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Minerals of the Kornerupine Group

by

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Abbreviations

BED: backscattered electron detector

EDXRF: energy-dispersive X-ray fluorescence spectrometry

FTIR: Fourier-transform infrared

FWHM: full width at half maximum

LWUV: long-wave ultraviolet

ND: not detectable

RI: refractive index (n)

SEM: scanning electron Microscope

SED: secondary electron detector

SWUV: short-wave ultraviolet

UV-Vis-NIR : ultraviolet-visible-near infrared

Introduction

The research project presented here was carried out as part of the preparation for the Diplôme d'Université de Gemmologie (DUG) of Nantes Université.

In September 2024, I travelled to Hong Kong together with Claudio Milisenda to represent the DSEF German Gem Lab during the Hong Kong Jewellery & Gem Fair and offer on site gemstone testing service. While I passed by a booth of a company specialised in tsavorites, my eyes fell upon a few emerald-green stones which looked different. They were actually kornerupines, the “auxiliary products” found together with tsavorites in Tanzania. The bright green colour of these kornerupines is lovely and I acquired two of them (respectively 0.45ct. and 2.39ct., Fig. 1). In November 2024, I participated in the DUG course in Nantes and chose kornerupine as the subject of my research project.



Fig. 1 Two kornerupines from Tanzania (Top left: 0.45ct., 5.06 x 4.13 mm)

It has been a trip full of discoveries and I feel truly lucky to have received so much support in many aspects.

For the research stones collection, my heartfelt thank goes to Emmanuel Fritsch (Nantes Université, Nantes), Tom Stephan (DgemG - German Gemmological Association, Idar-Oberstein), Michael Wild (Werner Wild e.K., Idar-Oberstein), M.T.M Haris (Emteem Gem Lab, Sri Lanka) and Fabian Schmitz (Rhein-Main-Gem-Consulting, Mainz) for having generously provided me with samples including those with uncommon colours.

I am infinitely grateful to my teachers Emmanuel Fritsch, Boris Chauviré, Stefanos Karampelas and Eloïse Gaillou for their teaching, guidance, encouragement and unconditional support,

to the members of the jury for their valuable feedbacks and suggestions which helped me to further develop this research project,

to Claudio Milisenda for his constant support and advice, for his comments to help me progress and for allowing me to carry out analysis with instruments of the DSEF German Gem Lab,

to Tom Stephan for his friendly help, the careful rereading, the motivating and inspiring discussions and for being available whenever I have questions,

to John Saul for kindly sharing with me his experience with discovery of kornerupines in East Africa,

and to my DUG promotion for the great time spent together and for all the enriching exchange.

Context of the project

History

Discovery

Kornerupine was first found at Fiskernæs, West Greenland, as material with a radiating columnar habit in translucent to transparent pieces of pale green to grey green colour. The mineral was reported upon in 1884 (but published in 1886) by J. Lorenzen who named it kornerupine in memory of Andreas Nicolaus Kornerup, a young Danish explorer, geologist and artist who made multiple research trips to Greenland.

In 1886, Sauer proposed the name prismatine for a prismatic mineral from a cut near the Waldheim railroad station, Saxony, Germany. This mineral resembled sillimanite and andalusite in appearance and staurolite in composition. At that time Sauer was presumably unaware of Lorenzen's (1886) name kornerupine for a mineral from Fiskernæs, Greenland, of the composition $\text{MgAl}_2\text{SiO}_6$ and resembling kyanite and sillimanite. Ussing (1889) compared Sauer's prismatine with Lorenzen's kornerupine and concluded that they were the same mineral on the basis of symmetry, cleavage and optical orientation; differences in optic angle, colour and specific gravity were presumed to be within the ranges found in isomorphous minerals.



A.N. Kornerup
Photo: Budtz Müller

Kornerupine group

Lacroix carried out research on the role of boron in kornerupines from Madagascar and suggested to integrate boron in the chemical formula of the mineral: $[\text{SiO}_4]_7\text{Mg}_8[(\text{Al}, \text{Fe}, \text{B})\text{O}]_{12}$ instead of the formula suggested for the material from Greenland $\text{SiO}_8 \text{Al}_2\text{O}_3 \text{MgO}$. (Lacroix et al., 1921)

Advances in the technology of ion- and electron-microprobe analysis and of crystal structure refinement made accurate measurement of boron in silicate minerals feasible. Analysis of boron using the ion microprobe and crystal structure refinement indicate that the boron content of one tetrahedral site in kornerupine ranges from 0 to 1. Kornerupine and prismatine, from their respective type localities of Fiskernæs, Greenland and Waldheim, Germany, are different minerals, members of an isomorphous series differing in boron content. For this reason, Sauer's name prismatine for kornerupines with $\text{B} > 0.5$ atoms per formula unit (apfu.) of $22(\text{O}, \text{OH}, \text{F})$ was re-introduced, and the name kornerupine *sensu stricto* is restricted to kornerupines with $\text{B} < 0.5$ apfu. Kornerupine *sensu lato* is an appropriate group name for kornerupine of unknown boron content. Both minerals form under granulite-facies conditions with sapphirine and phlogopite, but kornerupine *sensu stricto* is associated with anorthite and hornblende or gedrite, whereas prismatine is found with oligoclase (An9-13), sillimanite, garnet, and/or tourmaline. Occurrences at other localities suggest that increasing boron content extends the stability range of prismatine relative to that of kornerupine *sensu stricto*. (Grew et al., 1996)

In 1999, Wopenka et al. described a differentiation method between kornerupine *sensu stricto* and prismatine with Raman spectroscopy. According to this research work, two of the Raman vibrational modes of kornerupines *sensu lato* (at $\sim 803 \Delta\text{cm}^{-1}$ and at $\sim 884 \Delta\text{cm}^{-1}$) are sensitive to the presence of boron and their relative intensities can be used to distinguish kornerupine *sensu stricto* and prismatine. Based on the intensities of those boron-sensitive bands, Raman spectroscopy could potentially provide a semi-quantitative measure of the boron content of kornerupine.

See Fig. 2 for comparison of the fundamental Raman bands of boronfree, boron-poor, and boron-rich kornerupine-group minerals with 0° crystal orientation with respect to the polarisation orientation of the exciting laser beam. Bands C ($\sim 803 \Delta\text{cm}^{-1}$) and D ($\sim 884 \Delta\text{cm}^{-1}$) are sensitive to the presence and the concentration of boron in the mineral. Boron content of samples varied between 0.02 B apfu and 0.84 B apfu. Samples showing both boron-sensitive Raman bands at $\sim 803 \Delta\text{cm}^{-1}$ and $\sim 884 \Delta\text{cm}^{-1}$ could be identified as “boron-rich,” i.e., prismatine ($B > 0.5$ apfu) by Raman spectroscopy. In “boron-poor” kornerupines ($0.5 > B > 0.1$ apfu), i.e., kornerupine *sensu stricto*, only the stronger of the two boron-sensitive bands (the one at $\sim 884 \Delta\text{cm}^{-1}$) is detected in the Raman spectrum. For samples with $B < 0.1$ apfu, neither one of the two boron-sensitive Raman bands is detected. (Wopenka et al., 1999)

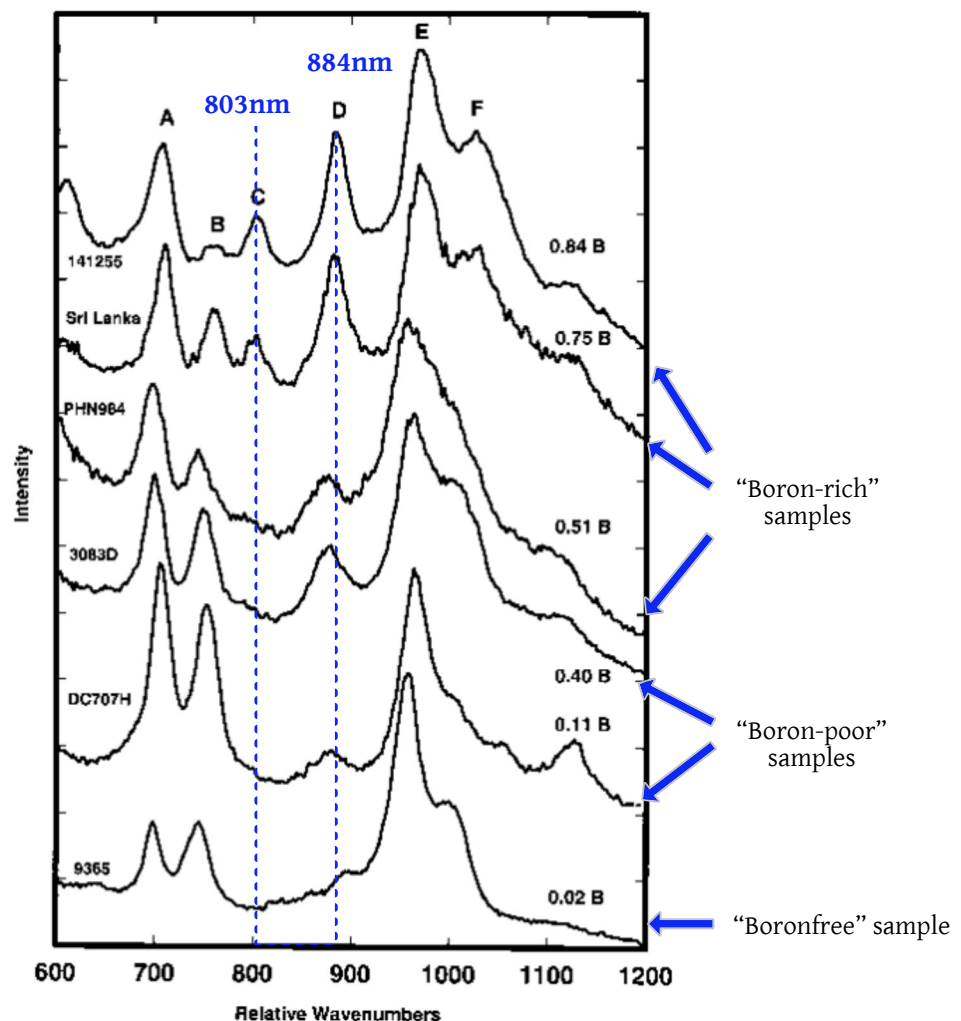


Fig. 2 Comparison of the fundamental Raman bands of boronfree, boron-poor and boron-rich kornerupine-group minerals (Wopenka et al., 1999)

Localities

Kornerupine *sensu stricto* and prismatine, the B-poor and B-rich members of the kornerupine group (Grew et al., 1996; Braga et al., 2003), have been reported from some 70 localities worldwide.

The material from Greenland is scarce and has no gem significance. In 1912, an olive green variety of kornerupine, found as transparent crystals, was discovered at Betroka, Madagascar (Lacroix, 1938), and later, in 1922, another deposit of similar coloured material was found at Itrongay on the same island. About 1936, some deep brownish-green cut stones from the illam of Ceylon were identified as kornerupine and a number of such stones have since been found in parcels of Ceylon gravel. In 1952, although a similar but unidentified stone had been known for some time, a green-coloured stone of fine quality was identified as kornerupine, and there is little doubt that the stone came from the Mogok Stone Tract of Burma. It has been credibly reported that a star-kornerupine has been found at this locality. Other sources of kornerupine, but not necessarily of gem quality, are Waldheim in Saxony, where the mineral was first known as prismatine; some opaque material has been found at Port Shepstone in Natal, South Africa, and material of two types, one a dark green and the other a yellow or greenish-yellow, comes from Lac Ste Marie, Gatineau, Quebec, Canada. (Webster, 1977). Kornerupine cat's-eyes have been found in Sri Lanka (Milisenda, 2005).

Specimens of gem quality with bright green colours from the Kwale District, Kenya were described in 1974 (Schmetzer et al., 1974). They are found together with quartz, silimanite, kyanite, tourmaline, muscovite and biotite in prismatic crystals up to 10cm length. John Saul kindly shared his experience with the discovery of kornerupines in East Africa: "Gem kornerupines with an attractive yellowish tint and strong dichroism were found near the town of Daluni in north east Tanzania in the early 1970s. A few rolled gem pebbles found in the Uмба River were either kornerupines or sillimanites or both. Crystal-sections, 1 to 3 cm in length, with 'woody' surface alteration were found, perhaps near the south east Kenya-north east Tanzania border c.1972. The specimens looked like crushed logs with bright green broken ends. When cut, they looked like tsavorites. This was very nice material. My impression was that everything came from a one-day find in hardrock. There is a chance I was not told the truth concerning the locality, in which case, the locality would be 'eastern East Africa'."

Bluish-green and blue kornerupines from Kenya (district of Namanga) and Tanzania (southern part of the Usambara Mountains or Daluni in the Uмба Region) were described by Schmetzer et al. in 1979. These stones are distinctly different in their optical features from the green kornerupine crystals from the Kwale District, Kenya (Schmetzer et al., 1974). They have been detected in lots of other minerals such as green tourmalines or green garnets and partly offered as single stones under other names (e.g. sillimanite). (Schmetzer et al., 1979)

According to Claudio Milisenda, the geology of the East African bright green and bluish-green to blue kornerupines is possibly related to the East African Mozambique belt, in whose terranes in Kenya and Tanzania numerous V-bearing minerals occur.

Gemmological properties

Generalities

Kornerupine *sensu lato*, approximately $(\text{Mg,Fe}^{2+},\text{Al},\square)_{10}(\text{Si,Al,B})_5\text{O}_{21}(\text{OH,F})_2$ (IMA Formula), also $(\square,\text{Mg,Fe}^{2+})\text{Al}_4(\text{Mg}_3\text{Al}_2)[\text{O}_4|(\text{OH},\text{O})|\text{Si}_2\text{O}_7|(\text{Si}(\text{Al},\text{B})\text{Si})_{\Sigma 3}\text{O}_{10}]$ (Strunz & Nickel, 2001), is a magnesium iron aluminium boron-silicate mineral group occurring in Mg-Al-rich rocks, magnesian metapelites and, very rarely, pegmatites in upper amphibolite- and granulitefacies terrains; it includes kornerupine *sensu stricto* ($0 \leq B < 0.5$ apfu) and prismatine ($1 > B > 0.5$ apfu) (Grew et al., 1999).

Transparent crystals can be cut as gemstones. They are usually green to blue-green, or brownish-green to greenish-brown, or yellow-brown to brownish-yellow in colour and display strong pleochroism. Blue specimens are rare (Henn et al., 2019). The crystallization is orthorhombic. The hardness is 6½ on Mohs scale and the density varies from 3.20 to 3.45. The refractive indices' ranges are as below, with a negative biaxial birefringence between 0.013 and 0.015 (Henn and Milisenda, 2004):

$$n_x = 1,660 - 1,671$$

$$n_y = 1,673 - 1,683$$

$$n_z = 1,675 - 1,684$$

Colouring agents

Schmetzer et al. analysed specimens of gem quality with light green colours from Kenya and attributed the green colour to vanadium (1974). Analysis of the bluish-green and blue kornerupines *sensu lato* from Kenya led to the following description of the colour variation of vanadium- and chromium-containing East African kornerupines: $V > Cr \Rightarrow$ green, $V \approx Cr \Rightarrow$ blue-green, $Cr > V \Rightarrow$ blue (Schmetzer, 1982). Iron-bearing kornerupines *sensu lato* in the colour range brown-yellow-green are known to occur in Sri Lanka, Madagascar and Burma (Schmetzer et al., 1974; Henn, 1985).

Luminescence

Robert Webster described that kornerupines *sensu lato* show a yellow glow under both long and short wavelengths of ultra-violet light. Those found in East Africa show “an even stronger yellow glow”.

GIA Gem Database recorded the fluorescence of a kornerupine *sensu lato* (1.64 ct.) from Kwale District (Kenya) which belongs to Edward J. Gübelin Collection: weak yellowish green with even distribution under LWUV and yellowish green with even distribution under SWUV (GIA Gem Database, 2011).

Pleochroism

Pleochroism of kornerupines *sensu lato* has been described in various publications. Bank et al. reported in 1974 and 1975 the strong pleochroism of transparent gem-quality kornerupines from south of Handeni in Tanzania. A comparative table (Table 1) published by Schmetzer et al. in 1977 (in German) and 1979 (in English) summarised the pleochroism of kornerupines from different localities.

Table 1 Pleochroism of kornerupines from different localities (Schmetzer et al., 1977&1979)

	Ceylon and Madagascar	Kwale District, Kenya	Kenya and Tanzania, various localities, somewhat different due to contents of trace elements		
X	yellowish-brown	intensely green	emerald-green	emerald-green	
Y	brown	slightly green	bluish-grey	reddish-purple	Y and Z show only small differences
Z	greenish	greenish-yellow	reddish-purple	bluish-grey	

Inclusions

Zircons, negative crystals, needle-like crystals, oriented hollow tubes, apatite, fluid inclusions, two-phase inclusions, etc. have been described as inclusions in kornerupine in the literature. (Henn, 1985; Henn et al., 2004; C. C. Milisenda, 2005; C. C. Milisenda et al., 2009)

Synthetics

Boron-free kornerupines were synthesised for the first time in 1969 by Schreyer & Seifert (Schreyer et al., 1969). Synthesis experiments suggest that boron incorporation occurs summarily for Al³⁺ (K. Schmetzer, 1979). Synthesised boron-bearing kornerupine was described by G. Werding and W. Schreyer in 1978.

Materials and Methods

Materials

Description

Twelve kornerupines *sensu lato*, with colours ranging from yellowish-green to emerald-green, green-blue to blue-violet and yellow-brown to brown-green, were analysed. Not all the origins of the samples are known. (Fig. 3-4, Table 2). The twelve kornerupines were grouped into **the Green-Blue-Violet series** and **the Brown-Yellow-Green series** according to their colours. One andalusite was measured for the purpose of comparative analysis of luminescence. Further description of the andalusite sample will be detailed in the session on luminescence.



Fig. 3 Twelve kornerupines *sensu lato* :

- Left: the Green-Blue-Violet series (KUD5: 7.64 x 5.54 mm)
- Bottom: the Brown-Yellow-Green series (KUD3: 10.14 x 9.10 mm)

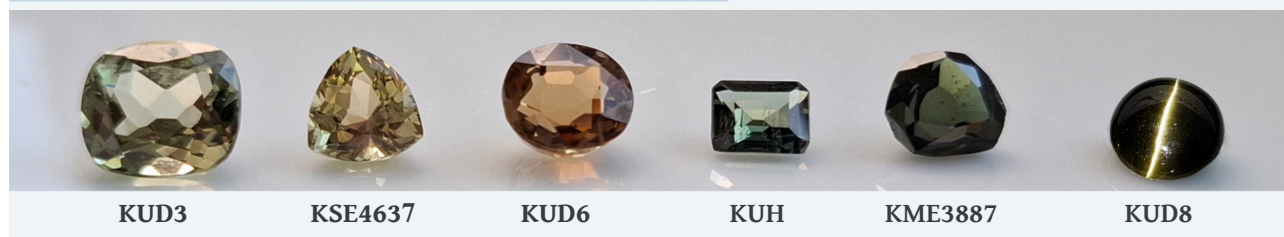


Fig. 4 Andalusite sample AUE4100 (8.08 x 6.64 mm)

Table 2 Description of twelve kornerupines *sensu lato* and one andalusite AUE4100

Sample N°	Colour	Weight	Dimensions (mm)	Cut	Form	Optical Effect	Origin
KTJ1	Green	0,45 ct.	5,06 x 4,13 x 2,97	Mixed Star/Step cut	Oval	-	Tanzania
KTJ2	Green	2,39 ct.	9,52 x 7,40 x 4,61	Mixed Star/Step cut	Oval	-	Tanzania
KUD5	Green	1,39 ct.	7,64 x 5,54 x 3,44	Step cut	Octagon	-	Unknown
KUD7	Green	1,53 ct.	9,02 x 5,37 x 3,46	Cabochon	Oval	Cat's-eye	Unknown
KUF	Green-blue	3,52 ct.	9,71 x 8,31 x 5,61	Mixed Star/Step cut	Cushion	-	Unknown
KTM	Blue-violet	2,08 ct.	8,98 x 7,03 x 5,23	Faceted	Oval	-	Tanzania
KUD6	Yellow-brown	3,13 ct.	8,66 x 7,96 x 5,57	Mixed Star/Step cut	Oval	-	Unknown
KUD3	Yellowish-green	3,88 ct.	10,14 x 9,10 x 5,53	Star cut	Cushion	-	Unknown
KSE4637	Greenish-yellow	1,83 ct.	7,66 x 7,47 x 5,28	Star cut	Rounded triangle	-	Sri Lanka
KUH	Brownish-green	1,06 ct.	6,51 x 5,38 x 3,43	Step cut	Octagon	-	Unknown
KME3887	Brownish-green	1,90 ct.	8,25 x 6,98 x 3,98	Faceted	Fancy	-	Madagascar
KUD8	Brown-green	1,54 ct.	7,30 - 7,39 x 3,26	Cabochon	Round	Cat's-eye	Unknown
AUE4100	Yellowish-brown	1,49 ct.	8,08 x 6,64 x 3,67	Star cut	Oval	-	Unknown

Among the research samples are:

- Two specimens with rare colours:
 - **Sample KTM**
 - 2.08 ct.
 - Colour: blue-violet
 - Origin: Tanzania
 - Collection Werner Wild, Idar-Oberstein
 - **Sample KUF**
 - 3.52 ct.
 - Colour: green-blue
 - Collection Fabian Schmitz, Mainz
- Two samples which show very sharp chatoyancy or cat's-eye effect:
 - KUD7 (green) and KUD8 (brown-green)
 - 1.53ct and 1.54 ct.
 - Collection DGemG, Idar-Oberstein



Methods

Classical gemmological instruments

Refractive indices were measured on a refractometer from Schneider Gemmologie. A hydrostatical balance was used to obtain specific gravity and a Mettler Toledo balance to measure the carat weight.

A digital sliding caliper is used to measure the samples dimensions.

short-wave (254 nm) and long-wave (365nm) UV lamps was used to observe luminescence of samples and Leica camera to photograph luminescence.

A ZEISS Stemi 508 Stereo microscope was used for observation of inclusions and of pleochroism by placing a London dichroscope between the sample and objective lens.

For microphotography as well as macrophotography of part of the samples, a Samsung Galaxy A55 cellphone was used.

Raman spectroscopy

Raman (Renishaw)

Most Raman spectra were obtained on a Renishaw InVia confocal Raman microscope equipped (with a 50x objective) with a 514 nm laser excitation. The spectral acquisition time was 10 seconds and laser power adapted.

Raman T64000

Part of the Raman scattering spectra were also measured with an Ar⁺ argon excitation laser at 514.5nm, using a T64000 Horiba Jobin-Yvon spectrometer equipped with a microscope in backscattering configuration.

Ultraviolet-visible-near infrared (UV-Vis-NIR) spectroscopy

Optical absorption spectra UV-Vis-NIR spectra were acquired on a PerkinElmer UV-Vis-NIR spectrometer Lambda 950s equipped with a deuterium and a halogen lamps (lamp change at 319.20nm) and three detectors PbS, InGaS and PMT (detector change at 814.40 nm). Spectra were acquired over a range from 200 to 1500 nm, the sampling was carried out with a step size of 1 nm and a scanning speed of 306.67 nm/min.

Fourier-transform infrared (FTIR) spectroscopy

FTIR spectra were acquired on a Nicolet iS50 FTIR spectrometer, with spectral sampling of 4 cm^{-1} for 128 scans in absorption and reflection modes in the range of $7500\text{-}400\text{ cm}^{-1}$.

Luminescence spectroscopy

The emission spectra, excitation spectra and phosphorescence decay time spectra were acquired on a fluorimeter Horiba Jobin-Yvon Fluorolog 3. Essence. Filters were used to avoid artefacts. Integration time (0.1-0.2 second) and slits (from 2nm to 14nm Bandpass) were adapted to obtain spectra with adequate resolutions.

Energy-dispersive X-ray fluorescence (EDXRF) analysis

Quantitative EDXRF data were collected using an ARL QUANT'X EDXRF analyzer Thermo Scientific, vacuum atmosphere, with 3.5mm collimator. The parameters were set as routine analyses settings of the DSEF German Gem Lab. Known concentrations given to kornerupines previously to calculation: 3.30wt.-% B_2O_3 and 1.00wt.-% of H_2O .

Scanning electron microscope (SEM)

Scanning electron microscope JEOL JSM IT510 working at 15KV for a beam current in the 1nA range, providing sufficient statistics for the acquisition of spectra and maps by the integrated EDS detector. Images were acquired using either an Everhart-Thornley secondary electron detector or a dual PN junction backscattered electron detector.

Results

Classical gemmology

Gemmological properties

The density of the twelve kornerupine samples varies from 3.21 to 3.32 g/cm³.

The refractive index (RI) of individual samples are listed in Table 3, including spot reading values for two samples with cabochon cut (KUD7 & KUD8).

Except from one translucent to opaque sample (KUD8), all kornerupine samples are dichroic or trichroic. The specimens of the Green-Blue-Violet series (KTJ1, KTJ2, KUD5, KUD7, KUF and KTM) show distinct pleochroism (Fig. 5).

Table 3 Measurements of twelve kornerupines *sensu lato*

Sample	Colour	Weight	RI	Density	Pleochroism
KTJ1	Green	0.45 ct.	1.661-1.673	3.21 g/m ³	Yellowish-green/emerald green
KTJ2	Green	2.39 ct.	1.661-1.673	3.25 g/m ³	Brown/yellowish-green/emerald green
KUD5	Green	1.39 ct.	1.661-1.674	3.21 g/m ³	Brownish-yellow/yellowish-green/emerald-green
KUD7	Green	1.53 ct.	~1.660	3.24 g/m ³	Brown/yellow/green
KUF	Green-blue	3.52 ct.	1.661-1.673	3.27 g/m ³	Yellowish-green/purple/violet
KTM	Blue-violet	2.08 ct.	1.660-1.673	3.24 g/m ³	Yellowish-green/purple/violet
KUD6	Yellow-brown	3.13 ct.	1.661-1.675	3.25 g/m ³	Light-brown/brown
KSE4637	Yellowish-green	3.88 ct.	1.665-1.678	3.28 g/m ³	Brown/brownish-green
KUD3	Greenish-yellow	1.83 ct.	1.662-1.675	3.28 g/m ³	Brown/light brown
KME3887	Brownish-green	1.06 ct.	1.669-1.681	3.32 g/m ³	Brown/bluish-green/yellowish-green
KUH	Brownish-green	1.90 ct.	1.669-1.682	3.30 g/m ³	Brown/green/bluish-green
KUD8	Brown-green	1.54 ct.	~1.670	3.32 g/m ³	-



Fig. 5 Examples of pleochroism in KTJ2, KTM and KUF. Observed under stereo microscope with a dichroscope. From left to right: 9.52x7.40mm, 8.98 x 7.03mm and 9.71 x 8.31mm.

Inclusions

Inclusions observed under stereo microscope include zircons (Fig. 6), hollow tubes (Fig. 7), fluid inclusions, negative crystals, mineral inclusions, healing cracks, etc..

Raman spectroscopy confirmed the identity of the zircon inclusions (Fig. 6) in the sample KME3887 (Appendix KME3887).

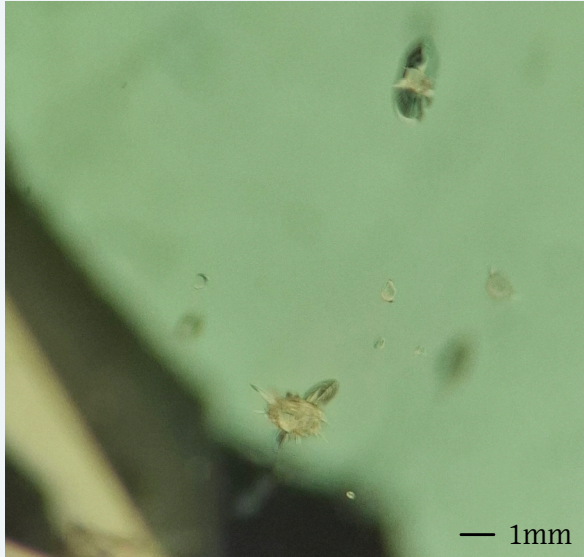


Fig. 6 Zircon inclusions with tension halos in the sample KME3887.

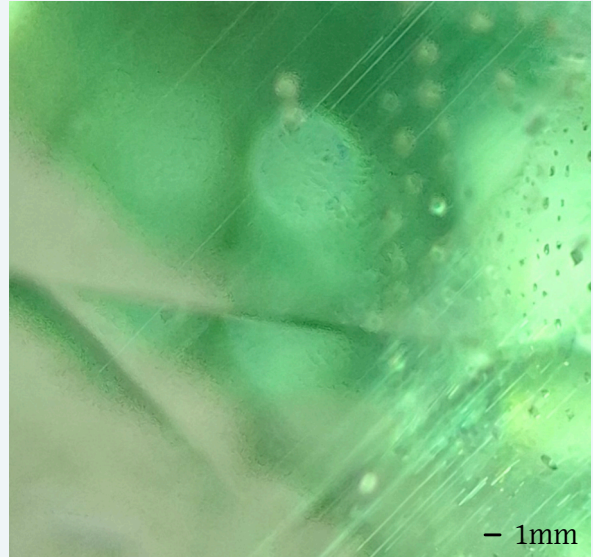


Fig. 7 Hollow tubes and two-phase inclusions in the sample KTJ1.

Luminescence

The six kornerupine samples of the Green-Blue-Violet series show distinct luminescence under short-wave UV (SWUV) and long-wave UV (LWUV) light, with LWUV > SWUV, unlike the andalusite sample, which shows a stronger SW luminescence and a very weak LW luminescence. (Table 4, Fig. 8)

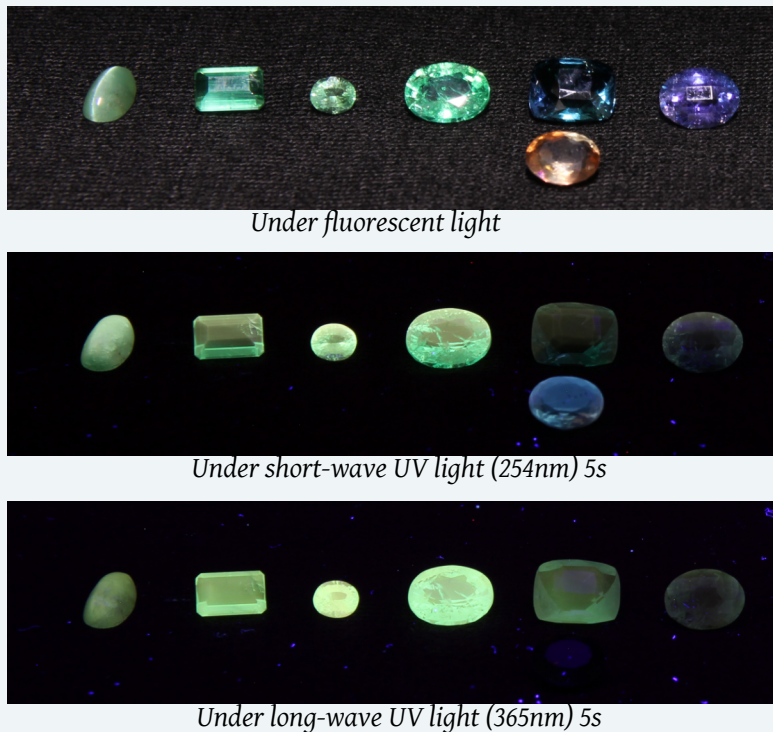


Fig. 8 Luminescence of six kornerupine samples and one andalusite (in the front)
(First sample on the left: 9.02 x 5.37 mm)

Table 4 Luminescence of kornerupine samples

Sample	Weight	SWUV Luminescence	LWUV Luminescence	SWUV vs LWUV
KTJ1	0.45 ct.	Yellow-green	Greenish-yellow	<
KTJ2	2.39 ct.	Yellowish-green	Yellowish-green	<
KUD5	1.39 ct.	Yellowish-green	Yellow-green	<
KUD7	1.53 ct.	Yellowish-green	Yellow-green	<
KUF	3.52 ct.	Weak green	Yellowish-green	<
KTM	2.08 ct.	Weak yellowish-green	Yellowish-green	<
KUD6	3.13 ct.	Weak orange	Orange	<
KUD3	3.88 ct.	Very weak brown	Greenish-brown	<
KSE4637	1.83 ct.	Very weak brown	Brown	<
KUH	1.06 ct.	Inert	Inert	-
KME3887	1.90 ct.	Inert	Inert	-
KUD8	1.54 ct.	Inert	Inert	-

Laboratory gemmology

Scanning Electron Microscopy

SEM provides possibilities of accurate identification of material with high magnification (Fig. 9). Besides inclusions already reported in the literature, SEM analysis of the sample KTJ1 identified further inclusions which have not yet been described in the literature:

- kornerupine as inclusion within the host kornerupine (**inclusion A**, Fig. 10-11),
- sphalerite (**inclusion B**, Fig. 12-13)
- and pyrite (**inclusion C**, Fig. 14-15).

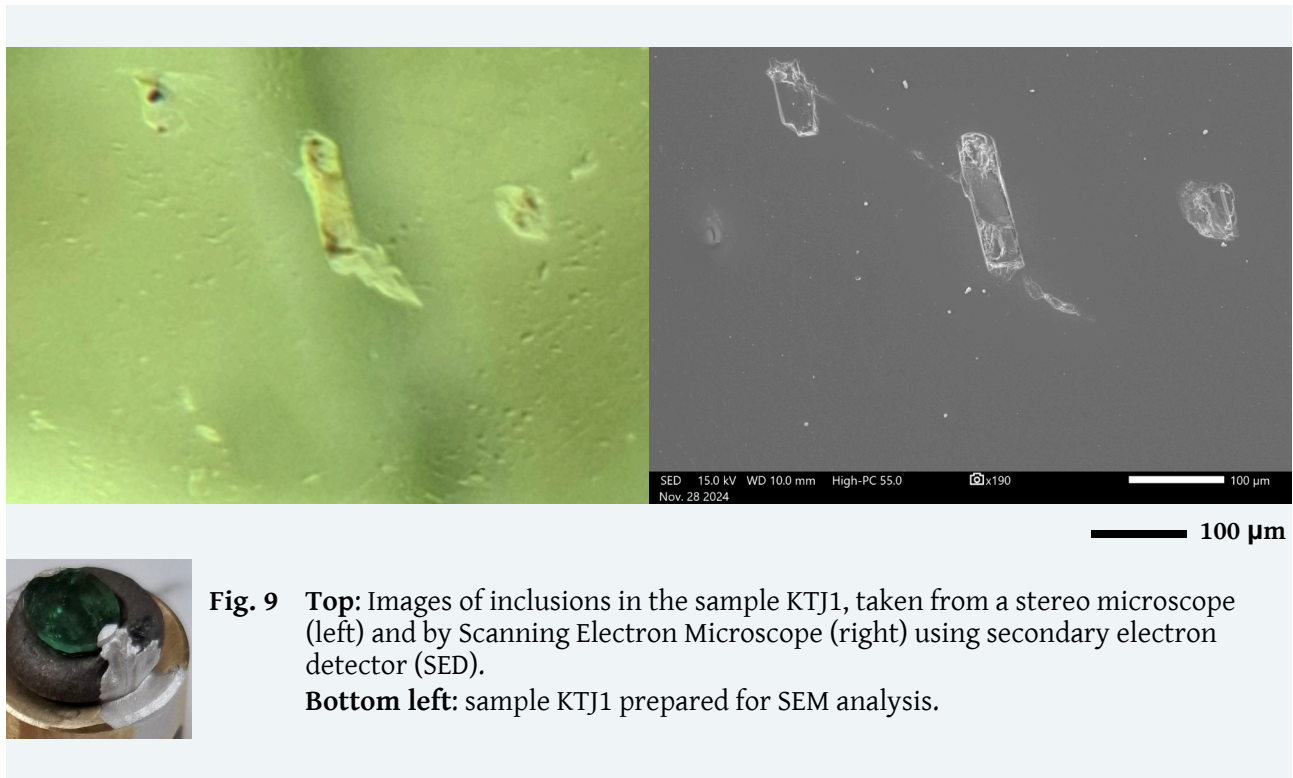


Fig. 9 **Top:** Images of inclusions in the sample KTJ1, taken from a stereo microscope (left) and by Scanning Electron Microscope (right) using secondary electron detector (SED).

Bottom left: sample KTJ1 prepared for SEM analysis.

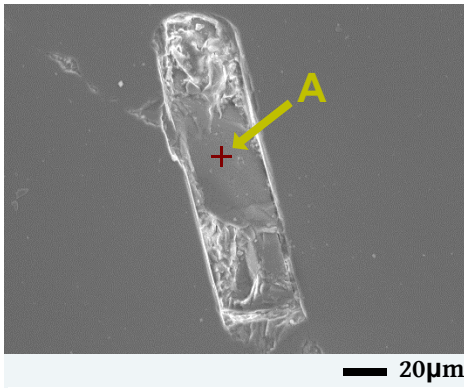
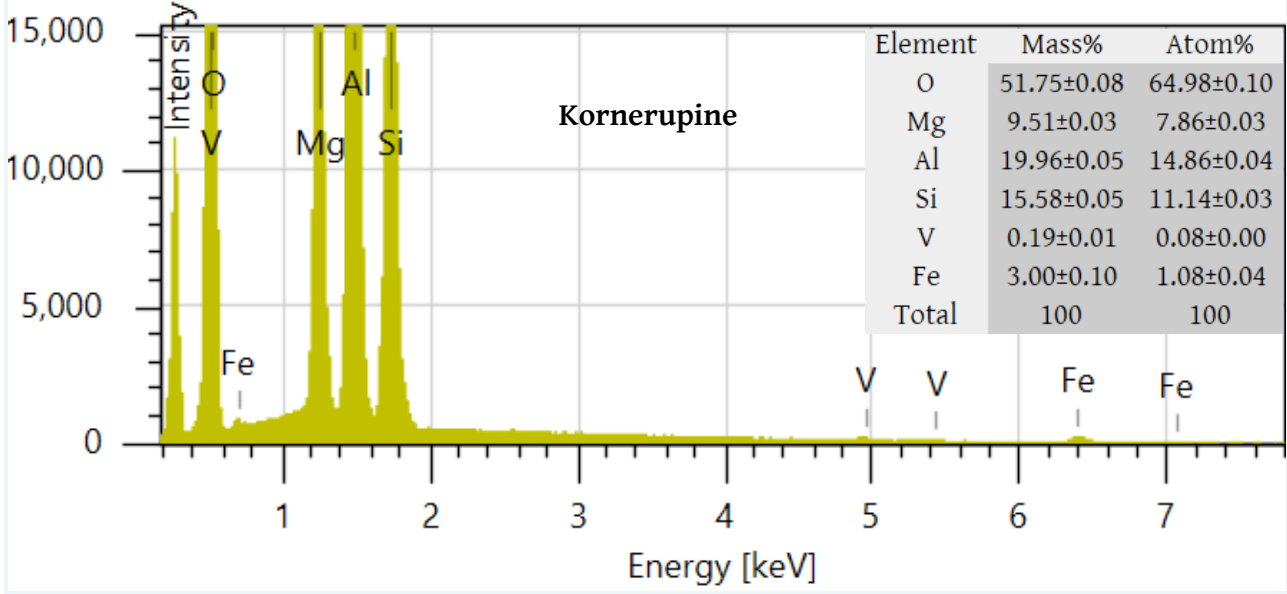


Fig. 10

Left: SEM image of a prismatic inclusion - inclusion A, taken with secondary electron detector (SED). Inclusion A was analysed at the position indicated by the arrow.

Below: chemical composition of inclusion A, identified as kornerupine.



The chemistry of the inclusion A (SEM analysis, Fig. 10) was compared with that of the host kornerupine KTJ1 (EDXRF analysis, Fig. 11). Despite the difference of calculation methods between the two analytic instruments, it is obvious that the kornerupine inclusion (inclusion A) has significantly higher iron concentration than the host kornerupine KTJ1. The eventuality of inclusion A being a negative crystal is excluded: placed between crossed polarisation filters under microscope, it shines as a birefringent mineral inclusion; furthermore, inclusion A hosts further solid inclusions (Fig. 12).

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	46.00	0.30	Al	24.34	0.16
SiO2	29.39	0.22	Si	13.74	0.10
MgO	19.48	0.20	Mg	11.75	0.12
CaO	0.162	0.008	Ca	0.116	0.006
TiO2	0.155	0.015	Ti	0.0927	0.0091
V2O5	0.145	0.009	V	0.0812	0.0050
MnO	0.112	0.009	Mn	0.0868	0.0066
Fe2O3	0.099	0.011	Fe	0.0694	0.0077
SO3	0.060	0.022	Sx	0.0239	0.0090
Sc2O3	0.0585	0.0033	Sc	0.0381	0.0021
Cr2O3	0.0147	0.0015	Cr	0.0101	0.0010
ZnO	0.0119	0.0008	Zn	0.0096	0.0006
K2O	0.0062	0.0021	K	0.0051	0.0017
Ga2O3	0.0054	0.0006	Ga	0.0040	0.0004

Fig. 11 EDXRF analysis of sample KTJ1

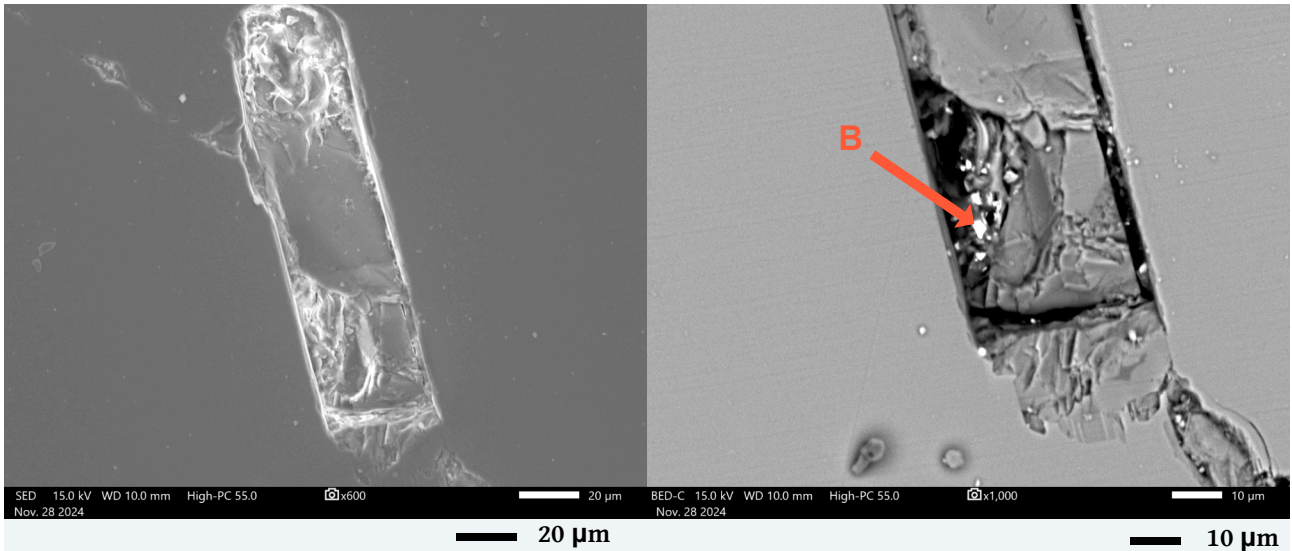
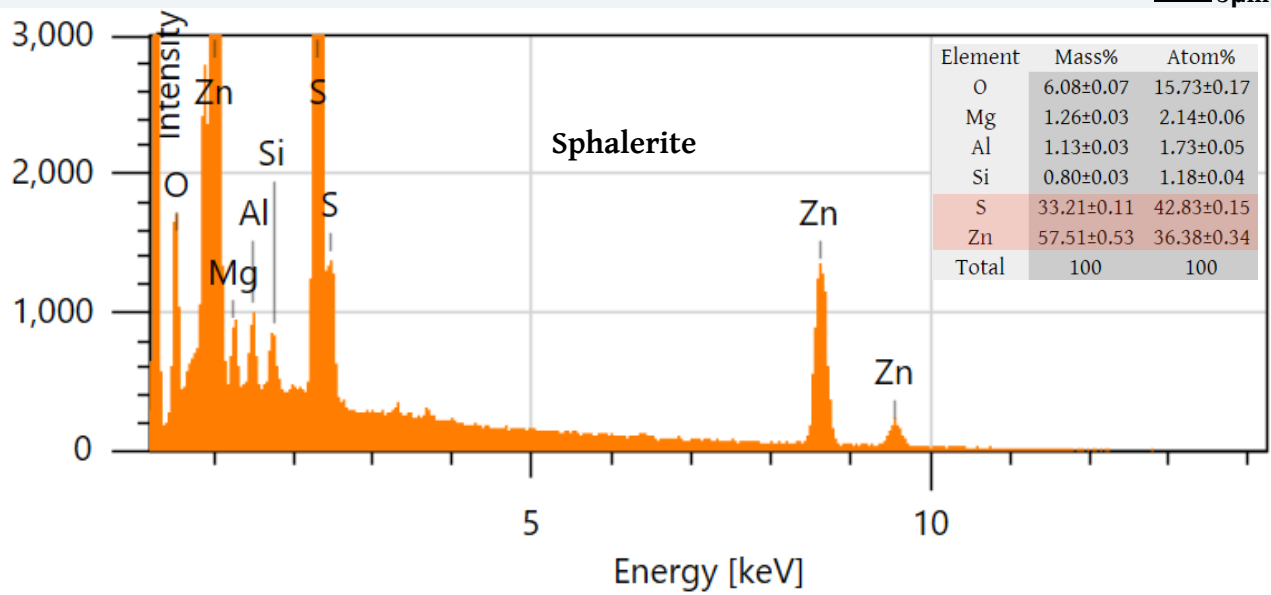
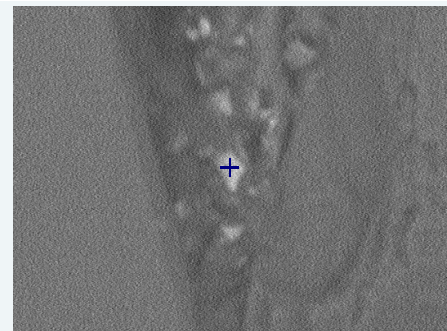


Fig. 12 Image taken with SED (left) and BED (right) of a prismatic inclusion identified as kornerupine (inclusion A) hosting the inclusion B.

Fig. 13 BED image (right) and chemical composition (bottom) of inclusion B, identified as sphalerite.



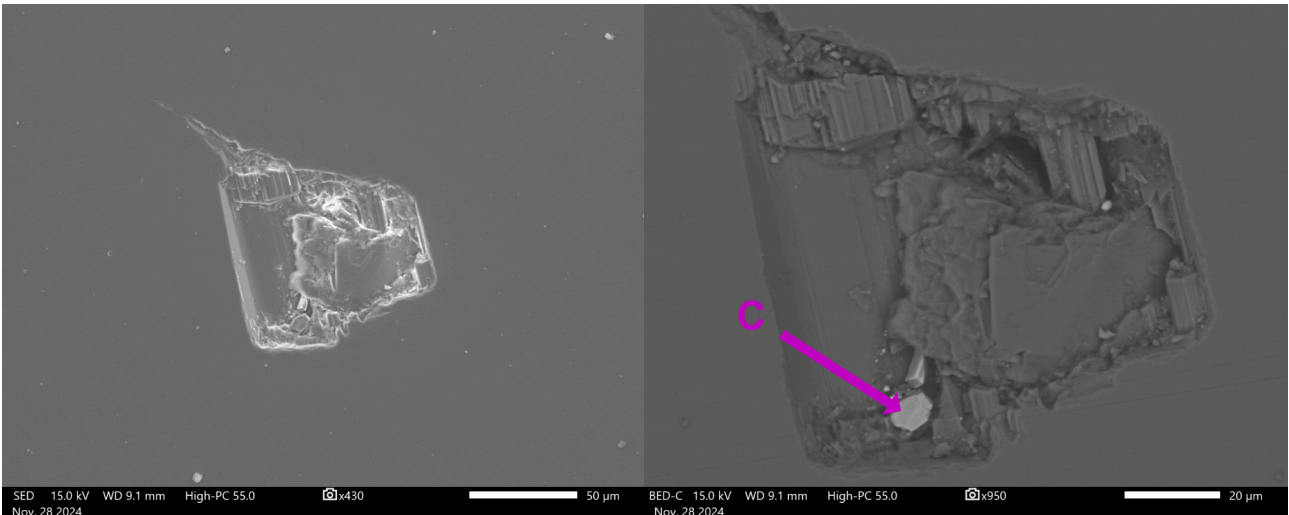
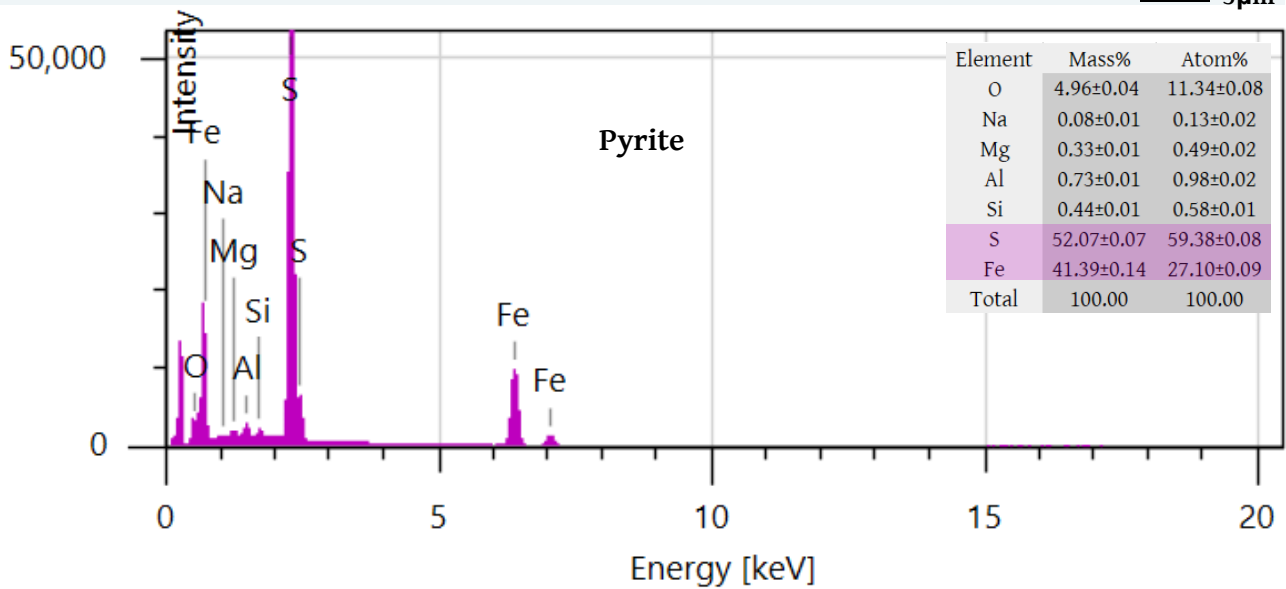
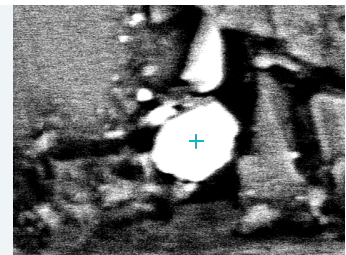


Fig. 14 SED (left) and BED (right) images of the inclusion C within its hosting inclusion.

Fig. 15 BED image (right) and chemical composition (bottom) of inclusion C, identified as pyrite.



Raman spectroscopy

Acquired Raman spectra were imported in CystalSleuth to compare with the reference data. All 12 kornerupines spectra match to the RRUFF reference spectra of kornerupine *sensu lato*. Fig. 16 shows two examples of search results.

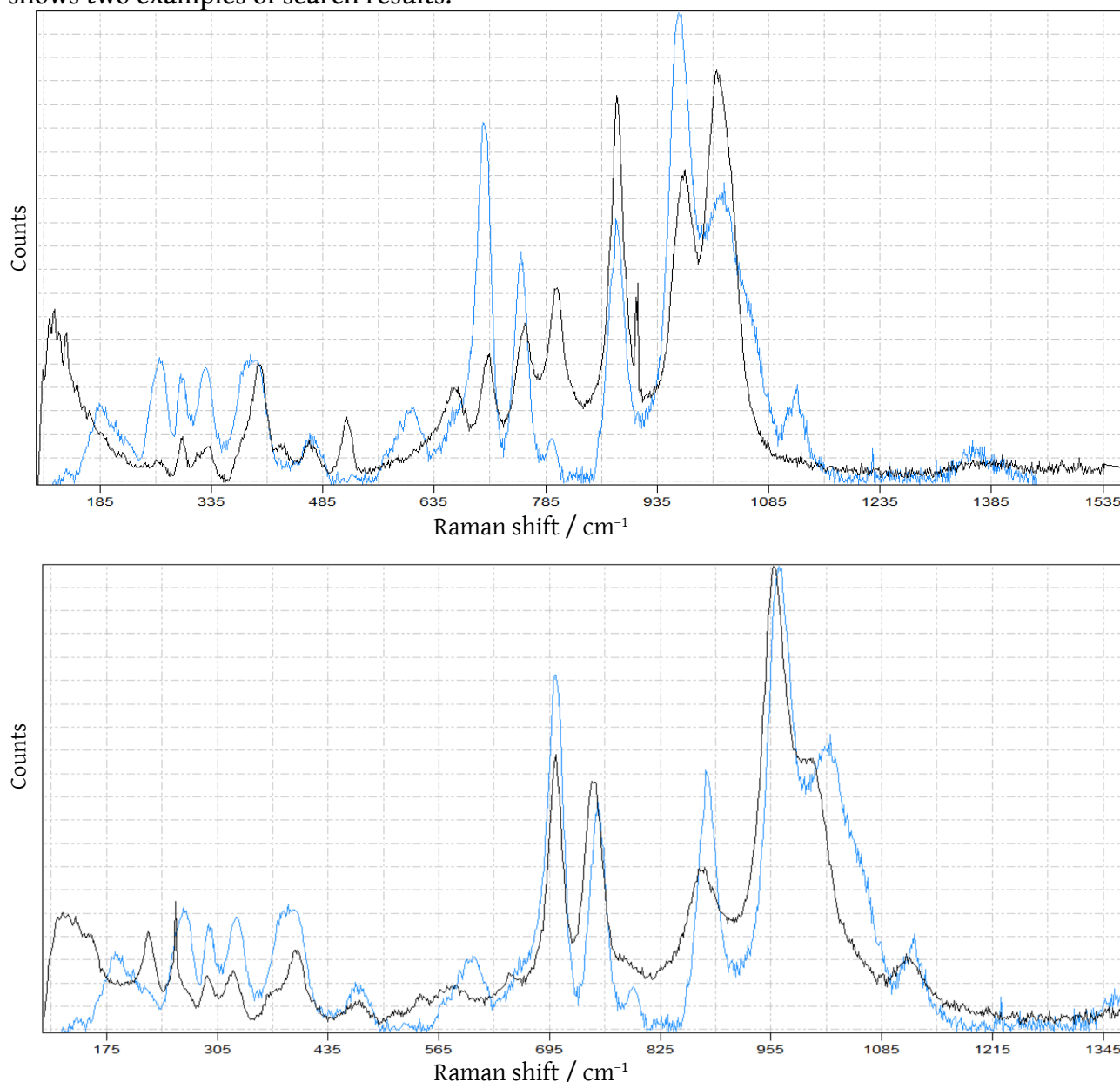


Fig. 16 Raman spectra (in black colour) of KUD3 (top) and KUD6 (bottom) match to those of kornerupine in RRUFF reference data (blue).

The distinction between kornerupine *sensu stricto* and prismatine among the kornerupine samples was made according to the method of Wopenka et al.(1999)(Fig. 2).

The Raman spectra of all twelve samples were analysed. The spectrum of one sample (KUD6) shows no peak at $\sim 803 \Delta\text{cm}^{-1}$ and a weak peak at $\sim 881 \Delta\text{cm}^{-1}$, all other samples shows peak at $\sim 803 \Delta\text{cm}^{-1}$ and strong peak at $\sim 881 \Delta\text{cm}^{-1}$. Sample KUD6 is identified as kornerupine *sensu stricto* and all other samples as prismatines (Table 5). Fig. 17 displays the Raman spectra of the kornerupine *sensu stricto* (KUD6) and two prismatine samples (KTJ2 & KUD3).

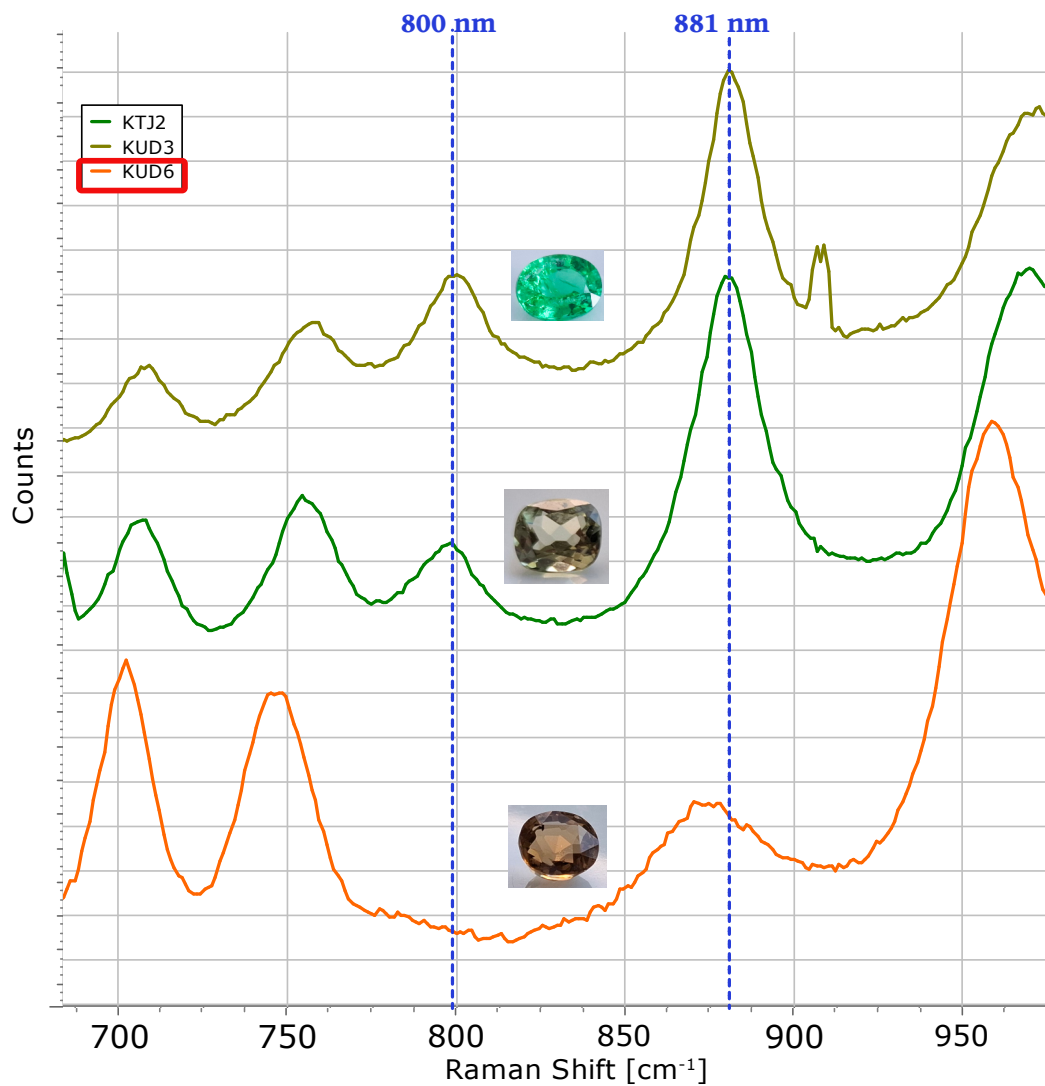


Fig. 17 Raman spectra of three kornerupine samples

Table 5 Result of Raman spectroscopy analysis

Sample	Weight	Result
KTJ1	0.45 ct.	Prismatine
KTJ2	2.39 ct.	Prismatine
KUD5	1.39 ct.	Prismatine
KUD7	1.53 ct.	Prismatine
KUF	3.52 ct.	Prismatine
KTM	2.08 ct.	Prismatine
KUD6	3.13 ct.	Kornerupine <i>sensu stricto</i>
KUD3	3.88 ct.	Prismatine
KSE4637	1.83 ct.	Prismatine
KUH	1.06 ct.	Prismatine
KME3887	1.90 ct.	Prismatine
KUD8	1.54 ct.	Prismatine

Energy-dispersive X-ray fluorescence (EDXRF) analysis

The EDXRF analysis was completed on all thirteen samples. Table 6 exposes the representative data, the complete data can be found in Appendix.

Table 6 Result of EDXRF analysis

Site	AND4100	KTJ1	KTJ2	KUD5	KUD7	KUF	KTM	KUD6	KSE4637	KUD3	KME3887	KUH	KUD8
Al ₂ O ₃	61.92	46.00	44.57	45.02	44.78	44.43	43.93	43.31	42.99	42.54	43.06	43.79	40.54
SiO ₂	36.80	29.39	29.89	29.87	30.43	30.26	30.25	27.92	30.13	29.92	29.07	28.46	29.01
MgO	0.93	19.48	20.56	19.99	19.32	20.27	21.04	19.75	20.33	19.91	19.22	17.63	15.14
CaO	0.00	0.16	0.07	0.06	0.25	0.06	0.04	0.10	0.06	0.15	0.04	0.04	1.87
TiO ₂	0.01	0.16	0.11	0.01	0.13	0.05	0.03	0.15	0.05	0.03	0.03	0.00	0.30
V ₂ O ₅	0.01	0.15	0.18	0.23	0.17	0.08	0.01	0.02	0.03	0.01	0.00	0.00	0.06
MnO	0.00	0.11	0.17	0.20	0.27	0.12	0.06	0.01	0.02	0.02	0.15	0.11	0.19
Fe ₂ O ₃	0.22	0.10	0.06	0.05	0.06	0.17	0.08	1.38	2.04	3.05	4.04	5.57	8.05
BaO	0.00	0.00	0.03	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO ₃	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22
Sc ₂ O ₃	0.00	0.06	0.02	0.02	0.05	0.00	0.02	0.00	0.00	0.00	0.01	0.00	0.00
Cr ₂ O ₃	0.00	0.01	0.02	0.01	0.02	0.22	0.25	0.01	0.00	0.00	0.00	0.00	0.10
ZnO	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.02	0.06
K ₂ O	0.01	0.01	0.01	0.00	0.02	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.04
Cl	0.00	0.00	0.00	0.01	0.02	0.02	0.00	0.01	0.00	0.01	0.01	0.01	0.04
Co ₃ O ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.04	0.04	0.07
Ga ₂ O ₃	0.01	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.01
P ₂ O ₅	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
B ₂ O ₃ (fixed)	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30	3.30
H ₂ O (fixed)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) spectroscopy

The absorption spectra of samples of the Brown-Yellow-Green series share common features with two main absorption bands in the range of 315nm to 382nm and 1024nm to 1049nm, weaker absorption at 445nm, 500nm. The spectrum of KUD8 shows an extra band at 681nm and a shoulder at 760nm, and the spectrum of KUD6 shows an extra shoulder at 454nm.

The absorption spectra of the green kornerupine samples (KTJ1, KTJ2, KUD5 and KUD7) share common features with two main absorption bands at 418nm, 675nm and a weak shoulder at 454nm.

The absorption spectra of the blue to violet samples (KUF and KTM) share common bands/shoulders at 384nm, 434nm, 526nm, 578nm, 681nm and 760nm.

UV-Vis-NIR spectra of the samples are interpreted and further discussed in the section Discussion.

Fourier-Transform Infrared (FTIR) spectroscopy

FTIR absorption spectra were acquired for all kornerupine samples. A certain similarity of the spectral pattern could be observed among kornerupines of the Brown-Yellow-Green series and those of the Green-Blue-Violet series (Fig. 19-20). As all the FTIR absorption spectra show total absorption between 2000cm^{-1} and 400cm^{-1} , FTIR reflection spectra of two samples (KUD5&KUD6) were acquired to further explore this region (Fig. 21).

Fig. 18 illustrates the FTIR absorption spectrum of sample KUD5. The broad absorption bands observed between 3630cm^{-1} and 3000cm^{-1} is related to stretching of O-H. The sharp bands between 6000cm^{-1} and 4000cm^{-1} could be the combination of stretching and bending of water including fluids and water in the structure. The strong absorption bands around 7000cm^{-1} is related to stretching of O-H.

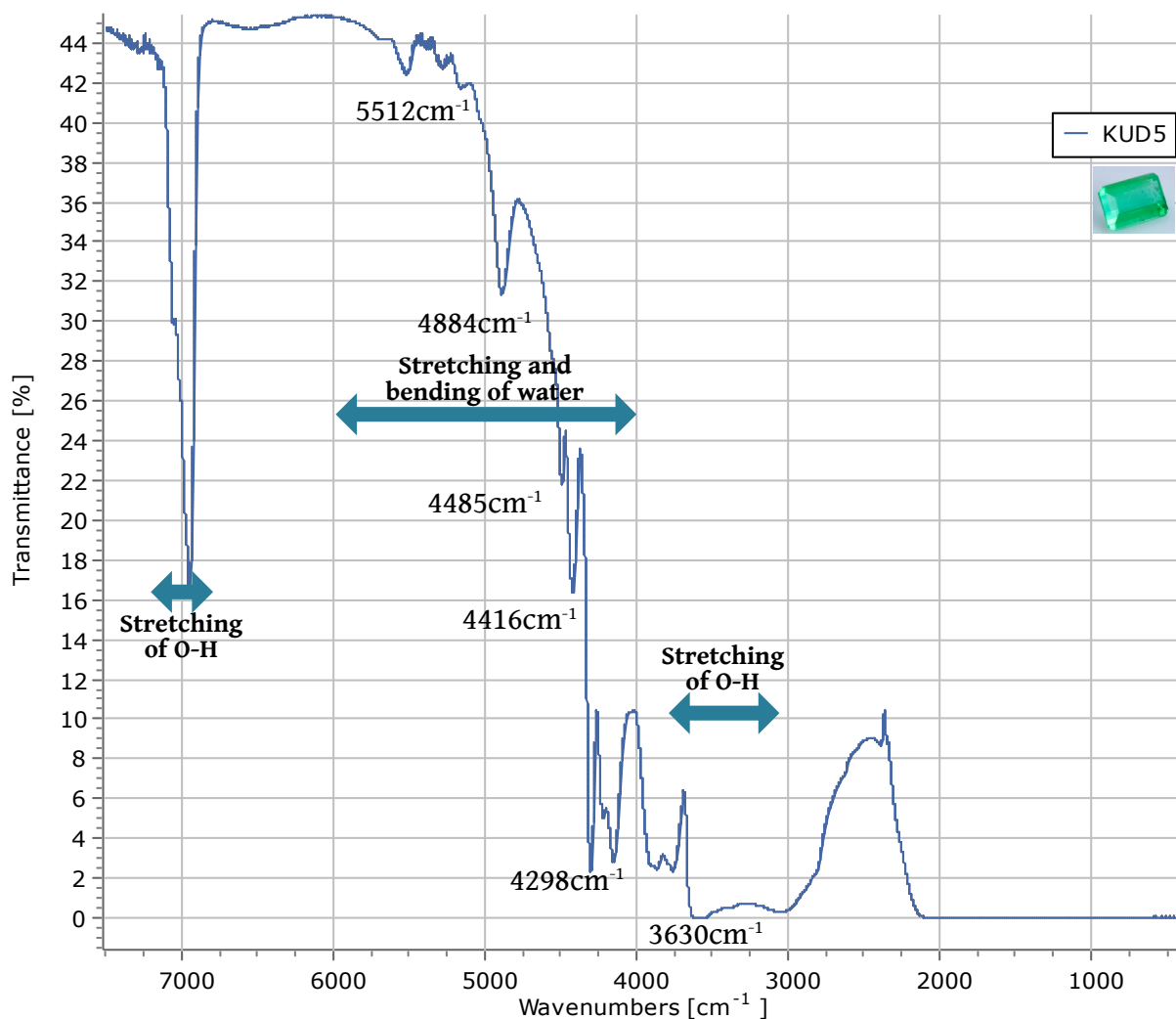


Fig. 18 FTIR absorption spectrum of sample KUD5

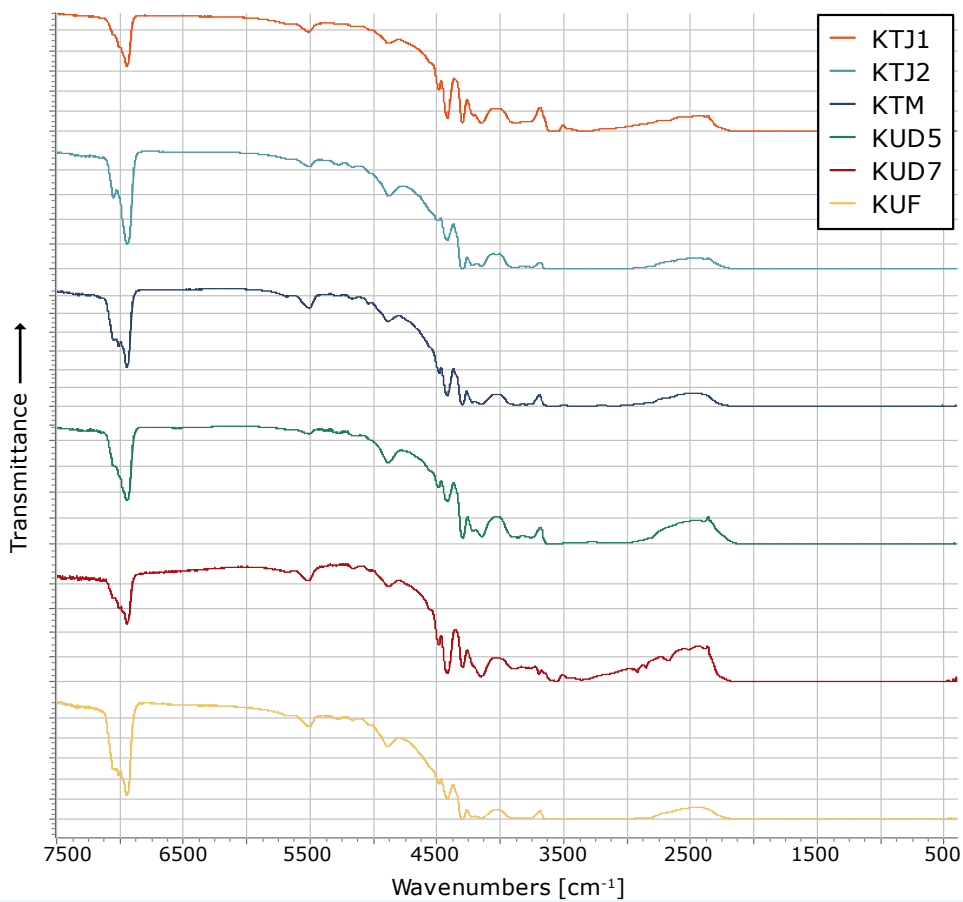


Fig. 19
FTIR absorption spectra of Green-Blue-Violet series

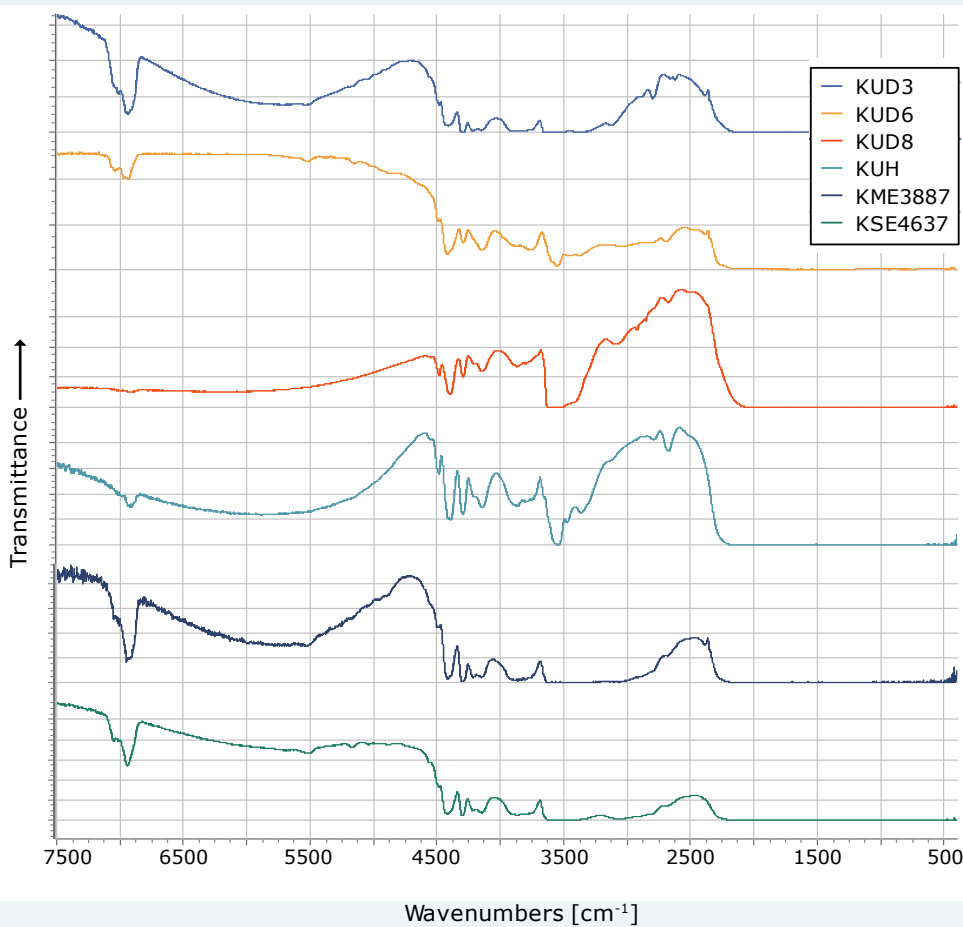


Fig. 20
FTIR absorption spectra of Brown-Yellow-Green series

Moenke researched on the recognition of BO_3 and BO_4 in different boron silicates including kornerupine through FTIR spectra. According to Moenke, the absorption bands in the fingerprint region of the FTIR spectrum show vibrations of tetrahedral boron in kornerupine (Fig. 21). Subsequent X-ray structural analyses and infrared studies confirmed the implications of these assignments for borosilicate structures. (1974).

FTIR reflection spectra of samples KUD5 and KUD6 are illustrated in Fig. 22. It turns out that, except from some minor shift which might be partly related to the stretching and bending of Si-O, the positions of major bands (Fig. 22) match to those in Fig. 21. As samples KUD5 and KUD6 have been identified respectively as prismatic and kornerupine *sensu stricto*, the difference or the correlation of fingerprint region of FTIR spectra between kornerupine *sensu stricto* and prismatic deserves further investigation.

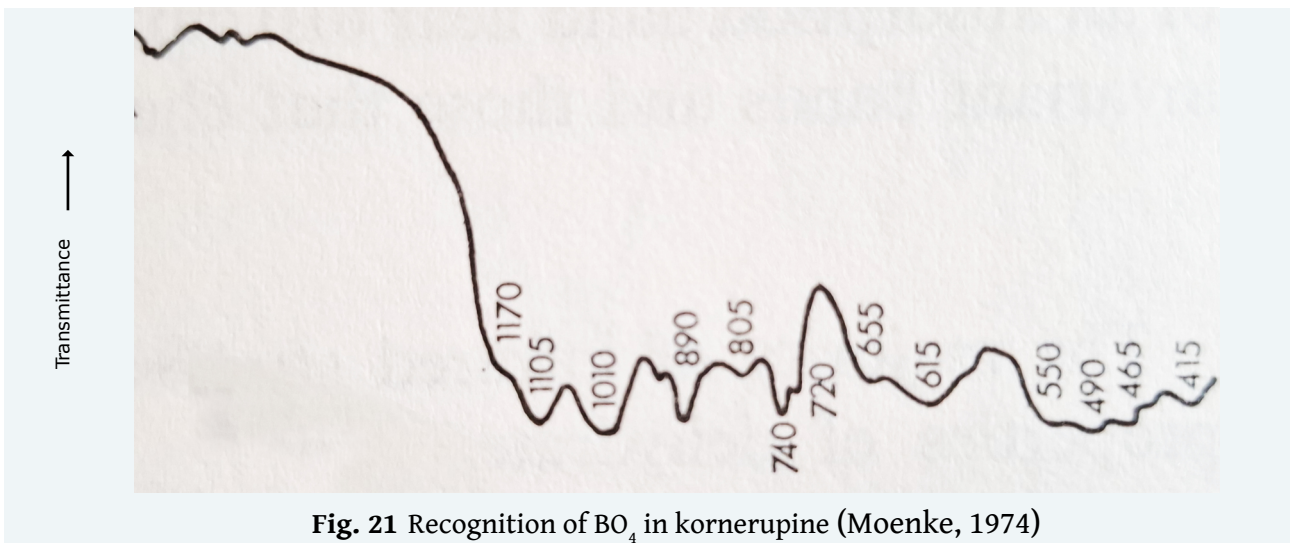


Fig. 21 Recognition of BO_4 in kornerupine (Moenke, 1974)

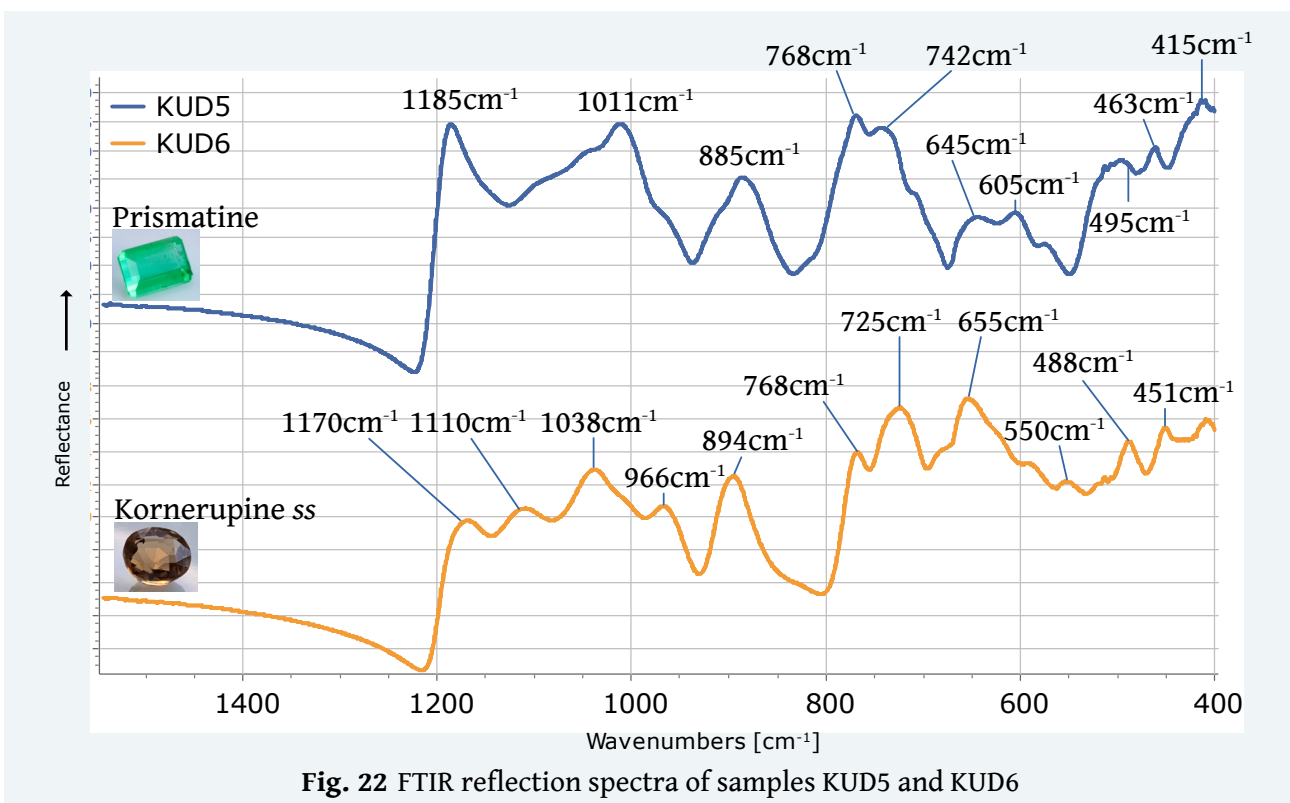


Fig. 22 FTIR reflection spectra of samples KUD5 and KUD6

Discussion

Colouring agents

Colours of kornerupine *sensu lato*, caused by traces of the elements iron, chromium and vanadium, have been described in the literature. Iron-bearing and thus Fe-coloured kornerupines range in colour from brown to yellow to green. V³⁺-coloured green kornerupines of gem quality have been found in Kenya since the early 1970s. Schmetzer describes the colour variation in vanadium- and chromium-bearing East African kornerupines as follows:

- V > Cr => green,
- V ≈ Cr => blue-green,
- Cr > V => blue.

(Schmetzer et al., 1974; Schmetzer, 1977; Schmetzer, 1982; Henn, 1985; Milisenda and Wehr, 2009; Henn, 2019)

EDXRF analysis result (Table 7) of the twelve kornerupine samples shows:

- Iron concentration is predominant (9,660–56,300 ppmw) in the samples of Brown-Yellow-Green series (illustrated in brown) - KUD6, KSE4637, KUD3, KME3887, KUH and KUD8.
- Vanadium concentration is predominant (812–1260 ppmw) in the green samples (illustrated in green) - KTJ1, KTJ2, KUD5 and KUD7, with lower concentration of iron (349–694 ppmw) and significantly lower concentration of chromium (92–146 ppmw).
- Chromium concentration is predominant (1480–1720 ppmw) in the green-blue and blue-violet samples (illustrated in blue) - KUF and KTM, with a lower concentration of iron (532–1,170 ppmw) and significantly lower concentration of vanadium (35–439 ppmw).

Table 7 Concentration of V, Cr and Fe in the twelve kornerupine samples (EDXRF analysis)

Sample	Element (ppmw)		
	V	Cr	Fe
KTJ1	812	101	694
KTJ2	1,010	146	418
KUD5	1,260	92	349
KUD7	946	143	387
KUF	439	1,480	1,170
KTM	35	1,720	532
KUD6	85	86	9,660
KSE4637	147	ND	14,300
KUD3	53	ND	21,300
KME3887	ND	ND	28,300
KUH	ND	ND	39,000
KUD8	308	681	56,300

The following terms are used for samples with similar colouring agents (Fig. 23):

- Iron kornerupine – high concentration of iron, ND or significantly lower concentration of chromium and vanadium;
- Vanadium kornerupine – high concentration of vanadium, significantly lower concentration of chromium and iron;
- Chromium kornerupine – high concentration of chromium, lower concentration of iron, significant lower concentration of vanadium.



Fig. 23 Kornerupine samples according to colouring agents

The UV-Vis-NIR Absorption spectra acquired are mainly unpolarised due to the fact that the samples are all cut stones.

Fig. 24 illustrates the UV-Vis-NIR spectra of three kornerupine samples belonging respectively to vanadium kornerupine (KTJ1), chromium kornerupine(KTM) and iron kornerupine (KUH).

- The green colour of sample KTJ1 originates from:
 - absorption bands related to V^{3+} at 454nm and 675nm
 - and transmission window with maximum at 528nm in the green range of visible region.
- The blue-violet colour of sample KTM is due to:
 - absorption bands related to Cr^{3+} at 384nm, 434nm, 526nm and 578nm,
 - transmission window with maximum at 470nm in the violet-blue range of visible range.
- The brownish-green colour of sample KUH results from:
 - absorption of Fe^{3+} at 445nm and 500nm,
 - weak transmission at 480nm in the blue range and a continuum starting from transmission at 525nm in the green range toward absorption of Fe^{2+} in the near infrared region.
- Absorption bands in the region 1420-1450nm are related to water.
- Absorption band at 1050nm of sample KUH is related to Fe^{2+} .

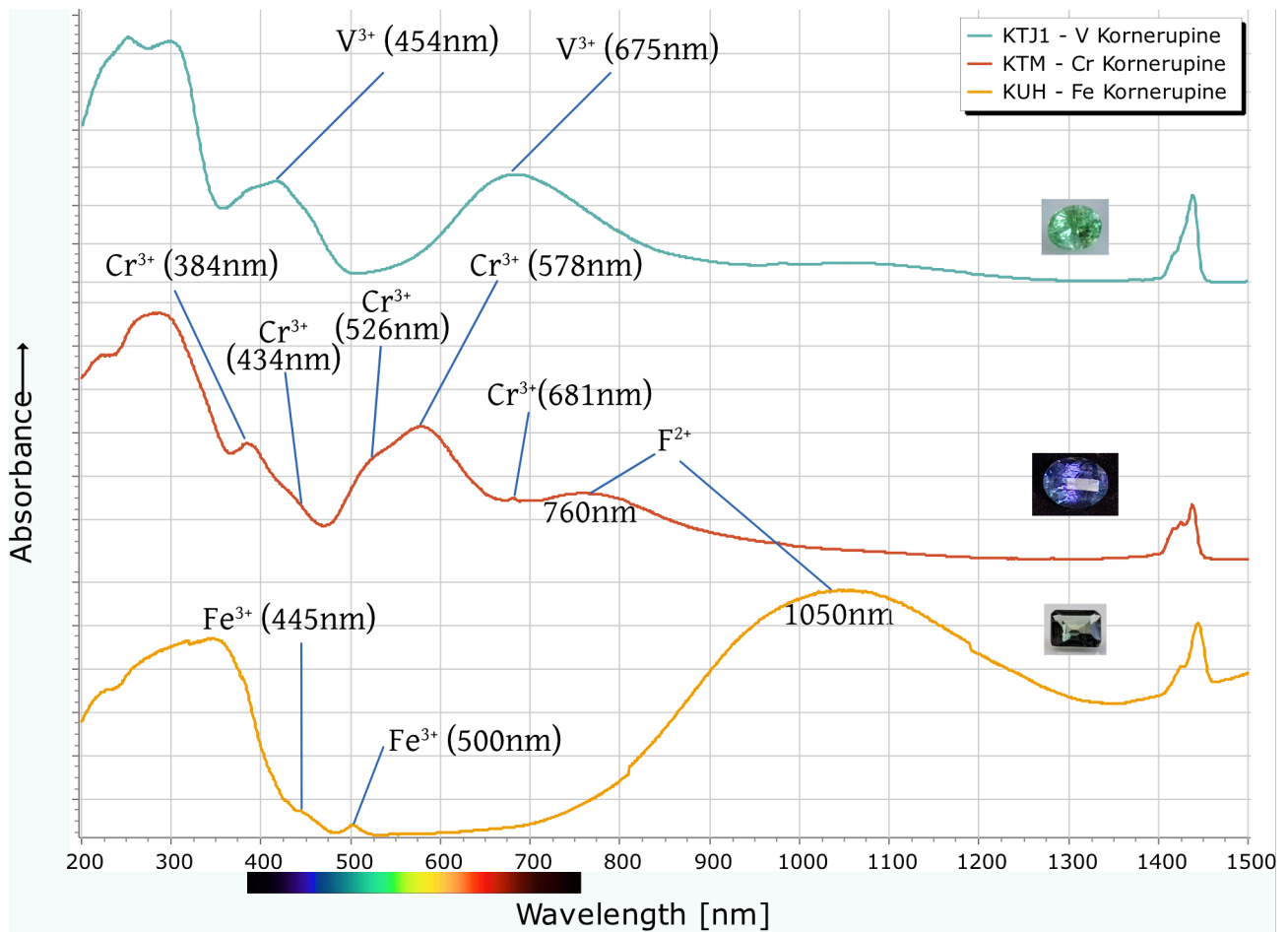


Fig. 24 UV-Vis-NIR spectra of vanadium, chromium and iron kornerupines

Polarised UV-Vis-NIR spectra were acquired for sample KUD7 (Fig. 25), a green kornerupine with cat's-eye effect. The measurement of polarised spectra for this sample was possible due to the orientation of hollow tubes which are not only responsible to the cat's-eye effect but also helps to give a hint on the crystal axes. The polarised spectra show the absorption bands which are predominantly related to V^{3+} and secondarily related to Cr^{3+} , two colouring agents responsible to the green colour of the sample KUD7.

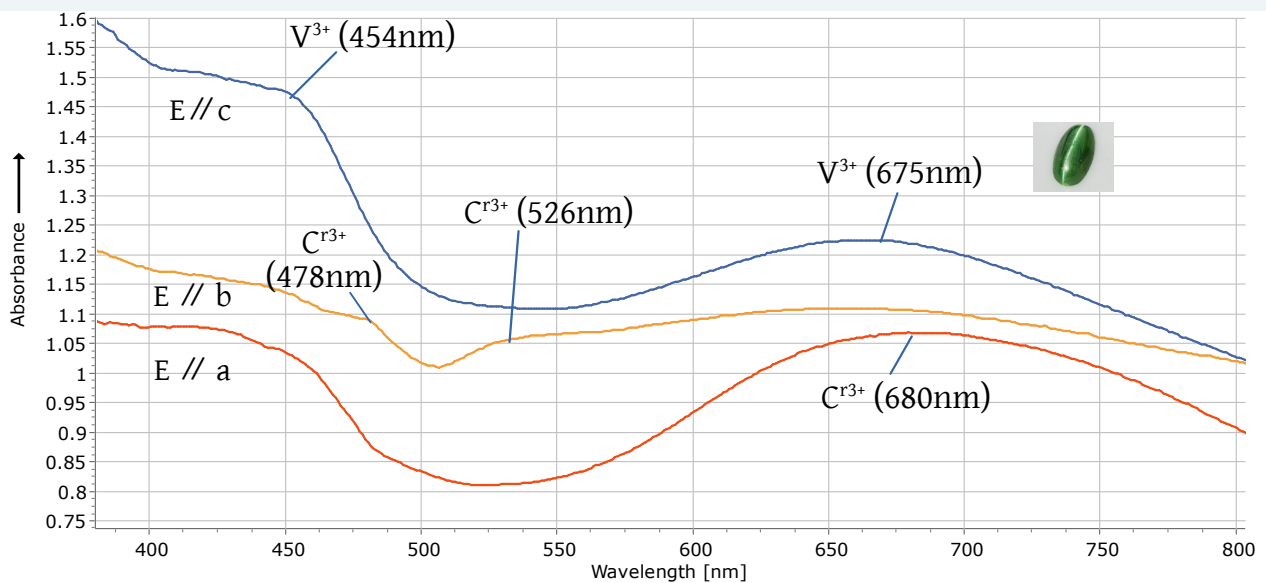


Fig. 25 Polarised UV-Vis-NIR spectra of sample KUD7

Luminescence

Distinct luminescence was observed in the andalusite sample and six kornerupine samples of the Green-Blue-Violet series (Fig. 8). The emission and excitation maxima of all seven samples are located at similar areas, which explain their luminescence colours in the range of yellow and green (Table 4).

Fig. 26 illustrates the emission and excitation spectra of sample KUD5 under respectively 254nm excitation and 565nm emission:

- Emission spectrum under short-wave 254nm excitation displays an intensive broad band emission with maximum at 559nm, with full width at half maximum (FWHM) ~150nm;
- Excitation spectrum under 565nm emission peaks at 273nm in the short-wave to middle-wave range, with FWHM ~70nm.

Luminescence decay time of sample KUD5 (see appendix) is:

- 22 microseconds under $\lambda_{ex} = 265\text{nm}$ and $\lambda_{em} = 550\text{nm}$;
- 14 microseconds under $\lambda_{ex} = 325\text{nm}$ and $\lambda_{em} = 550\text{nm}$.

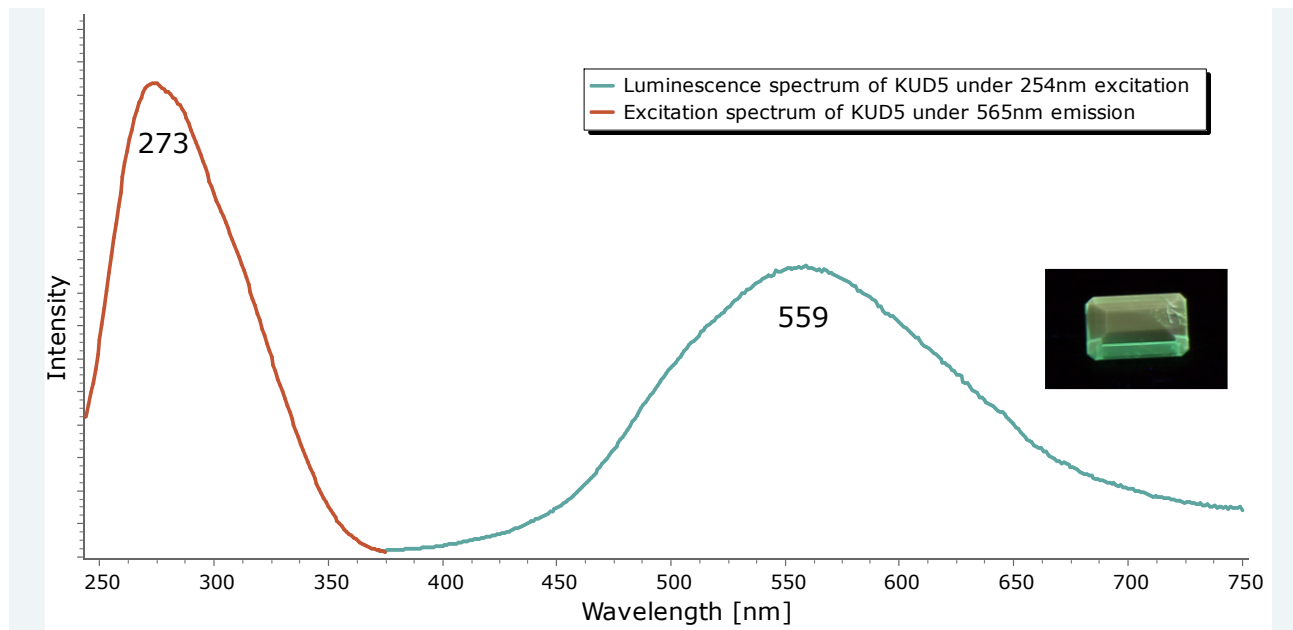


Fig. 26 Luminescence spectrum (on the right) and excitation spectrum (on the left) of sample KUD5

Table 8 Emission and excitation maxima of the andalusite sample and kornerupine samples of the Green-Blue-Violet series at room temperature.

Sample	Emission Maxima		Excitation Maxima
	$\lambda_{ex} = 254 \text{ nm}$	$\lambda_{ex} = 365 \text{ nm}$	
AUE4100	441	437	257
KTJ1	552	567	289
KTJ2	557	551	271
KUD5	559	551	273
KUD7	575	575	261
KUF	541	551 ($\lambda_{ex} = 318\text{nm}$)	317
KTM	568	435	292

Similar spectroscopic characteristics are observed in the luminescent samples (Fig. 27-28):

- All emission spectra display a broad band
 - centred between 441nm and 575nm under short-wave excitation and between 437nm and 575nm under long-wave excitation
 - with an average full width at half maximum (FWHM) of ~150nm.
- All excitation spectra display an asymmetric band
 - centred between 257nm and 317nm
 - with an average FWHM of ~70nm

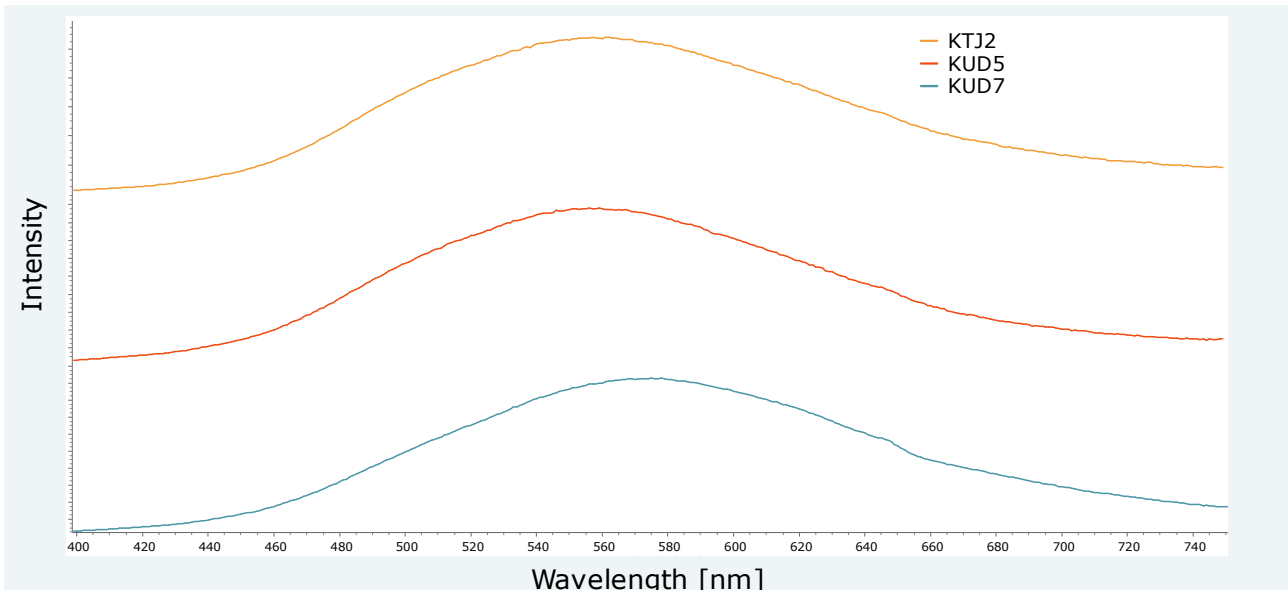


Fig. 27 Emission spectra of three green kornerupine samples under $\lambda_{ex} = 254$ nm at room temperature

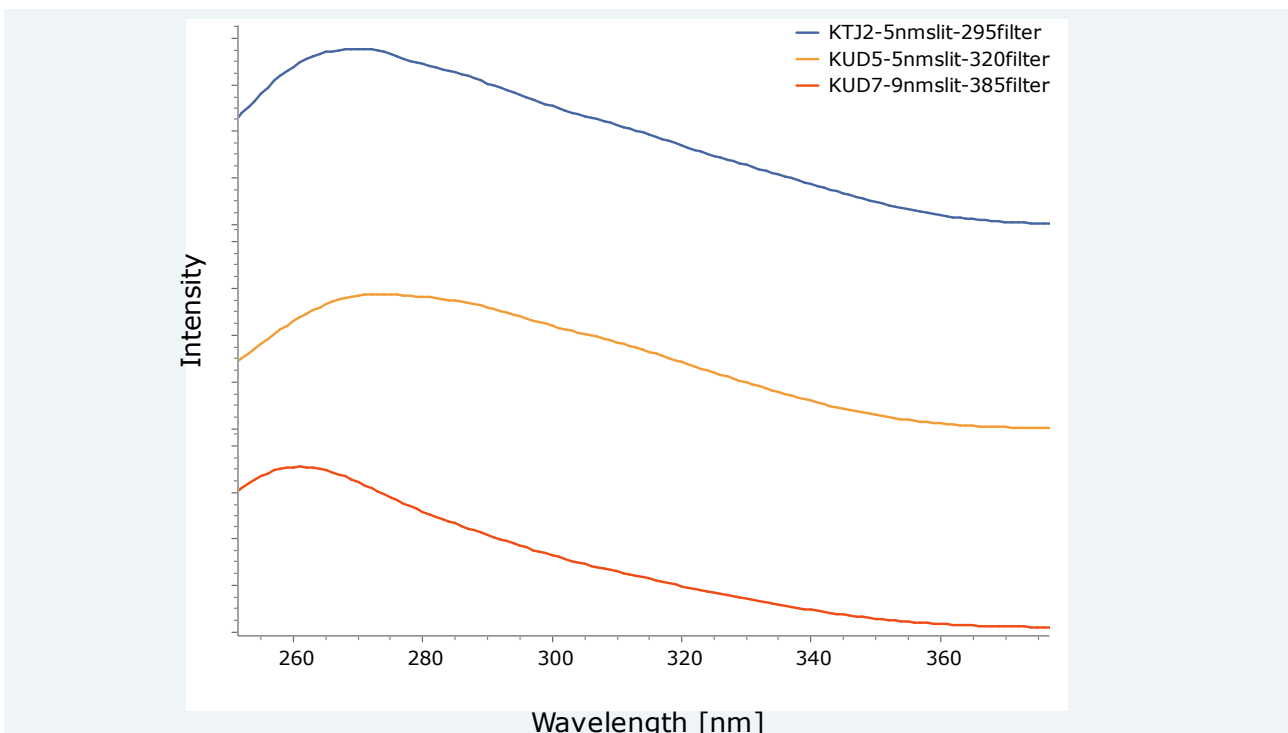


Fig. 28 Excitation spectra of three green kornerupine samples under $\lambda_{em} = 550$ nm for sample KTJ2, $\lambda_{em} = 565$ nm for sample KUD5 and $\lambda_{em} = 570$ nm for KUD7 at room temperature

Luminescence decay time was measured for four samples and it varies from 8 to 28 microseconds.

The above mentioned luminescence characteristics of the seven samples are similar to those of titanate emission described by Gaft et al. (2015) and Vigier et al. (2023):

- A broad emission short-wave UV with
 - maximum 420-480 nm
 - FWHM ~100 nm
- Excitation spectrum
 - peaking in the short-wave UV to middle-wave UV range
 - FWHM ~50 nm
- Luminescence decay time is about 20 microseconds in average.

An example of intrinsic luminescence emission spectra of benitoite, titanium-bearing mineral $\text{BaTiSi}_3\text{O}_9$, show the above mentioned characteristics (Fig. 29).

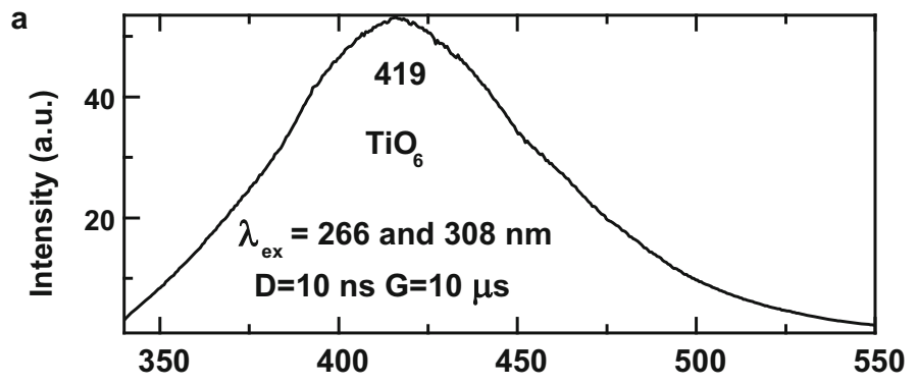


Fig. 29 Laser-induced time-resolved luminescence spectra of benitoite demonstrating TiO_6 centre (Gaft et al., 2015)

Table 9 Concentration of Ti and Fe from EDXRF analysis

Sample		Element (ppmw)	
		Ti	Fe
Luminescent	AUE4100	82	1,550
	KTJ1	927	694
	KTJ2	649	418
	KUD5	761	349
	KUD7	786	387
	KUF	270	1,170
	KTM	260	532
Faintly Luminescent	KUD6	902	9,660
	KSE4637	314	14,300
	KUD3	152	21,300
Inert	KME3887	308	28,300
	KUH	ND	39,000
	KUD8	1,800	56,300

The chemistry of the luminescent samples (Table 9) provides a further support to a possible correlation between intensity of luminescence and concentration of titanium in kornerupine: under both SWUV and LWUV light, the yellow-green range luminescence of the samples with higher concentration of titanium, unless quenched by a high concentration of iron, seems to be more intense than those with lower concentration of titanium.

Many titanium-containing minerals are known to have blue-to-blue-green short-wave-excited luminescence but titanate related luminescence is not restricted to blue short-wave ultraviolet luminescence. Some minerals emit a green to a yellow luminescence with the same excitation spectrum and similar lifetimes to blue short-wave luminescence. This is recorded for natural minerals such as andalusite, topaz, cassiterite, lorenzite, talc, uvarovite, baghdadite , chrysoberyl: alexandrite and enstatites. (Vigier et al., 2023)

Although one andalusite sample was included for this research work, it would be helpful to collect more andalusite samples and especially those display a distinct so called “mustard-coloured” luminescence, with the aim of a more effective comparison to kornerupine on luminescence.

Analysis of luminescence parameters combined with chemistry of the luminescent kornerupine samples suggests a possible luminescence activator in kornerupine *sensu lato*: titanate.

Conclusion

Minerals of the Kornerupine Group/*Kornerupine sensu lato* include *kornerupine sensu stricto* and prismaticine, members of an isomorphic series differing in boron content. Analytical technology such as Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) allows detection of the boron content in the mineral. Raman spectroscopy turns out to be an effective method for the separation between *kornerupine sensu stricto* and prismaticine.

Pyrite, sphalerite and kornerupine were detected as inclusions in minerals of the kornerupine group.

V^{3+} , Cr^{3+} and Fe^{3+} are the colouring agents of *kornerupine sensu lato*. The correlation between vanadium, chromium and iron within the sample has direct impact on the colour and pleochroism of kornerupine.

Titanate could be the luminescence activator of *kornerupine sensu lato*.

The assumption stays still exploratory at this stage. Further research needs to be carried out.

Appendix

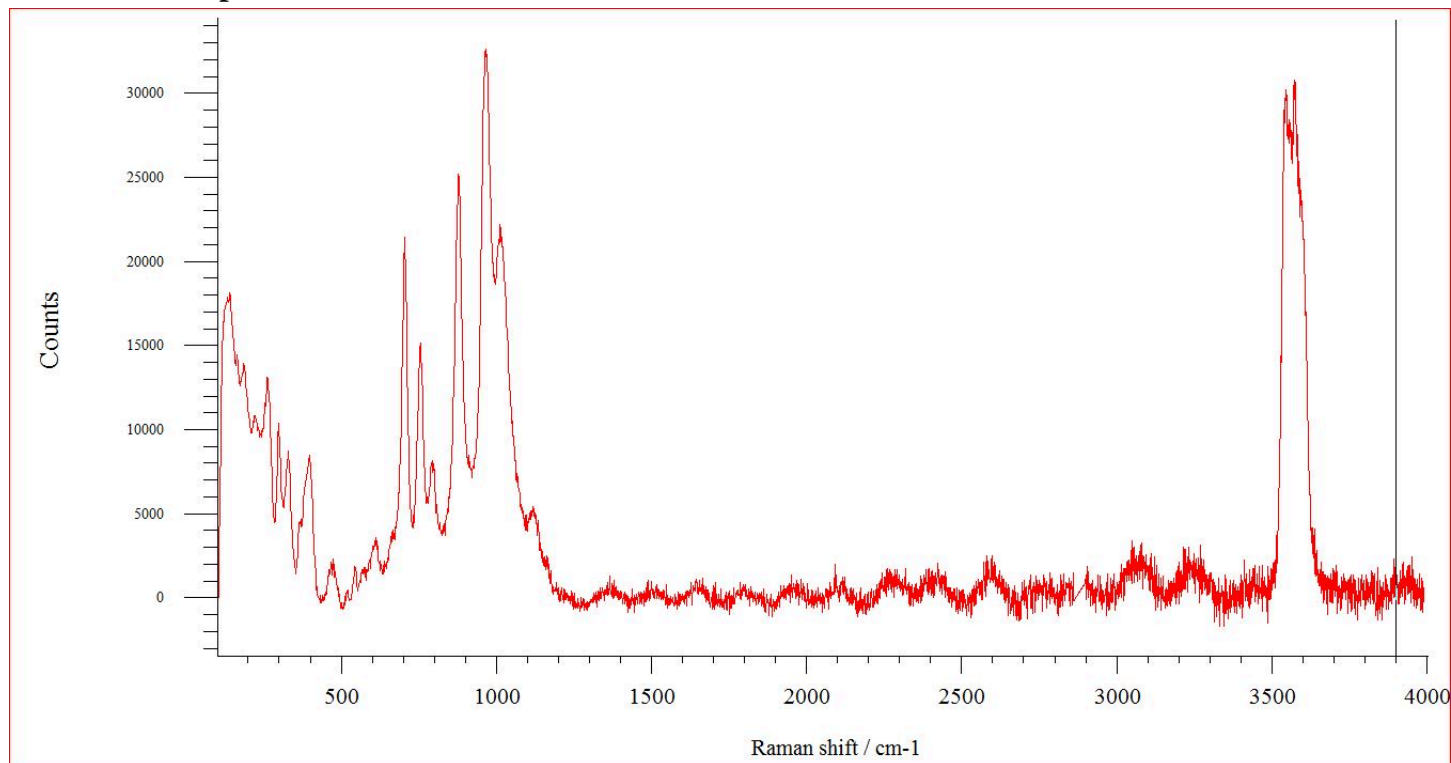
Sample KTJ1



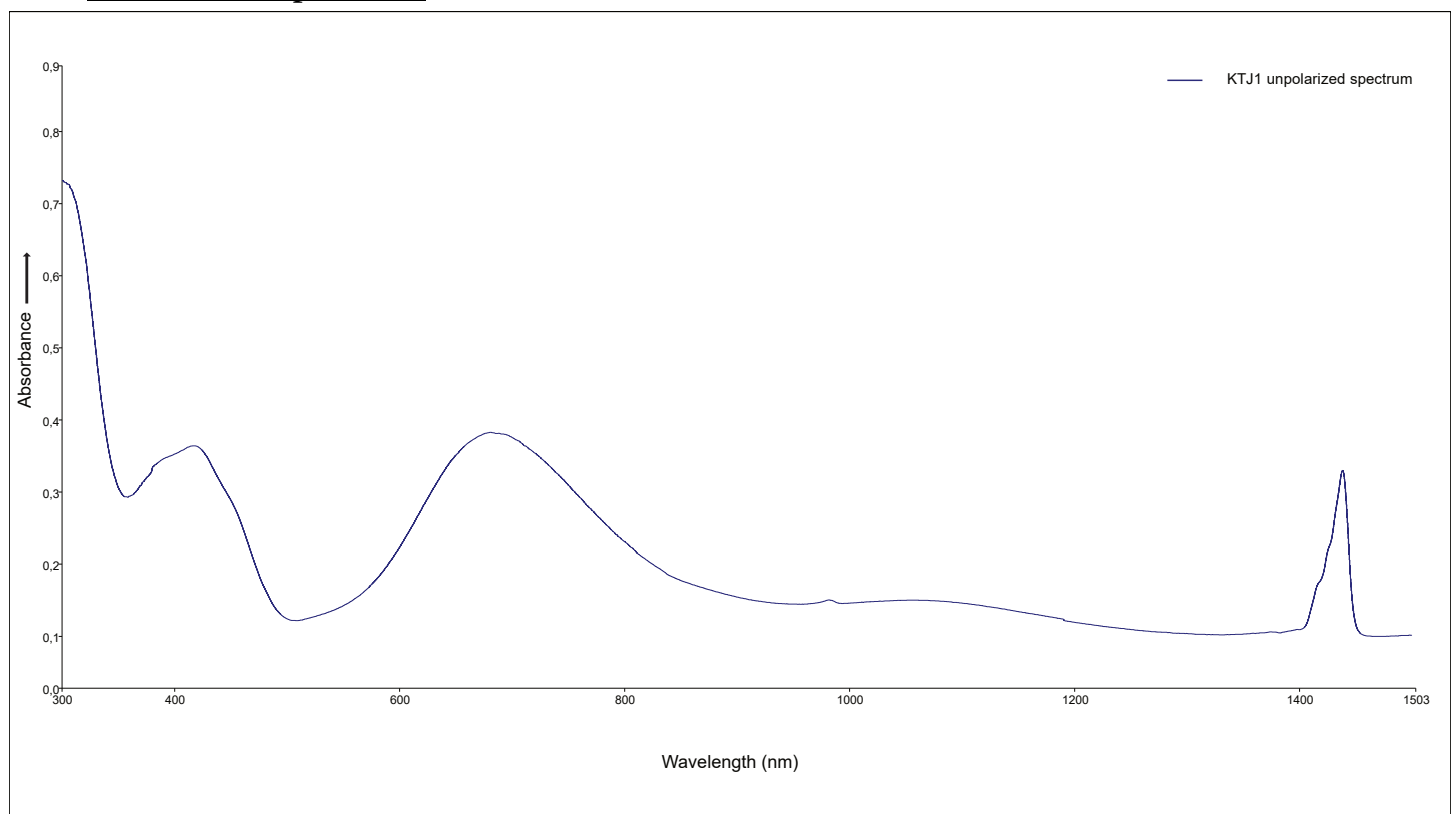
KTJ1

5.06 x 4.13 x 2.97 mm

Raman spectrum



UV-Vis-NIR spectrum

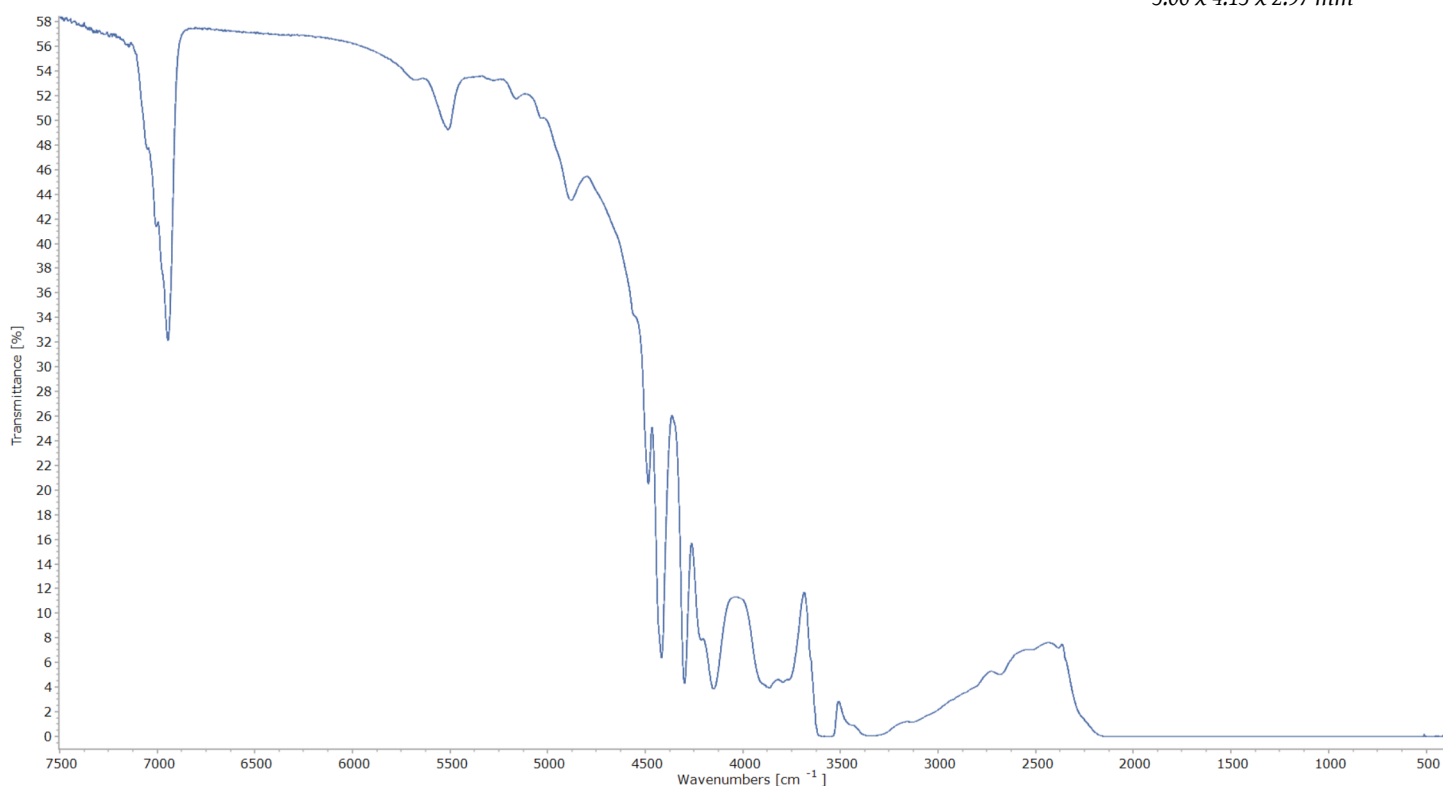




KTJ1

5.06 x 4.13 x 2.97 mm

FTIR spectrum



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	46.00	0.30	Al	24.34	0.16
SiO2	29.39	0.22	Si	13.74	0.10
MgO	19.48	0.20	Mg	11.75	0.12
CaO	0.162	0.008	Ca	0.116	0.006
TiO2	0.155	0.015	Ti	0.0927	0.0091
V2O5	0.145	0.009	V	0.0812	0.0050
MnO	0.112	0.009	Mn	0.0868	0.0066
Fe2O3	0.099	0.011	Fe	0.0694	0.0077
S03	0.060	0.022	Sx	0.0239	0.0090
Sc2O3	0.0585	0.0033	Sc	0.0381	0.0021
Cr2O3	0.0147	0.0015	Cr	0.0101	0.0010
ZnO	0.0119	0.0008	Zn	0.0096	0.0006
K2O	0.0062	0.0021	K	0.0051	0.0017
Ga2O3	0.0054	0.0006	Ga	0.0040	0.0004

KnownConc= 3.30 B2O3

REST= 1.00 H2O

D/S= 0

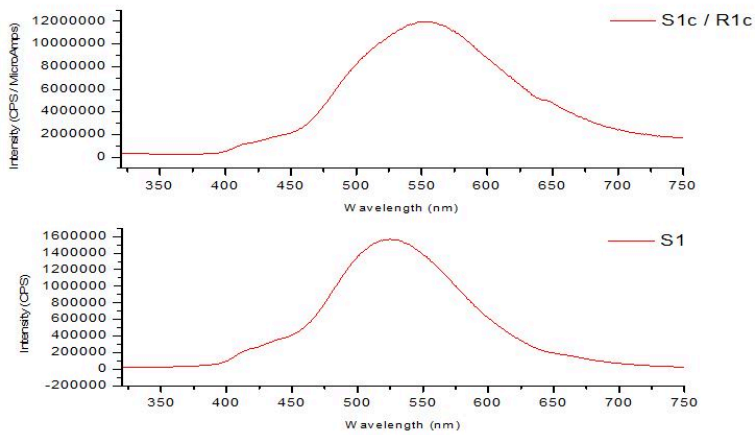
Sum Conc's before normalisation to 100% : 59.0 %



KTJ1

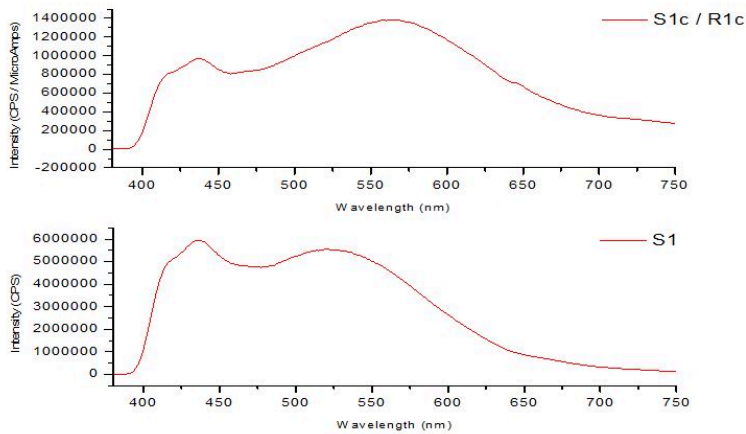
5.06 x 4.13 x 2.97 mm

Emission spectra



Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature

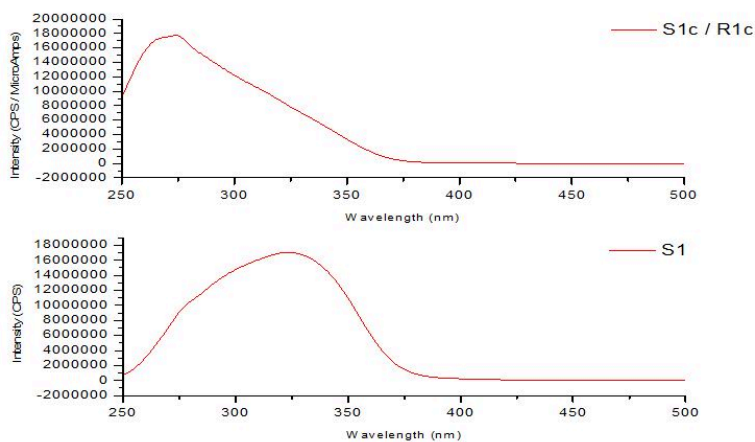
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 550\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

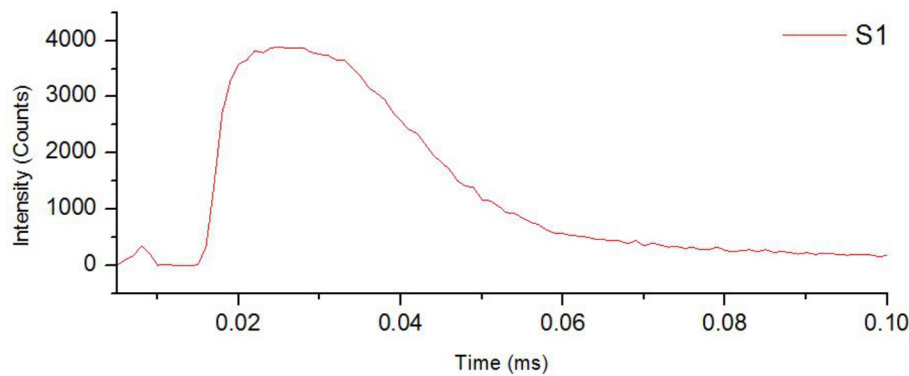
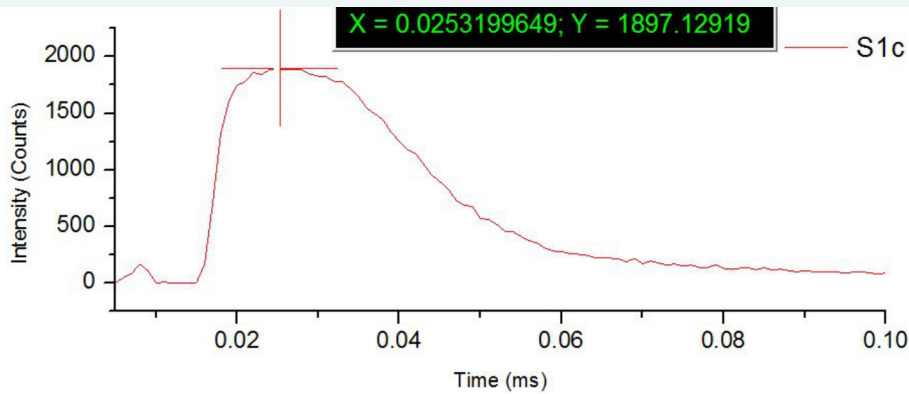
Phosphorescence decay time spectra

- $\lambda_{ex} = 265\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit

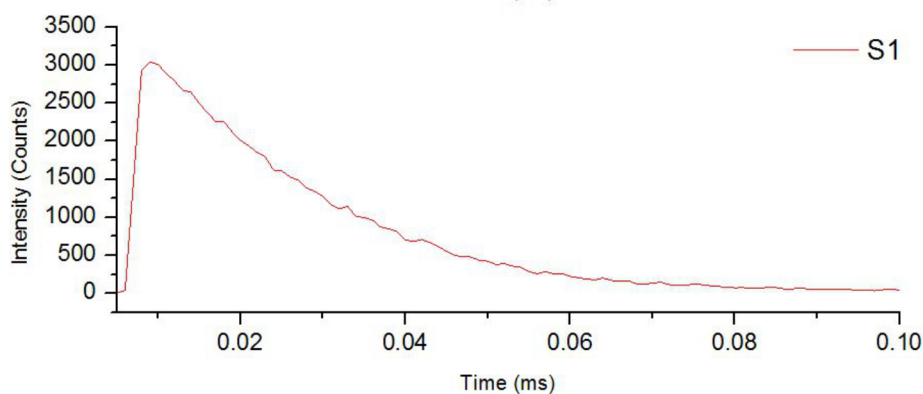
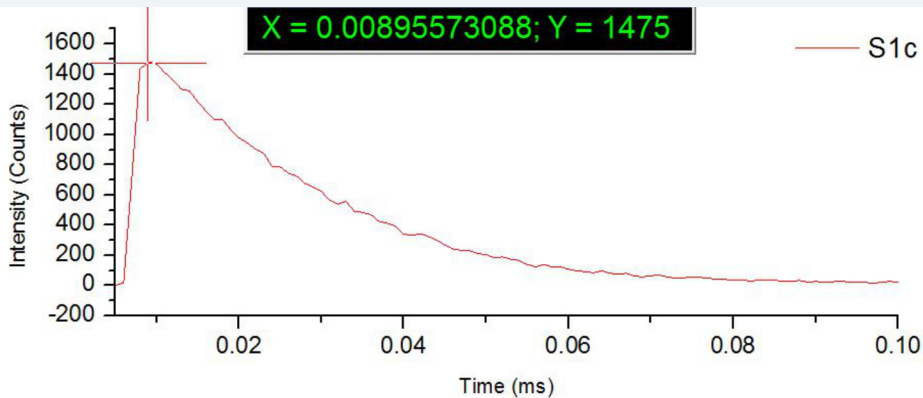


KTJ1

5.06 x 4.13 x 2.97 mm



- $\lambda_{ex} = 325\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit



Appendix

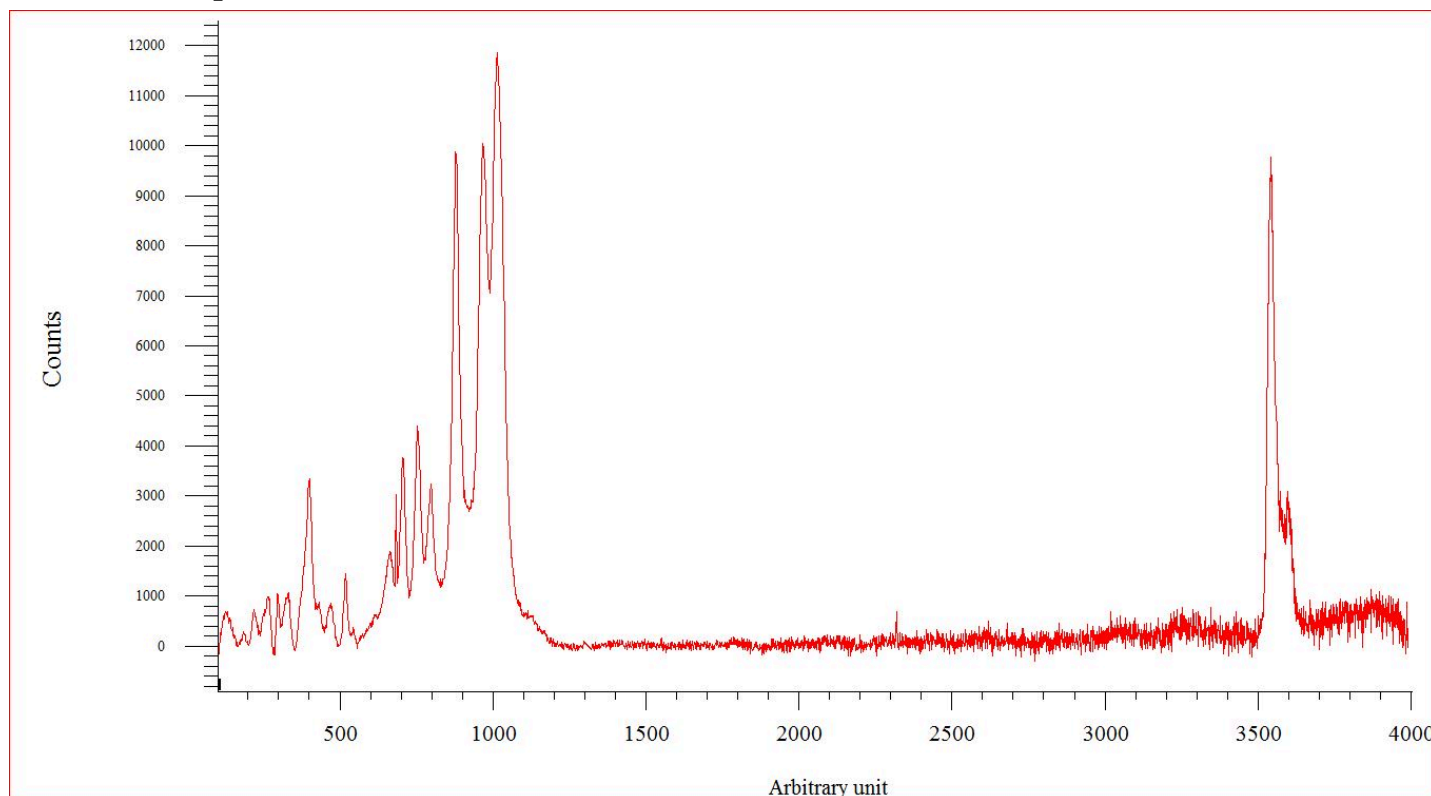
Sample KTJ2



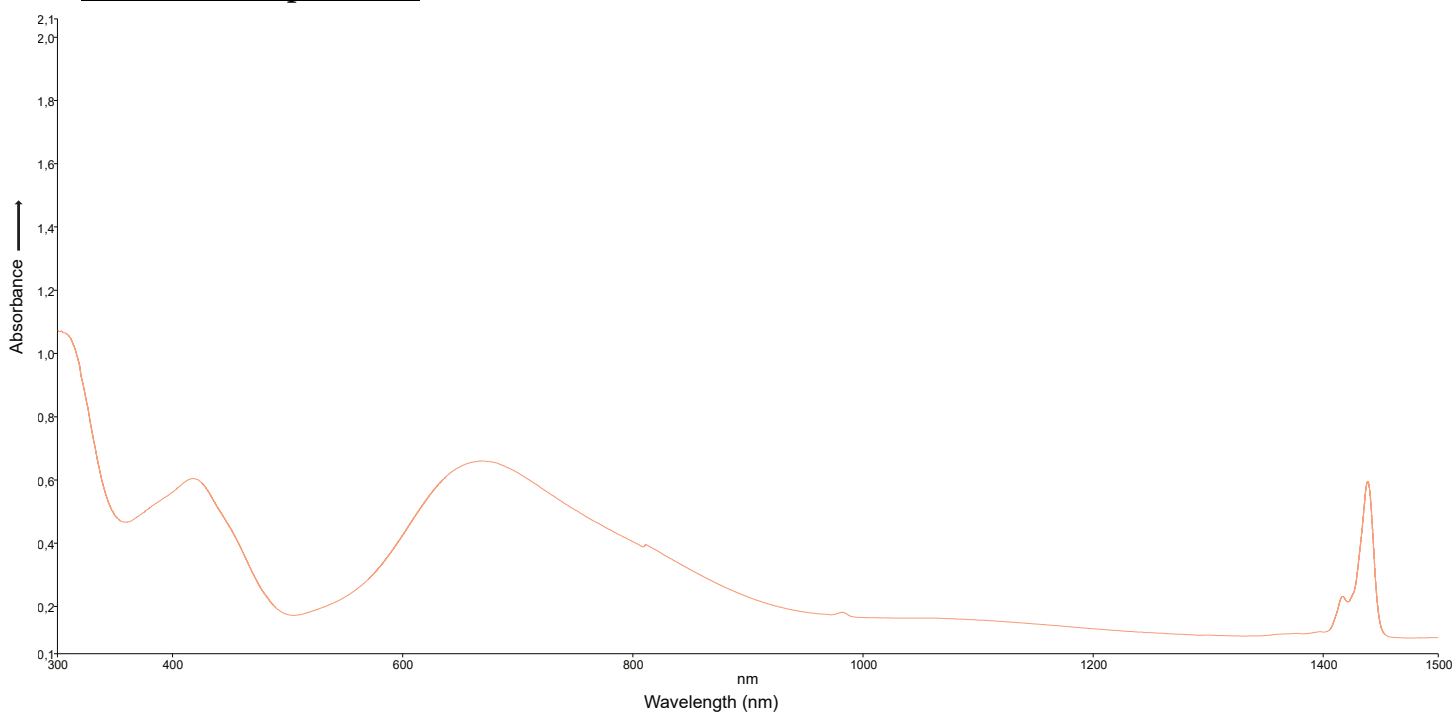
KTJ2

9.52 x 7.40 x 4.61 mm

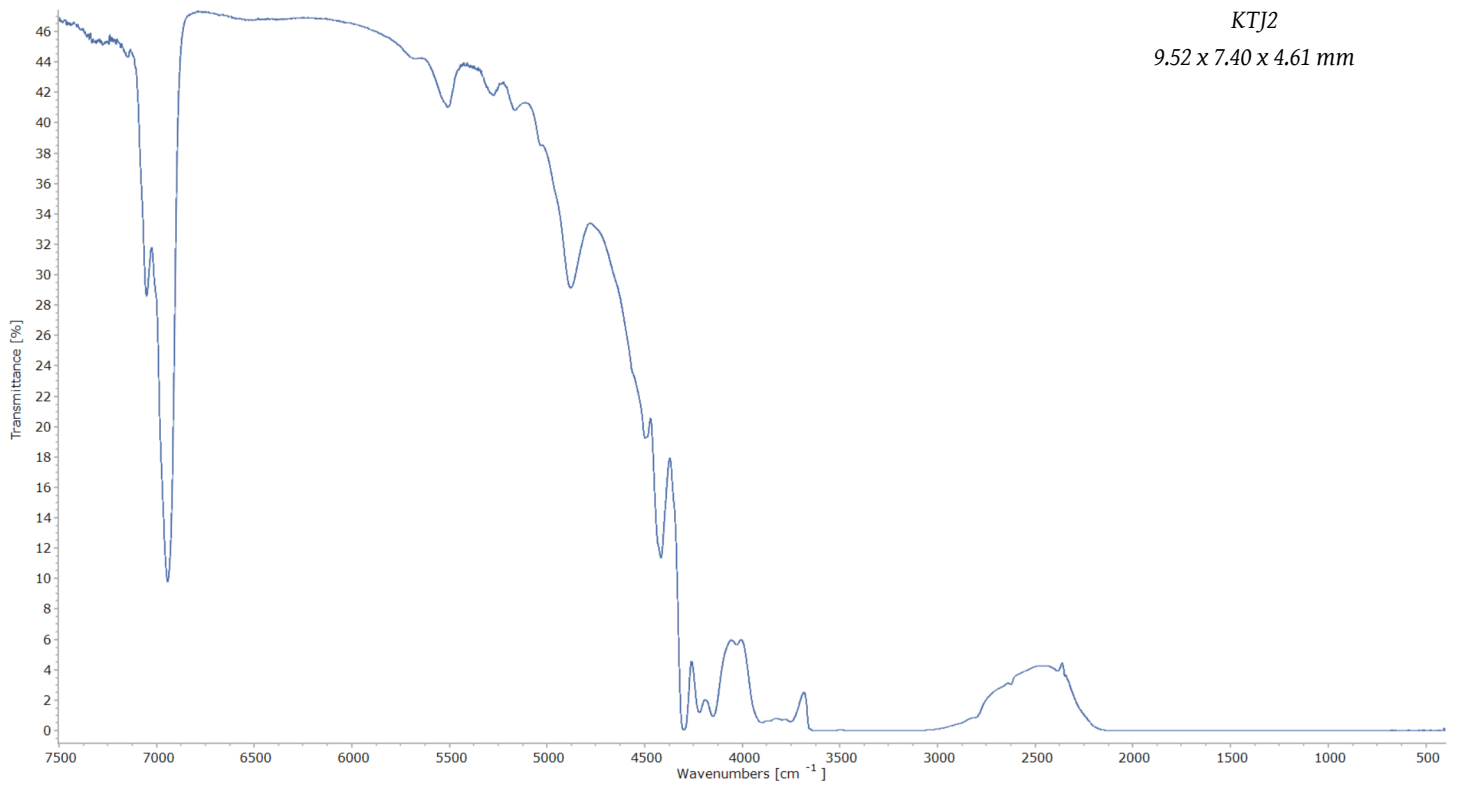
Raman spectrum



UV-Vis-NIR spectrum



FTIR spectrum



KTi₂

9.52 x 7.40 x 4.61 mm

EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	44.57	0.26	Al	23.59	0.14
SiO2	29.89	0.22	Si	13.97	0.10
MgO	20.56	0.20	Mg	12.40	0.12
V2O5	0.180	0.011	V	0.101	0.006
MnO	0.167	0.013	Mn	0.129	0.010
TiO2	0.108	0.011	Ti	0.0649	0.0064
CaO	0.0656	0.0033	Ca	0.0469	0.0023
Fe2O3	0.0598	0.0066	Fe	0.0418	0.0046
BaO	0.0286	0.0082	Ba	0.0256	0.0074
Sc2O3	0.0217	0.0018	Sc	0.0141	0.0012
Cr2O3	0.0213	0.0017	Cr	0.0146	0.0012
K2O	0.0103	0.0017	K	0.0086	0.0014
ZnO	0.0095	0.0006	Zn	0.0076	0.0004

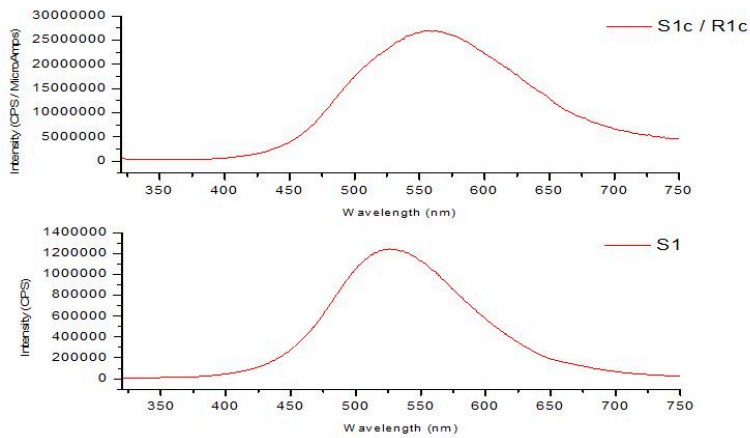
KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
 Sum Conc's before normalisation to 100% : 86.3 %



KTJ2

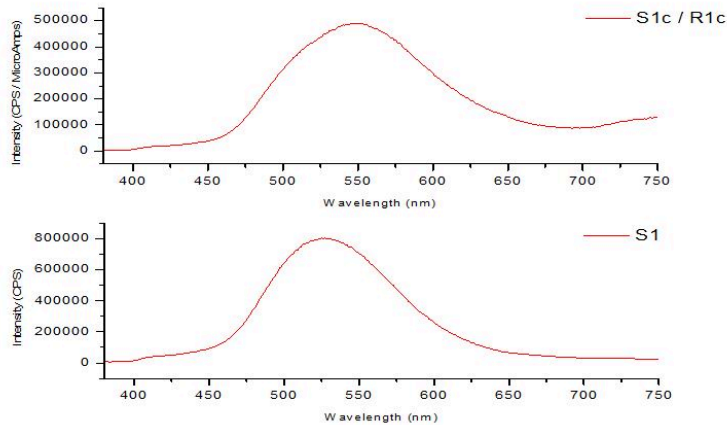
9.52 x 7.40 x 4.61 mm

Emission spectra



Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature

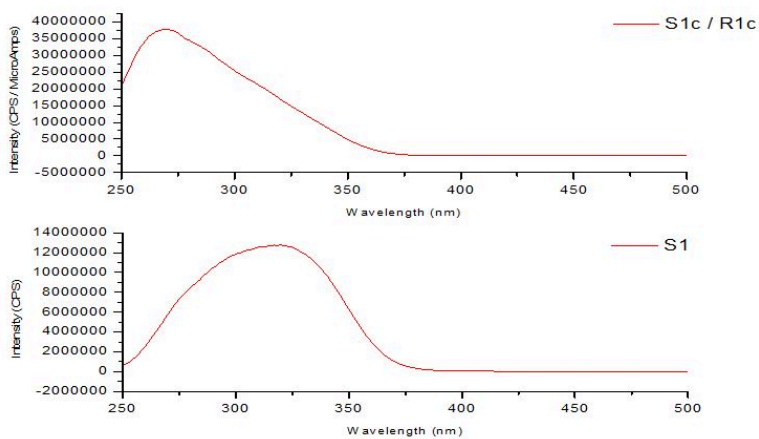
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 550\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

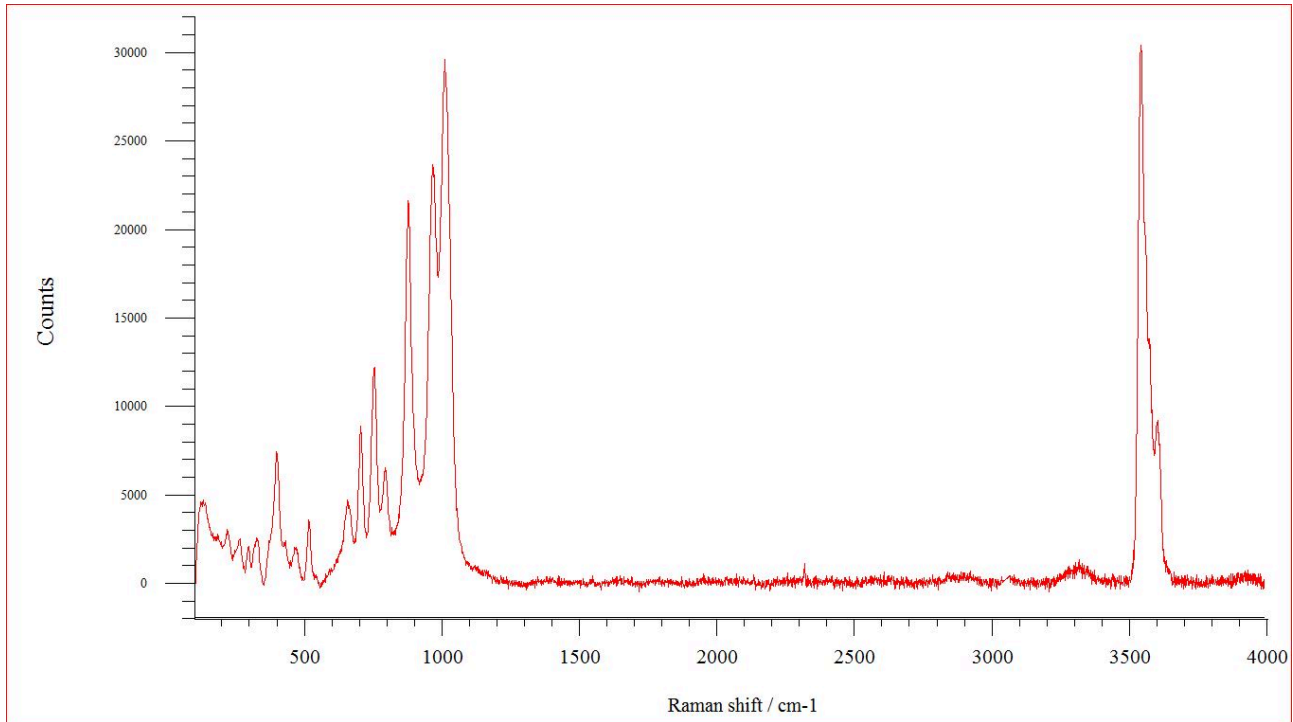
Appendix

Sample KUD5

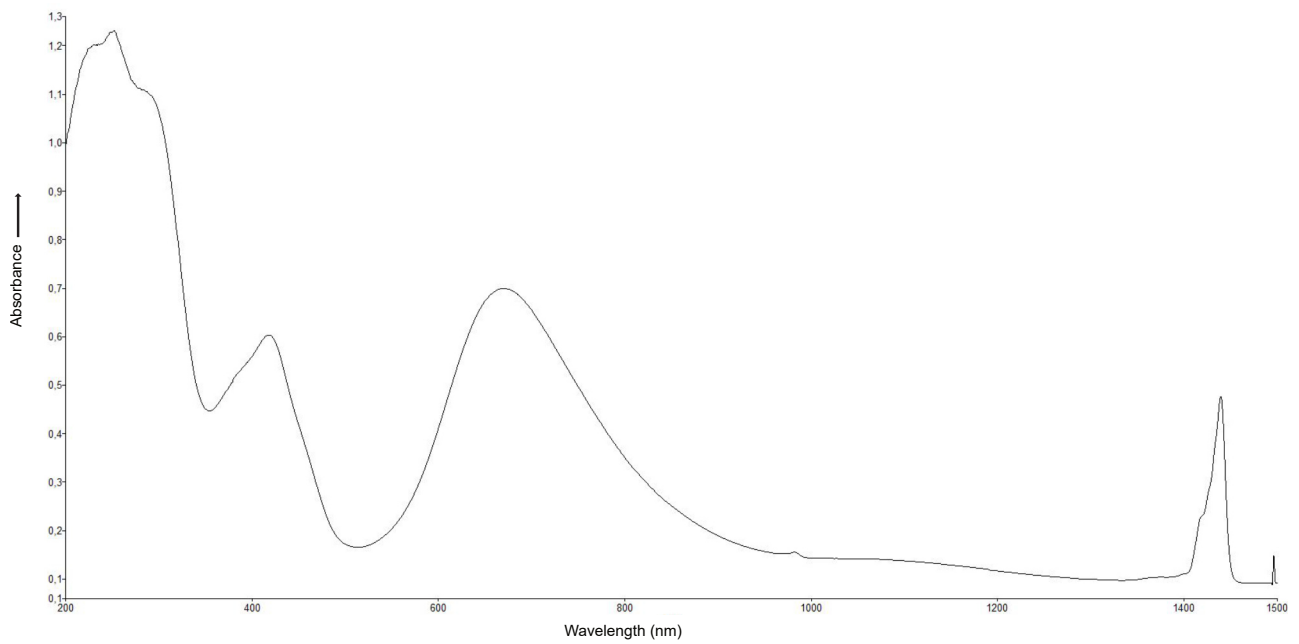
Raman spectrum



KUD5



UV-Vis-NIR spectrum

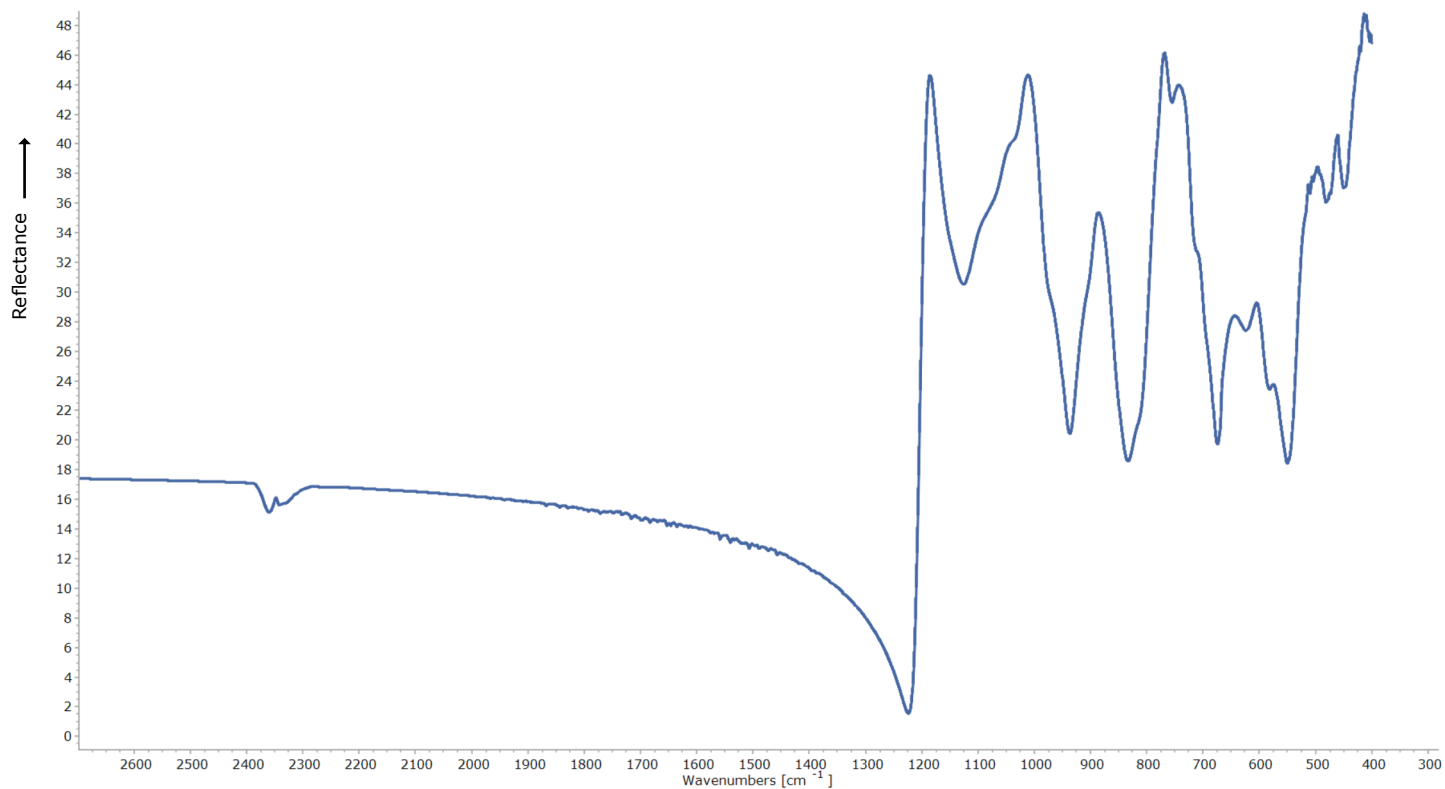
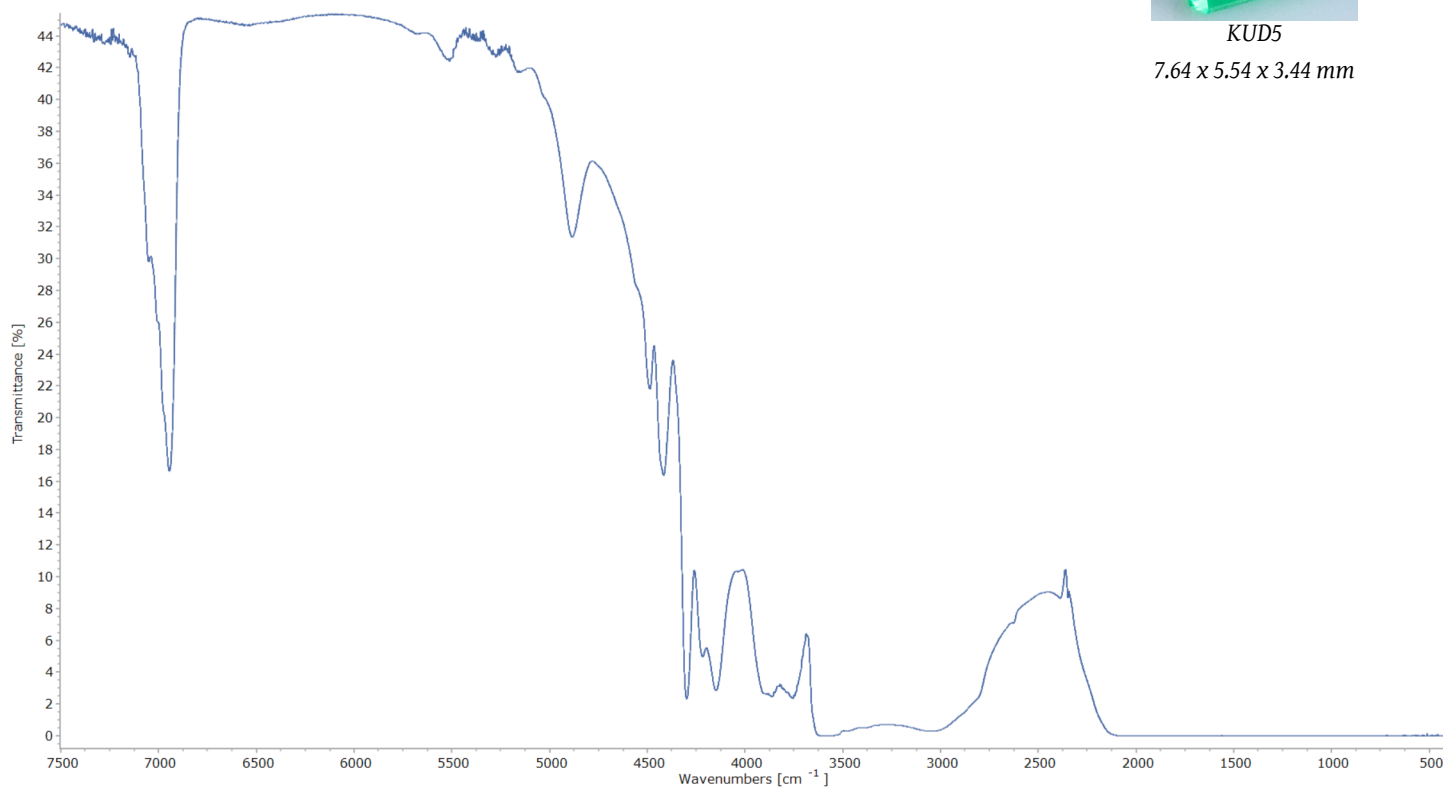


FTIR spectra (absorption & reflectance)



KUD5

7.64 x 5.54 x 3.44 mm





KUD5

7.64 x 5.54 x 3.44 mm

EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	45.02	0.26	Al	23.82	0.14
SiO2	29.87	0.22	Si	13.97	0.10
MgO	19.99	0.20	Mg	12.06	0.12
V2O5	0.225	0.014	V	0.126	0.008
MnO	0.220	0.017	Mn	0.171	0.013
TiO2	0.127	0.012	Ti	0.0761	0.0075
SO3	0.085	0.018	Sx	0.0340	0.0072
CaO	0.0587	0.0030	Ca	0.0420	0.0021
Fe2O3	0.0499	0.0055	Fe	0.0349	0.0039
Sc2O3	0.0245	0.0019	Sc	0.0160	0.0013
Cr2O3	0.0135	0.0022	Cr	0.0092	0.0015
Cl	0.0090	0.0030	Cl	0.0090	0.0030

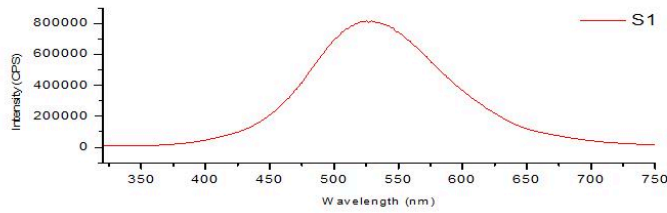
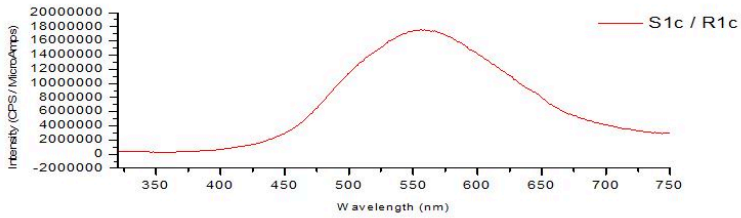
KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
 Sum Conc's before normalisation to 100% : 76.3 %

Emission spectra



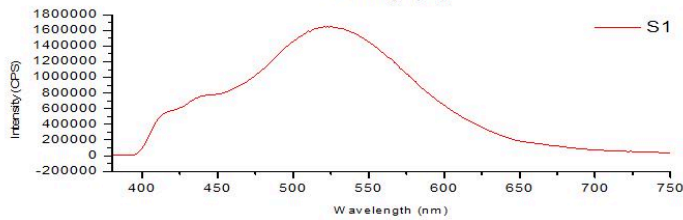
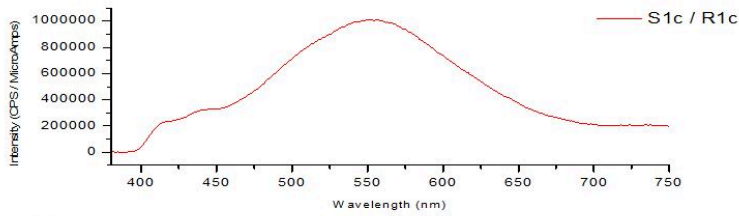
KUD5

7.64 x 5.54 x 3.44 mm



Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature

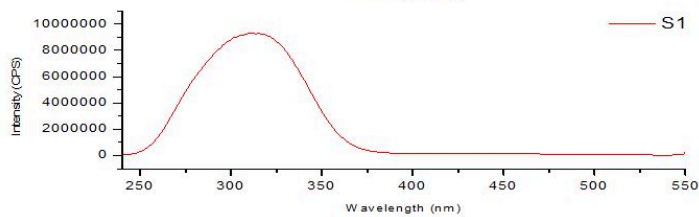
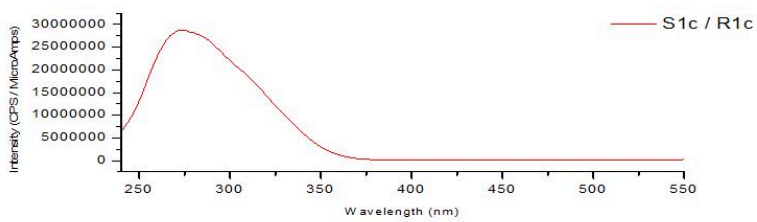
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 565\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

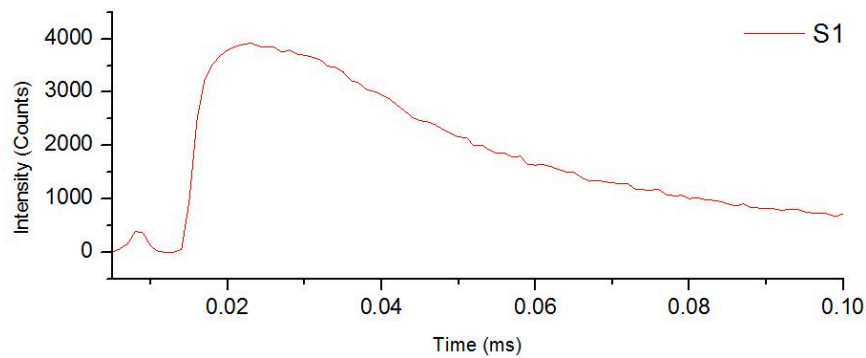
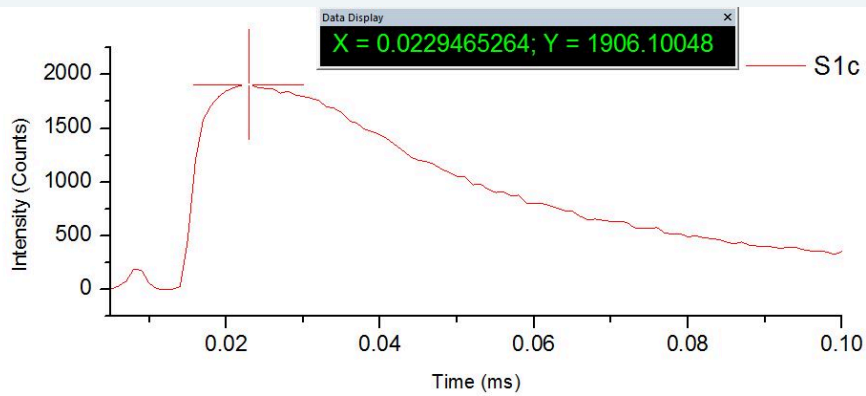
Phosphorescence decay time spectra

- $\lambda_{ex} = 265\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit

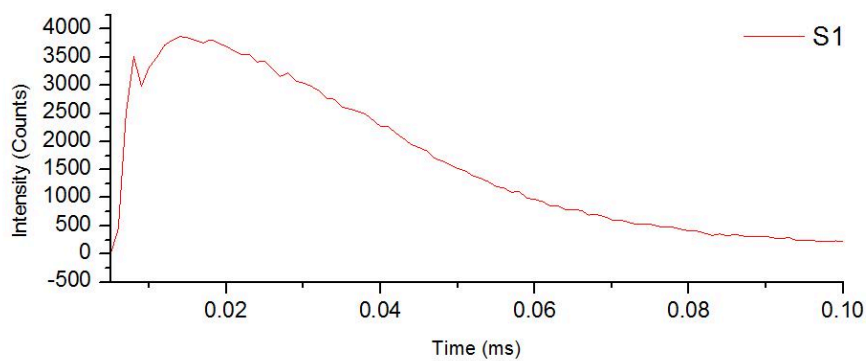
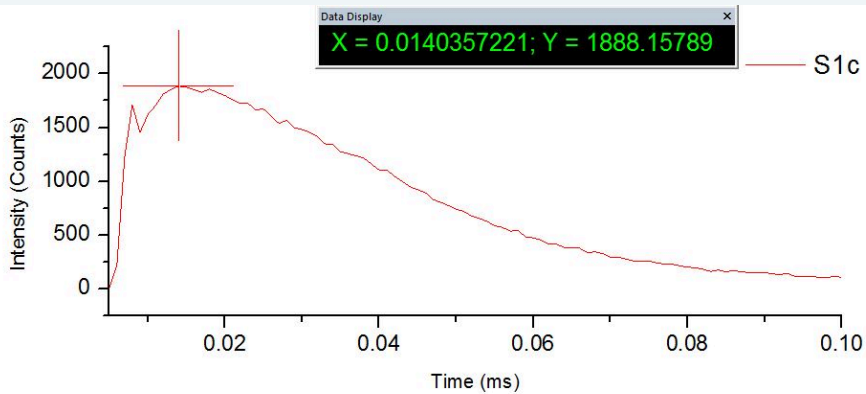


KUD5

7.64 x 5.54 x 3.44 mm



- $\lambda_{ex} = 325\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit



Appendix

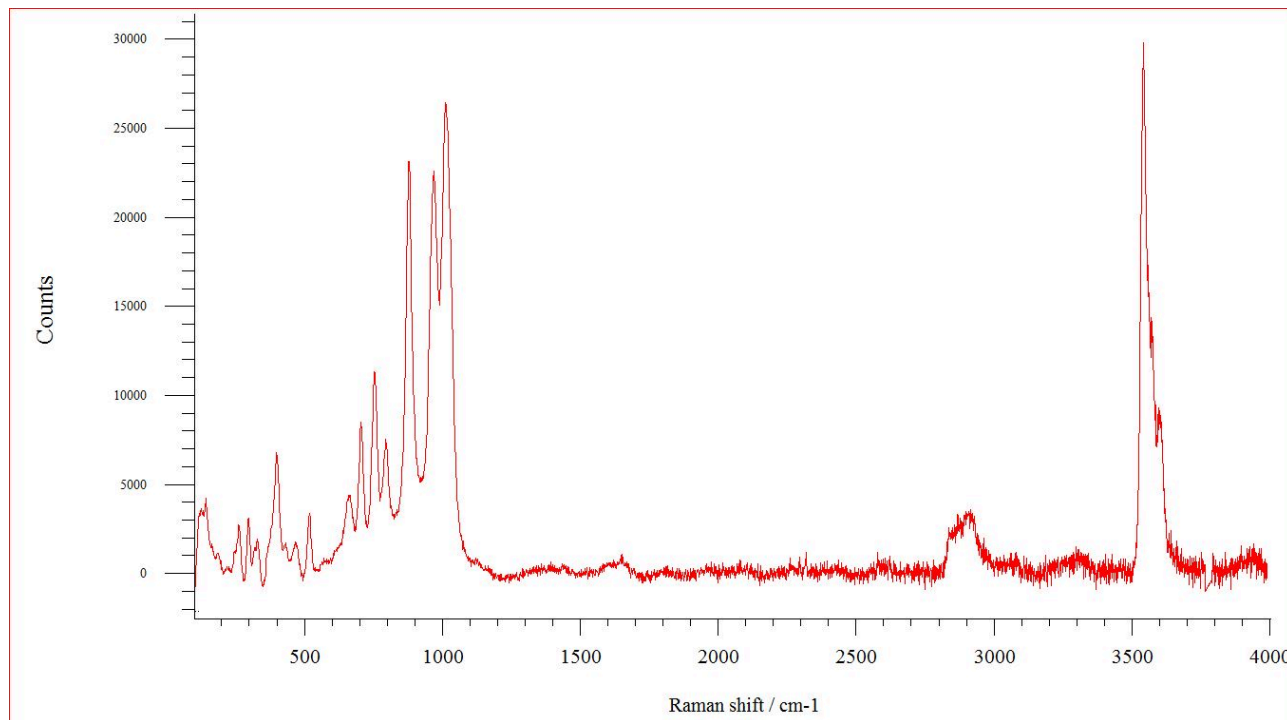
Sample KUD7



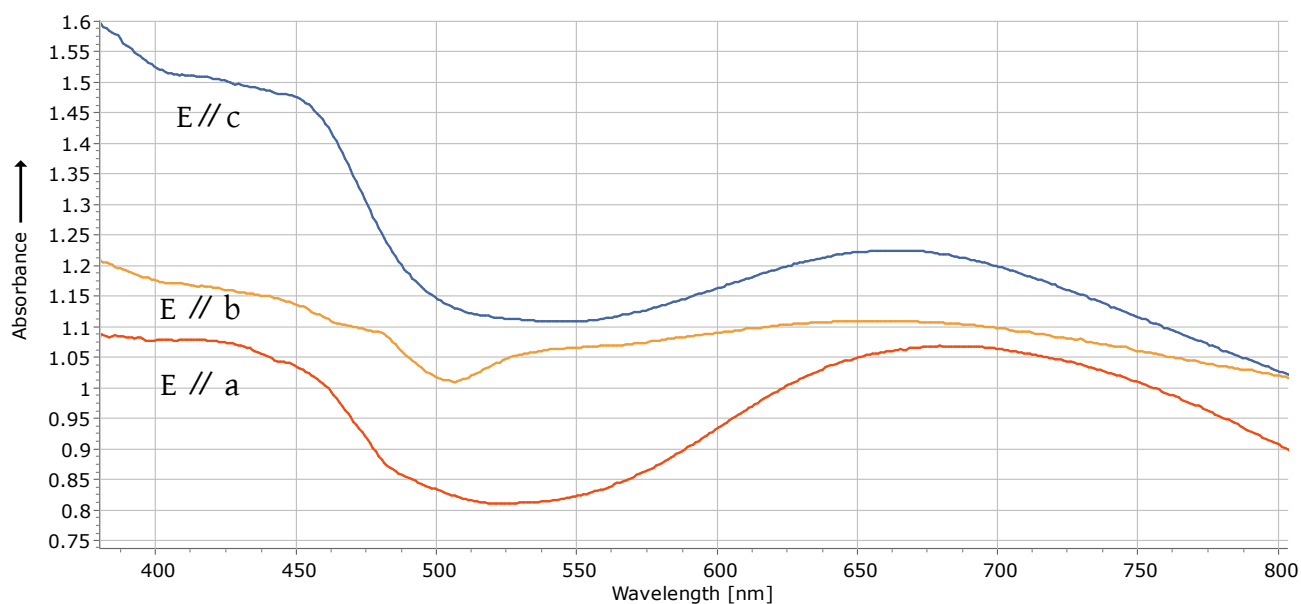
KUD7

9.02 x 5.37 x 3.46 mm

Raman spectrum



UV-Vis-NIR spectrum (polarised)

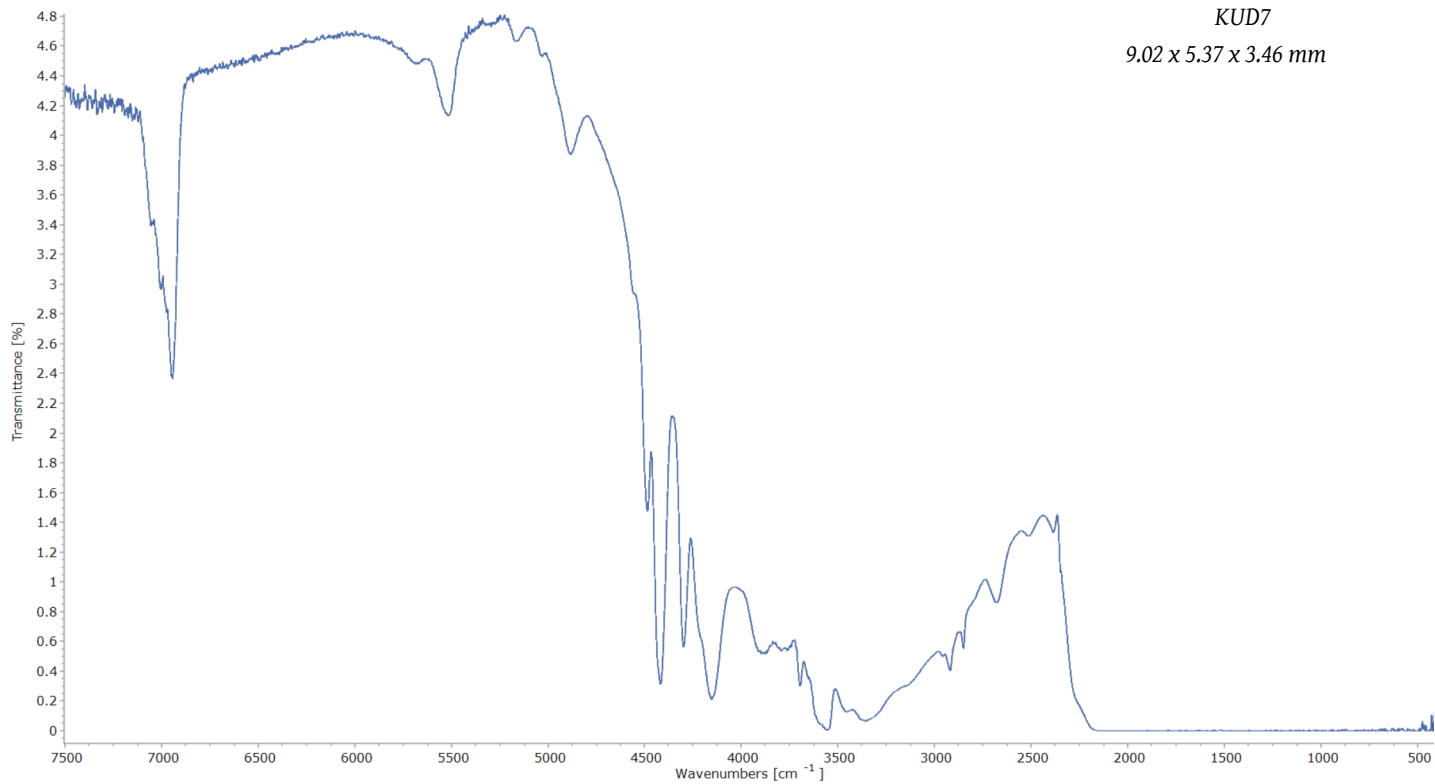


FTIR spectra



KUD7

9.02 x 5.37 x 3.46 mm

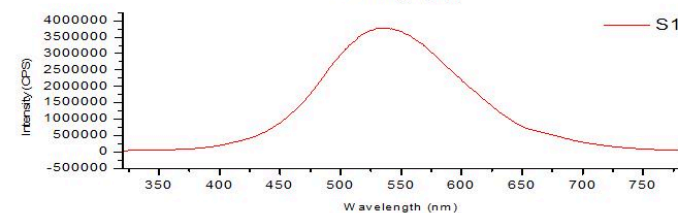
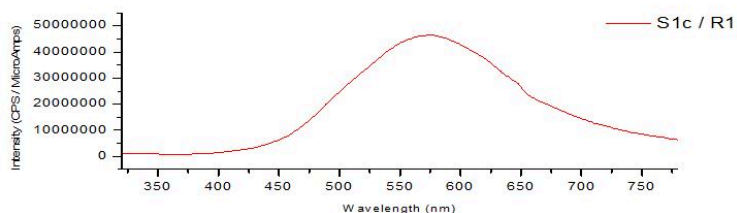


Emission spectra



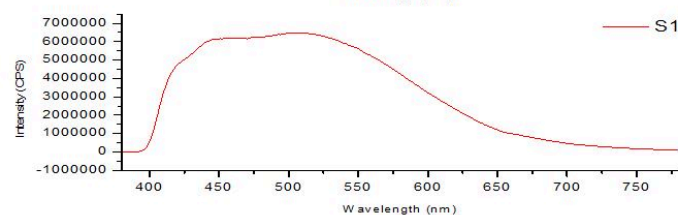
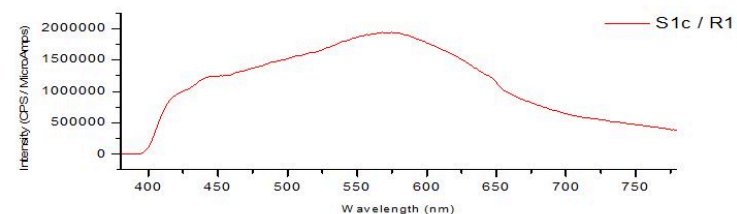
KUD7

9.02 x 5.37 x 3.46 mm



Emission spectra
under $\lambda_{ex} = 254\text{nm}$
at room temperature

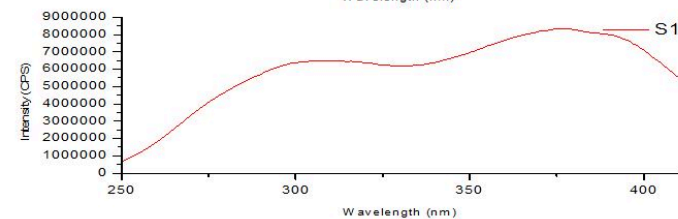
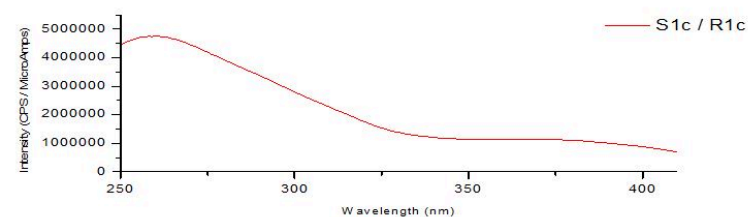
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$
at room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 445\text{nm}$
at room temperature

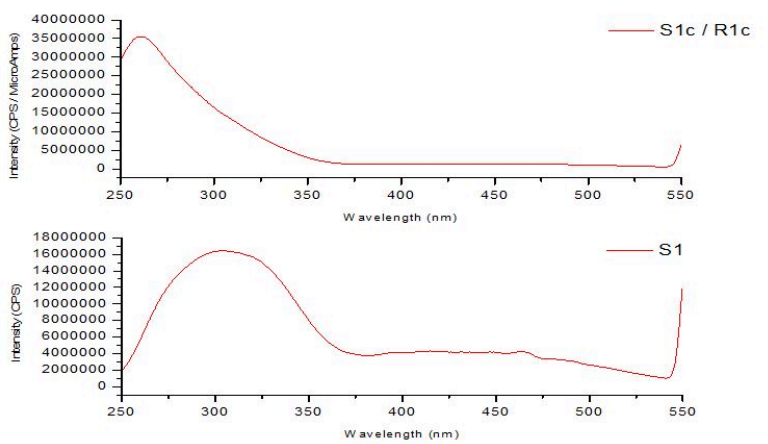
S1: measured
S1c/R1c: corrected

Excitation spectra



KUD7

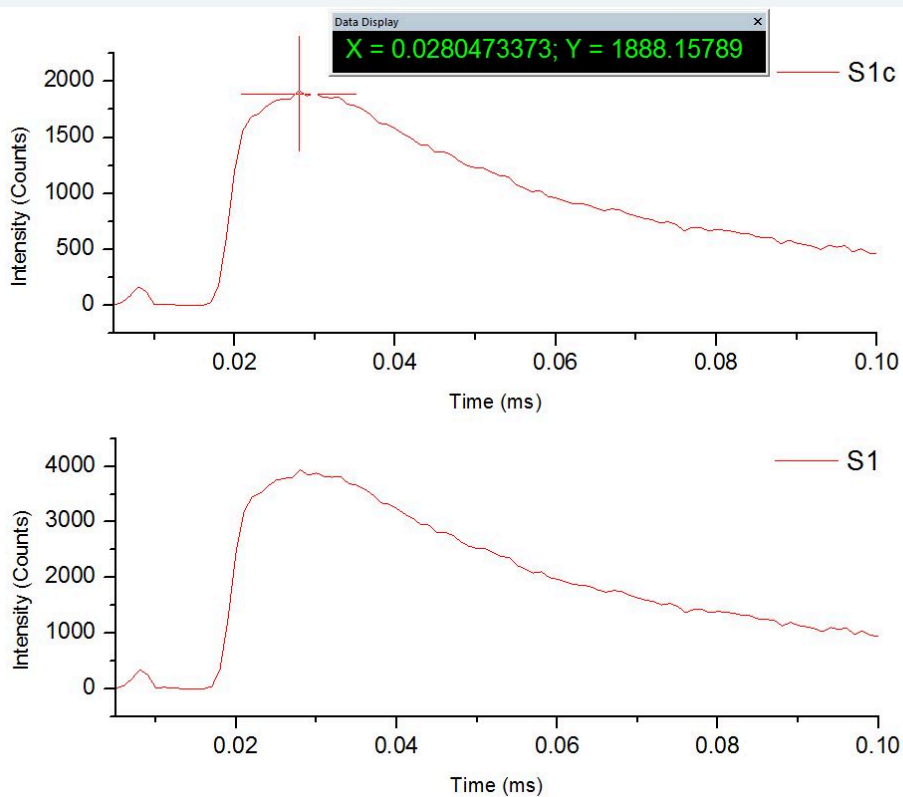
9.02 x 5.37 x 3.46 mm



Excitation spectra
under $\lambda_{em} = 570\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected

Phosphorescence decay time spectra

- $\lambda_{ex} = 265\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit

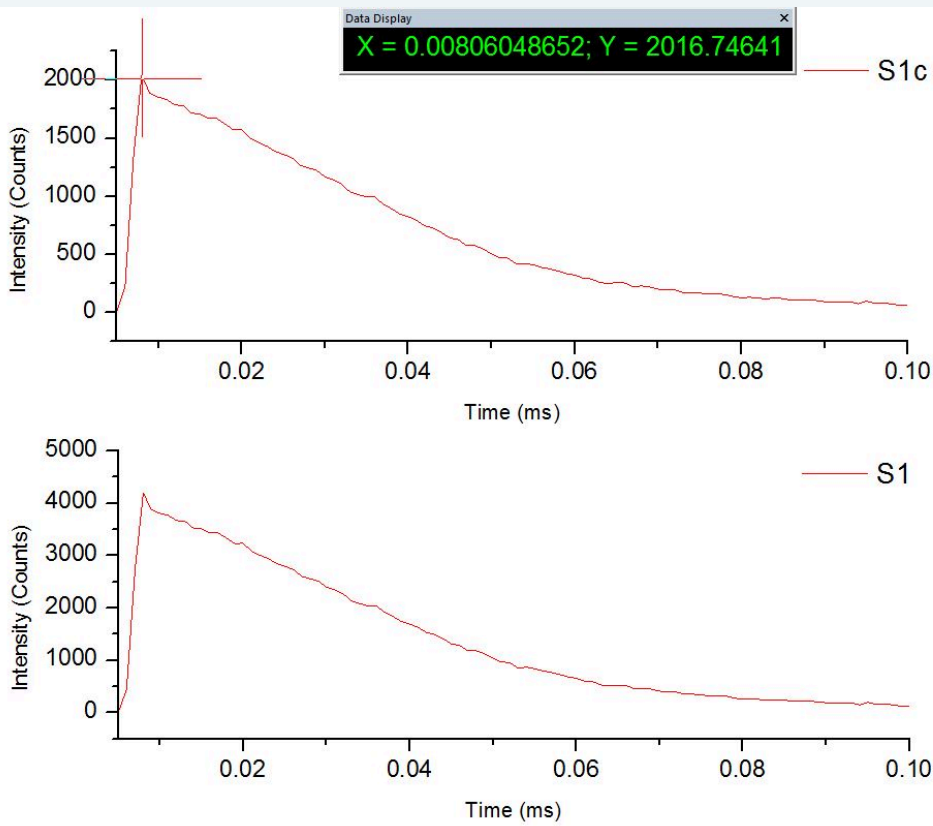


- $\lambda_{ex} = 325\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit



KUD7

9.02 x 5.37 x 3.46 mm



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	44.78	0.27	Al	23.70	0.14
SiO2	30.43	0.23	Si	14.23	0.11
MgO	19.32	0.20	Mg	11.65	0.12
MnO	0.270	0.021	Mn	0.209	0.016
CaO	0.249	0.012	Ca	0.178	0.009
V2O5	0.169	0.010	V	0.0946	0.0058
SO3	0.163	0.025	Sx	0.0654	0.0100
TiO2	0.131	0.013	Ti	0.0786	0.0077
Fe2O3	0.0553	0.0061	Fe	0.0387	0.0043
Sc2O3	0.0456	0.0028	Sc	0.0297	0.0019
BaO	0.0265	0.0089	Ba	0.0237	0.0079
Cr2O3	0.0209	0.0018	Cr	0.0143	0.0012
Cl	0.0165	0.0041	Cl	0.0165	0.0041
K2O	0.0158	0.0024	K	0.0131	0.0020

KnownConc= 3.30 B203

REST= 1.00 H2O

D/S= 0

Sum Conc's before normalisation to 100% : 72.8 %

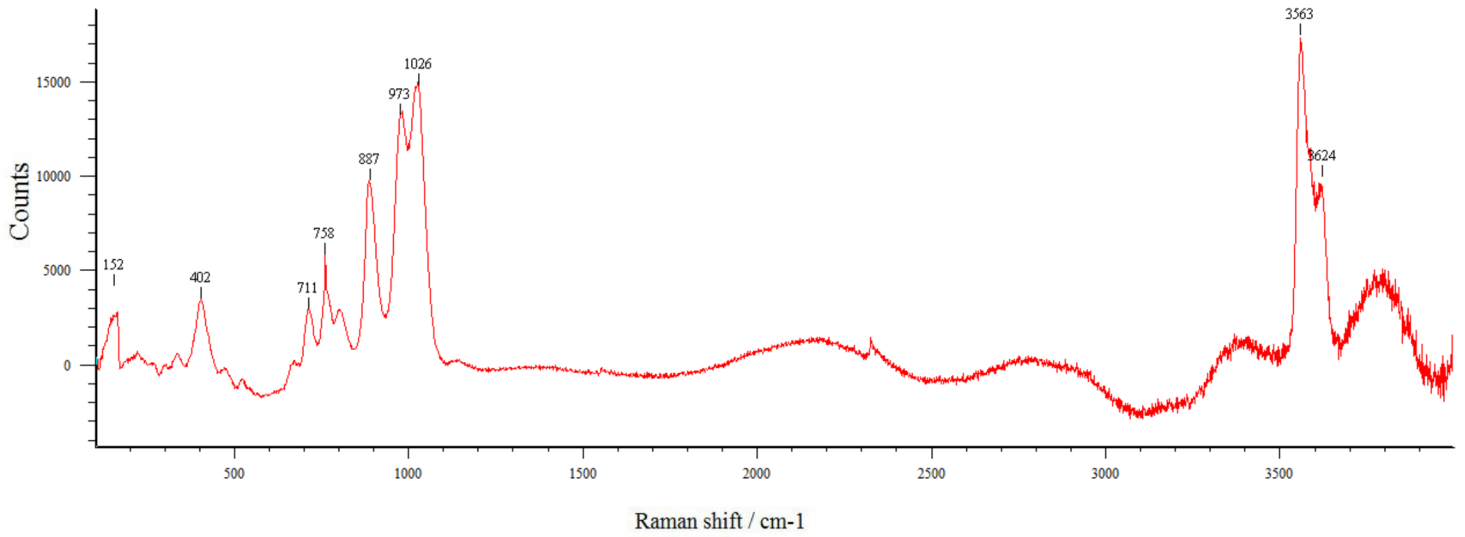
Appendix

Sample KUF

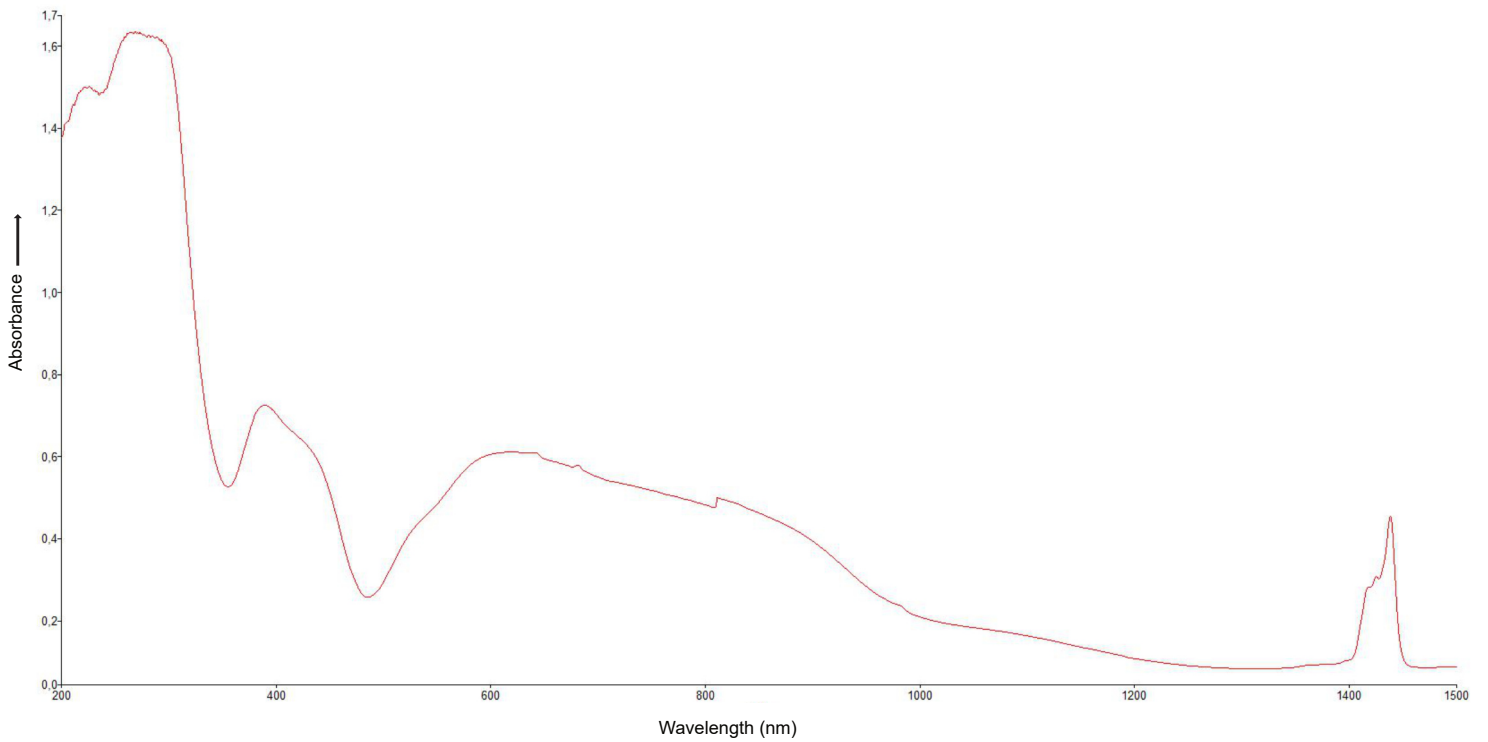
Raman spectrum



KUF
9.71 x 8.31 x 5.61 mm



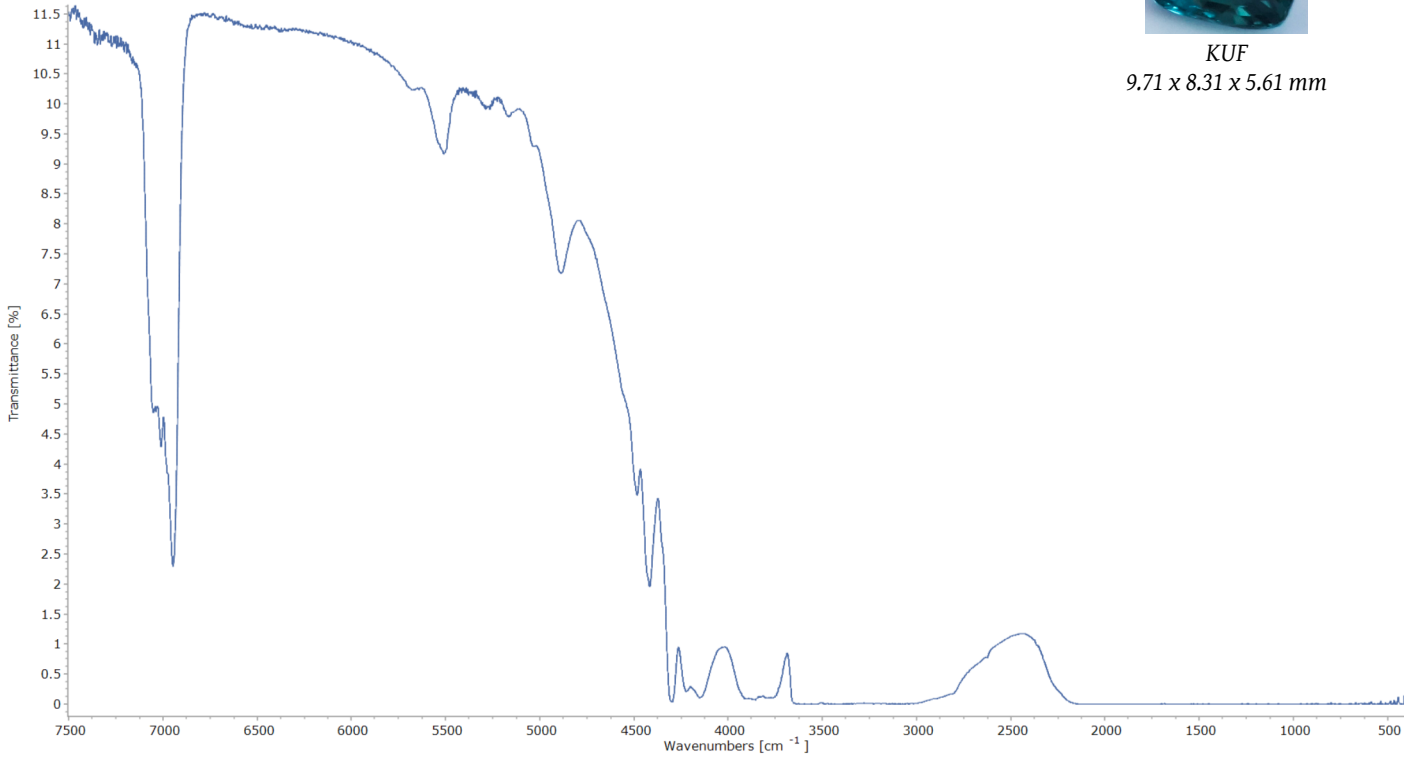
UV-Vis-NIR spectrum



FTIR spectra



KUF
9.71 x 8.31 x 5.61 mm



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	44.43	0.30	Al	23.51	0.16
SiO2	30.26	0.23	Si	14.15	0.11
MgO	20.27	0.20	Mg	12.23	0.12
Cr2O3	0.216	0.014	Cr	0.148	0.010
Fe2O3	0.167	0.018	Fe	0.117	0.013
MnO	0.115	0.009	Mn	0.0892	0.0068
V2O5	0.0784	0.0048	V	0.0439	0.0027
CaO	0.0566	0.0036	Ca	0.0405	0.0026
TiO2	0.0451	0.0044	Ti	0.0270	0.0026
Cl	0.0162	0.0046	Cl	0.0162	0.0046
K2O	0.0145	0.0025	K	0.0120	0.0020
ZnO	0.0135	0.0009	Zn	0.0108	0.0007
Ga2O3	0.0101	0.0007	Ga	0.0075	0.0005

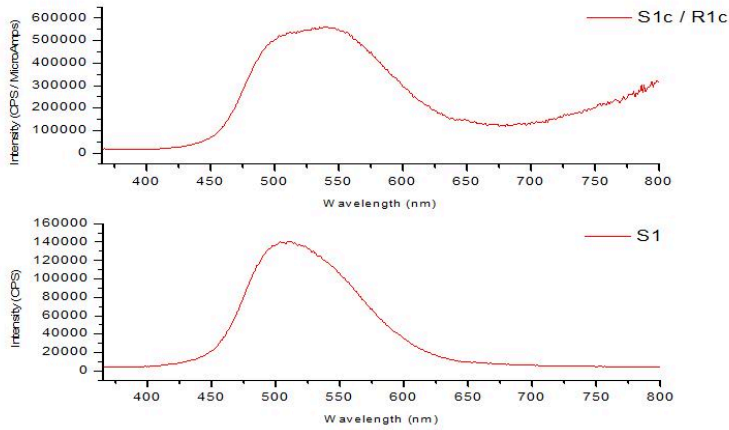
KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
 Sum Conc's before normalisation to 100% : 54.2 %



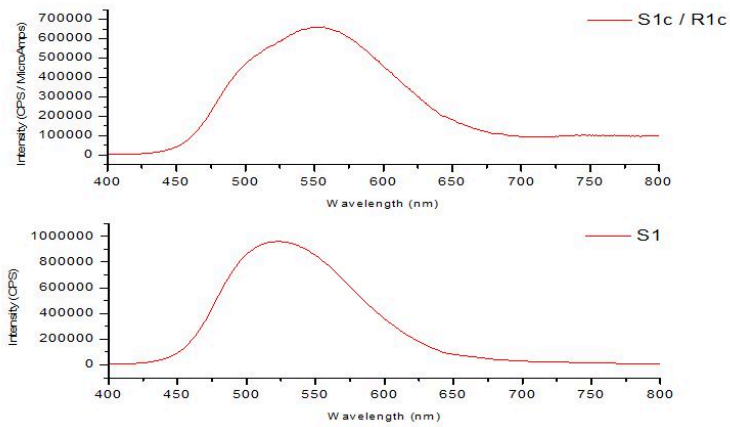
KUF

9.71 x 8.31 x 5.61 mm

Emission spectra

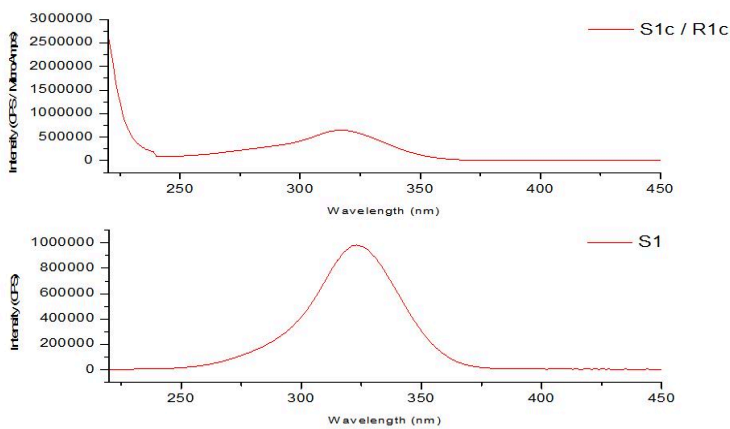


Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 318\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 540\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected

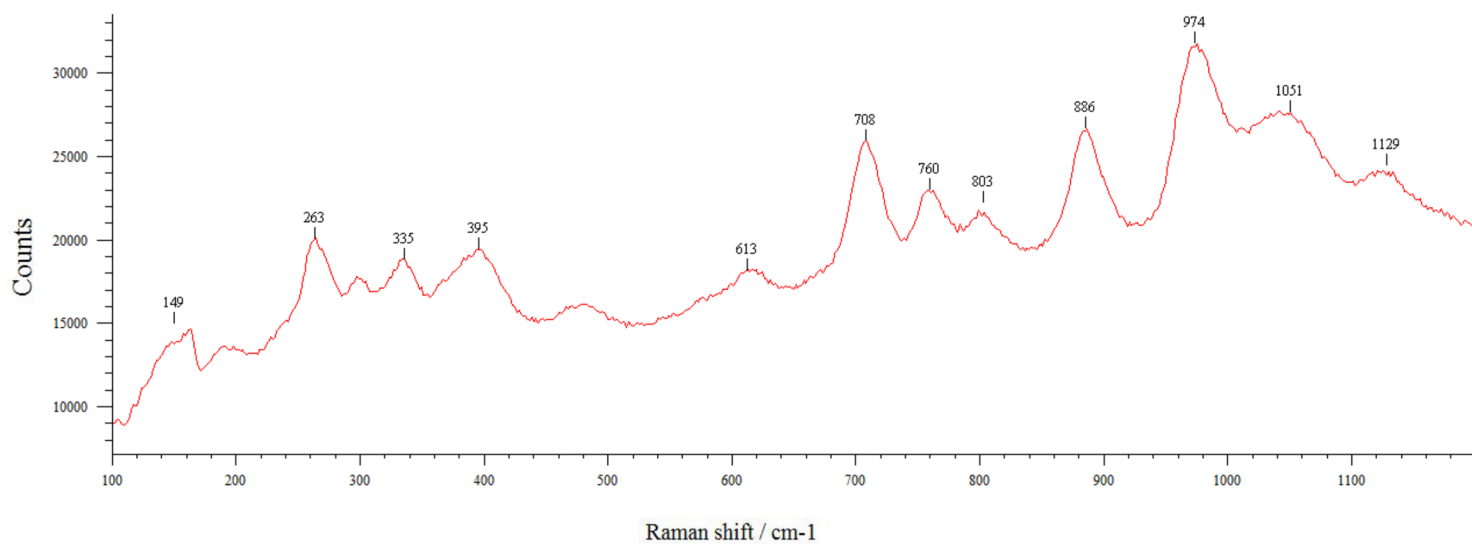
Appendix

Sample KTM

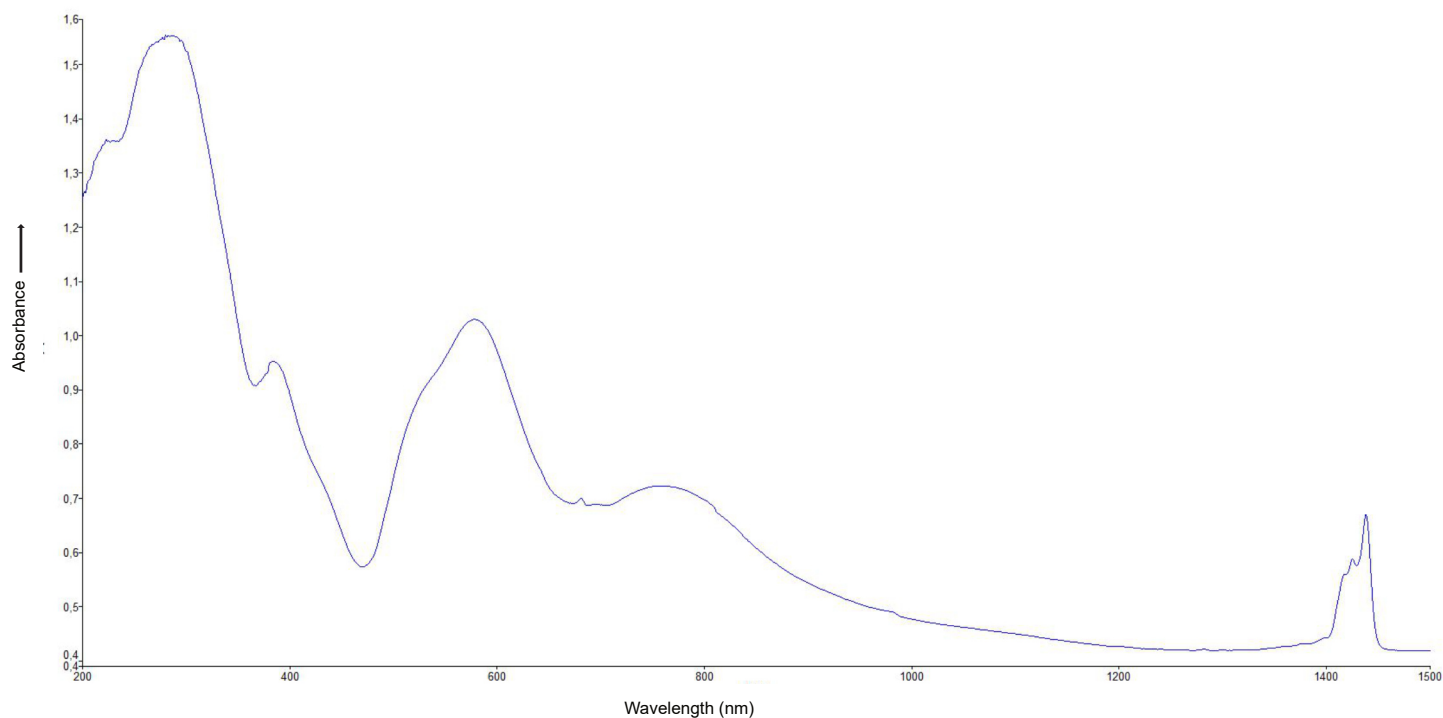
Raman spectrum



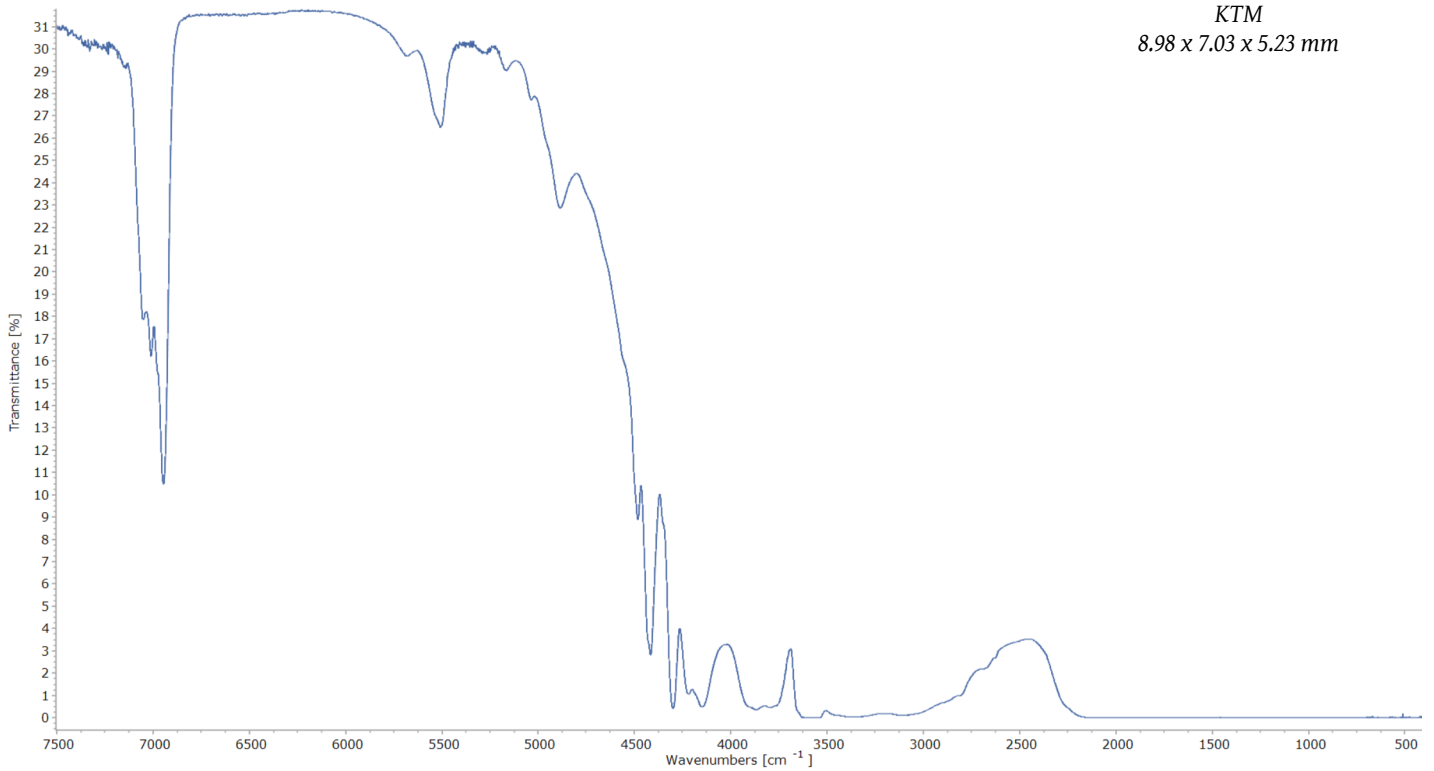
KTM
8.98 x 7.03 x 5.23 mm



UV-Vis-NIR spectrum



FTIR spectrum



KTM
8.98 x 7.03 x 5.23 mm

EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	43.93	0.26	Al	23.25	0.14
SiO2	30.25	0.23	Si	14.14	0.11
MgO	21.04	0.20	Mg	12.69	0.12
Cr2O3	0.251	0.017	Cr	0.172	0.011
Fe2O3	0.0760	0.0084	Fe	0.0532	0.0059
MnO	0.0632	0.0048	Mn	0.0489	0.0037
CaO	0.0392	0.0025	Ca	0.0280	0.0018
TiO2	0.0260	0.0025	Ti	0.0156	0.0015
Sc2O3	0.0194	0.0018	Sc	0.0126	0.0012
V2O5	0.0063	0.0011	V	0.0035	0.0006
Ga2O3	0.0051	0.0005	Ga	0.0038	0.0004

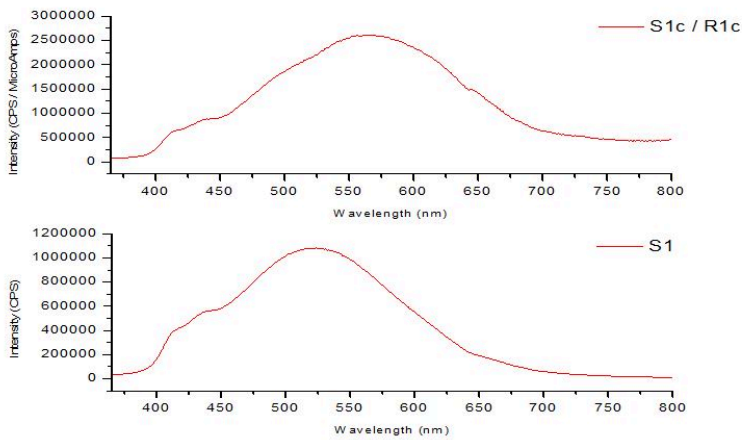
KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
Sum Conc's before normalisation to 100% : 77.5 %

Emission spectra

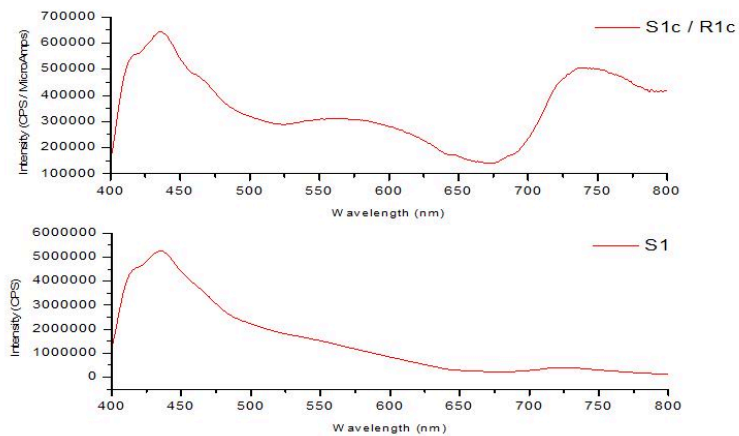


KTM

8.98 x 7.03 x 5.23 mm

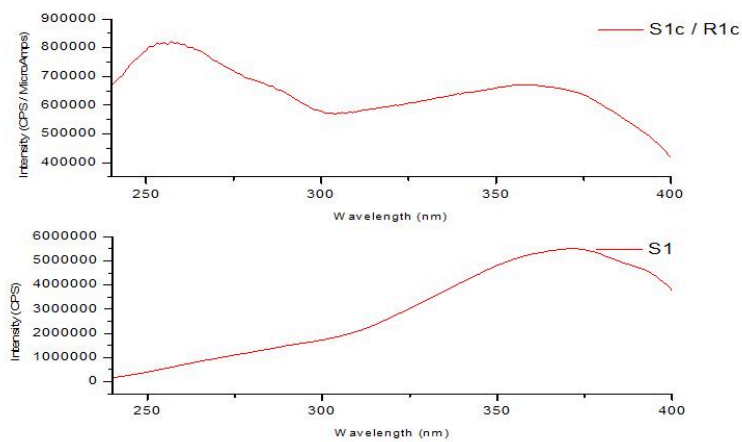


Emission spectra
under $\lambda_{ex} = 254\text{nm}$
at room temperature
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$
at room temperature
S1: measured
S1c/R1c: corrected

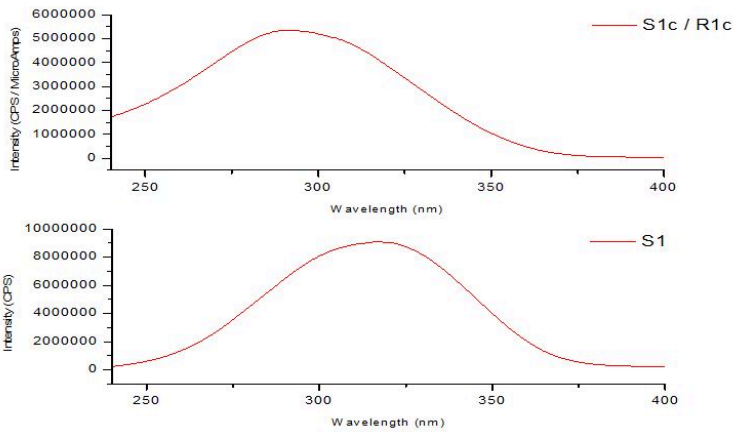
Excitation spectra



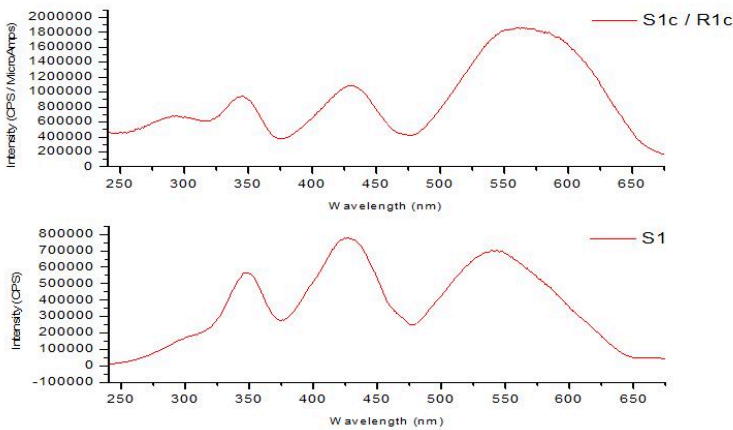
Excitation spectra
under $\lambda_{em} = 435\text{nm}$
at room temperature
S1: measured
S1c/R1c: corrected



KTM
8.98 x 7.03 x 5.23 mm



Excitation spectra
under $\lambda_{em} = 565nm$ at
room temperature
S1: measured
S1c/R1c: corrected



Excitation spectra
under $\lambda_{em} = 740nm$ at
room temperature
S1: measured
S1c/R1c: corrected

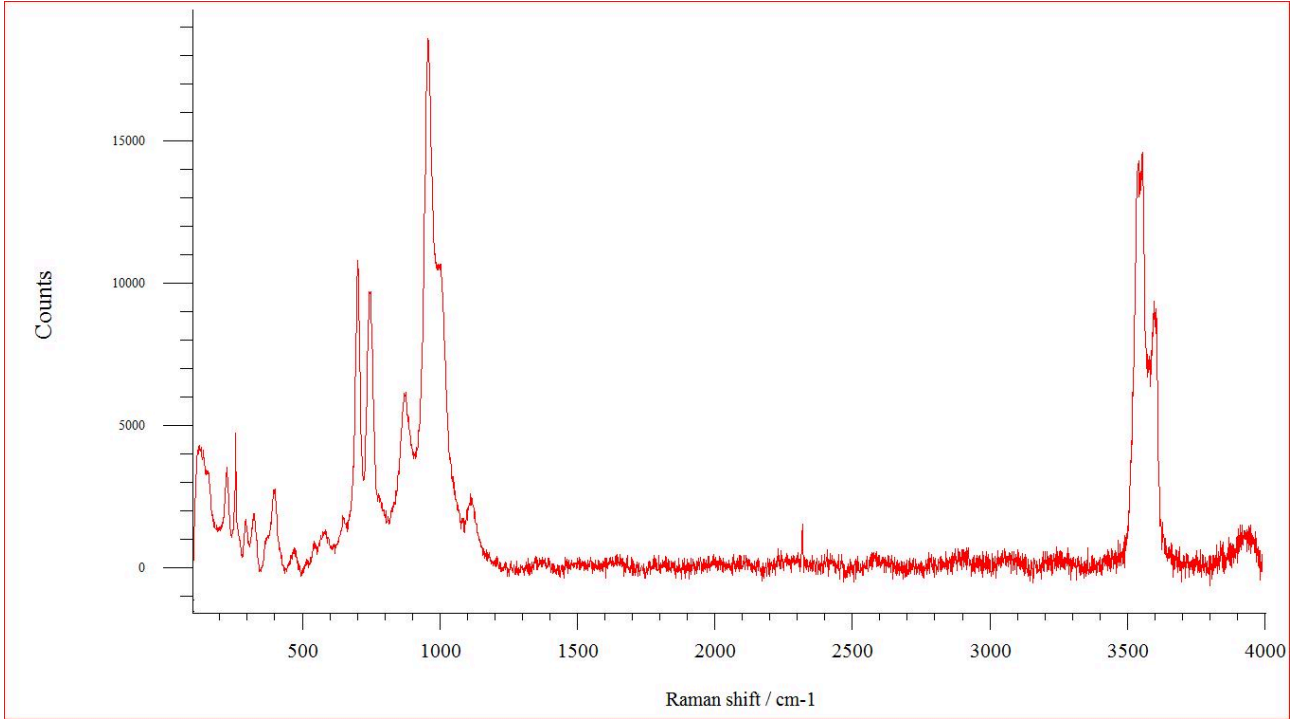
Appendix

Sample KUD6

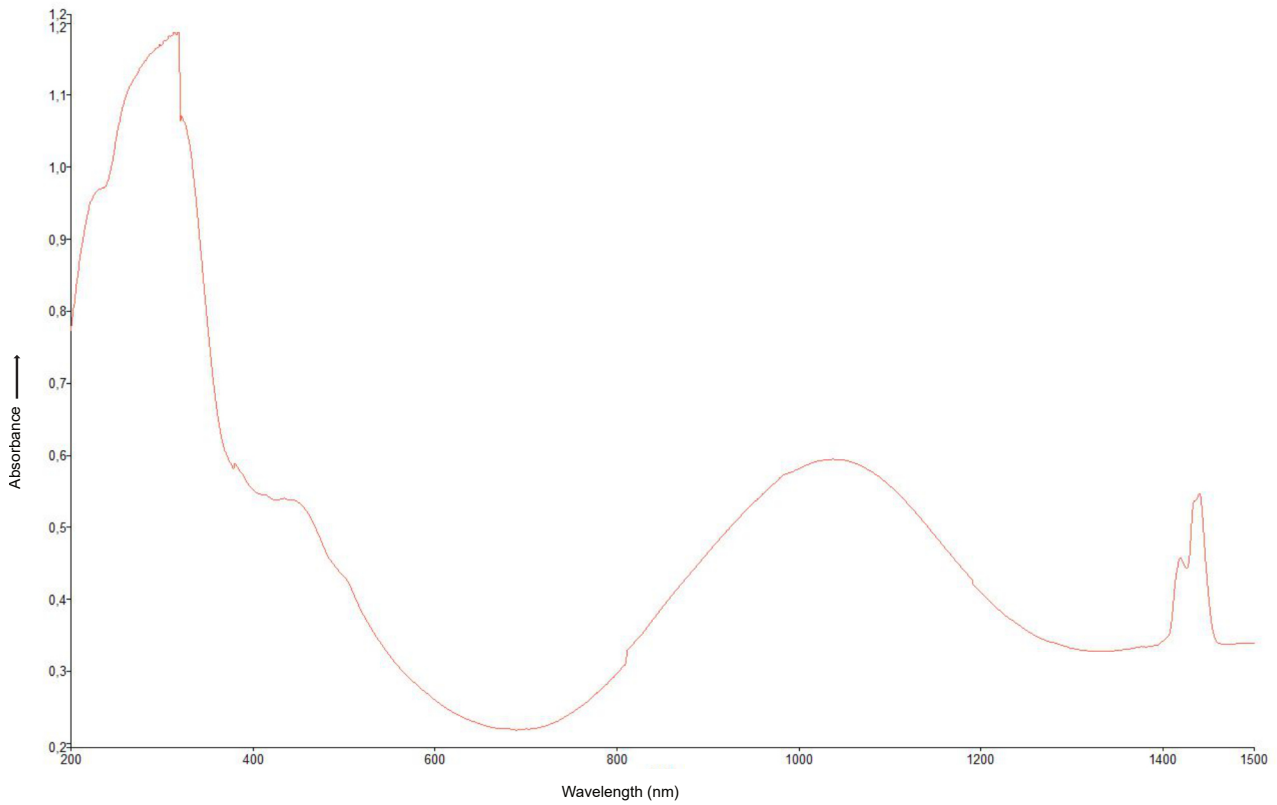


KUD6
8.66 x 7.96 x 5.57 mm

Raman spectrum



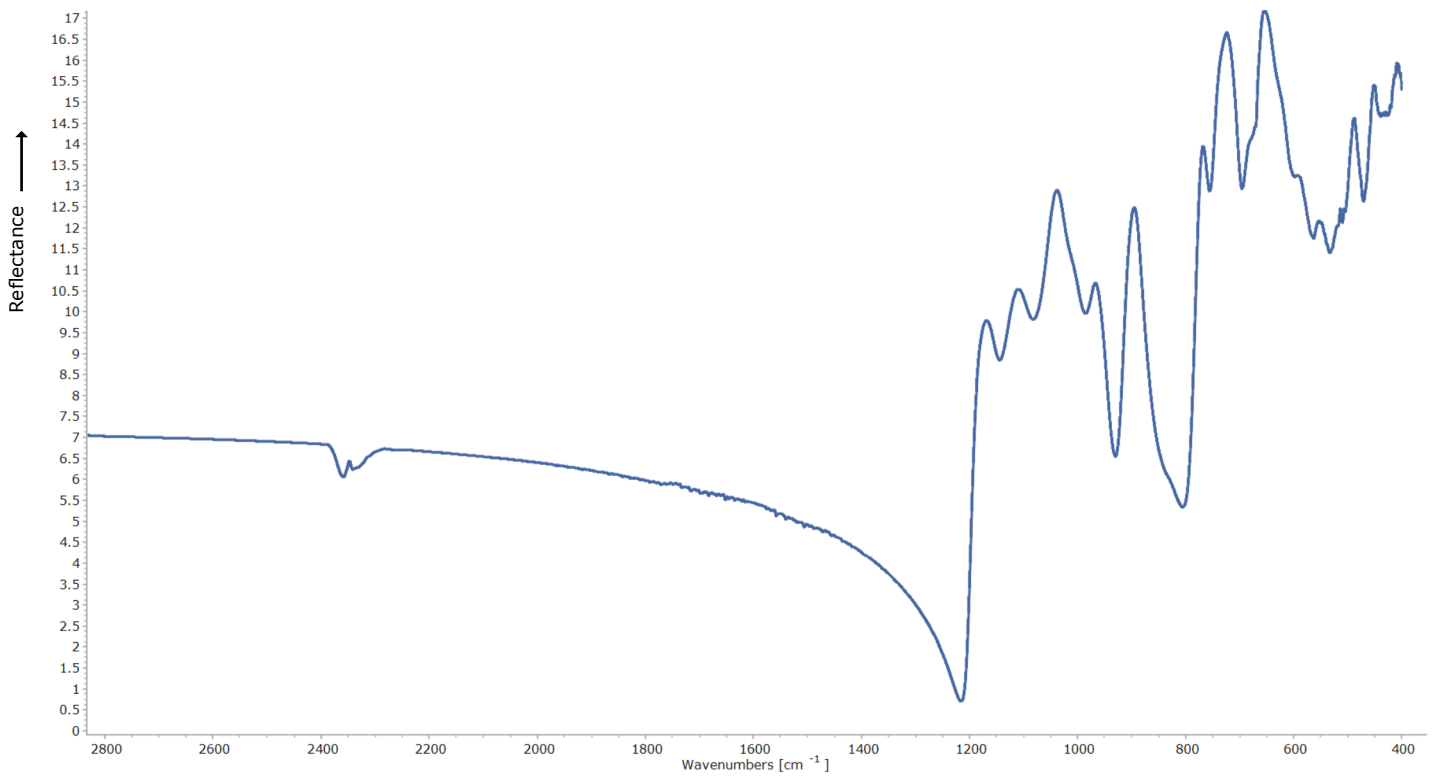
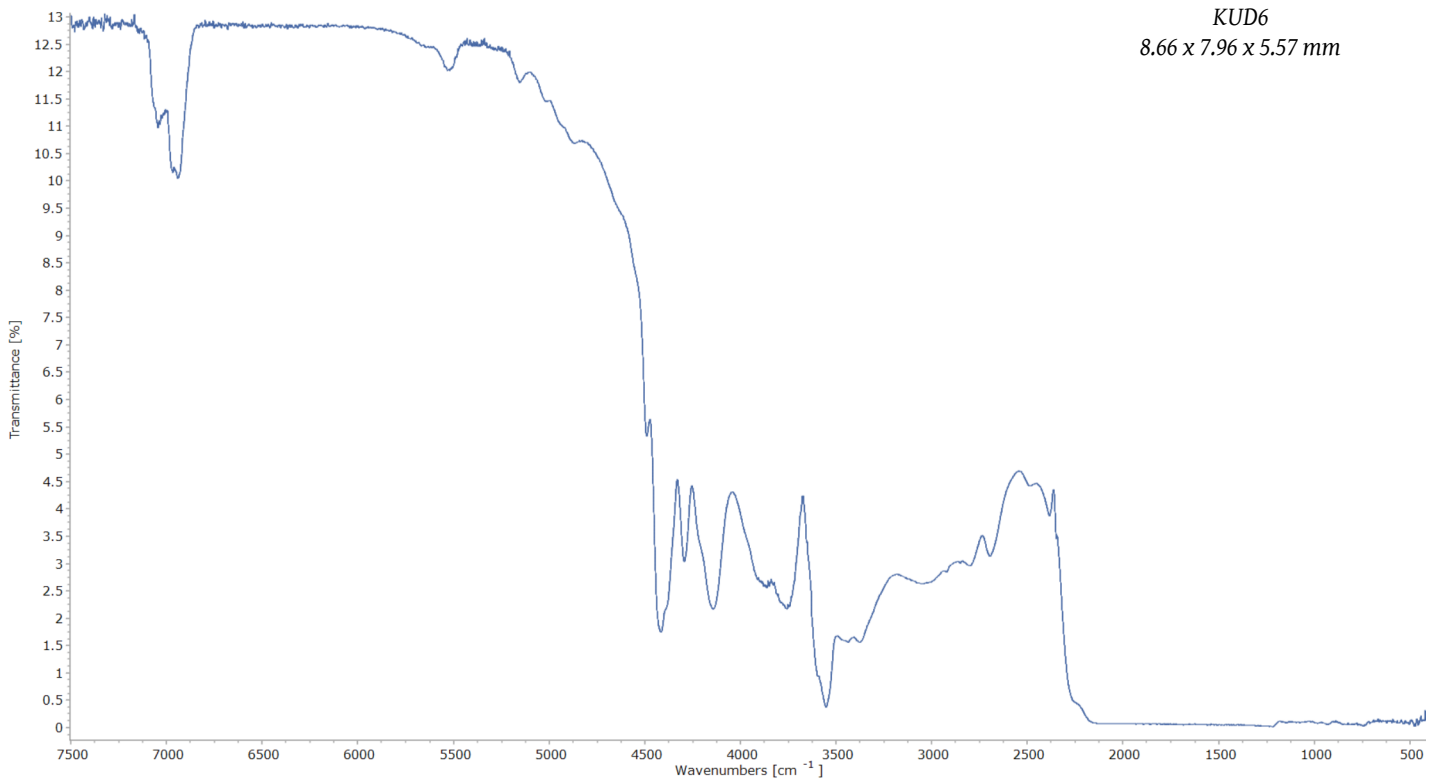
UV-Vis-NIR spectrum



FTIR spectra (absorption & reflectance)



KUD6
8.66 x 7.96 x 5.57 mm





KUD6

8.66 x 7.96 x 5.57 mm

EDXRF analysis

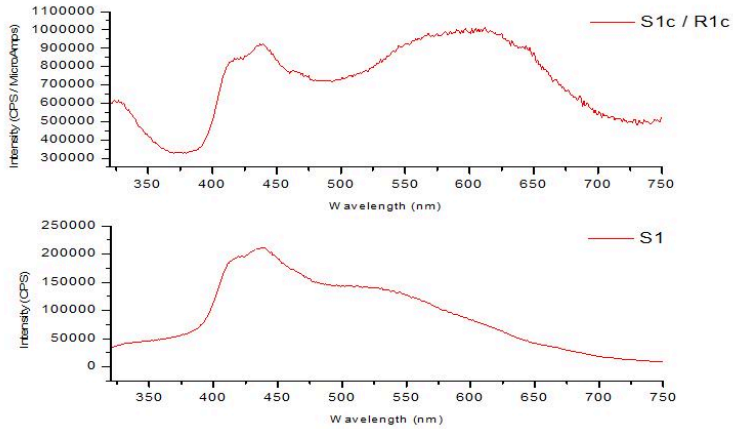
Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	46.31	0.26	Al	24.51	0.14
SiO2	27.92	0.22	Si	13.05	0.10
MgO	19.75	0.20	Mg	11.91	0.12
Fe2O3	1.38	0.13	Fe	0.966	0.091
TiO2	0.150	0.015	Ti	0.0902	0.0088
CaO	0.101	0.005	Ca	0.0726	0.0036
V2O5	0.0152	0.0017	V	0.0085	0.0009
MnO	0.0149	0.0017	Mn	0.0115	0.0013
Cr2O3	0.0125	0.0009	Cr	0.0086	0.0006
Co3O4	0.0122	0.0033	Co	0.0090	0.0024
Cl	0.0104	0.0031	Cl	0.0104	0.0031
K2O	0.0066	0.0016	K	0.0055	0.0013

KnownConc= 3.30 B203 REST= 1.00 H20 D/S= 0
 Sum Conc's before normalisation to 100% : 76.0 %

Emission spectra

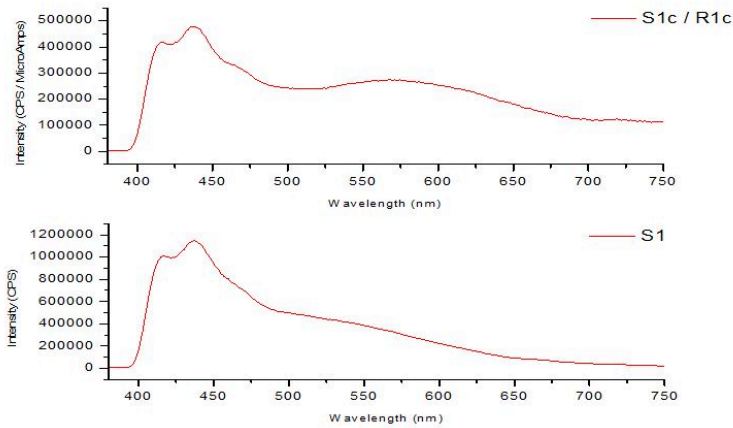


KUD6
8.66 x 7.96 x 5.57 mm



Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature

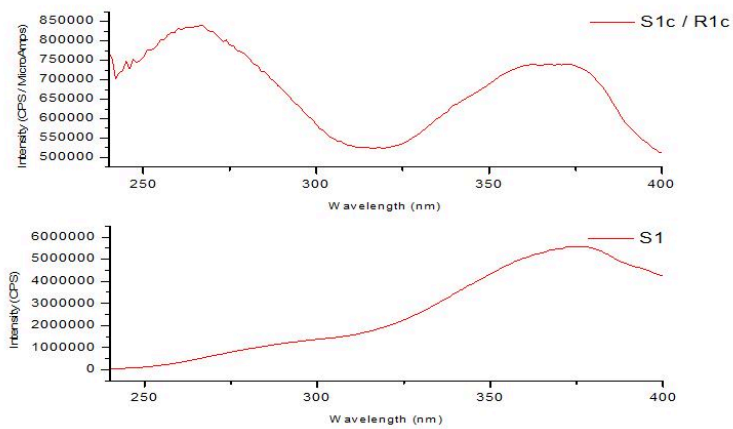
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra

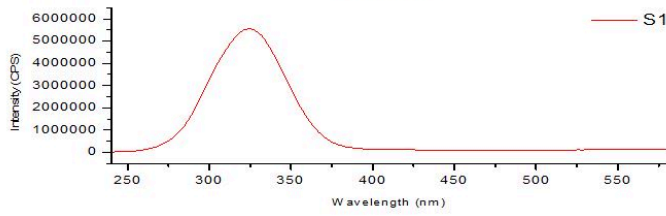
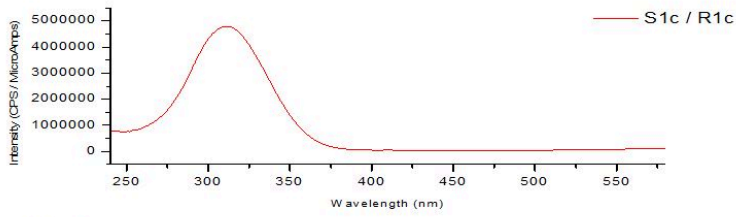


Excitation spectra
under $\lambda_{em} = 430\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected



KUD6
8.66 x 7.96 x 5.57 mm



Excitation spectra
under $\lambda_{em} = 610\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected

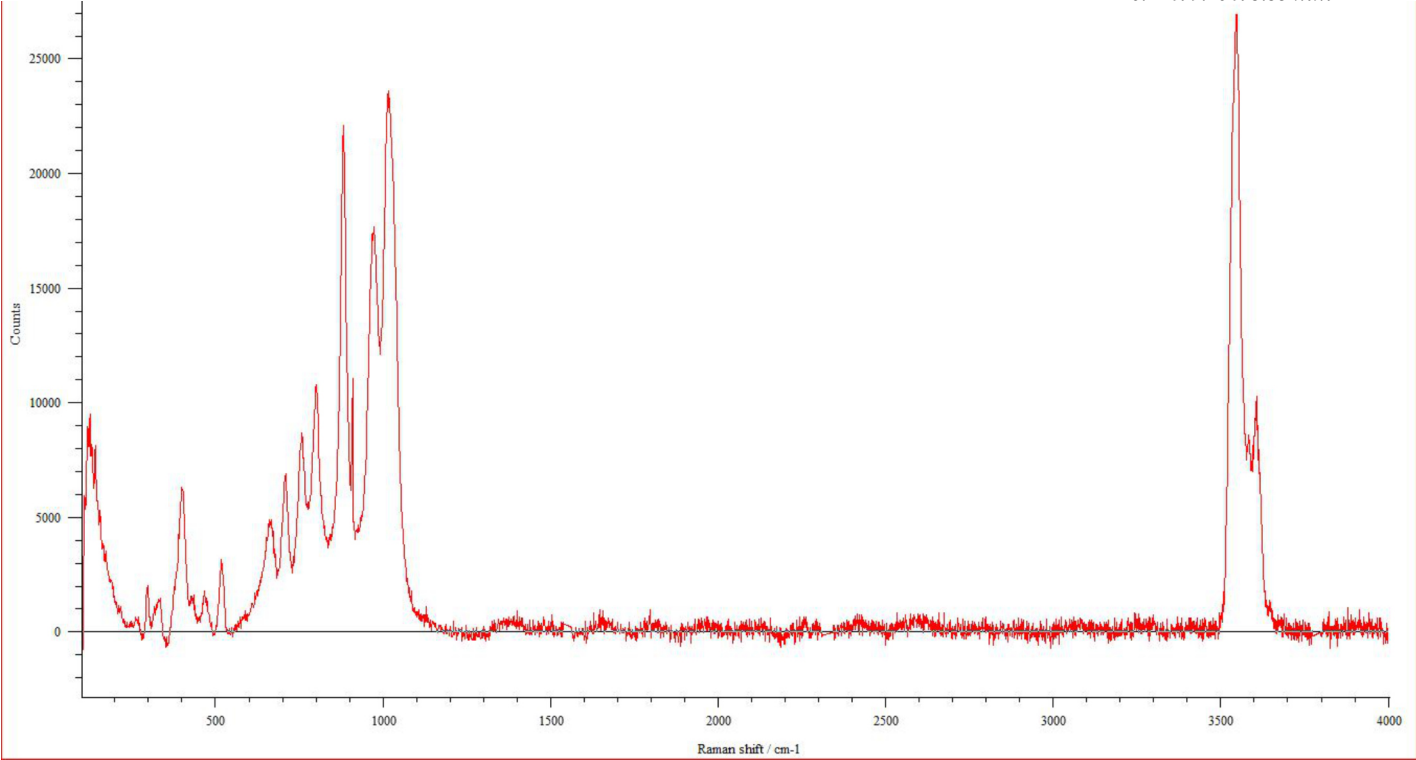
Appendix

Sample KUD3

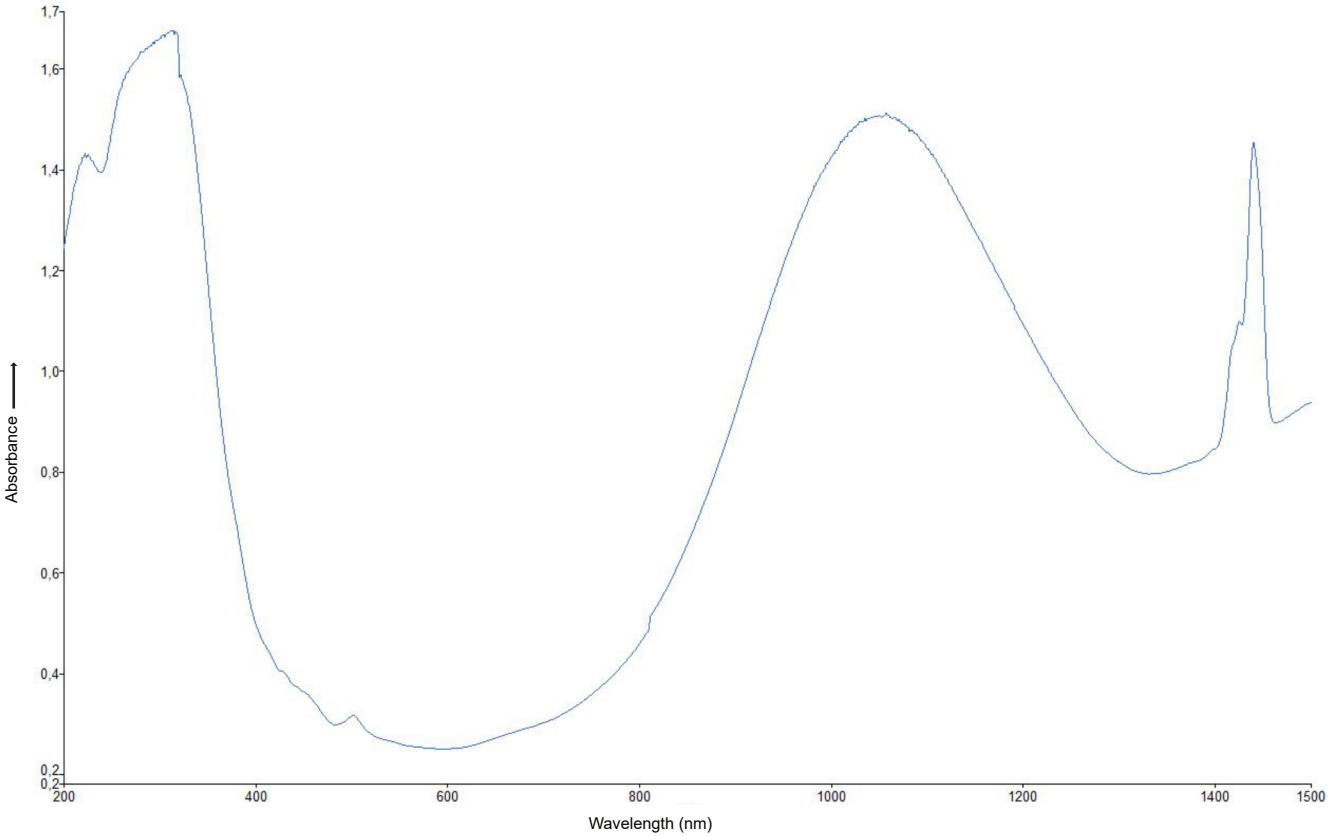
Raman spectrum



KUD3
10.14 x 9.10 x 5.53 mm



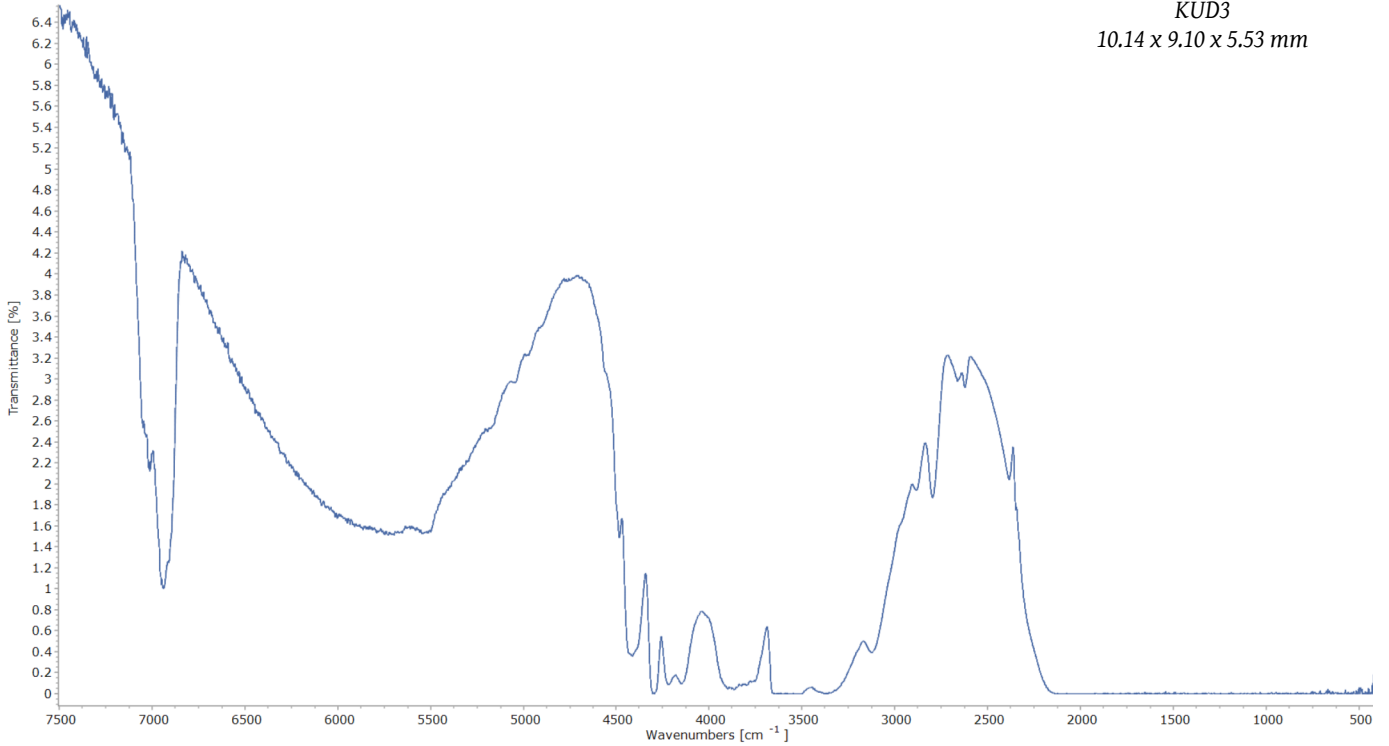
UV-Vis-NIR spectrum



FTIR spectrum



KUD3
10.14 x 9.10 x 5.53 mm



EDXRF analysis

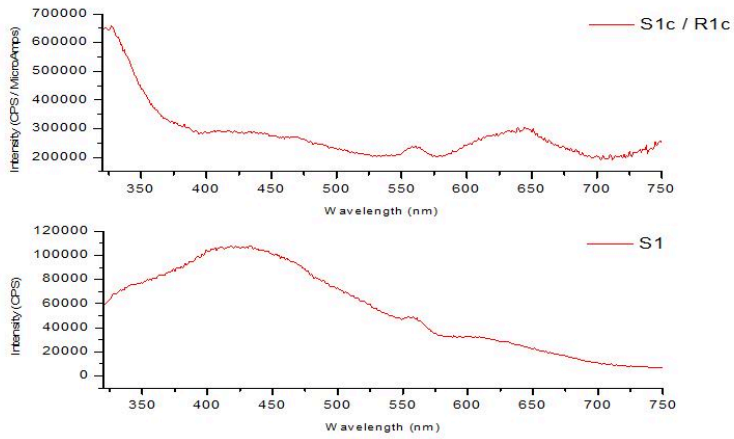
Compound	m/m%	StdErr	EL	m/m%	StdErr
Al2O3	42.54	0.26	Al	22.51	0.14
SiO2	29.92	0.22	Si	13.99	0.10
MgO	19.91	0.20	Mg	12.01	0.12
Fe2O3	3.05	0.19	Fe	2.13	0.13
CaO	0.147	0.007	Ca	0.105	0.005
Co3O4	0.0309	0.0073	Co	0.0227	0.0053
TiO2	0.0254	0.0025	Ti	0.0152	0.0015
MnO	0.0187	0.0019	Mn	0.0145	0.0015
ZnO	0.0109	0.0006	Zn	0.0088	0.0005
Cl	0.0101	0.0032	Cl	0.0101	0.0032
V2O5	0.0094	0.0011	V	0.0053	0.0006
K2O	0.0093	0.0017	K	0.0077	0.0014
Ga2O3	0.0073	0.0006	Ga	0.0054	0.0005

KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
 Sum Conc's before normalisation to 100% : 85.7 %

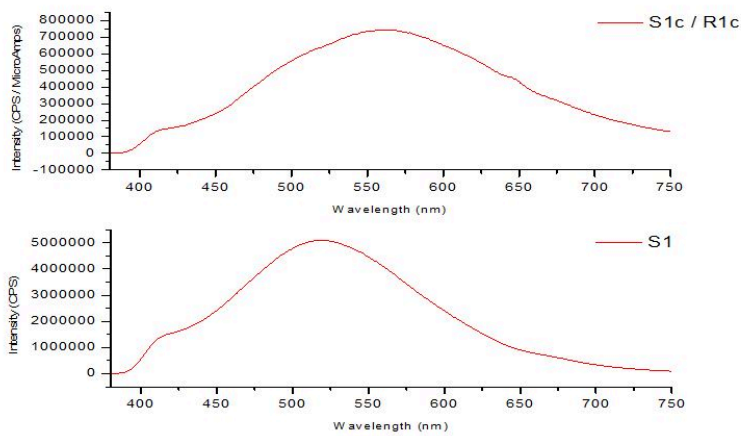
Emission spectra



KUD3
10.14 x 9.10 x 5.53 mm

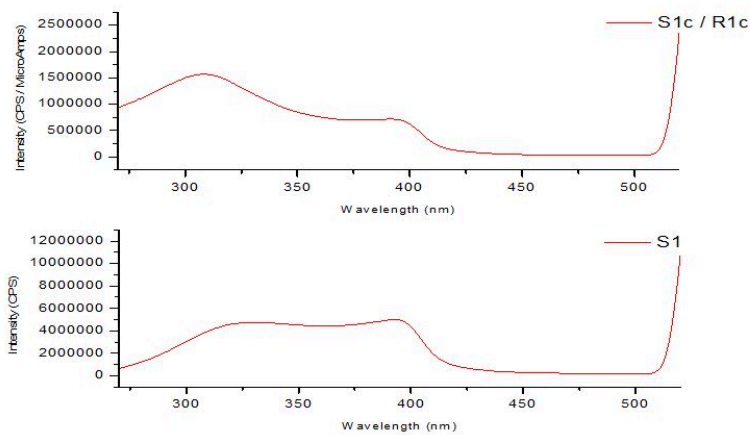


Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 550\text{nm}$ at
room temperature
S1: measured
S1c/R1c: corrected

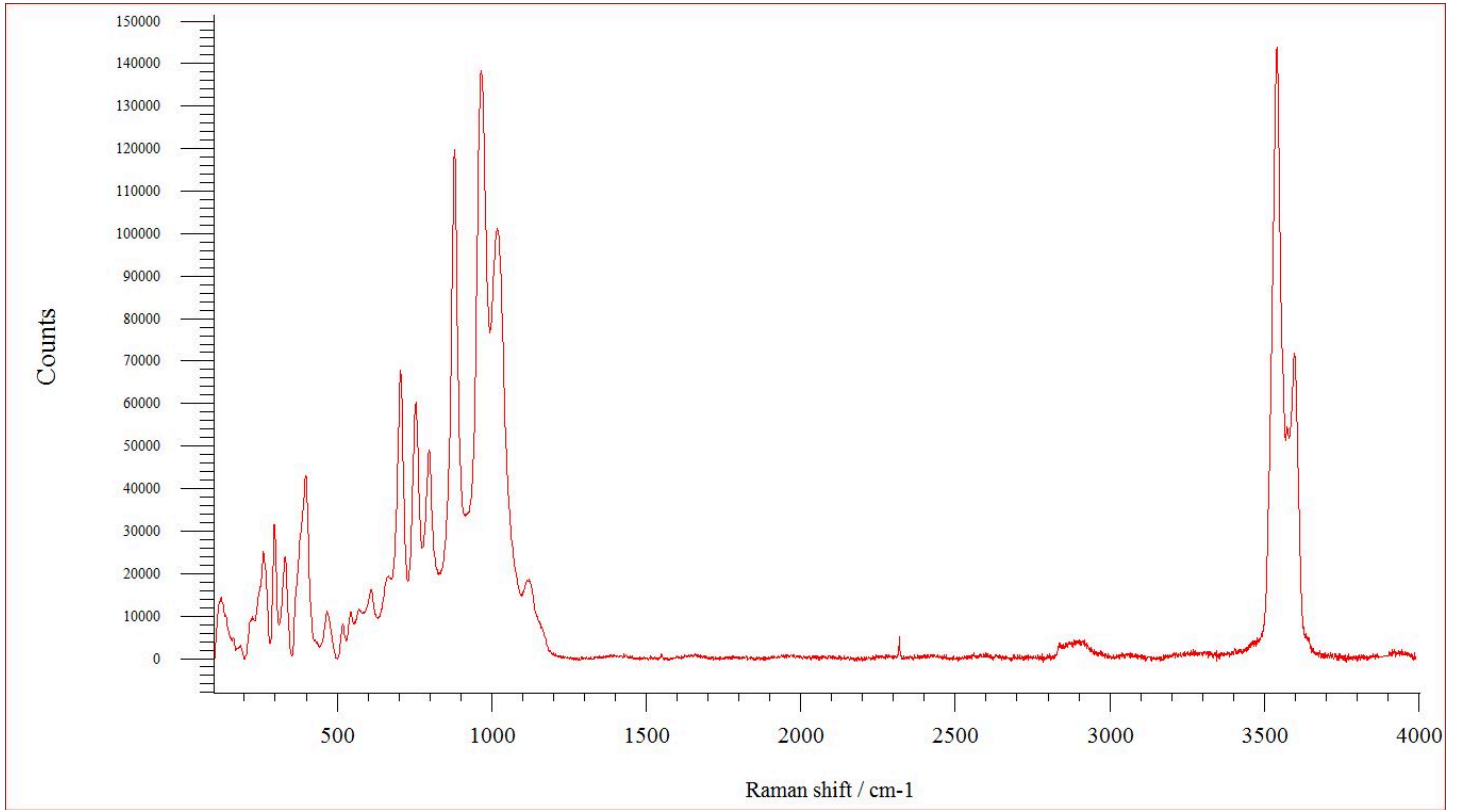
Appendix

Sample KSE4637

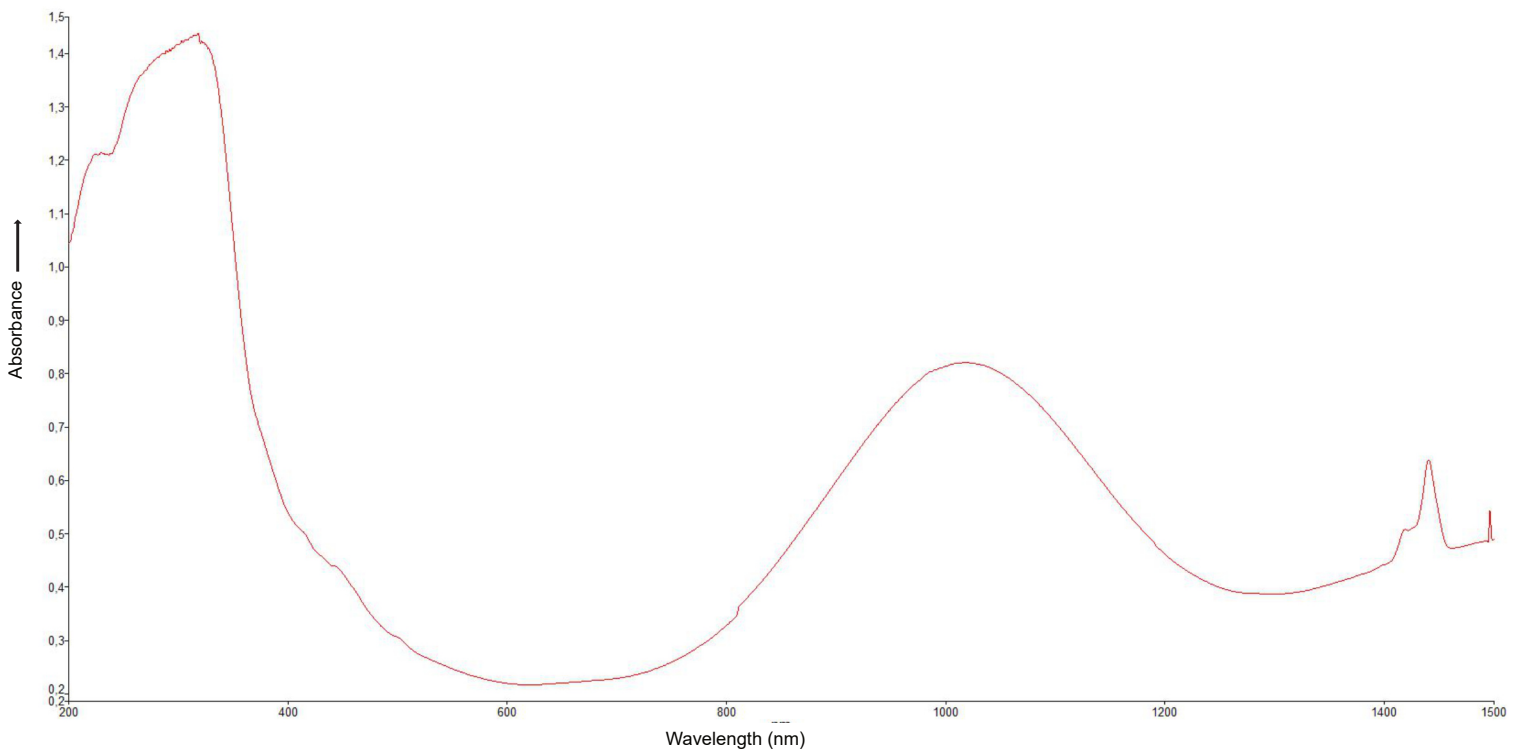
Raman spectrum



KSE4637
7.66 x 7.47 x 5.28 mm



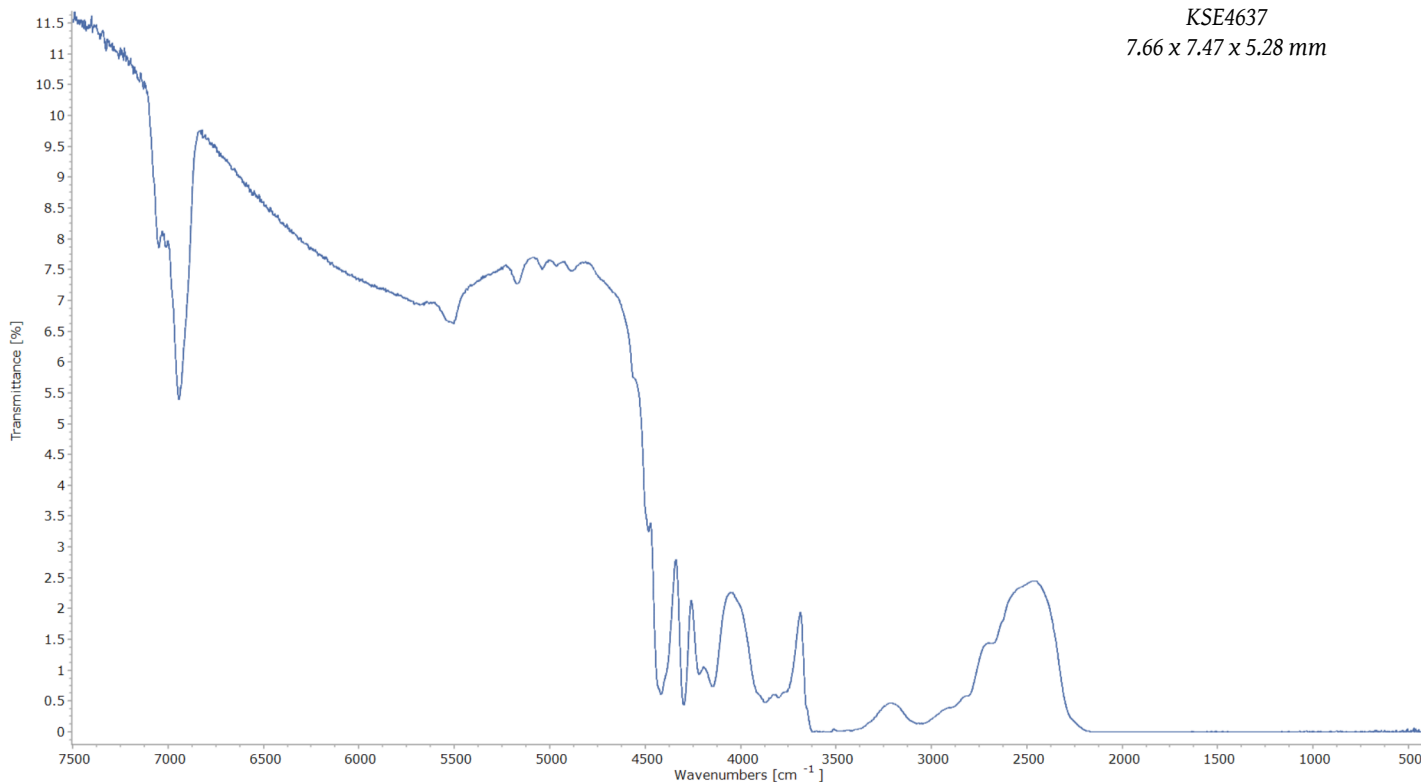
UV-Vis-NIR spectrum





KSE4637
7.66 x 7.47 x 5.28 mm

FTIR spectrum



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	42.99	0.26	Al	22.75	0.14
SiO2	30.13	0.22	Si	14.08	0.11
MgO	20.33	0.20	Mg	12.26	0.12
Fe2O3	2.04	0.16	Fe	1.43	0.11
CaO	0.0585	0.0029	Ca	0.0418	0.0021
TiO2	0.0523	0.0051	Ti	0.0314	0.0031
V2O5	0.0263	0.0016	V	0.0147	0.0009
MnO	0.0245	0.0020	Mn	0.0190	0.0016
Co3O4	0.0180	0.0049	Co	0.0132	0.0036
K2O	0.0143	0.0020	K	0.0119	0.0017

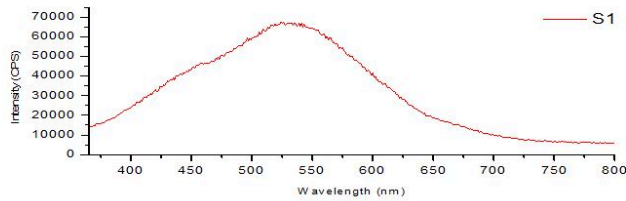
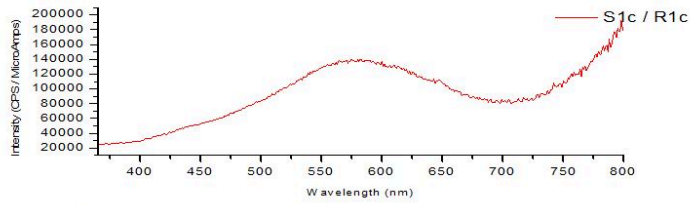
KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
Sum Conc's before normalisation to 100% : 82.0 %



KSE4637

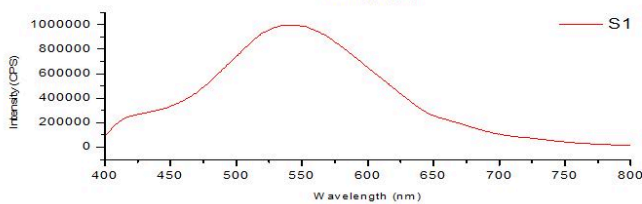
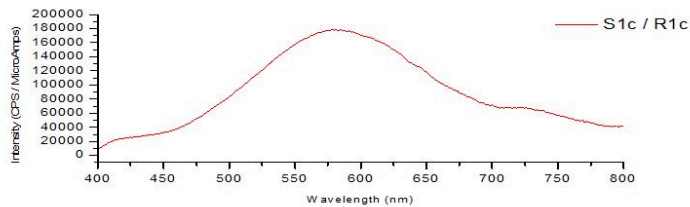
7.66 x 7.47 x 5.28 mm

Emission spectra



Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature

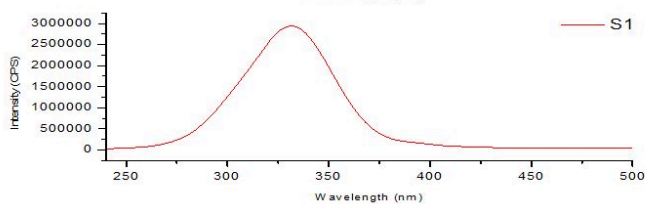
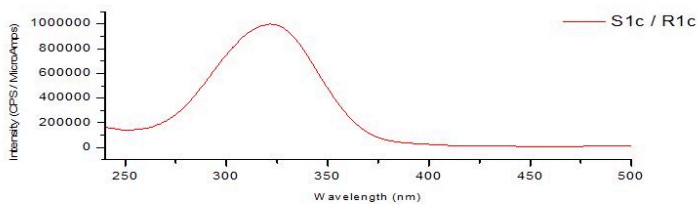
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 580\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

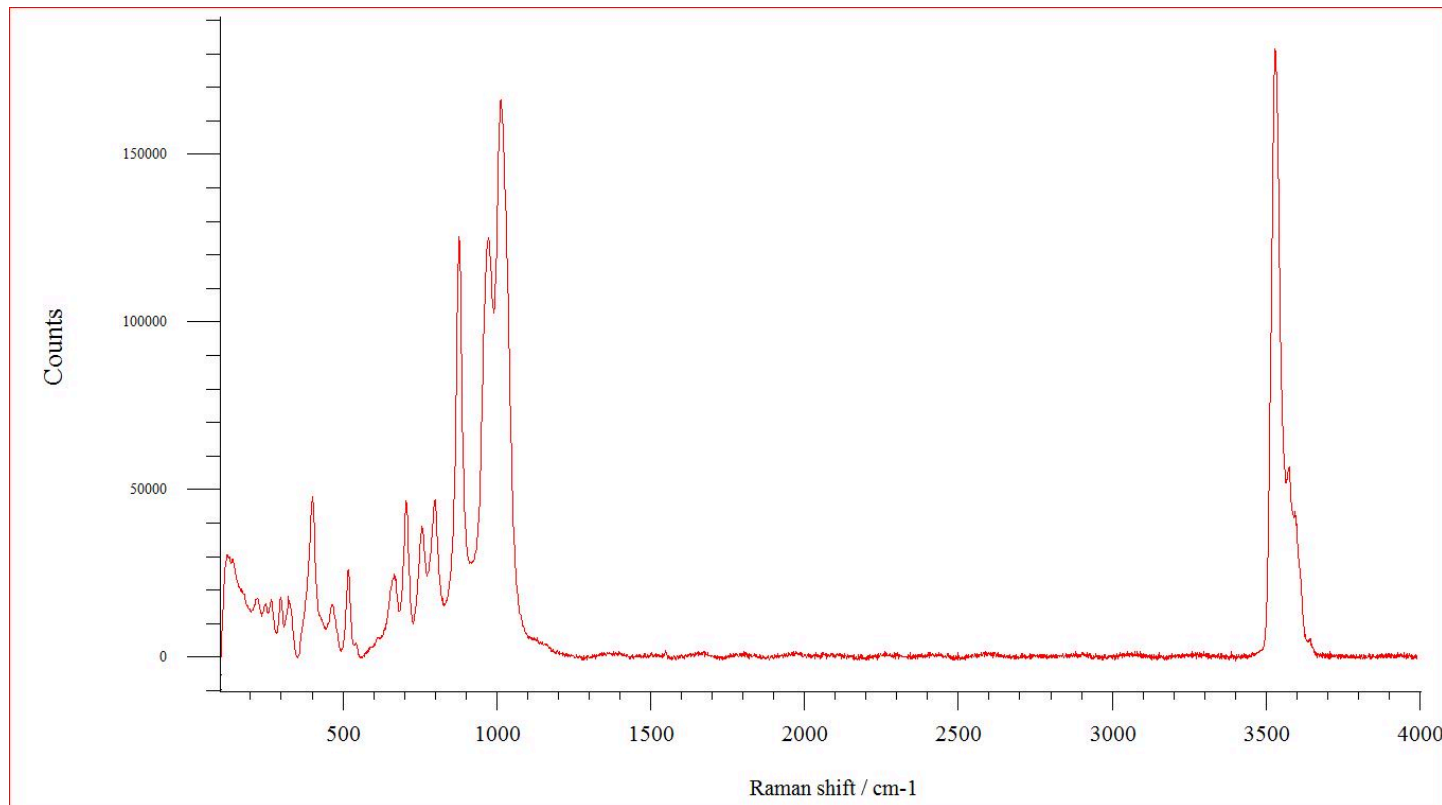
Appendix

Sample KUH

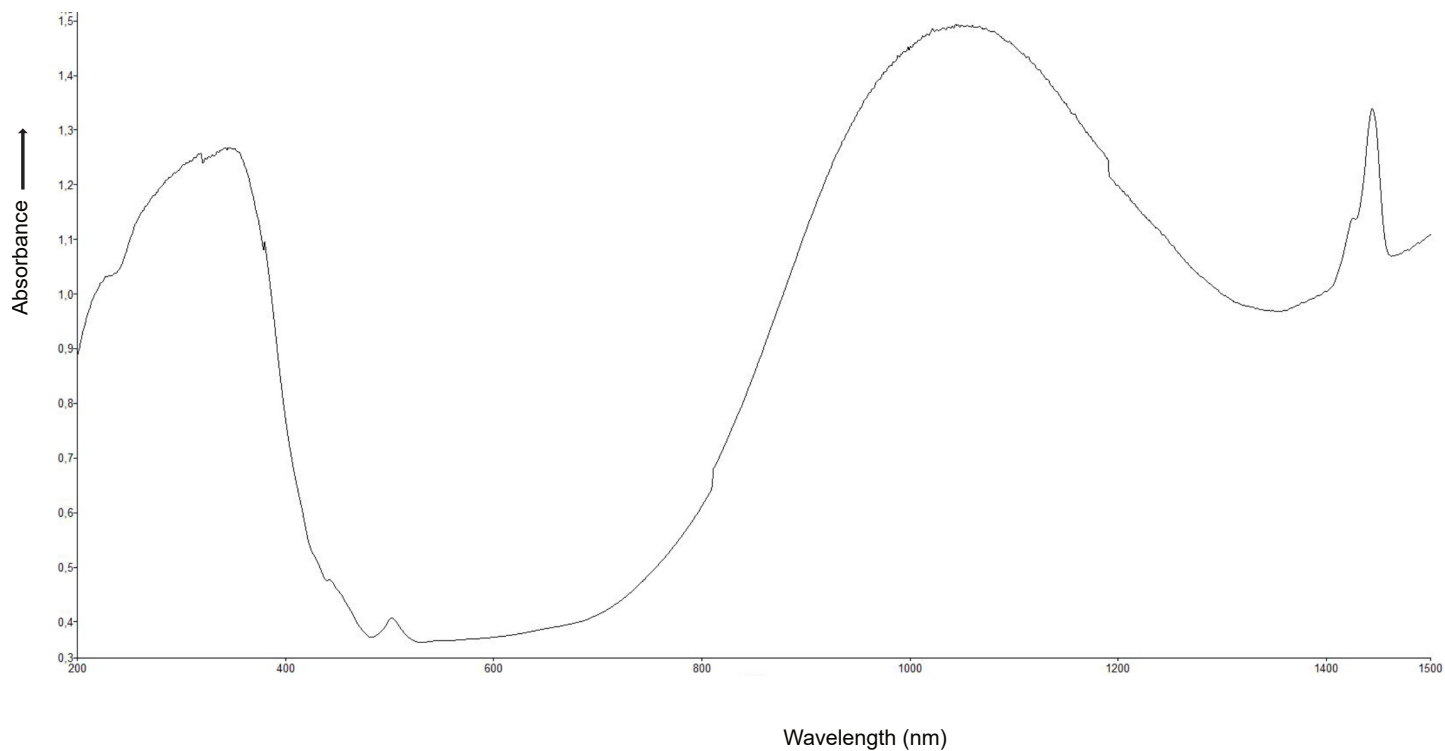
Raman spectrum



KUH
6.51 x 5.38 x 3.43 mm



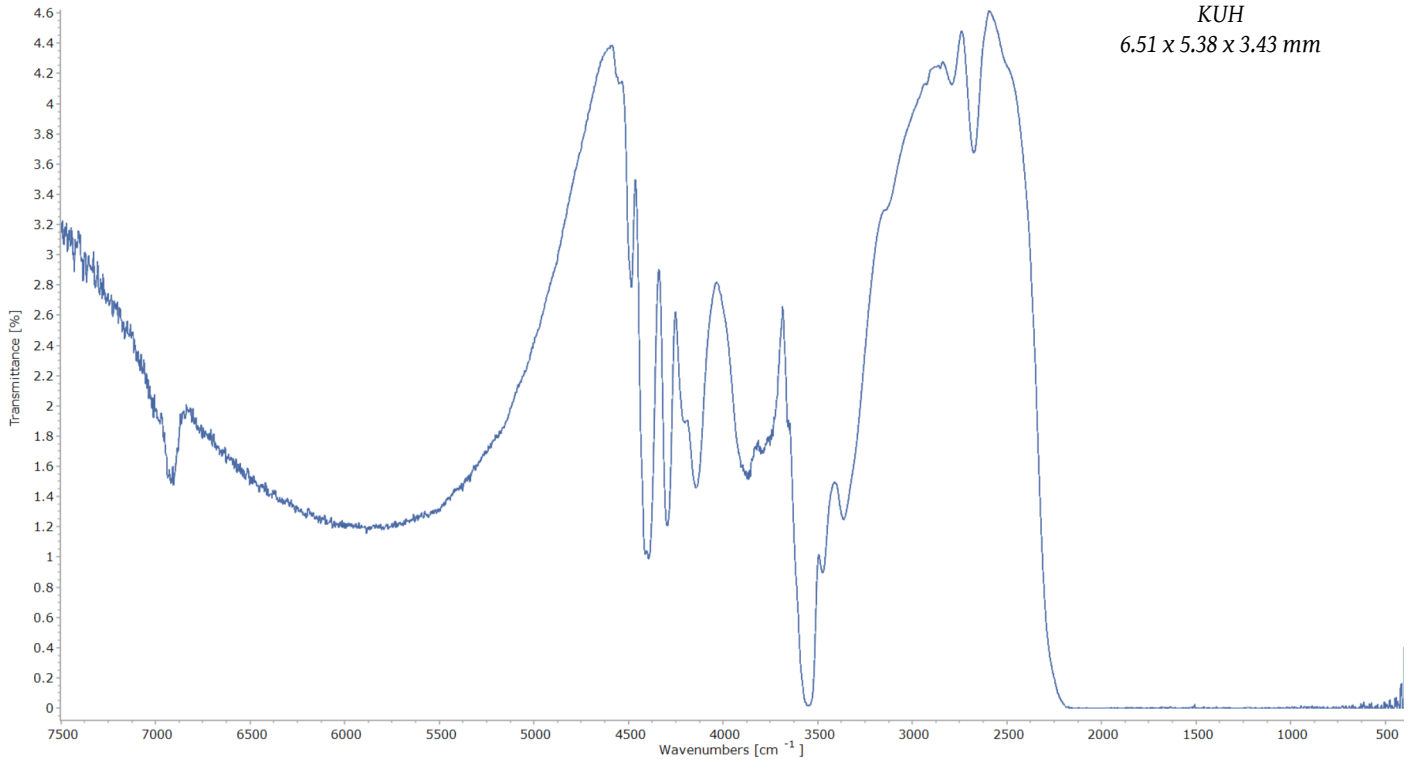
UV-Vis-NIR spectrum



FTIR spectrum



KUH
6.51 x 5.38 x 3.43 mm



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	43.79	0.26	Al	23.18	0.14
SiO2	28.46	0.22	Si	13.31	0.10
MgO	17.63	0.19	Mg	10.63	0.11
Fe2O3	5.57	0.25	Fe	3.90	0.18
MnO	0.111	0.008	Mn	0.0859	0.0065
CaO	0.0442	0.0027	Ca	0.0316	0.0019
Co3O4	0.041	0.013	Co	0.0298	0.0097
ZnO	0.0180	0.0009	Zn	0.0145	0.0007
Ga2O3	0.0123	0.0008	Ga	0.0091	0.0006
Cl	0.0064	0.0031	Cl	0.0064	0.0031

KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
 Sum Conc's before normalisation to 100% : 77.4 %

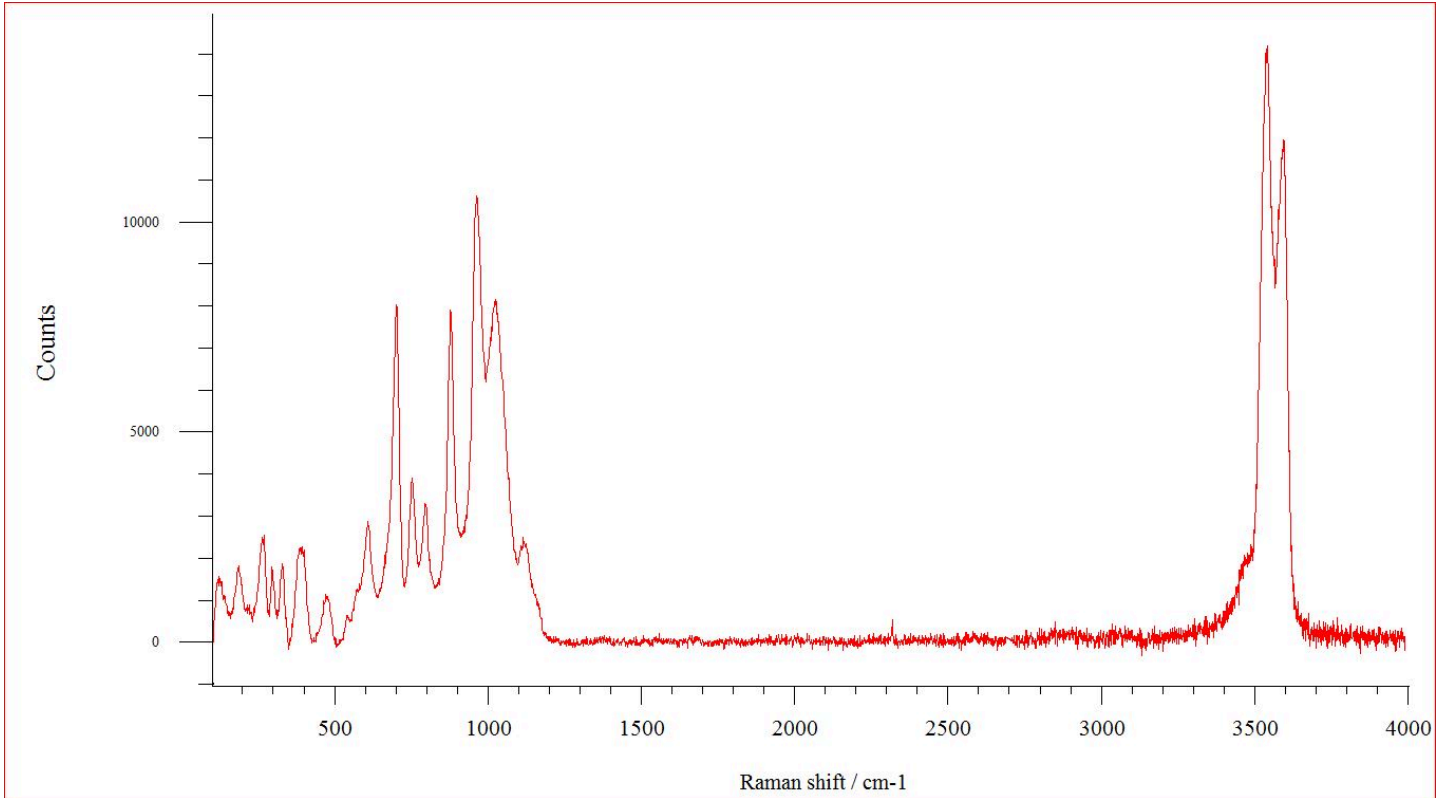
Appendix

Sample KME3887

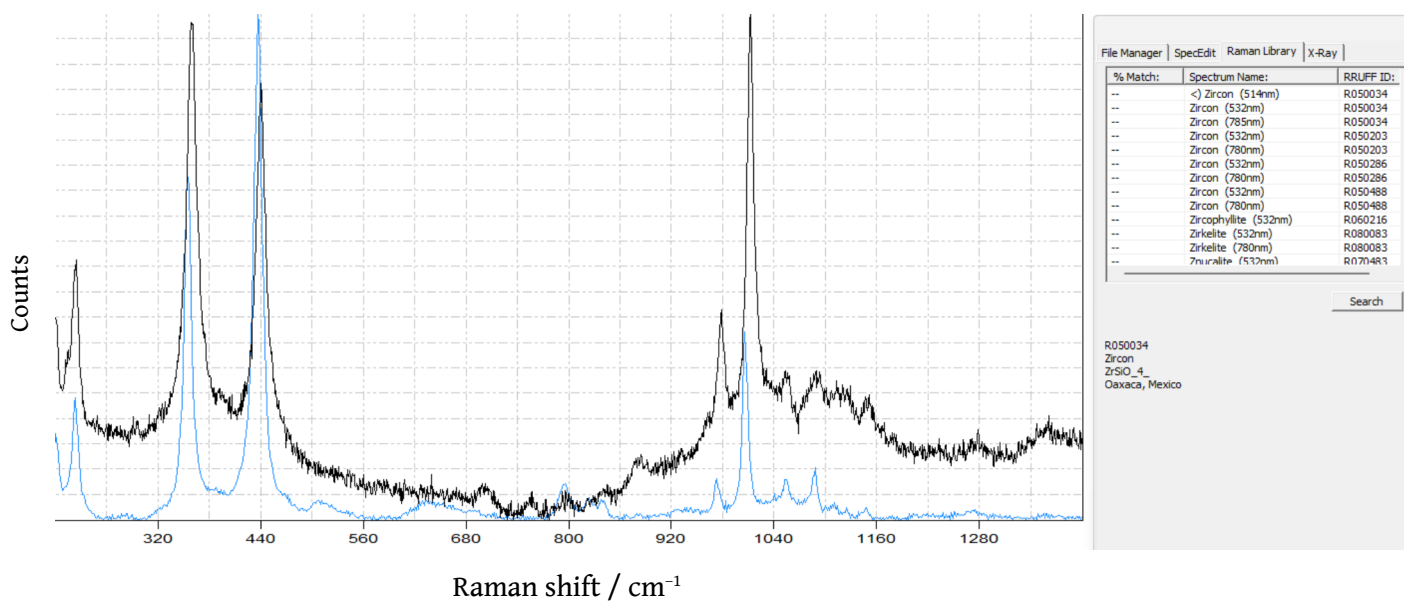


KME3887

Raman spectrum of the sample



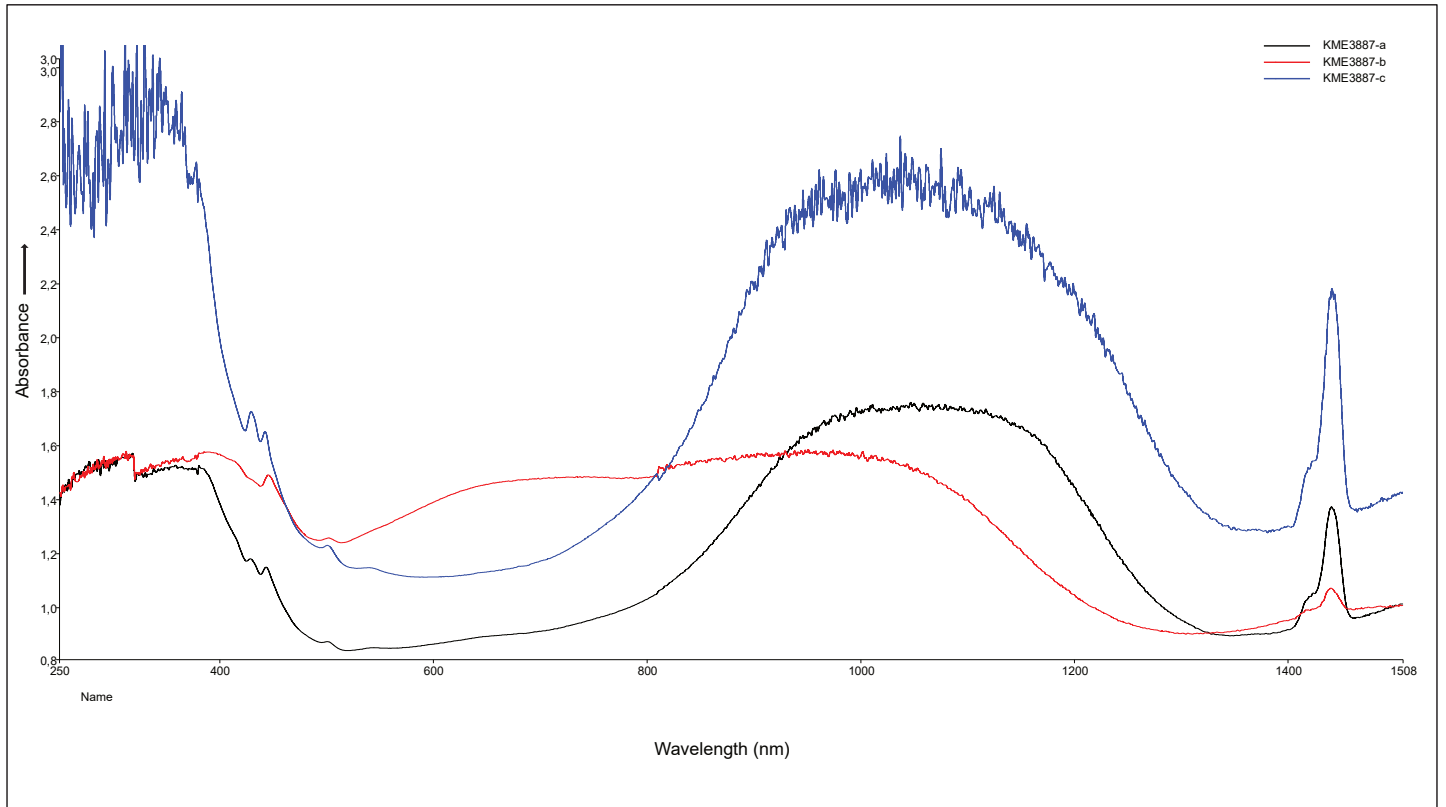
Raman spectrum of the zircon inclusion (black) matching to that of zircon in RRUFF reference data (blue)



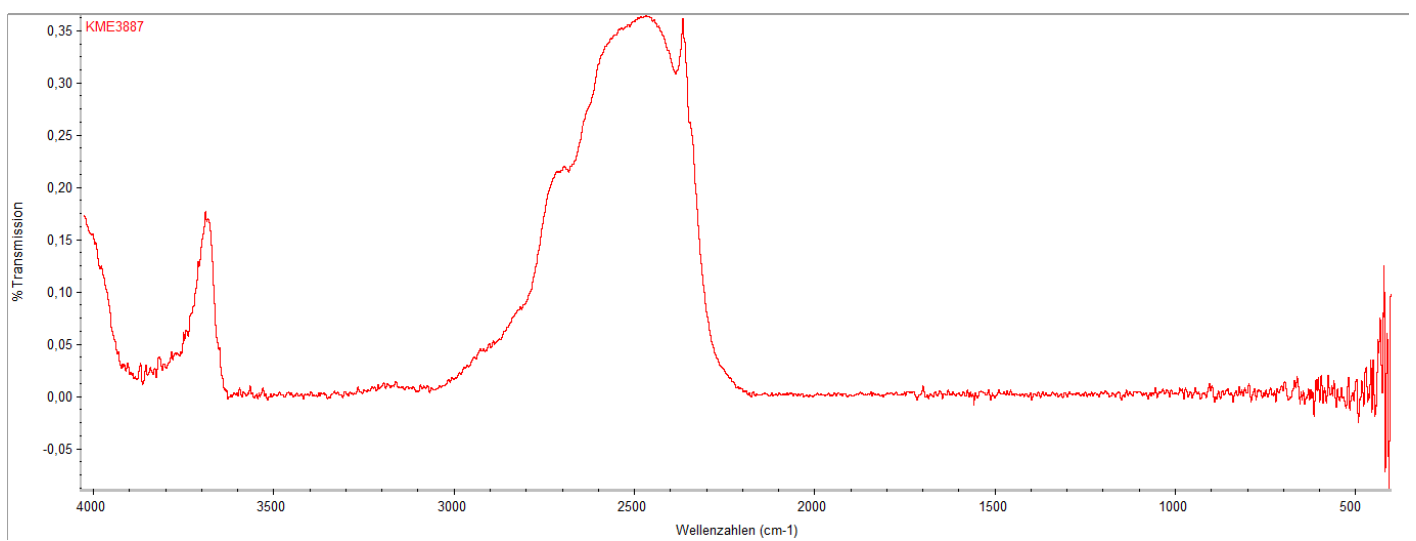


KME3887
8.25 x 6.98 x 3.98 mm

UV-Vis-NIR spectra (polarised)



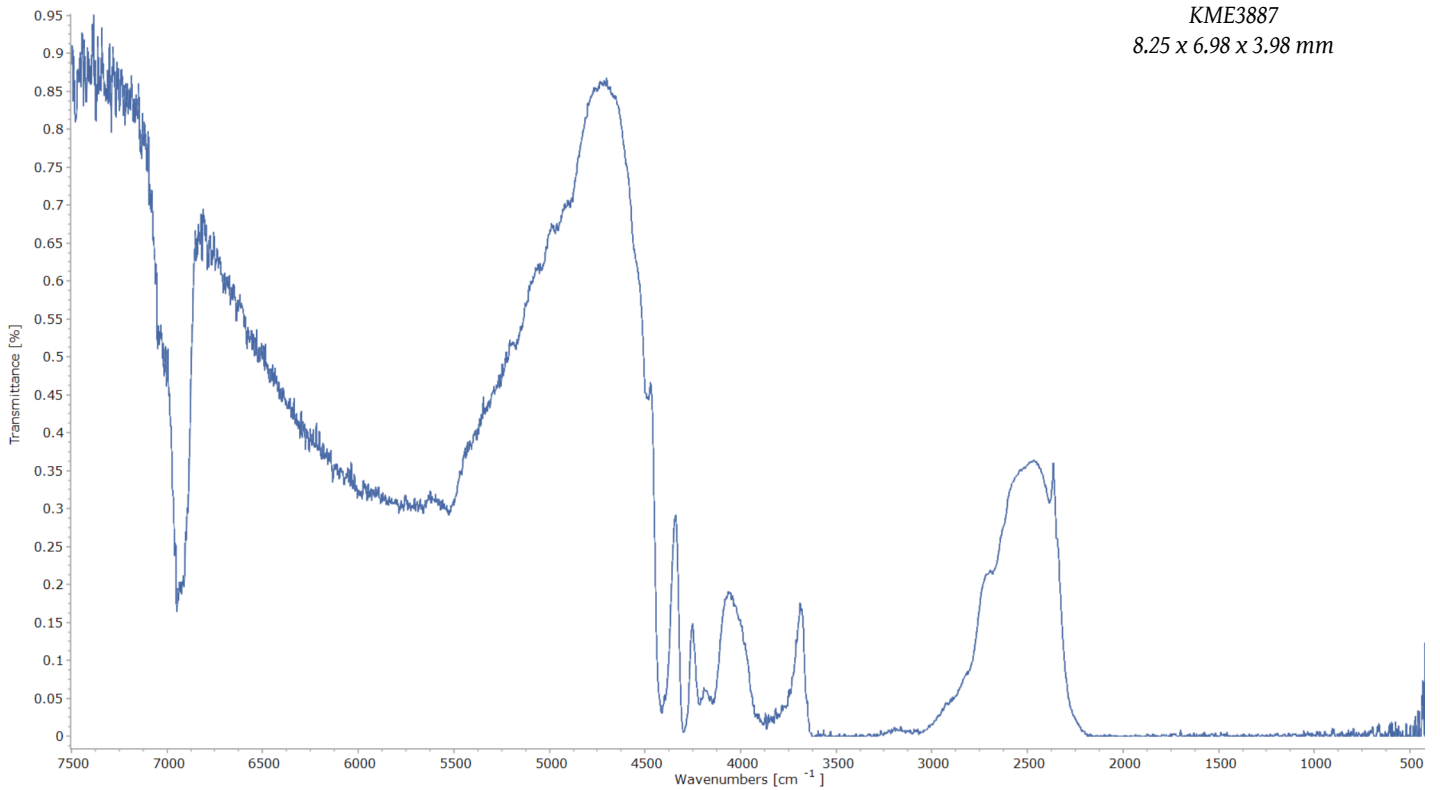
FTIR-Transmission spectrum



FTIR spectrum



KME3887
8.25 x 6.98 x 3.98 mm



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	43.06	0.26	Al	22.79	0.14
SiO2	29.07	0.22	Si	13.59	0.10
MgO	19.22	0.20	Mg	11.59	0.12
Fe2O3	4.04	0.22	Fe	2.83	0.15
MnO	0.147	0.011	Mn	0.114	0.009
CaO	0.0360	0.0023	Ca	0.0257	0.0016
Co3O4	0.0350	0.0096	Co	0.0257	0.0070
TiO2	0.0308	0.0030	Ti	0.0185	0.0018
ZnO	0.0119	0.0007	Zn	0.0096	0.0006
Sc2O3	0.0108	0.0014	Sc	0.0070	0.0009
ZrO2	0.0104	0.0005	Zr	0.0077	0.0004
Cl	0.0095	0.0028	Cl	0.0095	0.0028
K2O	0.0057	0.0013	K	0.0047	0.0011
Y2O3	0.0052	0.0003	Y	0.0041	0.0002

KnownConc= 3.30 B2O3

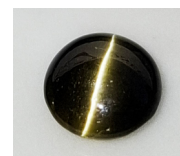
REST= 1.00 H2O

D/S= 0

Sum Conc's before normalisation to 100% : 84.3 %

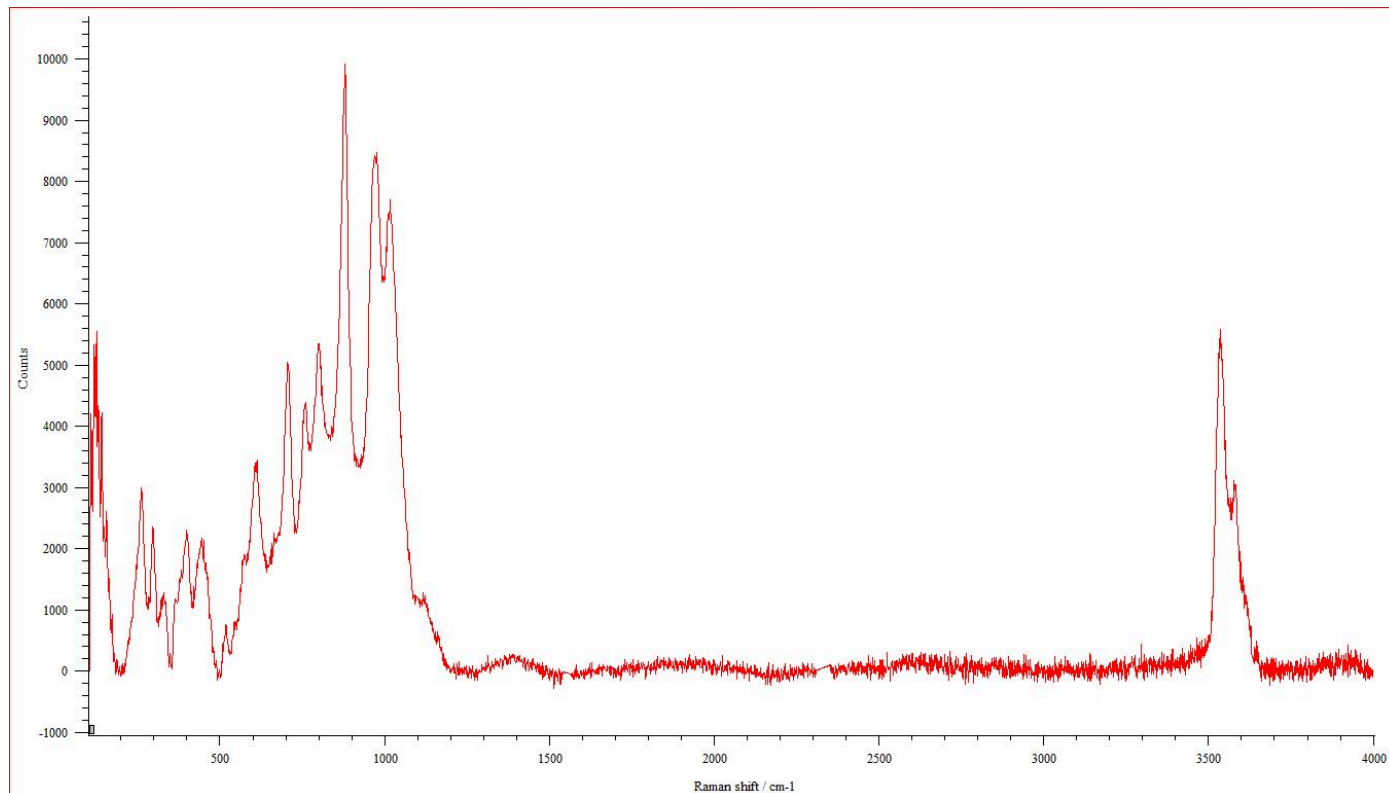
Appendix

Sample KUD8

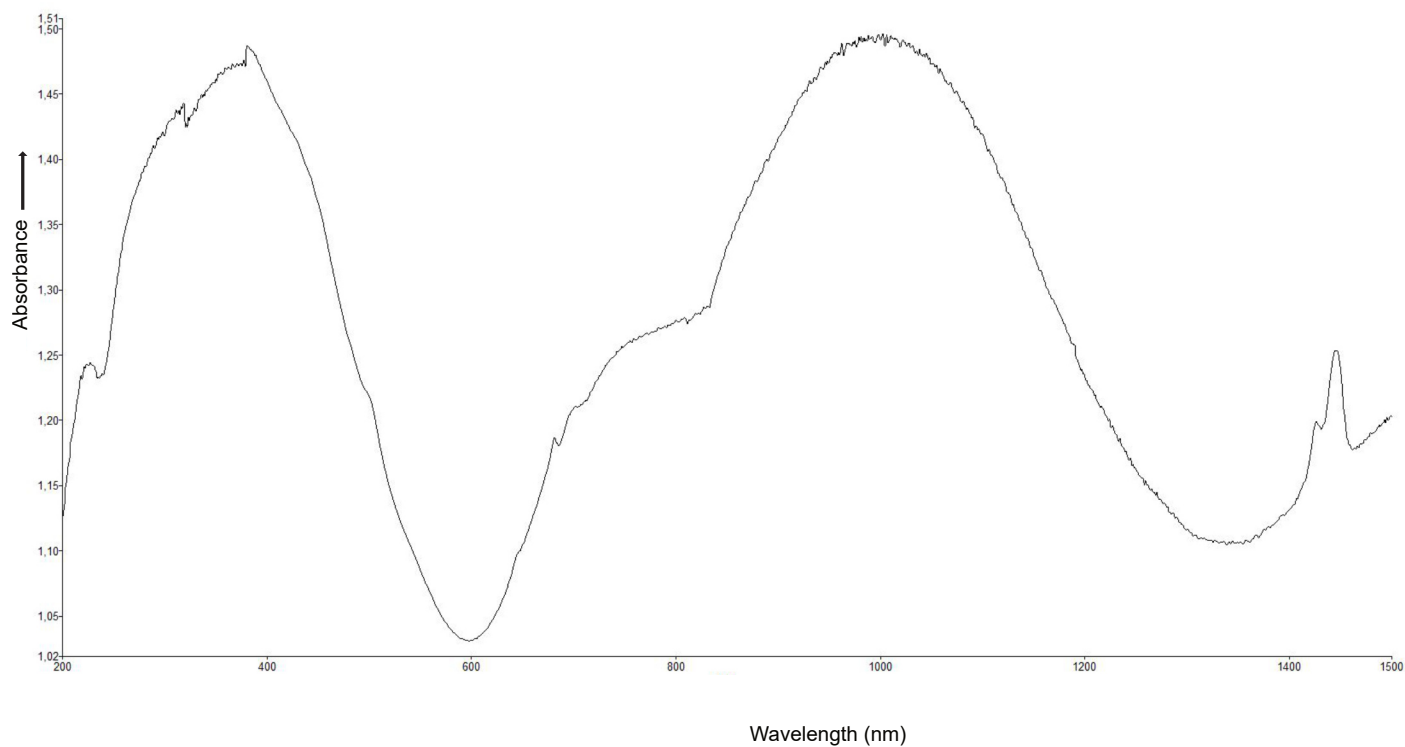


KUD8
7.30 - 7.39 x 3.26 mm

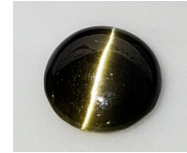
Raman spectrum



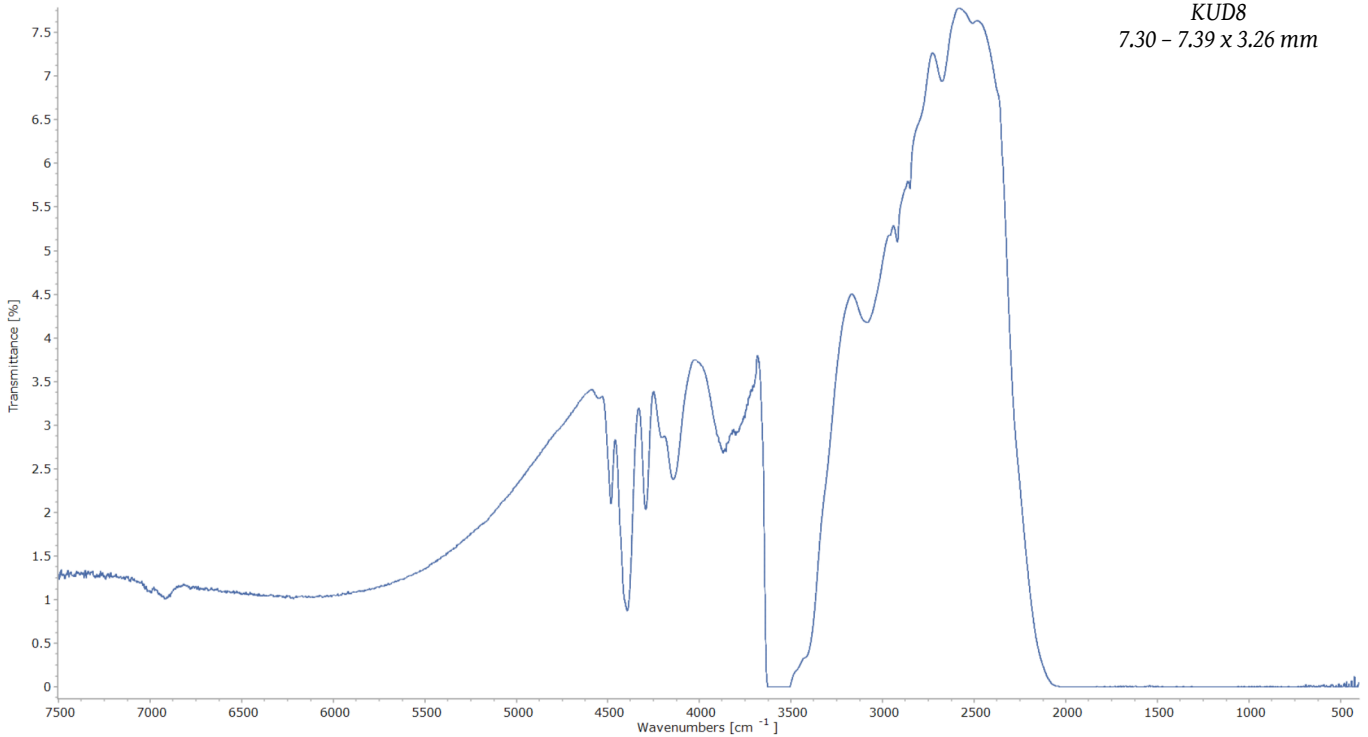
UV-Vis-NIR spectrum



FTIR spectrum



KUD8
7.30 - 7.39 x 3.26 mm



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	40.54	0.38	Al	21.45	0.20
SiO2	29.01	0.22	Si	13.56	0.10
MgO	15.14	0.18	Mg	9.13	0.11
Fe2O3	8.05	0.30	Fe	5.63	0.21
CaO	1.87	0.07	Ca	1.34	0.05
TiO2	0.301	0.029	Ti	0.180	0.018
SO3	0.221	0.034	Sx	0.088	0.014
MnO	0.188	0.014	Mn	0.146	0.011
Cr2O3	0.0995	0.0066	Cr	0.0681	0.0045
Co3O4	0.066	0.019	Co	0.049	0.014
ZnO	0.0631	0.0027	Zn	0.0507	0.0022
V2O5	0.0550	0.0034	V	0.0308	0.0019
Cl	0.0418	0.0070	Cl	0.0418	0.0070
K2O	0.0382	0.0037	K	0.0317	0.0031
Ga2O3	0.0108	0.0010	Ga	0.0080	0.0007
ZrO2	0.0052	0.0007	Zr	0.0038	0.0005

KnownConc= 3.30 B2O3 REST= 1.00 H2O D/S= 0
 Sum Conc's before normalisation to 100% : 66.4 %

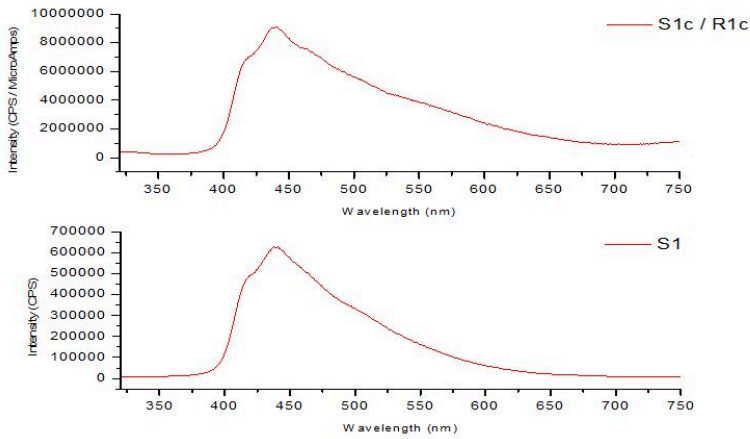
Appendix

Sample AUE4100



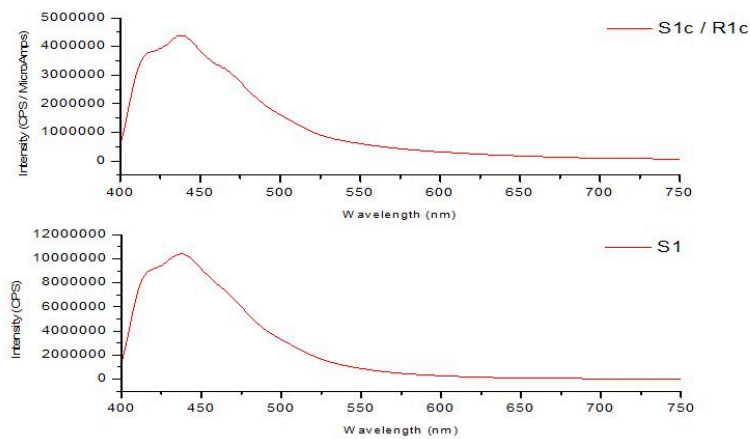
AUE4100
8.08 x 6.64 x 3.67 mm mm

Emission spectra



Emission spectra
under $\lambda_{ex} = 254\text{nm}$ at
room temperature

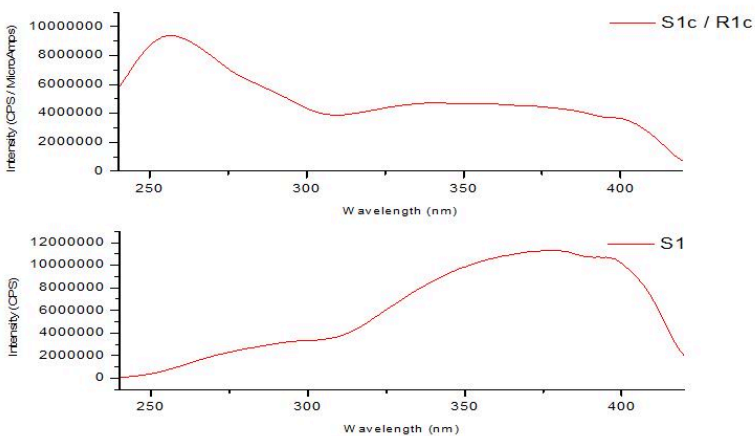
S1: measured
S1c/R1c: corrected



Emission spectra
under $\lambda_{ex} = 365\text{nm}$ at
room temperature

S1: measured
S1c/R1c: corrected

Excitation spectra



Excitation spectra
under $\lambda_{em} = 435\text{nm}$ at
room temperature

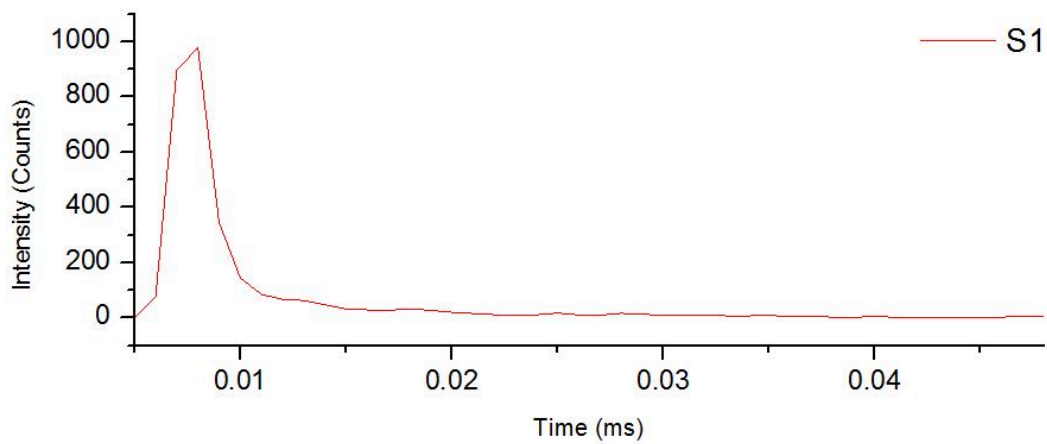
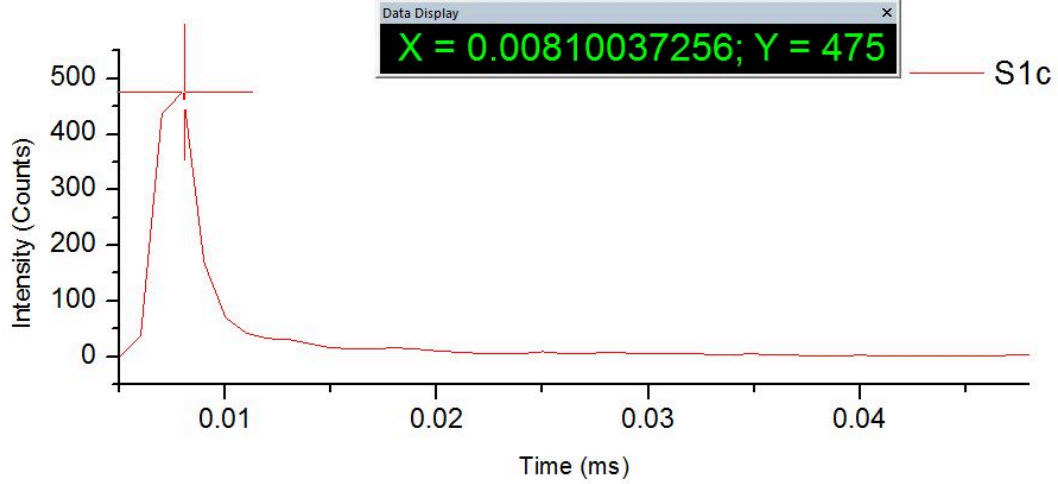
S1: measured
S1c/R1c: corrected

Phosphorescence decay time spectra

- $\lambda_{ex} = 325\text{nm}$
- $\lambda_{em} = 550\text{nm}$
- 10nm slit



AUE4100
8.08 x 6.64 x 3.67 mm mm



EDXRF analysis

Compound	m/m%	StdErr	El	m/m%	StdErr
Al2O3	61.92	0.25	Al	32.77	0.13
SiO2	36.80	0.24	Si	17.20	0.11
MgO	0.928	0.053	Mg	0.560	0.032
Fe2O3	0.222	0.025	Fe	0.155	0.017
P2O5	0.077	0.012	Px	0.0335	0.0053
K2O	0.0142	0.0020	K	0.0118	0.0017
TiO2	0.0136	0.0013	Ti	0.0082	0.0008
V2O5	0.0101	0.0011	V	0.0057	0.0006
Ga2O3	0.0076	0.0006	Ga	0.0057	0.0004

KnownConc= 0

REST= 0

D/S= 0

Sum Conc's before normalisation to 100% : 74.0 %

References

- Wikipedia page Andreas Nicolaus Kornerup https://da.wikipedia.org/wiki/Andreas_Nicolaus_Kornerup
- A. Lacroix and A. De Gramont (1921): Sur la recherche spectrale du bore et sur sa présence dans quelques silico-aluminates naturels. *Bulletin de la Société française de minéralogie*, 44-4-5, pages 67-77.
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