Spectroscopic examination of commercially available quartz varieties
- A gemmological perspective

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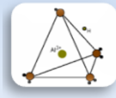
Introduction

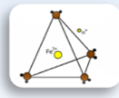
- Lack of inclusions and visible growth features (colour zoning) makes the separation of colourless natural and synthetic quartz quite challenging.
- Though found colourless in nature, it can also be produced by heating other quartz varieties, such as amethyst, citrine, smoky, green (praseolite), and greenish yellow (lemon).
- Rock crystal, the purest variety of quartz (SiO_2), often contains aluminium (Al^{3+}) impurities where the charge imbalance is compensated by a nearby interstitial alkali ion (figure 1); this is a precursor for smoky quartz, which is produced by natural or artificial irradiation.
- Iron impurities, having different charge states, result in green (Fe^{2+}), yellow (Fe^{3+}), and violet (Fe^{4+}).
- As a result, both natural and synthetic materials can be heated at 235-550ºC to produce the colourless variety. However, heating produces other colours as well, depending on the temperatures applied.
- In this paper, an attempt is made to produce the colourless variety by heating other available colours in the market place and study the changes in the common spectroscopic techniques available in a gem laboratory.

a. Pure Quartz



b. Smoky Quartz

c. Amethyst



d. Citrine

Figure 1: Substitution and charge balance scheme of quartz

Methodology

- Natural and synthetic rough samples were procured and fashioned as cubes ranging from 6 mm to 10mm of Amethyst, Citrine, Rock crystal, Smoky, Green and Lemon quartz.
- The cubes were fashioned in a way that the optic axis or ‘c’ axis intersects one of the faces of the cube enabling proper orientation of the samples.
- 10 samples each for natural and synthetic were used for all the varieties mentioned above. We could not obtain synthetic lemon quartz and synthetic green quartz, but we were able to use a sample which was actually bi-coloured green-yellow quartz.
- Infra red, UV-Vis, and Laser Raman spectra were measured for all samples in two directions; one along the optic axis and the other perpendicular to the optic axis. These were recorded before as well as after heating experiments.
- The main objective of performing heating experiments was to produce the colourless variety.
- Heating of half of the samples i.e. 5 each was conducted in a muffle furnace with digital temperature controls. Time, temperature and results obtained are given in Table 1.

Table 1: Results of heating experiments on various colours of quartz

Variety	Temperature (in ºC)	Time after temperature reached (in hours)	Total time	Changes observed	Remarks
Natural Amethyst	510	2.5	4.5	Yellow - milky yellow	Contained numerous inclusions
	550	3	5	Milky, partially yellow tint	
Synthetic Amethyst	510	2.5	4.5	Colourless , slight yellow tint	Strongly zoned; violet zones turned yellow; shades of yellow to orange
	550	3	5	2 pieces went slightly milky with a point colour zone; 3 others did not convert	
Natural Citrine	550	3	5	3pcs milky to colourless ; 2 darker colour pieces - lightened slightly	Contained fluid inclusions
	650	4	6	Milky and colourless	
Synthetic Citrine	280 - 350	2	3	No change	Zonal changes observed
	510	3	5	Slightly lightened	
	550	3	5	Milky zones with yellow tint	
Natural Smoky	235	1	2	Partially to lemon	Colour zones remained light smoky to lemon
	280	1	2	Mostly colourless; some remain partially smoky	
Synthetic Smoky	235	1	2	Partially colourless and smoky; parallel zones of smoky	
	280	1	2	Colourless	
Natural Lemon	280	1	2.5	Colourless	
Natural Green	280	1	2.5	Colourless	
Synthetic Green / Bi-coloured (Green-Yellow)	280 - 510	2 -3	3	No change	
	550	3	5	Green part turned milky; yellow became colourless	
	650	4	6	Green part turned more milky and bluish	

About the authors

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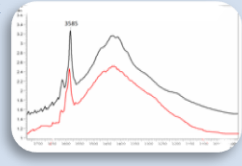
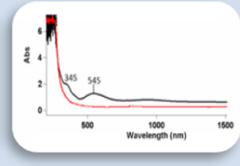
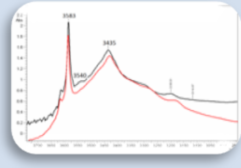
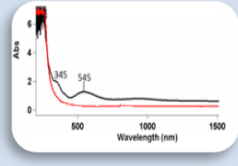
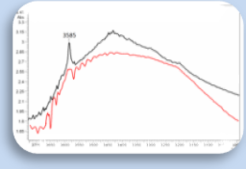
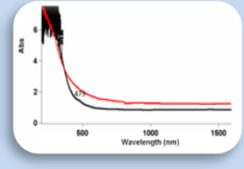
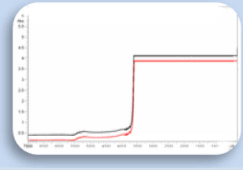
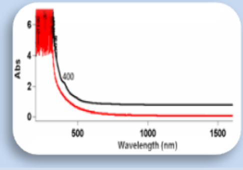
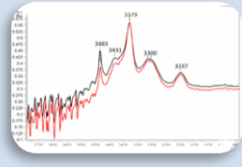
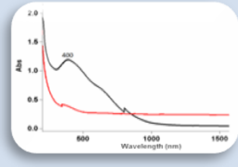
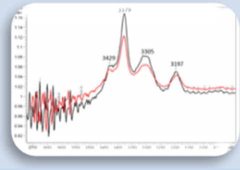
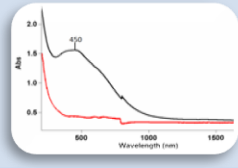
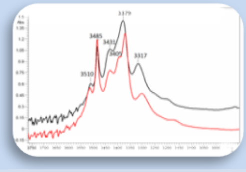
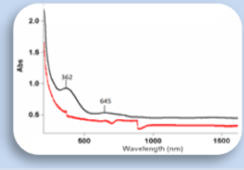
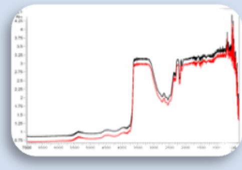
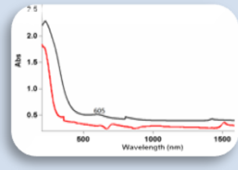
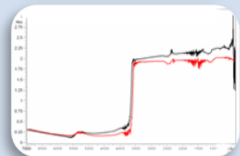
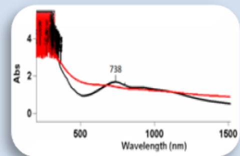
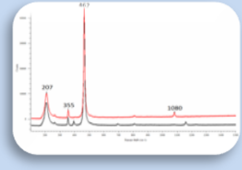
Results

Table showing IR and Raman spectra of **Natural and Synthetic Quartz**, before and after heating experiments

Variety	IR Spectra	Visible Range
Amethyst Natural		
Synthetic		
Citrine Natural		
Synthetic		
Smoky Natural		
Synthetic		
Lemon Natural		
Green Natural		
Synthetic		

Raman spectra - all quartz varieties
- natural and synthetic



All spectra in red are after heating

Discussion and Conclusion

Infra red spectra offered the most valuable means for differentiating between natural and synthetic varieties, and only minute difference in the absorption patterns was observed after heating those samples. IR spectra majorly displayed, Al-OH/Li, Al-OH, Si-O / Al-OH, and Si-O related peaks. ***Visible range*** spectra displayed variations where body colour was changed / modified; however did not helped in separating natural and synthetic counterparts. ***Raman spectra*** was similar for all quartz varieties, irrespective of natural or synthetic origin. Minute differences were observed after heating.

Distinguishing natural from synthetic rock crystal: The most important peak was at 3481 cm^{-1}, present in natural. ***Synthetic amethyst:*** Peak at 3540 cm^{-1} was characteristic to differentiate synthetic from the natural counterpart.
On heating 3540 cm^{-1} disappeared. The body colour became pale yellow, similar to citrine and the absorption pattern now overlaps with the natural citrine.

- No changes were observed in natural or synthetic samples of citrine, green and smoky quartz after heating.
- ***In lemon quartz,*** a peak at 3403 cm^{-1} developed on heating.

On comparing natural rock crystal with other natural varieties after heating,

- Majority of the peaks were similar.
- Exception was 3585 cm^{-1} present in amethyst and citrine.
- Similarity in spectral features of rock crystal, smoky and lemon quartz at 3481, 3430, 3379 and 3197 cm^{-1}.
- Heating smoky quartz produces rock crystal through the intermediate lemon colour and hence due to the similarity in their structures, the absorption patterns are similar.

Synthetic rock crystal vs. other heated synthetic varieties.

- ***Synthetic rock crystal and heated synthetic smoky quartz (now colourless)*** was almost identical, with difference in peaks at 3377, 3430 and 3310 cm^{-1} present in synthetic smoky quartz (now colourless); the latter being present only along the optic axis direction.
- ***Heated synthetic amethyst*** displayed additional peaks at 3612, 3585 and 3435 cm^{-1}.
- Other varieties had completely different spectra as compared to natural or synthetic rock crystal, hence have not been taken under consideration in this comparison.

In the past studies in our laboratory and in literature, The peak at 3585 cm^{-1} has been found in synthetic rock crystals, which was not the case in this study. Difference in growth conditions could have been responsible for this variation. Therefore, if the peak at 3585 cm^{-1} is present in a rock crystal, it may be presumed that *the sample is either a synthetic (as grown) or a heat treated amethyst or citrine (natural or synthetic).*