



Figure 1: These deep blue gahnites from Jemaa, Nigeria, form part of the material examined for this study. The oval stone on the right weighs 1.34 ct. Photo by T. Stephan.

On the Colour Mechanism of Blue Gahnite from Nigeria

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ABSTRACT: Gem-quality blue gahnite from Jemaa in central Nigeria has gemmological properties (RI and SG) and a chemical composition indicating relatively pure gahnite (90.7–91.3%). The blue colour is caused by a region of transmission between a system of dominant Fe^{2+} - and Co^{2+} -related absorption bands centred in the orange-to-green spectral range and an absorption edge in the UV region. The UV edge is strongly temperature dependent and, upon heating of the gahnite to 1000°C and 1400°C, shifts towards the visible range, resulting in blue-green and green colouration, respectively. The green colour component is related to Fe^{3+} , whereas the blue hue of the unheated gahnite is due predominantly to Co^{2+} .

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Among the minerals of the spinel supergroup, the zinc member gahnite (ideally ZnAl_2O_4) is found only sporadically in gem quality. Transparent green specimens from Brazil were described by Bank (1975). Green-to-blue material from Nigeria was characterised in detail by Jackson

(1982). The latter locality, in the Jemaa region of central Nigeria, is associated with granitic pegmatites (Jacobson & Webb 1946). In recent years, some parcels of rough deep blue gahnite from Nigeria (e.g. Figure 1) entered the gem trade, and short notes were published in the gemmological literature (Boehm & Laurs 2018; Hain & Sun 2019).

Jackson (1982) attributed the blue colour of Nigerian gahnite to Fe^{2+} , and mentioned an interesting colour modification from blue to blue-green and dark 'olive' green when the material is heated to temperatures of 1000°C and 1400°C, respectively. Subsequent detailed research on the causes of green-to-blue colouration in Nigerian gahnite (Fregola *et al.* 2014) proved the blue material to be coloured by a combination of absorption features associated with Fe^{2+} , Fe^{3+} and Co^{2+} . The role of Co^{2+} as a chromophore in Nigerian gahnite, in addition to Fe^{2+} , was also mentioned briefly by Hain and Sun (2019).

Generally, higher Fe contents in gahnite produce a stronger UV absorption edge extending into the visible spectral range that causes a green colour, while specimens with lower Fe that also contain Co show green-blue to blue colouration (Taran *et al.* 2005; Fregola *et al.* 2014). The aim of this study is to further investigate this interdependency of Fe and Co, mainly to show how strongly Co^{2+} influences the colour of blue Nigerian gahnite, as well as to document and interpret the annealing effect described by Jackson (1982).

CRYSTAL CHEMISTRY

Minerals with the spinel structure are found in a wide range of geological environments—both on Earth and in extraterrestrial contexts—making them important for scientific research. The structure and crystal chemistry of spinel-group minerals have been the focus of many studies, starting with initial publications in 1915 and continuing to the present (for a thorough review, see Bowles *et al.* 2011).

The spinel structure is generally characterised by close-packed oxygen atoms with metal atoms in tetrahedral and octahedral sites. To date, the spinel supergroup consists of 56 minerals with the general chemical formula AB_2X_4 (Bosi *et al.* 2019). The occupancy of the X position differentiates the oxyspinel (oxygen), thio-spinel (sulphur) and selenospinel (selenium) groups. Gem-quality spinel minerals belong to the oxyspinel group, with the general chemical formula $\text{A}^{2+}\text{B}_2^{3+}\text{O}_4$, where A and B represent divalent or trivalent metal ions (M^{2+} or M^{3+} , respectively). The spinel subgroup contains several species with Al^{3+} as the dominant B cation, the most common being:

- Spinel (MgAl_2O_4)
- Hercynite (FeAl_2O_4)
- Gahnite (ZnAl_2O_4)
- Galaxite (MnAl_2O_4)

These end members form complete solid solutions. Gem-quality spinels are usually Mg rich (i.e. the mineral spinel, or 'common' spinel; MgAl_2O_4). Mixed crystals of spinel and gahnite, the so-called gahnospinel, have less significance as gems, and relatively pure gahnite is rare in gem quality.

The colour range of gem spinel varies from red and purple to blue, green-blue and bluish green. The chromophores Cr^{3+} , V^{3+} , Fe^{2+} , Fe^{3+} and Co^{2+} , as well as Mn^{3+} , are responsible for this wide range of colours (Schmetzer *et al.* 1989).

MATERIALS AND METHODS

The study samples consisted of 81 crystals and crystal fragments (3–6 mm in size), and six faceted stones (0.22–1.34 ct), from Jemaa, Nigeria (e.g. Figure 1). The majority of the samples were loaned or donated by Gemstore24 and Arnoldi International, and some were from the collection of the German Gemmological Association. All of them were transparent, and most were deep blue in colour, although a few showed a slightly greenish hue. Some of the crystals were euhedral octahedra, but most showed a flattened or distorted octahedral shape. The waterworn appearance of their edges indicates they were mined from a secondary occurrence.

For comparison, several additional samples were investigated for their chemical composition (especially Co contents) and optical absorption spectra. These included four faceted (0.41–1.53 ct) and three rough (with parallel-polished windows) Fe ± Co-bearing blue spinels from other localities (Sri Lanka, Vietnam and an unspecified location), and a flux-grown Co-bearing synthetic spinel (Figure 2).

All six faceted Nigerian samples were tested by standard gemmological methods at the German Gemmological Association. RI was measured with a digital refractometer (Presidium Refractive Index Meter II) and SG was determined hydrostatically. The rough material was identified, and the identity of the cut stones was confirmed, by Raman spectroscopy using a Magilabs GemmoRaman instrument. Internal features were studied with a gemmological microscope, and inclusions were identified with Raman micro-spectroscopy using a Renishaw inVia unit with 514 and 785 nm laser excitation.

The chemical composition of the six faceted Nigerian gahnites, and all the comparison samples, was analysed at the Institute of Geosciences (Johannes Gutenberg University Mainz, Germany) with a JEOL JXA-8200 electron probe micro-analyser (EPMA) equipped with five wavelength-dispersive spectrometers. Analytical



Figure 2: This 0.47 ct flux-grown synthetic spinel is coloured by cobalt. Photo by T. Stephan.

conditions were 20 kV accelerating voltage, 20 nA beam current and a beam diameter of 5 μm . The counting time was generally 30 s (or 40 s for Fe and Mn). For analysis, $K\alpha$ -lines were used for each element, and special care was taken with overlapping peaks such as Fe($K\alpha$) and Co($K\alpha$). Standards consisted of well-characterised natural and synthetic oxide and silicate minerals. The matrix correction was done using a customised spinel program developed by the Petrology Working Group of the Institute of Geosciences. End-member composition was calculated with EMG software (End-Members Generator; Ferracutti *et al.* 2015).

Optical absorption spectra of all faceted and ten rough Nigerian gahnites, as well as the comparison samples, were collected at the DSEF German Gem Lab with a PerkinElmer Lambda 950S ultraviolet-visible-near infrared (UV-Vis-NIR) spectrometer, in the 200–2500 nm range with a resolution of 1 nm. The rough samples were analysed through parallel-polished windows. Deuterium and tungsten halogen lamps were used as light sources. The major detector change took place at 810 nm; longer wavelengths were recorded with an InGaAs detector, and shorter wavelengths with a photomultiplier tube (PMT detector). In the 200–810 nm range the slot width was fixed to 4 nm, and for 810–2500 nm it was variable (2–4 mm). The device was equipped with an integration sphere to collect scattered light. For spectral fitting, MagicPlot non-linear curve-fitting software was used. The $L^*a^*b^*$ colour coordinates were calculated between 380 and 780 nm (using the CIE standard illuminant D65 and a 2° standard observer) with LabCognition Panorama 4.0 software.

Heat-treatment experiments were performed at the German Gemmological Association on two rough Nigerian gahnites with parallel-polished windows, using a Nabertherm LHT 02/18 electric furnace. The samples were placed in ceramic (Al_2O_3) crucibles and heated in air. First they were heated for one hour at 1000°C and then for one hour at 1400°C (with a one-hour ramp-up time to the final temperature). After each heating interval they were taken directly out of the furnace and allowed to cool to ambient conditions.

RESULTS

Gemmological Properties

The RI of the Nigerian gahnites ranged between 1.791 and 1.798, and their SG varied from 4.34 to 4.66. These properties fall within the general ranges reported for gem-quality gahnite (Bank 1975, 1983; Jackson 1982; Boehm & Laurs 2018; Hain & Sun 2019), and are relatively close to the values described for pure gahnite (Winchell & Winchell 1967): RI = 1.805 and SG = 4.62.

Most of the samples contained crystalline and liquid inclusions. The solid inclusions consisted of transparent, corroded crystal clusters (identified as quartz); euhedral hexagonal prisms (beryl); rounded, colourless to slightly yellow crystals (zircon), often surrounded by tension halos; black tabular inclusions (tentatively identified as columbite), also often surrounded by tension halos; flat, tabular, hexagonal crystals (mica); and reddish brown, often rounded inclusions (sphalerite). In addition, negative crystals and two-phase partially healed fractures were observed.

Chemical Composition

The analysed samples had a composition relatively close to end-member gahnite, with approximately 91% ZnAl_2O_4 (see Table I). Most of the remainder consisted of the hercynite component (FeAl_2O_4), while galaxite (MnAl_2O_4) and spinel (MgAl_2O_4) components were present in amounts less than 1%. The analyses correspond well to data previously reported for Nigerian gahnite (D'Ippolito *et al.* 2013).

Low contents of Co were detected, ranging between 0.02 and 0.03 wt.% CoO. Such traces of Co have been previously reported in blue 'cobalt spinel' and gahnite (Shigley & Stockton 1984; Chauviré *et al.* 2015; D'Ippolito *et al.* 2015; Schollenbruch *et al.* 2021). Our measurements revealed comparable Co concentrations to some cobalt spinels from Sri Lanka (0.02–0.04 wt.% CoO), while a reference sample from Vietnam showed a distinctly higher concentration (0.07 wt.% CoO).

Table I: Chemical composition by EPMA of six blue gahnites from Nigeria.

Sample	1	2	3	4	5	6
Oxides (wt.%)						
Al ₂ O ₃	56.47	57.08	56.99	57.31	57.30	57.55
FeO ^a	3.18	2.97	2.97	3.05	2.90	2.93
CoO	0.02	0.02	0.02	0.02	0.03	0.02
MnO	0.09	0.08	0.07	0.09	0.08	0.08
MgO	0.20	0.18	0.19	0.20	0.18	0.20
ZnO	39.97	39.59	39.64	39.23	39.41	39.14
Total	99.92	99.92	99.89	99.90	99.91	99.92
Cations per 4 oxygens						
Al	2.010	2.023	2.022	2.028	2.028	2.032
Fe ²⁺	0.080	0.075	0.075	0.077	0.073	0.074
Co	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Mn	0.002	0.002	0.002	0.002	0.002	0.002
Mg	0.009	0.008	0.009	0.009	0.008	0.009
Zn	0.892	0.879	0.881	0.870	0.874	0.866
Total^b	0.984	0.965	0.968	0.959	0.958	0.951
End members (%)						
Gahnite (ZnAl ₂ O ₄)	90.70	91.20	91.19	90.84	91.31	91.10
Hercynite (FeAl ₂ O ₄)	8.18	7.75	7.74	8.01	7.61	7.75
Galaxite (MnAl ₂ O ₄)	0.22	0.21	0.20	0.23	0.23	0.21
Spinel (MgAl ₂ O ₄)	0.90	0.84	0.87	0.92	0.85	0.94

^a All iron reported as FeO. ^b Includes all elements except Al.

Optical Absorption Spectra

The UV-Vis-NIR absorption spectra of our Nigerian blue gahnite samples showed three dominant absorption-band systems (Figure 3). The strongest was located in the NIR range, the second towards the UV and the third in the visible range. Interpretation and assignment of the absorption bands was carried out in comparison to reference data from the literature (Schmetzer *et al.* 1989; Taran *et al.* 2005, 2009; D'Ippolito *et al.* 2013, 2015; Fregola *et al.* 2014; Palke & Sun 2018). The most important absorption bands, and their attributions, are listed in Table II.

The dominant absorption band system in the NIR range below 8300 cm⁻¹ (above 1200 nm) is attributed to spin-allowed *d-d* transitions of tetrahedrally coordinated Fe²⁺. The Co-bearing samples showed some smaller bands between 9000 and 6500 cm⁻¹ (1100–1550 nm); as shown in Figure 3, these were prominent in some spectra (d and e) and weak in others (a and c). These bands were absent from samples coloured mainly by iron (Figure 3b).

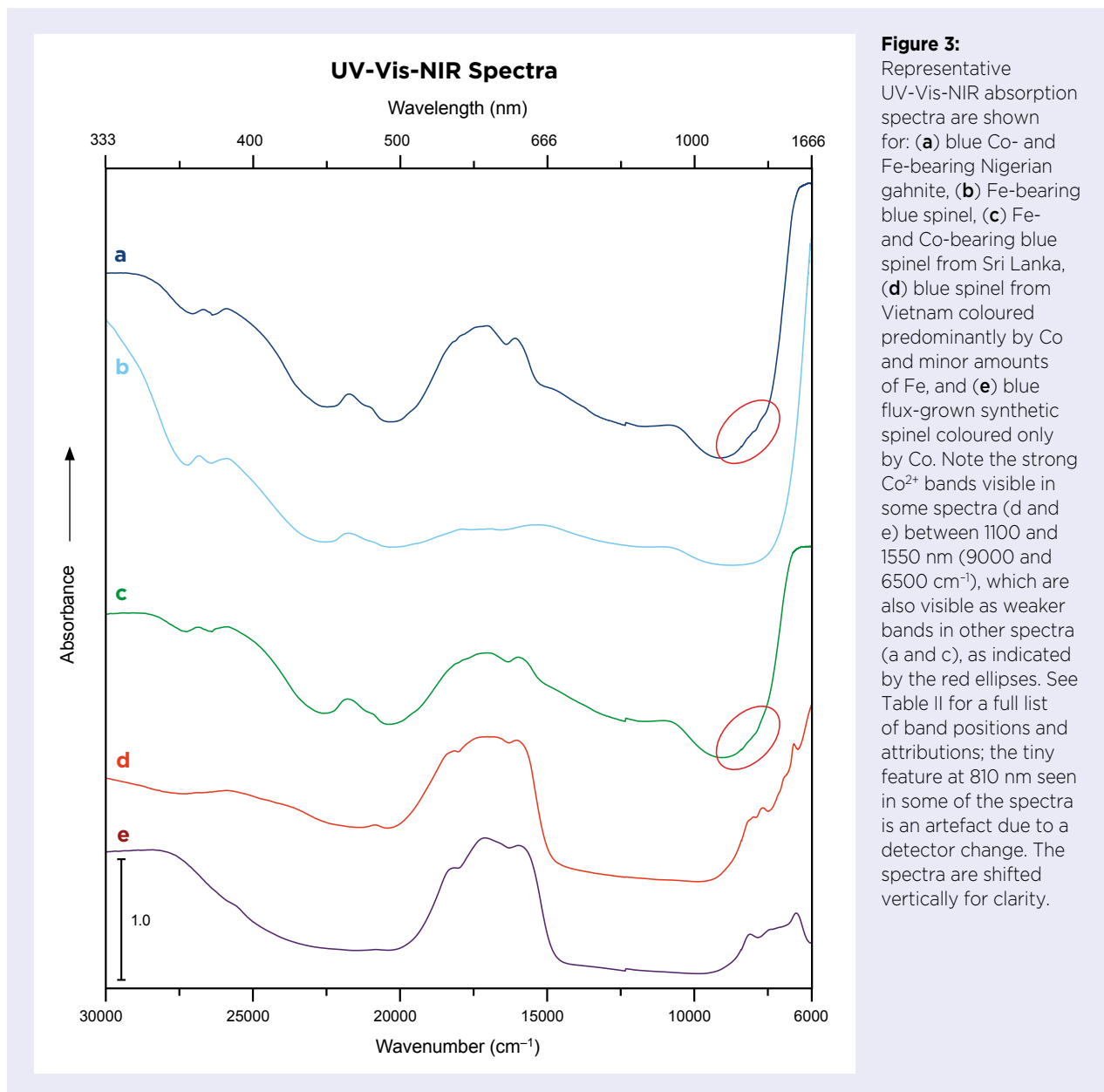
A strong band system towards the UV region is explained by oxygen-metal charge-transfer (OMCT) processes, mainly O²⁻ → Fe³⁺ and O²⁻ → Fe²⁺. These

OMCT bands form both a consistent increase in absorption towards the UV and an absorption edge at around 30,000 cm⁻¹ (330 nm).

Between these two strong band systems, a series of weaker bands in the visible region is caused by a combination of mostly spin-forbidden, but also spin-allowed, transitions mainly of the chromophores Fe²⁺, Co²⁺ and (minor) Fe³⁺. In combination, their overlapping absorption bands create a transmission window in the blue region. To distinguish the individual bands, however, is difficult.

Spectral Fitting and Colour Mechanism

To demonstrate the influence of Co²⁺ on gahnite colouration, the absorption spectra were mathematically deconvoluted by spectral fitting. For spectral fitting, the absorption spectra were plotted on a wavenumber (cm⁻¹) scale. The wavenumber values are proportional to the photon energy of the light, which facilitates comparison of diagnostic features such as HWHM (half width at half maximum) across the entire spectrum. For colour calculation, the fitted spectra were recalculated to a wavelength (nm) scale.

**Figure 3:**

Representative UV-Vis-NIR absorption spectra are shown for: (a) blue Co- and Fe-bearing Nigerian gahnite, (b) Fe-bearing blue spinel, (c) Fe- and Co-bearing blue spinel from Sri Lanka, (d) blue spinel from Vietnam coloured predominantly by Co and minor amounts of Fe, and (e) blue flux-grown synthetic spinel coloured only by Co. Note the strong Co^{2+} bands visible in some spectra (d and e) between 1100 and 1550 nm (9000 and 6500 cm^{-1}), which are also visible as weaker bands in other spectra (a and c), as indicated by the red ellipses. See Table II for a full list of band positions and attributions; the tiny feature at 810 nm seen in some of the spectra is an artefact due to a detector change. The spectra are shifted vertically for clarity.

Development of the Co^{2+} Model. To develop the Co^{2+} model, we used the blue flux-grown synthetic spinel coloured by Co^{2+} (Figure 2), without a significant influence of Fe in the visible-range absorption spectrum. Chemical analysis of this sample identified it as almost pure spinel, with 72.43 wt.% Al_2O_3 and 26.96 wt.% MgO , as well as 0.11 wt.% FeO and 0.05 wt.% CoO . Both Zn and Mn were below detection limit.

After modelling the background (Figure 4a), the residual spectrum was fitted with 12 Gaussian curves (Figure 4b). In the visible range, three bands from 18,314 to 15,816 cm^{-1} (546–632 nm) are described in the literature for Co^{2+} (see Table II). Due to their asymmetry, however, for each of these three bands we used two Gaussian curves to describe them with the MagicPlot software

(which only allows symmetrical Gaussian curves). The bands in the NIR region are strongly present in the absorption spectrum of the synthetic spinel (Figure 3e) and are seen as shoulders in the absorption spectra of the natural Co-bearing gahnites and spinels (Figure 3a, c, d). These NIR bands were also fitted using a total of six Gaussian curves, and Table III shows the band positions, HWHMs, amplitudes and areas calculated for these curves.

To develop the Co^{2+} model, the band positions and HWHMs were fixed, and then all 12 Gaussian curves were joined together by setting the area of the curve for the ' Co^{2+}_1 ' band in Table III to a factor of 1, and expressing the area of the other 11 bands as multiples of that factor. When using this model, the described parameters (band positions and HWHMs) must be fixed, and then the

Table II: Maxima of the major absorption bands in the UV-Vis-NIR spectra of blue gahnite from Nigeria (calculated by spectral fitting) compared to literature data.^a

Wavenumber (cm ⁻¹) ^b	Fitted position (cm ⁻¹)	Fitted position (nm)	Assignment
26850-26640	26674	375	^{IV} Fe ²⁺
25730-15989	25899	386	^{IV} Fe ²⁺
24870-24675	24937	401	^{VI} Fe ³⁺
21826-21656	21667	462	^{VI} Fe ³⁺
21120-20833	20982	477	^{IV} Fe ²⁺
<i>18314-17943</i>	18389 and 18236 (Co ²⁺) 17875 (Fe ²⁺)	544 and 548 (Co ²⁺) 559 (Fe ²⁺)	^{IV} Co ²⁺ ^{IV} Fe ²⁺
<i>17059-16932</i>	17375 and 16554 (Co ²⁺) 16740 and 16017 (Fe ²⁺)	576 and 603 (Co ²⁺) 597 and 624 (Fe ²⁺)	^{IV} Co ²⁺ ^{IV} Fe ²⁺
<i>15911-15816</i>	15872 and 15434	630 and 647	^{IV} Co ²⁺
14945-14814	14559	687	^{VI} Fe ²⁺ - ^{VI} Fe ³⁺ -IVCT ^{IV} Fe ²⁺ - ^{VI} Fe ³⁺ -ECP
12778-12604	12863	777	^{VI} Fe ²⁺ ^{IV} Fe ²⁺ - ^{VI} Fe ³⁺ -ECP
10939-10629	10690	935	^{VI} Fe ²⁺
<i>8200^c</i>	—	1220 ^c	Presumably ^{IV} Co ²⁺
<i>8000^c</i>	—	1250 ^c	Presumably ^{IV} Co ²⁺
<i>7750^c</i>	—	1290 ^c	Presumably ^{IV} Co ²⁺

^a Abbreviations: ECP = exchange-coupled pair, ^{IV} = tetrahedral coordination, IVCT = intervalence charge transfer, ^{VI} = octahedral coordination. Unless stated otherwise, wavenumber values are from D’Ippolito *et al.* (2015).

^b Bands related to Co²⁺ are shown in italics.

^c These three bands have been documented by the authors only in Co-bearing spinel and gahnite, but they have not been mentioned in the literature (probably because they are on the flank of the strong Fe²⁺-related system in the near-infrared region). The wavenumber and wavelength positions given here are the maxima of the corresponding bands visually observed in absorption spectra. See Table III for the fitted positions (Co²⁺_6 to Co²⁺_12).

software can just vary the amplitudes of the curves—and since their areas are joined, the ratios between them always remain the same. This deconvolution method has the advantage that one can focus on peaks which do not strongly overlap those of other chromophores.¹

Applying the Co²⁺ Model to Nigerian Gahnite. The influence of Co²⁺ on the colouration of Nigerian gahnite was determined in three steps:

1. The background of the spectra of the Nigerian gahnite samples (e.g. Figure 5a) was modelled (see Figure 5b). The background system is a combination of the OMCT bands, the spin-allowed transition of Fe²⁺ and minor reflections at the surface of the samples.
2. The Co²⁺ model obtained from the synthetic spinel above was used to calculate the influence of Co²⁺ on the colour of the Nigerian gahnite (Figure 5c). The

¹ The best fit can be achieved when using a model for each chromophore, developed with samples coloured solely by that chromophore. The flux-grown synthetic spinel used to develop the Co²⁺ model is structurally different from gahnite, so slightly different band positions, HWHMs and symmetry would be expected when preparing such a model using gahnite coloured solely by Co²⁺ (which, to the authors’ knowledge, does not exist in either natural or synthetic form). Work is in progress to prepare models for Fe²⁺ and Fe³⁺ in spinel.

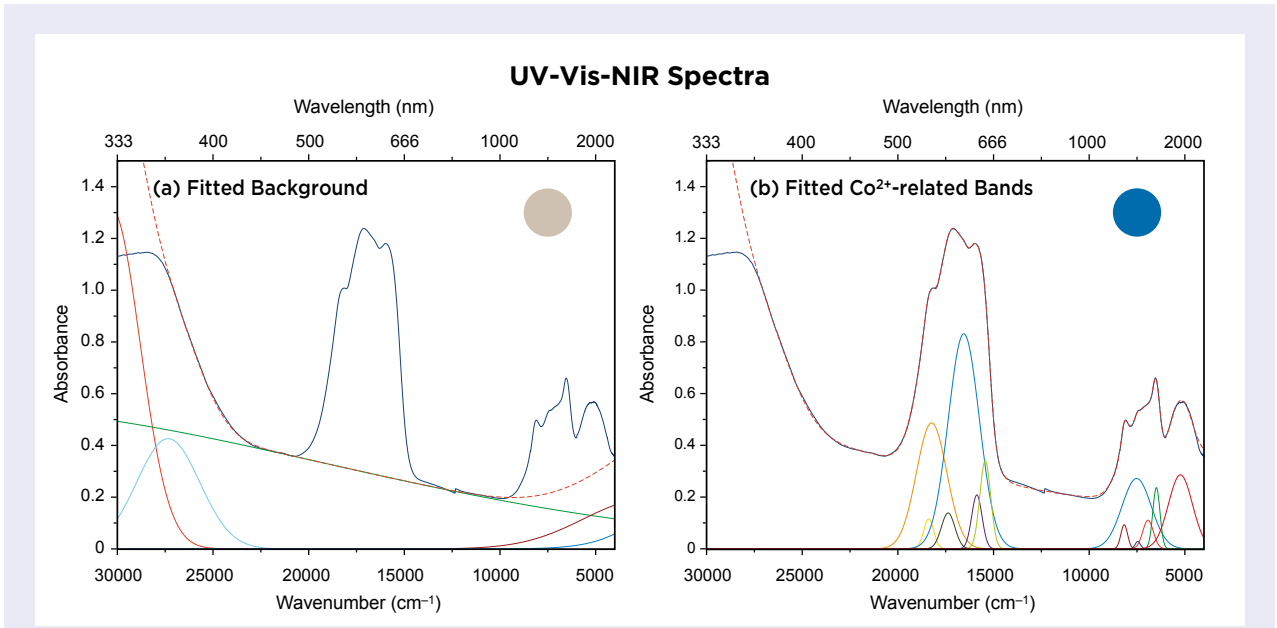


Figure 4: The absorption spectrum of a blue flux-grown synthetic spinel coloured only by Co was deconvoluted mathematically by spectral fitting, showing (a) the background band system and (b) the fitted Co²⁺-related bands. These latter bands were used to prepare a model in order to calculate the influence of Co²⁺ on the colour of Nigerian gahnite. The colour circles depict the corresponding colour calculated from the fitted spectrum (dashed red line), and the deconvoluted spectral curves are shown at the bottom on the x-axis.

intensity of this band system was evaluated using the Co bands between 9000 and 6500 cm⁻¹ (1100–1550 nm), since these bands are not strongly overlapped by Fe bands.

3. The residual component was spectrally fitted to demonstrate the influence of the Fe-related bands (see Figure 5d and Table IV). This is a combination of spin-allowed and spin-forbidden transitions, mainly of

Table III: Parameters used to develop the model for demonstrating the influence of Co²⁺ on the colour of Nigerian gahnite.*

Band	Position (cm ⁻¹)	HWHM (cm ⁻¹)	Amplitude	Area	Factor
Co ²⁺ _1	18388.79	306.84	0.12	75.58	1.00
Co ²⁺ _2	18235.54	936.02	0.49	969.54	12.83
Co ²⁺ _3	17375.02	414.89	0.14	122.36	1.62
Co ²⁺ _4	16553.93	953.13	0.83	1686.35	22.31
Co ²⁺ _5	15872.28	318.79	0.21	141.30	1.87
Co ²⁺ _6	15434.31	333.73	0.34	241.54	3.20
Co ²⁺ _7	8169.78	206.81	0.09	40.87	0.54
Co ²⁺ _8	7520.48	899.86	0.27	520.81	6.89
Co ²⁺ _9	7461.57	162.21	0.03	9.68	0.13
Co ²⁺ _10	6924.62	325.18	0.11	76.50	1.01
Co ²⁺ _11	6489.05	220.21	0.24	110.93	1.47
Co ²⁺ _12	5231.87	735.51	0.29	447.62	5.92

* Each value is rounded to two decimals. Position and HWHM values must be fixed to use the model.

Fe²⁺ and minor Fe³⁺. Both, but especially Fe³⁺, have a strong influence on the OMCT bands. This influence was included in the ‘background system’ in step 1.

Based on the results obtained with the deconvolution method described above, both Fe and Co have a strong influence on the colour of the blue Nigerian gahnite. The colour circles calculated from the spectral fitting (see Figure 5), however, demonstrate that the background system and the Fe-related bands mainly influence tone, whereas the blue hue is predominantly produced by Co²⁺, despite its low concentration (only 0.02–0.03 wt.% CoO).

HEAT TREATMENT

Generally, gahnites with a higher Fe content show green colouration due to the stronger OMCT band system towards the UV region (Taran *et al.* 2005), while those containing lower Fe content and additionally with Co²⁺ show blue-green to blue colours (Fregola *et al.* 2014). This, however, is not consistent with the description given by Jackson (1982), who mentioned a colour modification from blue to green by heat treatment, since heating does not change Fe content.

To investigate this further, heat treatment experiments were performed on two of the rough Nigerian

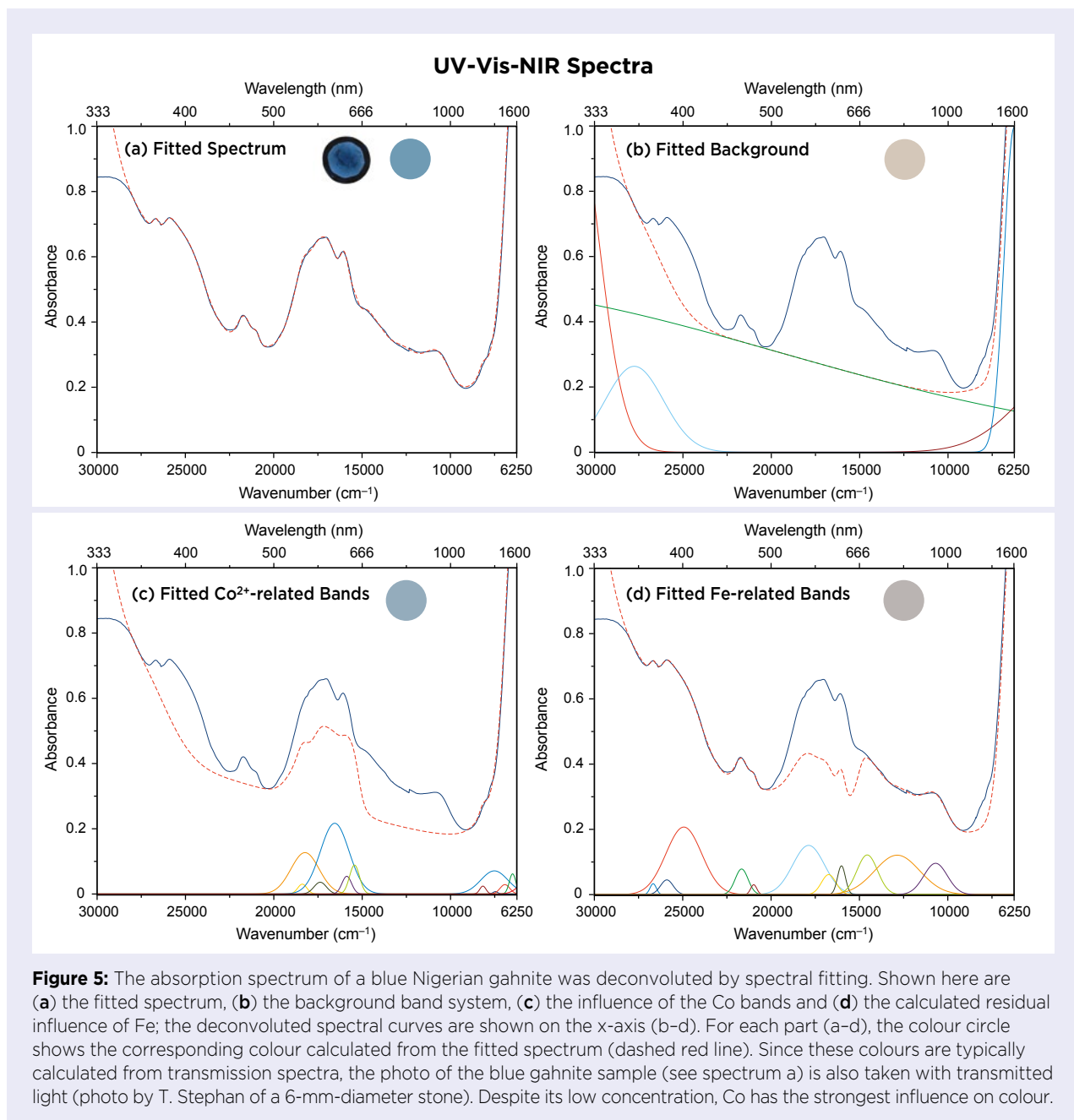


Table IV: Parameters obtained in this study for the Fe-related bands in blue gahnite from Nigeria.*

Band	Position (cm ⁻¹)	HWHM (cm ⁻¹)	Amplitude	Area
Fe ²⁺ _1	26673.56	211.04	0.03	15.02
Fe ²⁺ _2	25898.92	421.14	0.05	40.40
Fe ³⁺ _1	24937.46	1191.89	0.21	525.42
Fe ³⁺ _2	21667.03	430.37	0.08	71.86
Fe ²⁺ _3	20981.55	205.54	0.03	13.24
Fe ²⁺ _4	17875.05	1057.03	0.15	339.62
Fe ²⁺ _5	16740.08	480.93	0.06	62.80
Fe ²⁺ _6	16016.78	263.72	0.09	49.50
Fe ²⁺ /Fe ³⁺ -IVCT_1	14559.16	688.24	0.12	178.12
Fe ²⁺ /Fe ³⁺ -IVCT_2	12863.19	1498.85	0.12	385.67
Fe ²⁺ _7	10689.95	781.55	0.10	159.66

* These have not been fitted with respective models for the influence of iron on gahnite colouration, but are the mathematical best description of the residual spectral component after applying the Co²⁺ model.

gahnite samples. After heating at 1000°C they became darker greyish blue with a slightly greenish hue, and after heating at 1400°C they became dark bluish green. The corresponding absorption spectra are shown in Figure 6.

D'Ippolito *et al.* (2013) mentioned that the colour of gahnite is highly sensitive to variations in the oxidation state of Fe. In the spectra shown in Figure 6, with increasing temperature there is a strong increase in the intensity of the band at 21,667 cm⁻¹ (462 nm) assigned to spin-forbidden Fe³⁺ transitions. The shoulder at 24,937 cm⁻¹ (401 nm), also assigned to Fe³⁺, increased in intensity as well, but is hidden by the more intense absorption edge after heat treatment. Most important is the stronger overall absorption in the blue-to-violet range, which shifts the transmission window towards the green spectral region. For heating of corundum, this is mainly explained by the formation of defect centres (trapped holes involving Mg²⁺ and Fe³⁺; e.g. Emmett & Douthit 1993, 2017). The increasing intensities of the spin-forbidden Fe³⁺ transitions, however, indicate that Fe²⁺ is partly oxidised to Fe³⁺. Based on this, we infer that the greater absorption in the blue-to-violet range is due to a stronger O²⁻ → Fe³⁺ charge transfer. Additional experiments are needed to prove whether the colour

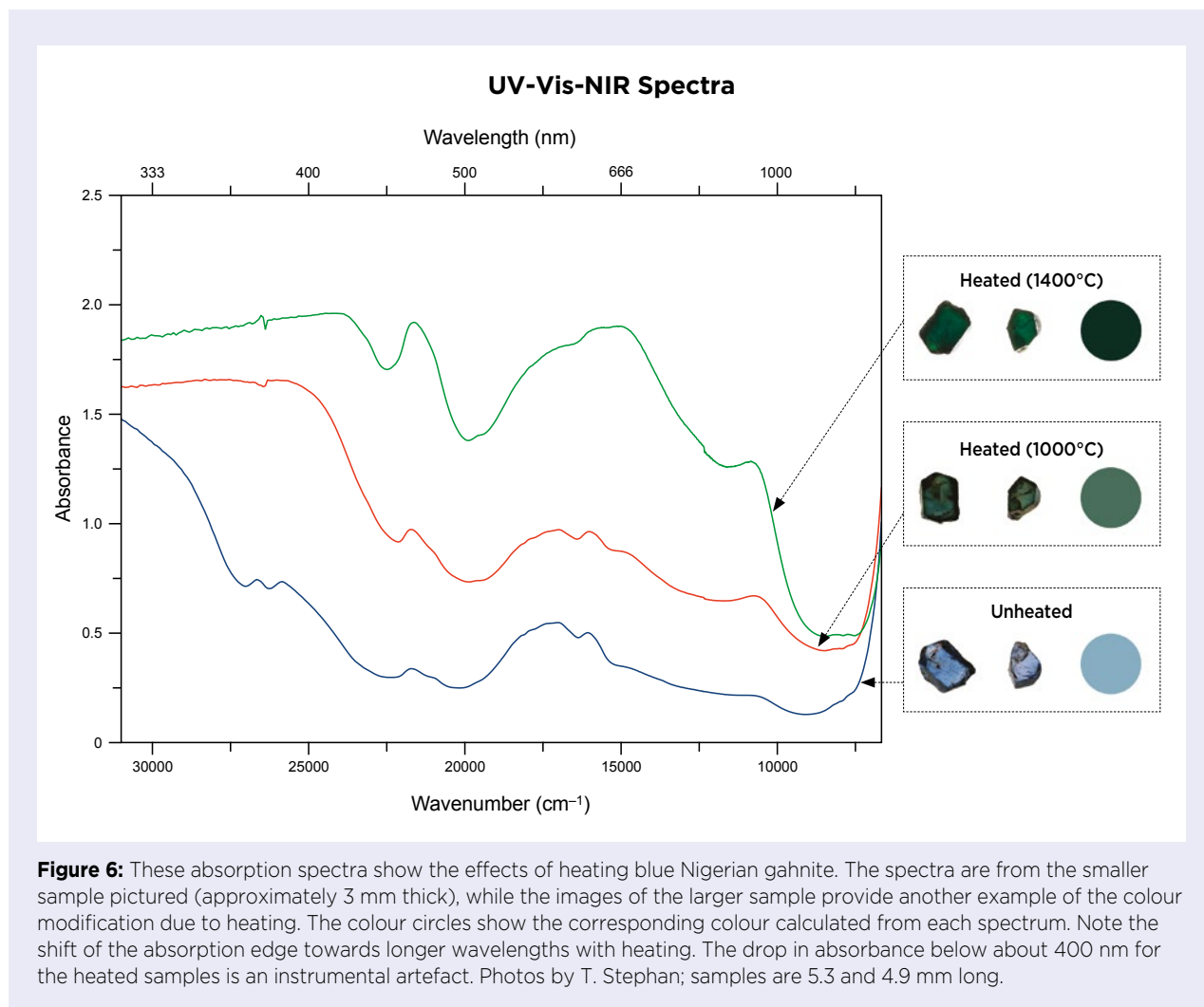
modification is reversible in a reducing atmosphere.

To the authors' knowledge, the heat treatment of blue Nigerian gahnite in oxidising conditions is not of commercial interest to the gem market, since the colours produced are not of an attractive hue and/or are generally over dark.

CONCLUSION

The availability of blue Co- and Fe-bearing gahnites from Nigeria is an interesting addition to the trade and for gem collectors. Their deep blue colour is due to a combination of Co²⁺ and Fe²⁺, as well as minor Fe³⁺. The optical absorption spectrum is mainly dominated by the Fe²⁺ band system, but—despite its low concentration—Co²⁺ is mainly responsible for the blue colour.

Heating to 1000°C and 1400°C in oxidising conditions produces darker greyish-greenish blue to dark bluish green colours, caused mainly by more intense O²⁻ → Fe³⁺ charge-transfer bands, due to the oxidation of Fe²⁺ to Fe³⁺. Consequently, the green colour does not depend on the Fe content, as previously described, but on the amount of Fe³⁺, as reported by D'Ippolito *et al.* (2013).



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