower content in Fe (< 150 ppm) and Ti (< 40 ppm), while V is often absent (except in R5).

Table 2. Concentrations (ppm) of trace elements detected in the studied rubies and sapphires.

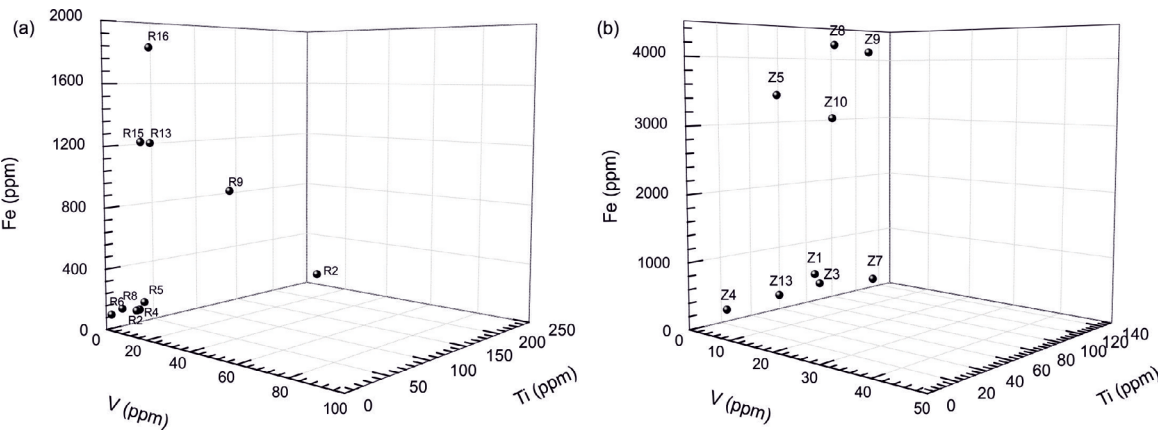| Corundum variety	Sample	Ti	V	Cr	Mn	Fe	Cu	Zn	Pb	Zr
RED	R2	230	12.10	903	44	119	163	21	b.d.l.	b.d.l.
	R4	17	b.d.l.	1554	30	116	169	23	b.d.l.	b.d.l.
	R5	24	7.91	1472	36	174	166	22	b.d.l.	b.d.l.
	R6	32	b.d.l.	2465	24	82	162	19	b.d.l.	b.d.l.
	R8	35	b.d.l.	2526	25	84	160	18	b.d.l.	b.d.l.
	R9	75	26.80	1410	64	902	170	62	4062	80
	R10	6	b.d.l.	2175	23	91	163	19	b.d.l.	b.d.l.
	R13	48	b.d.l.	235	62	1204	163	20	b.d.l.	b.d.l.
	R15	38	b.d.l.	593	56	1215	167	22	b.d.l.	b.d.l.
	R16	48	b.d.l.	1420	45	1838	167	21	b.d.l.	b.d.l.
BLUE	Z1	87	b.d.l.	b.d.l.	60	441	159	19	b.d.l.	b.d.l.
	Z3	90	b.d.l.	b.d.l.	63	268	162	24	b.d.l.	b.d.l.
	Z4	24	b.d.l.	b.d.l.	60	177	161	18	b.d.l.	b.d.l.
	Z5	59	b.d.l.	b.d.l.	78	3424	167	20	b.d.l.	b.d.l.
	Z7	111	7	b.d.l.	63	336	160	18	b.d.l.	b.d.l.
	Z8	103	b.d.l.	b.d.l.	78	4239	174	26	b.d.l.	b.d.l.
	Z9	131	b.d.l.	b.d.l.	77	4132	162	20	b.d.l.	b.d.l.
	Z10	101	b.d.l.	b.d.l.	76	3023	166	22	b.d.l.	b.d.l.
	Z13	60	b.d.l.	b.d.l.	64	223	162	19	b.d.l.	b.d.l.

Figure 3. Ternary diagrams V–Ti–Fe for (a) rubies and (b) sapphires.

Considering the origin of these rubies, by combining information from previous Raman spectroscopy studies (Barone et al. 2016b), microscopic observations and trace-element chemistry, it is possible to classify gems R2, R9, R13, R15 and R16 as natural rubies (being characterized by the highest percentages in Fe, Ti and V and by the presence of Ga). Quite interesting is the case of sample R9, in which Pb and Zr have been also detected. Usually, Pb is considered a proof of synthetic origin; however, from previous studies (Barone et al. 2016b), we know that this corundum has been certainly subjected to glass filling and invasive heat treatments (gained from the association of zircon and baddeleyete crystals). Therefore, we can conclude that Pb cannot be always used as origin indicator, as it can possibly be related to glass infiltration treatments, detectable only by complementary microscopic observation and micro-Raman analysis. For the other samples (R4, R5, R6, R8 and R10) characterized by lower Fe and Ti levels than the others, a synthetic origin can be assessed. A criticism could be proposed for sample R5, in which a low content of V and the presence of Ga has been detected. However, it is known that V cannot be considered alone a proof of natural origin, as both natural and synthetic gems can contain low V content. Moreover, regarding Ga, it is known that synthetic corundum obtained by Knischka, Douros, and Ramaura synthesis methods can contain trace of this element (Muhlmeister et al. 1998).

About sapphires, the inspection of a V–Ti–Fe graph allows us to separate samples in two groups (see Figure 3 (b)), characterized by different levels of Fe and Ti. In detail, Z5, Z7, Z8, Z9 and Z10 samples exhibit the higher contents of Fe (> 3000 ppm) and Ti (> 100 ppm), while in the other blue corundum (Z1, Z3, Z4 and Z13) the lowest percentages of these elements have been detected.

It is interesting that this discrimination is approximately in agreement with previous studies in which an hypothesis on origin were proposed on the basis of laboratory observations and Raman spectroscopy analysis (Barone et al. 2014). Specifically, a natural origin was suggested or Z1, Z8, Z9 and Z10 samples, while gems Z3, Z4, Z5, Z7 and Z13 were supposed to be synthetic. Based on trace-element chemistry, new insights can be finally proposed. Samples Z8, Z9 and Z10 seem to be natural, being grouped among sapphires exhibiting the higher Fe and Ti contents; however, this chemical group includes also Z5 and Z7, previously identified as synthetic gems. Of great interest is that all these five gems exhibited, in their Raman spectra, two low-frequency bands (at 190 and 240 cm^{-1}) not clearly interpreted; generally, these bands are not present in synthetic Al_2O_3 and are probably related to defects in natural minerals. Therefore, by combining chemical data and previous studies, it is possible to conclude that samples exhibiting the higher percentage in Fe and Ti (Z5, Z7, Z8, Z9 and Z10) are natural sapphires, while the other ones (Z3, Z4, Z13) are synthetic crystals. An exception is represented by sample Z1, for which the low contents in Fe and Ti might suggest a synthetic origin; however, in this case, the sole chemistry can lead to wrong conclusions. In fact, with Fe and Ti being responsible for the color of sapphires, the scarce content in these elements has to be related to the colorless of the Z1 gem, for which a natural origin can be assumed from the results gained from previous Raman spectroscopic analysis (due to the identification of rutile needles, typical of natural gemstones).

5 Conclusions

In this study, we have demonstrated the high potential of portable XRF in discriminating corundum gems of different origin, natural and synthetic. The method can be therefore recommended for gems characterization being non-invasive and non-destructive. However, in some cases, the study of trace-element chemistry might not be sufficient on its own. For example, the presence of specific elements usually considered proof of origin can be effectively related to invasive treatments suffered by natural gemstones. The concentration of discriminating elements can depend on the hue of the gem and only additional studies focused on inclusions can support the determination of origin. Therefore, even if chemical evidences are available, it is always important to combine chemical data with gemological observations and other techniques. A possible gem testing standard might include preliminary portable Raman spectroscopy analysis for the mineralogical identification of a gem. Once the discrimination between valuable gems and copies or fakes is achieved, portable-XRF spectroscopy can be used to discriminate natural from synthetic crystals. Of

course, when possible, microscopic observations and micro-Raman studies can certainly improve the basic knowledge acquired by using portable methods.

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