

PHASE TRANSFORMATIONS AS IMPORTANT MARKERS FOR HEAT TREATMENT DETECTION OF CORUNDUM AND OTHER GEMSTONES

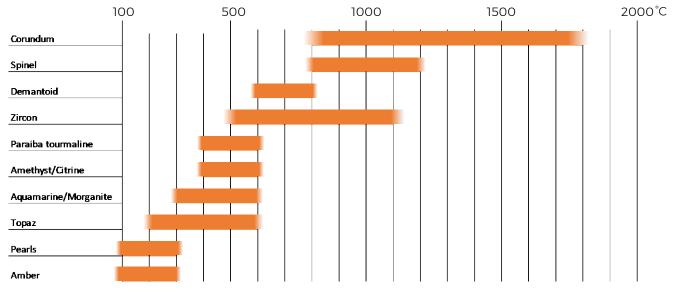
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HEAT TREATMENT OF GEMSTONES



approx. temperature ranges as by gemmological literature

- Depending on the gemstone, different heating temperatures are required to result in an enhancement.
- In most cases, heat treatment results in a change/shift of colour.
- In certain cases may also reduce turbidity or create other desired (optical) effects.



DETECTION OF HEATING:

Microscopy



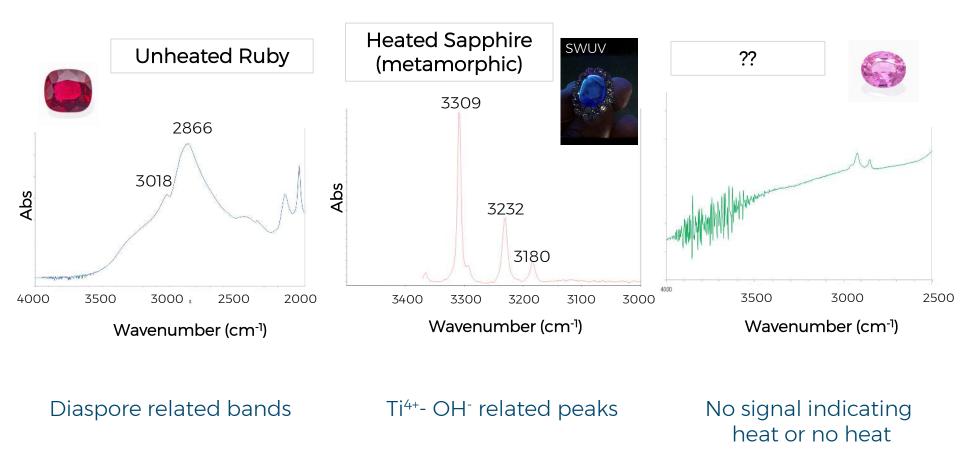
Atoll-structures (discoid extension features) and "burn marks" at the surface are proof of a heat treatment in this orange sapphire.

However, such features indicating heating are often absent, specifically in stones heated at lower temperatures (< 1000 °C)



DETECTION OF HEATING

FTIR Spectroscopy of Corundum





PHASE TRANSFORMATIONS

Classic examples: Diaspore (α -AlOOH) and Goethite (α -FeOOH)



and

P. GAY, M.A., Ph.D.

Dept. of Mineralogy and Petrology, Cambridge.

[Read 23 March 1961.]

Summary. Single crystal X-ray studies of the dehydration of goethite to hemati t low temperatures show that satellite reflections occur close to the hemati ilfraction spots. At higher temperature these satellites are replaced by diffunct ensity regions, which disappear on further heating. The satellites are situated c ach side of hematite spots on reciprocal lattice lines parallel to the σ^* -axis of the ematite; their spacing corresponds to a periodicity in direct space of about 32. t similar phenomenon is observed on the dehydration of diaspore to corundum, wi spacing for the satellites of about 39 Å.

The mode of occurrence of the satellites, both in position and intensity, cou

37 Disordered structural states in the dehydration of goethite and diaspore.

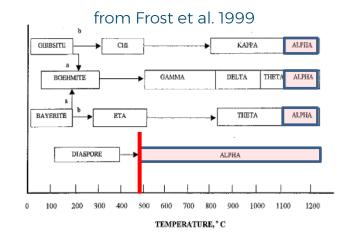
By J. LIMA-DE-FARIA

Dehydration of diaspore and goethite is known and has been studied for many decades (Deflandre, 1932; Goldsztaub, 1935; Rooksby, 1951; Ervin, 1952; Francombe and Rooksby, 1959, etc).





PHASE TRANSFORMATIONS



Dehydration of diaspore to corundum:

De Faria & Gay P. 1963:400 °C (heated 20 days); 550 °C (heated ~20 minutes)Iwai et al. 1973:550 °C (heated 1 hour)Carim et al. 1997:above 400 °C (138 h)Annealing in air: direct and more rapid than in vacuum!Frost et al. 1999:500 to 530 °C over small temperature range!

Dehydration of goethite to hematite:

De Faria & Gay P. 1963: Pomiès et al. 1998: Ruan et al. 2002: de Faria & Lopes 2007:

Wells et al. 2006:

300 °C (heated 19 h); **351 °C** (heated ~20 minutes) 250 to 270 °C 250 to 300 °C 300 °C (regardless if 1 or 40 hours) however rather large bandwidths (lower crystallinity) 250 to 300 °C Al-substituted goethite at slightly higher temperatures



PHASE TRANSFORMATIONS



Gemmological literature:

from Koivula 2013

Koivula J.I. 1987: Goethite inclusion alteration during the heat conversion of amethyst to citrine. *The Australian Gemmologist*, Vol. 16, No. 7, pp. 271–272.

Kammerling R.C. & Koivula J.I., 1989. Thermal alteration of Inclusions in "rutilated" topaz. *Gems & Gemology*, 25, 3, 165-167. http://dx.doi.org/10.5741/GEMS.25.3.165

Koivula J.I., 2013. Useful visual clue indicating corundum heat treatment. *Gems &Gemology*, 49, 3, 160-161. http://dx.doi.org/10.5741/GEMS.49.3.160

Sripoonjan et al. 2016: Phase transformation of epigenetic iron staining: In dication of low-Temperature heat treatment in Mozambique ruby. JoG, 35 (2), 156-161. Gemmological Brief

Phase Transformation of Epigenetic Iron Staining: Indication of Low-Temperature Heat Treatment in Mozambique Ruby

Tasnara Sripoonjan, Bhuwadol Wanthanachaisaeng and Thanong Leelawatanasuk

In the past several years, Mozambious has emerged as one of the world's most important sources of multip and unbeated stances from this country arein particularly strong domaind. Nevertheless, it is common far these nubles to undergo low-bemperature meding (~1.000° G ar below to slightly immove them colour. The tracted stones may show very sublict on no alteration of interval features (e.g. minoral inclusions, "ingerprints", needles, slik, ed., Nevever, "inoral-stand" suffaces and the tractiles commonly disably a naticcably mare interuse collaur discr heating, Barnara and FIRs spectratory were used to document a transition fram goethile to hematite within stained fractures in samples heated to 500°C and 500°C. The identification of hematite within such fractures provides key evidence for the low-temperature usits.

Ris Annario Connisado 2012, 2015 da 125-131, 452/04 da agril 12906/46/2015.352.156 O 2316 The Germological Association of Grae Dilan

Sripoonjan et al. 2016



HEATING EXPERIMENT

Heating stage Linkam TS 1200 Coupled with Raman system for in-situ measurements



Electric muffle furnace Nabotherm LHT 18 - Heating similar to gem trade



Step-wise heating, $T_{\rm max}$ per step kept for 4 minutes only

Step-wise heating, T_{max} per step kept for 1 hour

Heating in air, step-by-step heating, Raman spectra only after cooling down



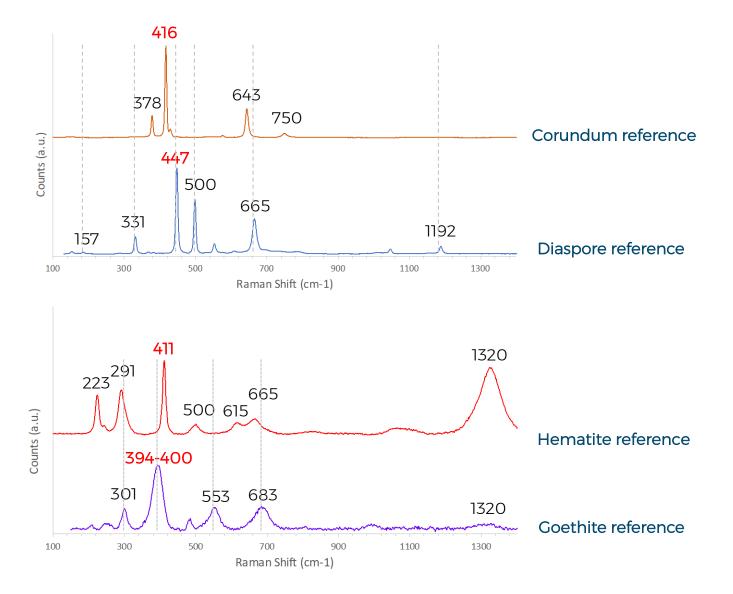
HEATING EXPERIMENT

Sample		ID	Weight (ct)	Shape	Colour	Origin	Heating	max T°C	Colour after Heating
97003	C	Diaspore	0.40	flat fragment	colourless	Muğla Prov., Turkey	Electric furnace	800	whitish
126993_6	Ó	Ruby with diaspore	0.19	polished slab	red	Mogok <i>,</i> Myanmar	Heating stage	700	no change
106424_21		Sapphire with diaspore	1.03	faceted	blue	Mogok, Myanmar	Heating stage	700	no change
85933_C3		Ruby with goethite	0.52	polished slab	red	Montepuez, Mozambique	Heating stage	400	no change
120553_B		Ruby with goethite	1.31	polished slab	red	Montepuez, Mozambique	Electric furnace	1000	no change

Important: none of the corundum samples showed any change of colour after our heating experiments reaching a maximum of 1000 °C.

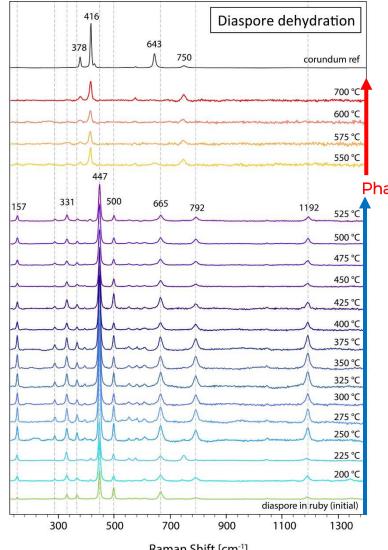


RAMAN SPECTRA OF PHASES





DIASPORE TO CORUNDUM



Raman Shift [cm⁻¹] dotted vertical lines: main diaspore peaks

Sample 120993_6 Diaspore in Burmese ruby (Mogok)

Experiment setup: Linkam heating stage

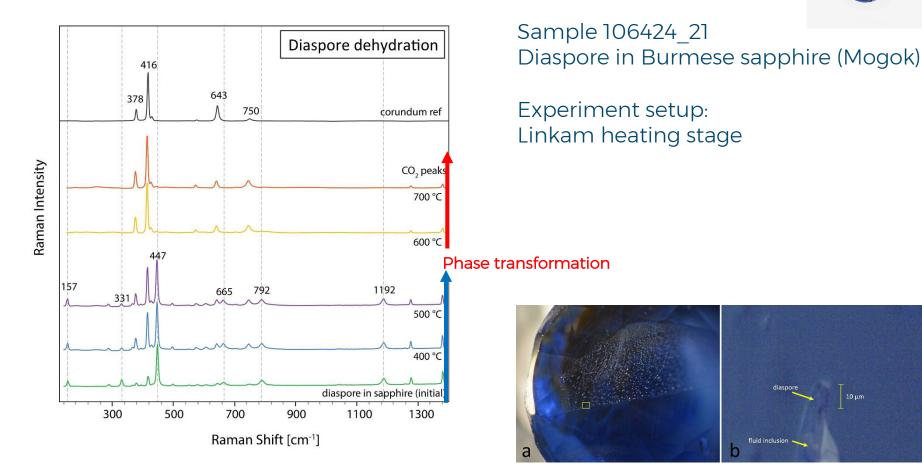
Phase transformation



Diaspore in ruby (image width 2mm).



DIASPORE TO CORUNDUM

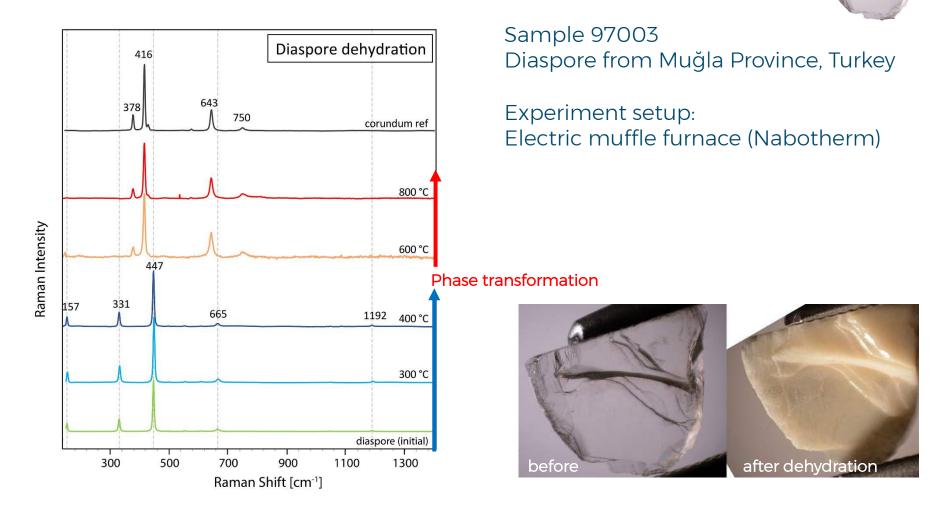


dotted vertical lines: main diaspore peaks

SSEF

Diaspore in fluid inclusion in sapphire (approx. 10 μ m).

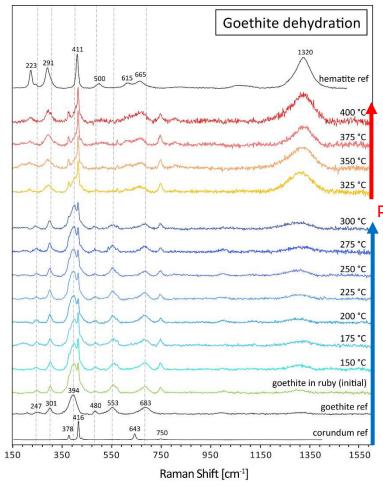
DIASPORE TO CORUNDUM



dotted vertical lines: main diaspore peaks



GOETHITE TO HEMATITE



Sample 85933_C3 Goethite in Mozambique ruby

Experiment setup: Linkam heating stage

Phase transformation



Goethite in fissure in ruby

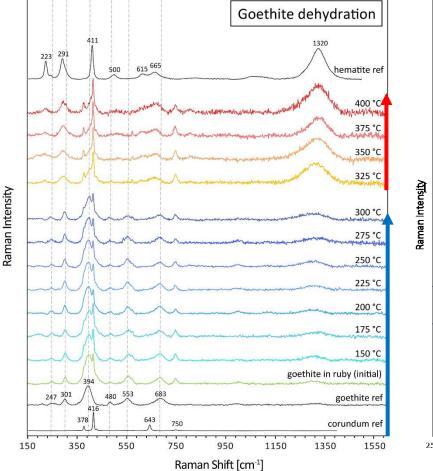
Raman Intensity

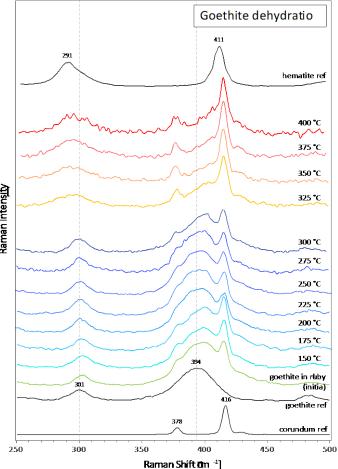
dotted vertical lines: main goethite peaks



GOETHITE TO HEMATITE



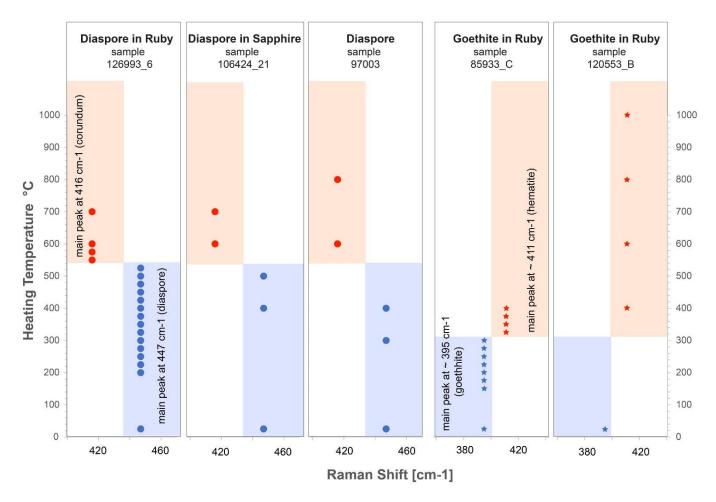




dotted vertical lines: main goethite peaks



RESULTS OF HEATING EXPERIMENTS

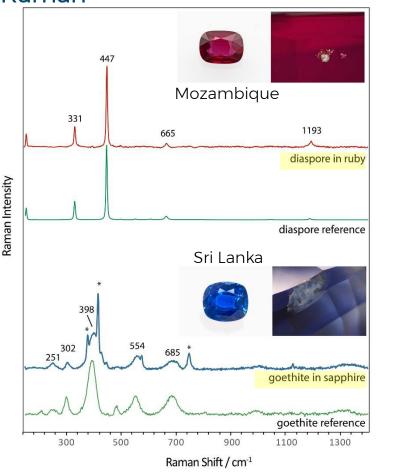


Regardless of size and position of the inclusion, the phase transitions (dehydration) of the diaspore and goethite can be observed in in all samples in their specific temperature range (diaspore about 525 °C; goethite about 325 °C)

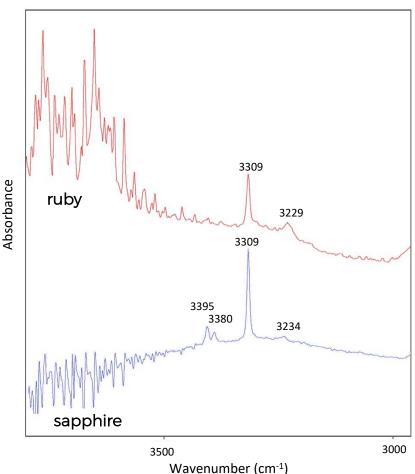


REAL CASES





FTIR



FTIR can be tricky, the peaks at 3229 and 3234 are not identical with the peak at 3232 cm⁻¹ commonly related to heating ! Corundum with similar FTIR spectra have already been identified as heated!

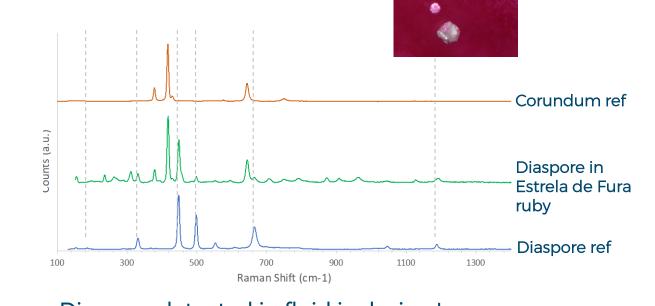




Estrela de Fura 55.22 ct

Sells at auction Sotheby's auction June 2023 for record \$34.8 million.





from Sotheby's International



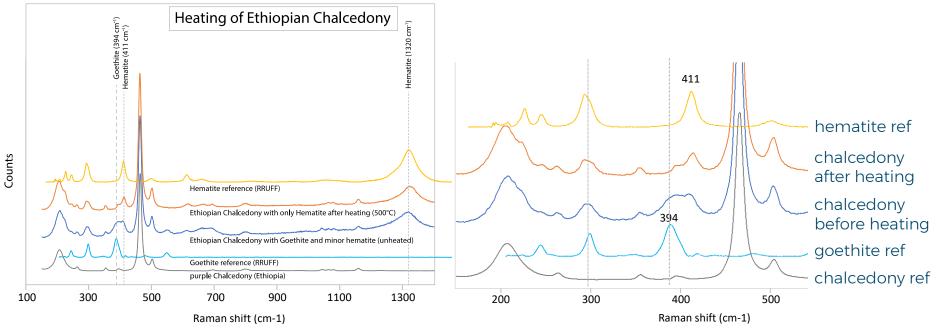


REAL CASES

Purple Chalcedony from Ethiopia: Heating Experiment

- 30 minutes for ramping up
- 120 minutes at **500 °C**
- 60 minutes cooling down
- Heating in air





Goethite present in this chalcedony transforms to hematite as a result of heating. Some hematite already present before heating!



CONCLUSIONS

- Diaspore and goethite are oxyhydroxides which dehydrate to anhydrous oxides when heated.
- Our experiments confirm phase transformation temperatures as reported in literature (goethite to hematite at ~325 °C; diaspore to corundum at ~ 550 °C).
- Phase transformation occurs in small temperature range, thus resulting in a quasi immediate switch in the Raman spectrum.
- Phase transformation cannot be stopped or shifted to higher temperatures, and affects all diaspore and goethite at the same moment.
- The presence of diaspore and/or goethite is a clear indication, that a corundum is not heated (either by low-T heating > 800 °C), even in cases when FTIR may reveal peaks which could be (mis)interpreted as related to heating or no information whether a stone is heated or not.
- The absence of diaspore or the presence of hematite is not enough to call a stone heated.
- Applicable on all kind of gemstones, as long as diaspore or goethite are present.



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