

# AGEE hydrothermal

By Dr H A Hanni and Lore Kiefert, Swiss Gemological Institute, Zurich

In June 1994 we were informed by R Y Durlabhji from Jaipur, India that a new product was intriguing the trade. Presumably synthetic emeralds which were hardly identifiable were disturbing the trade with natural emeralds. At the same time, advertisements in some journals were seen in which a company known as A G Japan was offering so-called "AGEE emeralds, refined and recrystallized." The company further explained that it used "Colombian rough emerald crushed into fine powder and purified with a laser process and recrystallized with a hydrothermal process,...no chemicals are added at any time..." We were very keen to get and analyze such material, since the described technique is not known so far, and we suspected an inadequate description of the production technique as well as an incorrect nomenclature of the product. Thanks to six samples kindly provided by Junko Shida (Gemological Association of All Japan, Tokyo) and by Mr Durlabhji we were finally in a position to do some research on the stones (Figure 1). In the meantime, Shyamala Fernandes (Gem Testing Laboratory, Jaipur) furnished her own findings regarding the new material.

The results of our preliminary study proved the new material to be usual hydrothermal synthetic emeralds. The misnomer used by the producers, "AGEE emeralds," is not in agreement with the worldwide accepted CIBJO nomenclature trade rules and should therefore be avoided.

Synthetic and imitation stones are artificial products which imitate a gem mineral that occurs naturally. While an imitation only resembles a natural stone by its external appearance (ie, green glass for emerald), a synthetic crystal is in many aspects identical to its

natural counterpart. The chemical composition, as well as the crystal structure, and therefore all physical constants such as refractive indices, density, hardness, cause of color, etc, must correspond with the natural counterpart. Only under these conditions can an artificially produced crystal be called a synthetic.

## Flux-grown synthetic crystals

The production of synthetic emeralds has been performed for a long time with variable success. In 1848 Ebelman was able to produce some of the first crystals. Before World War II Espig, from the IG Farbenindustrie AG in Germany, experimented with synthetic crystal growth and developed the fundamental technology for the production. The first commercially relevant results were scored by Carrol Chatham (USA) and Pierre Gilson (France) in the 1960s. The crystal growth technology they used was based on a melt of raw materials as oxides to which chromium was added. Usually the melt is kept at a temperature of approximately 800°C under normal pressure in a crucible made of precious metal. As soon as the melt is over-saturated crystallization may start with the formation of spontaneous nucleation. These germs go on growing until they are numerous enough to form crystal clusters. Thus, the reconsolidated material transforms into a multitude of small intergrown crystals. Spontaneous nucleation may be inhibited by installing

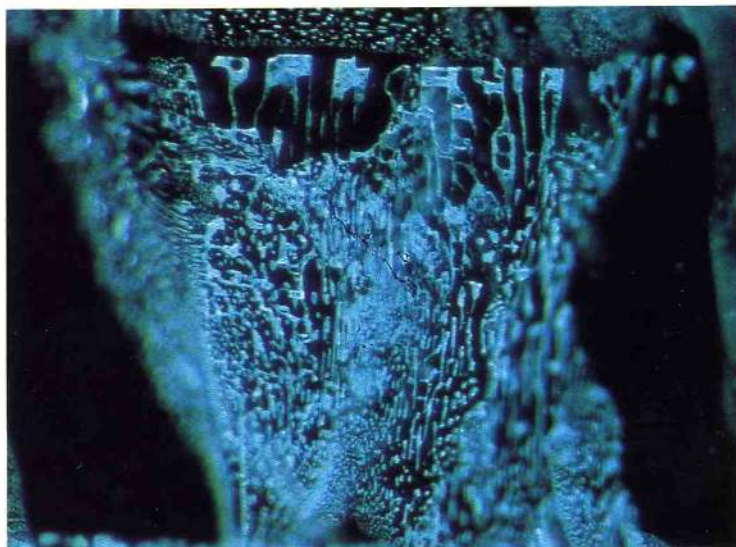


Figure 2—Flux synthetic emerald (Chatham) showing a veil of residual flux trapped in tiny cavities, the crystal nature of the fillings and tiny vacuum bubbles are sometimes visible. Magnification approximately 40x.



Figure 1—Six samples of hydrothermal synthetic emeralds distributed by A G Japan Ltd, showing different colors and degrees of transparency. The largest stone is 1.4 carats.



# synthetic emeralds

a seed plate, ie a slice of beryl which offers a pattern for the growing crystal which then continuously grows as long as the melt is over-saturated. Through this process all the dissolved material is attracted to the beryl plate and forms one single crystal. This is the best result for a crystal to be used as a gem.

The environment of the formation of these synthetics by the flux method differs sharply from the environment in which natural emerald is formed, notably by the lack of water. That is why such products (ie flux grown synthetic emeralds from Chatham, Gilson, etc) usually are rather easy to differentiate from natural emeralds. Gemologists may recognize veil-like residual flux droplets in tiny voids during a microscopic inspection (Figure 2).

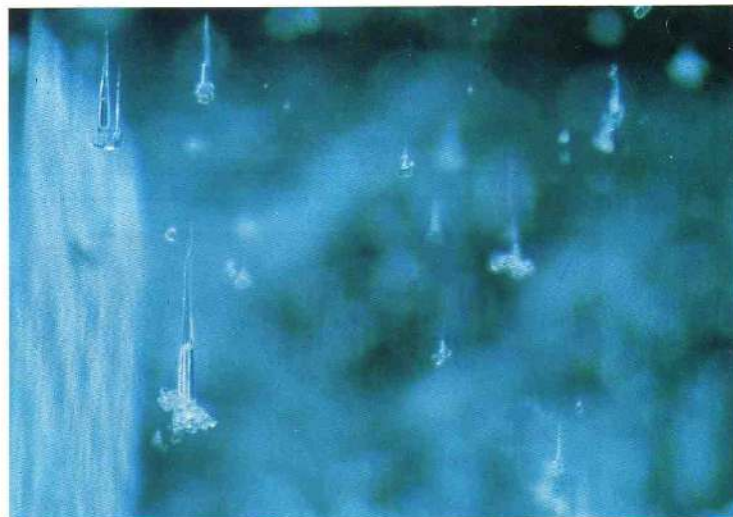
Nowadays flux synthetic emeralds are mainly produced in the USA (Chatham), Japan (Inamori) and Russia. The production of Gilson, formerly the most important producer in Europe, has moved to the Far East due to the sale of its license.

## Hydrothermal synthetic emerald

The first steps to produce synthetic emeralds by the hydrothermal method were made at the beginning of the 1960s. In a hydrothermal process the crystals do not grow in melt, but in overheated water. The raw materials, oxides or beryl, together with additional chromium (ie chromium chloride) are dissolved in an autoclave. An autoclave is comparable to a pressure cooker. In order to rise the solubility of the raw material the acting aqueous solution has to be extremely acid (ie pH 0.1). Under the influence of heat (550°C), pressure (1000 bar) and steam, the primary materials are dissolved. A lining made of precious metal (ie silver, gold or platinum) is required for the autoclave itself not to melt. Furthermore, it is important that within the autoclave there is a temperature gradient, a difference in temperature of about 60°C. In the hotter zone (under-saturation) the substances are dissolved, in the cooler zone (over-saturation) the chemical elements are deposited on the exposed seed plate. By means of vapor, the chemical components move atom per atom to the seed plate which grows. Synthetic emeralds are formed through this procedure.

Johann Lechleitner of Austria was the first who succeeded in growing synthetic emerald on faceted colorless beryl. Later on, Linde of the US produced larger synthetic emeralds of the hydrothermal method. These contained a seed plate of natural colorless beryl. Hydrothermal synthetic emeralds which have been produced since the 1960s have increased considerably in quality. Originally only a growth rate of a few millimeters was possible during each run of

hydrothermal growth, or per autoclave filling. Thus, the crystal or seed plate had to be covered many times until the coating was sufficiently thick. The first multilayer synthetic emeralds were called "sandwiches." Samples from this older type of hydrothermal emeralds usually exhibited a multitude of inclusions, most of them consisting of tiny phenakite clusters and acicular voids with a liquid and gas filling (Figure 3). Hydrothermal synthetic emeralds are today produced by Regency (formerly Linde, USA), Vassar (Russia) (compare Schmetzer, 1988), Kimberly (Biron, Australia) (compare Kane & Liddicoat, 1985; Hanni, 1993). The common growth peculiarity of these products are angular growth structures, such as shown in Figure 4, which are typical for the hydrothermal production technique.



**Figure 3—Hydrothermal synthetic emerald (Linde) with tiny crystal clusters (phenakite) from which spiky two-phase filled cavities emanate. Magnification 50x.**



**Figure 4—Hydrothermal synthetic emerald (Biron) with typical angular growth structure (chevrons). Magnification 40x.**



# AGEE hydrothermal synthetic emeralds

The six faceted stones which we could analyse so far were between 0.25 and 1.40 carats. They showed basically two types of color (see Table 1). A factor that could make the synthetic emeralds difficult to identify is the relative impurity compared to what we are used to seeing in synthetic material. Veils formed by tiny liquid droplets are frequent (Figure 5). In larger cavities, two-phase fillings were observed. Shining fine tension fractures were seen in all of the stones. Some of the

**Table 2: Trace element characteristics of 6 AGEE hydrothermal synthetic emeralds compared with fluorescence behaviour**

Nr.	shape	weight (ct)	colour	LW UV (366 nm)	Cr*	V*	Fe*
1	octagonal	1.404	light green	none	X	XXX	(x)
2	oval	1.164	dark green	red	XXX	XXX	(x)
3	oval	1.081	light green	none	(x)	XXX	(x) 1
4	round	0.736	dark green	red	XXX	XXX	(x)
5	square	0.503	light green	red	XXX	XXX	(x) 2
6	pear	0.247	med. green	red	XXX	XXX	(x)

\* Comparative trace element values obtained by EDS-XFA. XXX = abundant, X = present, (x) = near detection limit.

**Table 1: Physical and optical properties of 6 AGEE hydrothermal synthetic emeralds**

Nr.	shape	weight (ct)	colour	transparency	density	n <sub>e</sub>	n <sub>o</sub>	Δn
1	octagonal	1.404	light green	transparent	2.690	1.569	1.575	0.006
2	oval	1.164	dark green	transparent	2.688	1.570	1.576	0.006
3 ✓	oval	1.081	light green	transparent	2.689	1.570	1.576	0.006
4	round	0.736	dark green	transparent	2.696	1.572	1.579	0.007
5 ✓	square	0.503	light green	semi-transparent	2.690	1.569	1.575	0.006
6	pear	0.247	med. green	transparent	2.685	1.571	1.578	0.007



**Figure 5—Hydrothermal synthetic emerald (AGEE) with undulated healed fractures consisting of residual fluid in typical distribution.**



**Figure 6—Hydrothermal synthetic emerald (AGEE) with typical veils of fluid inclusions and angular growth structures (chevrons).**

fractures were even "oiled." Spiral-shaped and fan-shaped fluid inclusions are frequent. Due to the frequency of internal disturbance by the described inclusions, the most characteristic angular growth zoning, or "chevrons," as seen in most of the modern hydrothermal synthetic emeralds (Schmetzer, 1988) is sometimes hardly visible (Figure 6). Parallel narrow or wide spaced color zoning is common. Colorless (phenakite?) and brownish fine crystals (Figure 7) are often seen on planes probably parallel to the former seed plate. Hollow tubes were seen in one sample.

The physical properties (refractive indices and density) are overlapping with the lower end of the population formed by natural emeralds (Schrader, 1983). In fact, many Colombian emeralds (Bosshart, 1991) with low values cannot be separated by their constants from hydrothermal synthetic emeralds. In Table 1 the values of our samples are given. The data obtained by Ms Fernandes are similar, but show a higher variation than our results.

A brief chemical investigation by EDS-XFA (energy-dispersive X-ray fluorescence analysis) informed us about the trace element contents (Table 2). We remark basically on two types of stones. One type, the darker ones, showed similar amounts of chromium and vanadium (Figure 8). The other type, lighter in color,



**Figure 7—Hydrothermal synthetic emerald (AGEE) with small cavities filled with two-phases, and a horizontal growth plane decorated with dark dust particles. Magnification 50x.**



# Spectrace Instruments

Sample: AGEE hydrothermal synthetic emerald 0.736 ct

Energy dispersive X-ray fluorescence spectrum 19.07.94

tube voltage : 20 kV filter used: aluminium  
tube current : 0.03 mA livetime: 200 sec  
atmosphere: vacuum sample rotation: off

SSEF Swiss Gemmological Institute

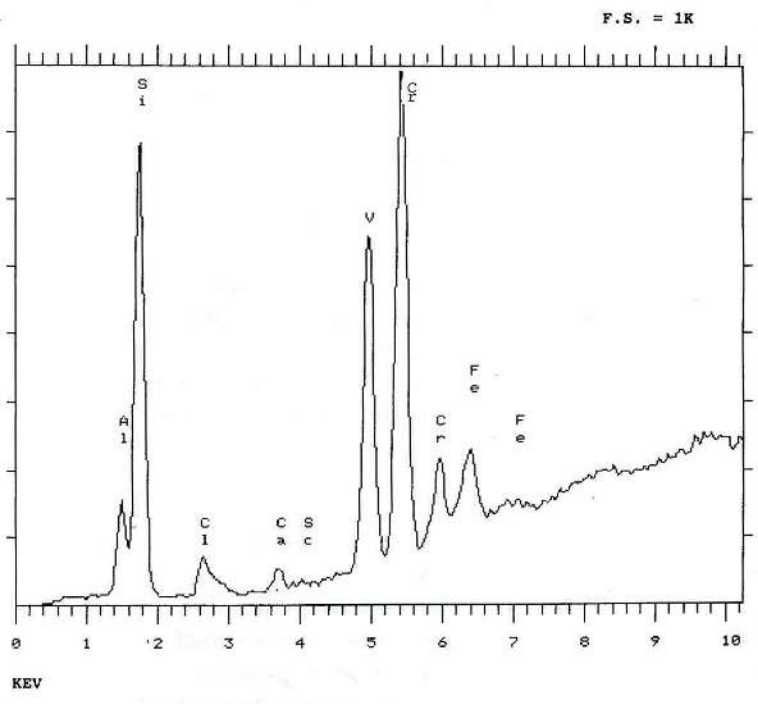


Figure 8—EDS-XRF spectrum of hydrothermal synthetic emerald (AGEE) with equal concentrations of vanadium and chromium, comparable to some Colombian emeralds. The chlorine peak reveals the synthetic nature of the stone.

# Spectrace Instruments

Sample: AGEE hydrothermal synthetic emerald 1.404 ct

Energy dispersive X-ray fluorescence spectrum 02.08.94

tube voltage : 20 kV filter used: aluminium  
tube current : 0.03 mA livetime: 200 sec  
atmosphere: vacuum sample rotation: off

SSEF Swiss Gemmological Institute

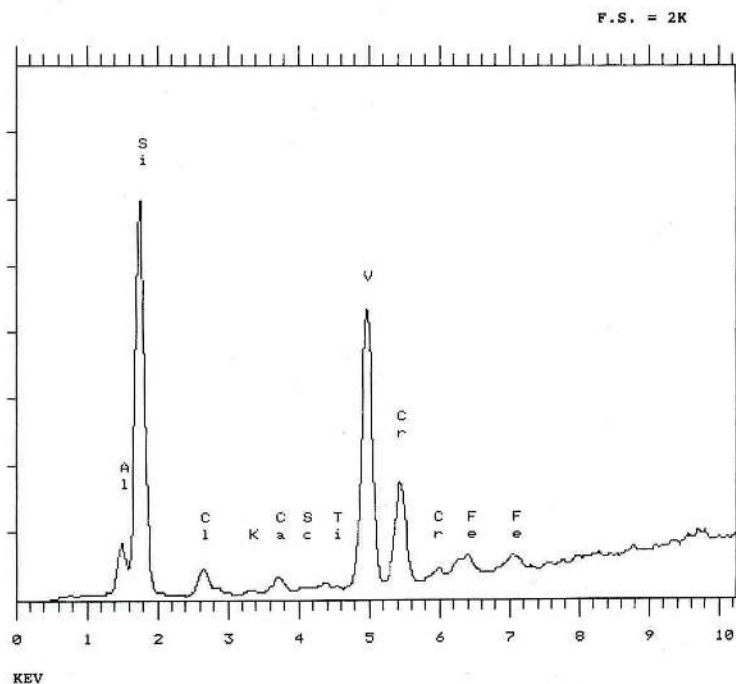
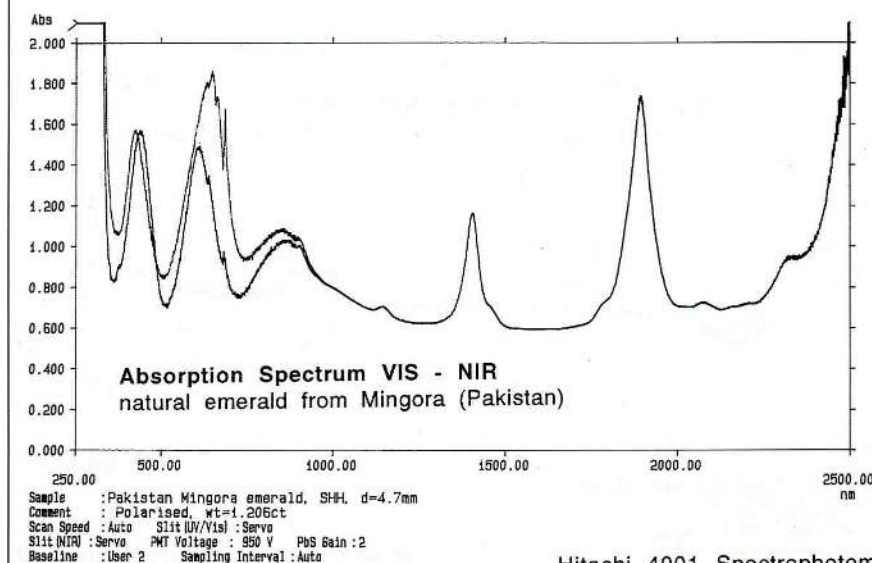


Figure 9—EDS-XRF spectrum of a hydrothermal synthetic vanadian-emerald (AGEE) with almost no chromium. The chlorine peak reveals the synthetic nature of the stone.

SSEF Swiss Gemmological Institute



Hitachi 4001 Spectrophotometer

Figure 10—VIS-NIR spectrum of a natural emerald from Mingora, Pakistan. The spectrum shows a very high absorption peak at 1900 nm attributed to H<sub>2</sub>O molecules, with very weak side peaks.

exhibited a prominent vanadium peak and only little chromium (Figure 9). Interesting to note is that the high Cr-samples show a moderate red fluorescence whereas the V-samples are inert to long-wave ultraviolet. In addition to the color causing trace elements V, Cr and Fe, we identified Si and Al from the beryl mineral formula and, interestingly, chlorine. It is well known that in hydrothermal synthetic emeralds Cl usually is present (Hanni, 1982). The feeding of Cr for the coloration of the products is usually done by adding chromium chloride, and the hydrothermal solution usually contains significant amounts of hydrochloric acid.

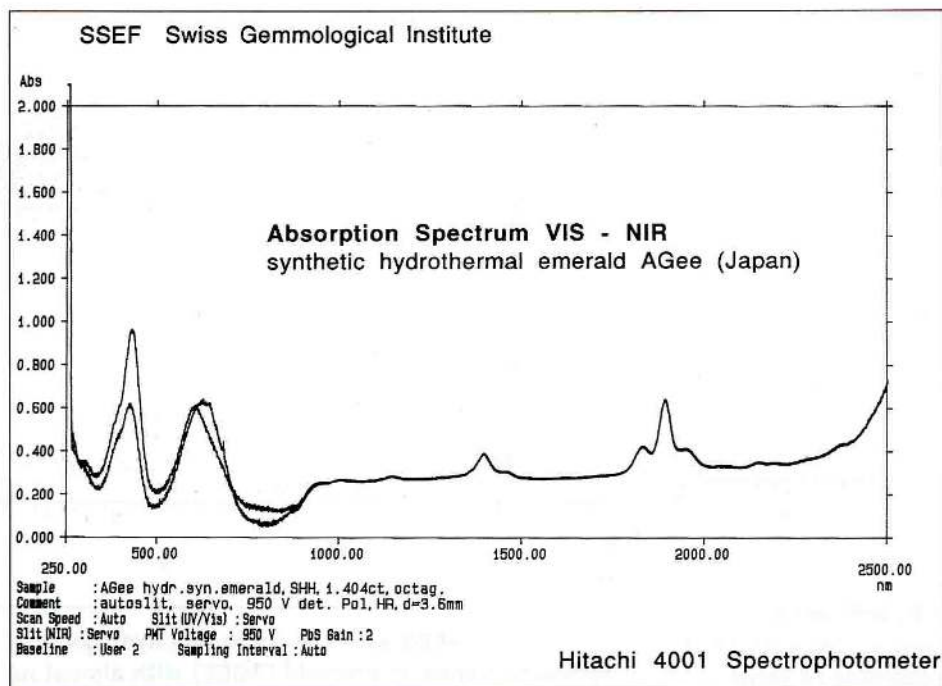
This observation proves the synthetic nature of

AGEE synthetic emeralds. Further, the statement of the producers that "...no chemicals are added at any time..." was refuted.

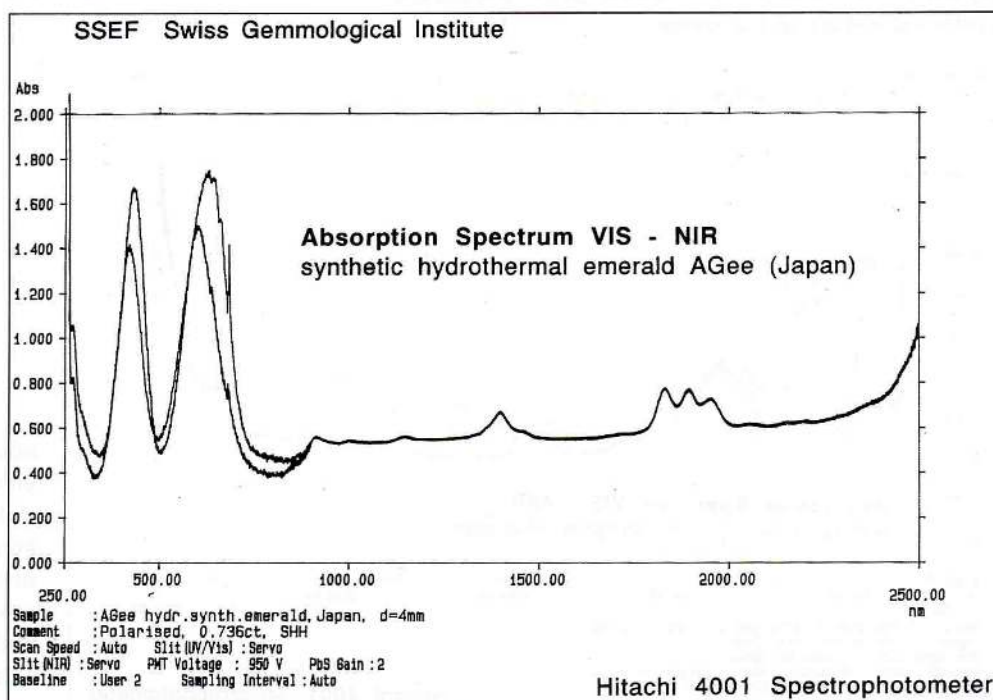
When we recorded VIS-NIR spectra on our Hitachi 4001 spectrophotometer, the Cr-samples performed a typical Cr-spectrum. With V-samples (with only little Cr), the typical Cr-line at 680 nm was only small. Most interesting are the absorption features in the near infrared region (NIR). In contrast to Colombian emeralds, the absorption peaks at 1900 nm are rather small. This feature, attributed to H<sub>2</sub>O molecules (Wood & Nassau, 1968), consists of a triplet of lines. In most natural emeralds, the central peak is very strong and the side peaks are only weak. This situation is demonstrated in Figure 10.

The synthetic V-samples (Figure 11) are producing higher 1900 nm peaks compared to Cr-samples (Figure 12), but both show much weaker intensities than the ones common in natural emeralds (ie from Mingora, Pakistan, as shown in Figure 10).

**Figure 11—VIS-NIR spectrum of a hydrothermal synthetic vanadate-emerald (AGEE). The spectrum shows a distinct absorption peak at 1900 nm attributed to H<sub>2</sub>O molecules, the side peaks are also visible.**



**Figure 12—VIS-NIR spectrum of a hydrothermal synthetic emerald with equal concentrations of chromium and vanadium. The triplet of absorption peaks at 1900 nm, attributed to H<sub>2</sub>O molecules, is small, all three peaks are equal in intensity.**





# Conclusions

Although harder to identify than former hydrothermal synthetic emeralds, the stones sold by A G Japan are different from natural emeralds in many cases. They do not show typical mineral inclusions, such as mica flakes, chromite grains, tremolite needles, etc as described by Gubelin & Koivula (1986) or Schwarz (1987). On the other hand, characteristic features which allow an identification may be present. Most important are structural features like the angular "chevron"-shaped growth and color zoning. Screw-like turns or fans of tiny healing fissures are sometimes visible, but of lesser diagnostic value because such features occur in similar aspect in natural emeralds (see Bosshart, 1991).

Chemical tests may be very helpful since the considerable content of Chlorine may be regarded as the most secure proof of these synthetic emeralds. In comparison with natural emeralds (see Kazmi & Snee, 1989) further chemical differences may also become evident. An inspection of the near-infrared spectral region will indicate a smaller H<sub>2</sub>O feature than found in most of the natural emeralds, including Colombian material.

In many ways, AGEE synthetic emeralds resemble hydrothermal synthetic emeralds produced by Biron. The stones have the same density values, and most similar refractive indices and chemical composition. Many of the inclusions observed in AGEE hydrothermal synthetic emeralds are also described for Biron hydrothermal synthetic emeralds by Kane & Liddicoat (1985). A difference to Biron hydrothermal synthetic emeralds we have seen so far is the relative impurity of the stones sold by AGEE. We could imagine that the lower quality sector of synthetic emeralds produced by Biron International Limited is sold via A G Japan Ltd.

## Acknowledgments

**Shyamala Fernandes**, Gem Testing Laboratory, Jaipur, India for communication of her findings regarding inclusions and physical values of AGEE synthetic emeralds.

**Junko Shida**, Gemmological Association of All Japan, Tokyo, and **R Durlabhji**, Jaipur, India for the donation of the investigated stones.

## References

- Bosshart, G (1991): Emeralds from Colombia (Part II). *Journal of Gemmology*. 22, 409-425.
- Gubelin, E & Koivula, J I (1986): Photoatlas of Inclusions in Gemstones. ABC Edition, Zurich.
- Hanni, H A (1982): A contribution to the separability of natural and synthetic emeralds. *Journal of Gemmology*. 18, 138-144.
- Hanni, H A (1993): Hydrothermal synthetic emeralds from Australia: Emeralds and pink beryls. *Swiss Watch and Jewelry Journal*, 1/1993, 133-136.
- Kane, R E & Liddicoat Jr, R T (1985): The Biron hydrothermal synthetic emerald. *Gems & Gemology* 21, 158-170.
- Kazmi, A H & Snee L W (Eds) (1989): Emeralds of Pakistan: Geology, Gemology, and Genesis. Van Nostrand Reinhold, New York.
- Schmetzer, K (1988): Characterization of Russian hydrothermally grown synthetic emeralds. *Journal of Gemmology*. 21, 145-164.
- Schrader, H W (1983): Contributions to the study of the distinction of natural and synthetic emeralds. *Journal of Gemmology*. 18, 530-543.
- Schwarz, D (1987): Esmeraldas—Inclusões em Gemas. Escola de Minas, Imprensa Universitaria, Universidade Federal de Ouro Preto, Brazil.
- Wood, D L & Nassau, K (1968): Characterization of beryl and emerald by visible and infrared absorption spectroscopy. *American Mineral*. 53, 777-800.