Natural Alexandrite with an Irregular Growth Pattern A Case Study

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作者們對一顆聲稱來自馬達加斯加，含有異常的、類似合成寶石包裹體的亞歷山大石進行檢測；並與馬達加斯加產出之一般天然亞歷山大石和金綠寶石，和日本精工廠生產的合成寶石作詳細檢測及比較，確定其為天然金綠寶石。

Abstract: The diagnostic properties of a faceted alexandrite, reportedly originating from Madagascar, with unusual microscopic features are described. The results of microscopic and chemical examination are compared with properties of natural alexandrite and chrysoberyl from Mananjary and Ilakaka in Madagascar and with those of synthetic gem materials grown by Seiko in Japan.

Introduction

Two different occurrences of gem quality alexandrites on the island of Madagascar have been mentioned to date. Chrysoberyls and alexandrites from the secondary deposits in the Ilakaka area in southern Madagascar are occasionally seen in the market (Hänni, 1999; Milisenda et al., 2001; Schmetzer et al., 2002), but alexandrites from the primary Mananjary emerald deposit in the eastern part of Madagascar are only rarely encountered as rough or faceted samples (Schmetzer, 2002). Therefore, faceted alexandrites from one of these deposits in Madagascar are always interesting, especially to complete the data base available for origin determination as a laboratory service for interested clients.

A sample of 1.10 ct (Fig. 1) reportedly originating from Madagascar was recently received for examination. This faceted alexandrite showed a pronounced irregular growth structure, which has, up to now, mainly been seen in synthetic alexandrites

Fig. 1 Faceted alexandrite of 1.10 ct in weight which is reported to originate from Madagascar in daylight (left) and incandescent light (right). Size 7.6 x 5.1 mm
Photo by K. Schmetzer

grown using the floating zone technique used by Seiko in Japan. Therefore, the authors used the opportunity to examine and describe briefly the diagnostic properties of this alexandrite and to compare these properties with those of other natural and synthetic samples.

Alexandrite with irregular growth pattern

The growth pattern of the sample depicted in Figure 1 is quite similar to the pattern of the synthetic material grown by Seiko in Japan. The sample shows several irregularly curved grain boundaries, which reveal a characteristic interference pattern under crossed polarisers (Fig. 2). However, in plane polarised light, the outline of the boundaries is somewhat weaker compared to the synthetic material produced by Seiko. In addition, an area with a series of plane growth faces was observed, which also shows some colour zoning (Fig. 3). No mineral inclusions of diagnostic value were observed in this sample.

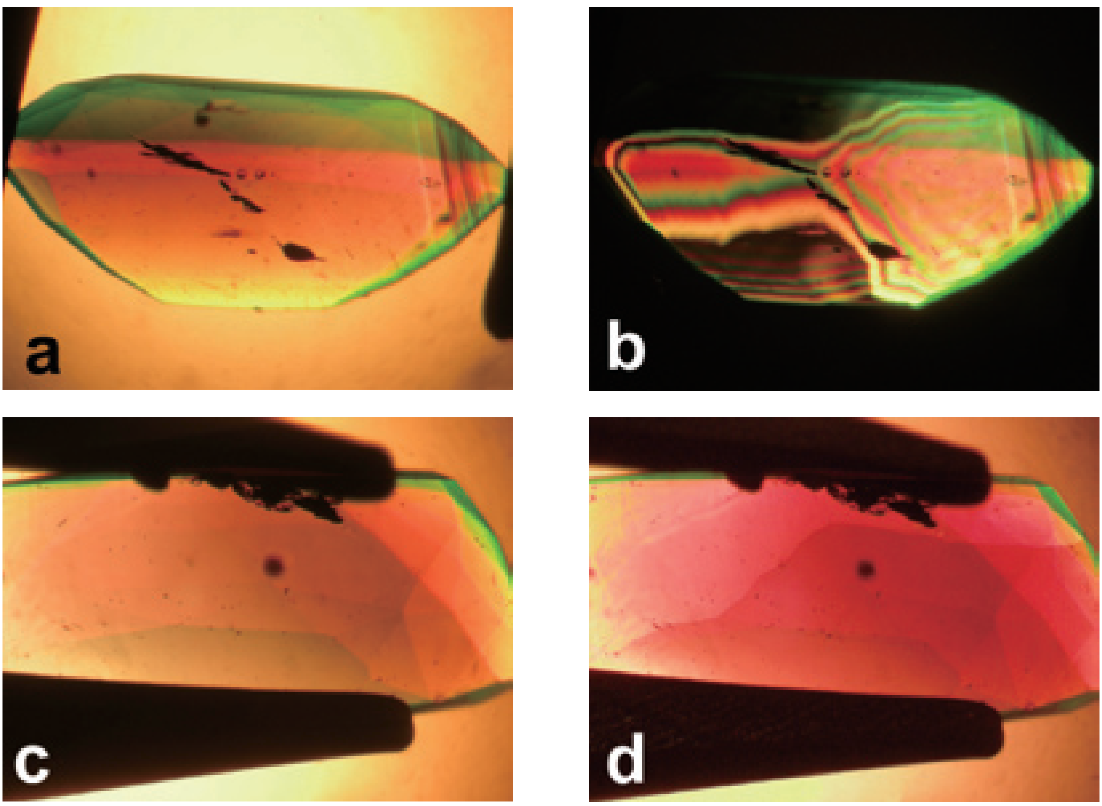

Fig. 2 Interference figures and irregularly curved grain boundaries in natural alexandrite of 1.10 ct in weight, size 7.6 x 5.1 mm (see Fig. 1) in two different orientations. The photos were taken in plane polarised light (a, c) and under crossed polarisers (b, d).
Photos by K. Schmetzer

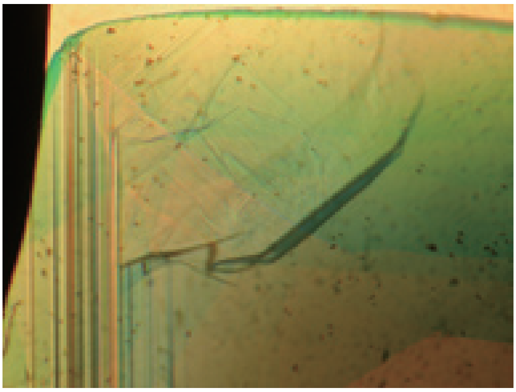

Fig. 3 The microscopic examination of a natural alexandrite of 1.10 ct (see Fig. 1) shows a series of plane parallel growth faces associated with colour zoning and irregularly curved grain boundaries. Immersion, 60X
Photo by K. Schmetzer

Investigations by infrared spectroscopy in the range 2000 - 4200 cm^{-1} revealed OH-related features contradicting a genesis by high-temperature synthesis, but in agreement with characteristics of natural alexandrite (Stockton and Kane, 2002).

Synthetic alexandrites from Seiko

Synthetic alexandrites from Seiko in Japan (Fig. 4) have been known in the trade since the 1980s. These samples are grown by the floating zone (FZ) technique, which is described in detail by Kochi (1980). A schematic outline of the experimental setting is given in Figure 5. A rod is pressed from powder consisting of the main components of chrysoberyl, BeO and Al_2O_3. For colouration, chromium oxide is added to the powder of beryllium and aluminium oxide and for the production of cat's-eyes, minor amounts of titanium oxide are added to the nutrient. The desired single crystals of chrysoberyl or alexandrite are produced by heating of the rods in a controlled atmosphere using infrared rays. A suitable source for the infrared light is a halogen lamp or a xenon lamp. The infrared rays are focused by an ellipsoidal reflector upon a restricted portion of the rod to form a melt zone which is moved along the rod. During the melting and crystallisation steps, the melt zone is moved upwards by moving the feed rod downwards under rotation of the ends of the rod.

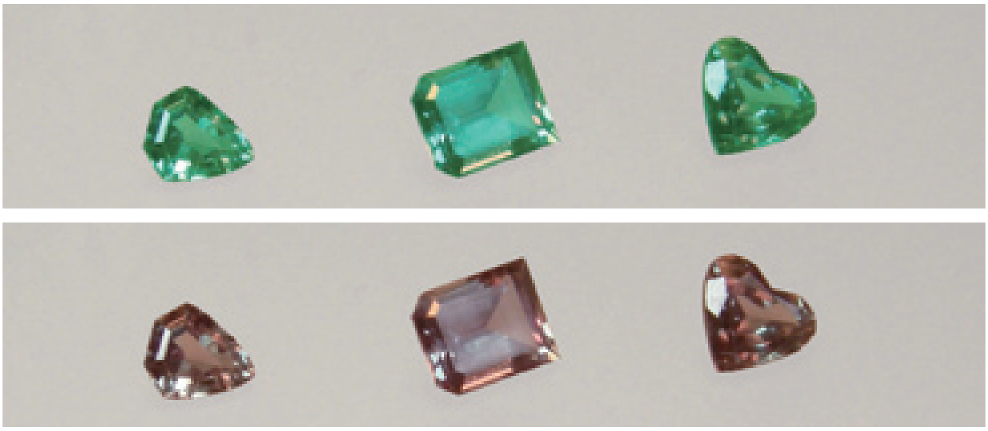

Fig. 4 Faceted synthetic alexandrites of 0.21 to 0.54 ct in weight grown by the floating zone technique by Seiko in Japan in daylight (above) and incandescent light. The sample in the centre weighs 0.54 ct and measures 5.1 x 4.2 mm. *Photo by K. Schmetzer*

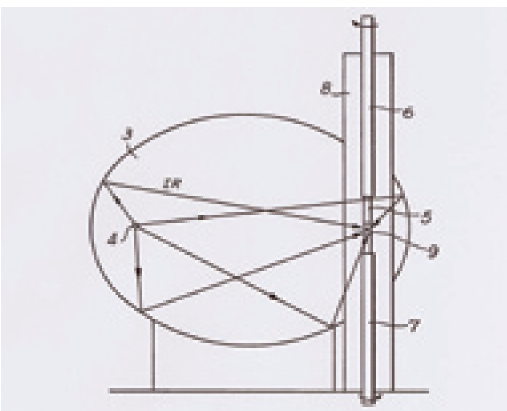

Fig. 5 Schematic outline of the floating zone technique which was used by Seiko in Japan to grow synthetic alexandrite single crystals: 3-ellipsoidal mirror; 4-halogen or xenon lamp; 5-feed rod; 6, 7-upper and lower rotation axes for the feed rod; 8-quartz tube; 9-melt zone, IR infrared rays. From US Patent 4,218,282, inventor: A. Kochi, applicant: Kabushiki Kaisha Suwa Seikoska

This specific production process is responsible for the most characteristic internal properties of this type of samples. Under the gemmological microscope, especially under immersion, irregularly curved grain boundaries are observed, which reveal a characteristic interference pattern under crossed polarisers (Fig. 6). Using plane polarised light it is evident, that the boundaries do not represent twin boundaries, simply because the parts of the alexandrites separated by these boundaries always show identical colours and not the different colouration of areas separated by twin boundaries. The governing twin law in chrysoberyl or alexandrite is reflection on (031) or $(0\bar{3}1)$ (see Schmetzer, 2010, 2011). In addition to the structural pattern described, gas bubbles are occasionally seen in the synthetic crystals grown by Seiko.

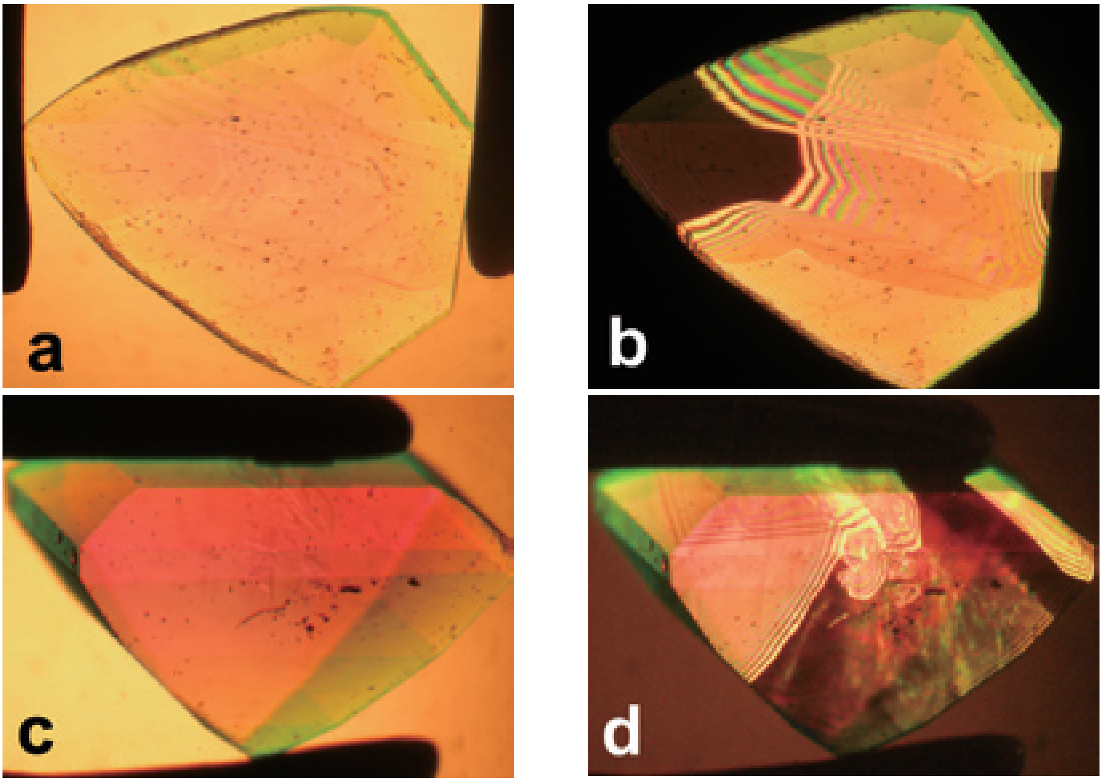

Fig. 6 Interference figures and irregularly curved grain boundaries in synthetic alexandrites grown by Seiko in Japan. Upper row, sample of 0.21 ct in weight, size 4.2 x 3.7 mm (see Fig. 4, left sample); lower row, sample of 0.54 ct in weight, size 5.1 x 4.2 mm (see Fig. 4, sample in the centre). The samples are shown in plane polarised light (a, c) and under crossed polarisers (b, d).
Photos by K. Schmetzer

Alexandrites from Mananjary, Madagascar

Alexandrites from the area of the primary emerald deposits in the Mananjary region of Madagascar originate from a phlogopite-bearing host rock (Fig. 7). Even larger crystals of about 71 ct in weight have been found (Fig. 8). These rough crystals show transparent, clear areas, but frequently also milky white zones (Figs 7, 8). In faceted samples, microscopic examination resolves these milky-white reflecting zones and shows numerous oriented needle-like particles. These reflecting particles are responsible for the milky white appearance of some samples when viewed from specific angles.

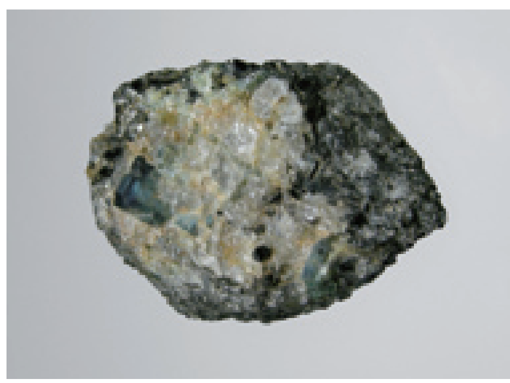

Fig. 7 Tabular alexandrite crystal from the Mananjary emerald deposit in Madagascar in matrix in daylight. The rock specimen (phlogopite schist) measures about 6 x 4 cm, the single crystal is about 1 cm wide.
Photo by K. Schmetzer

Fig. 8 Columnar alexandrite twin of 70.74 ct in weight from the Mananjary emerald deposit in Madagascar in daylight (top left) and incandescent light. Dimensions about 18 x 16 x 21 mm.
Photo by K. Schmetzer

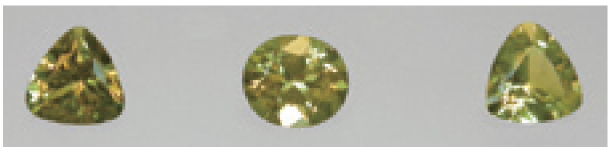

Fig. 9 Faceted greenish yellow chrysoberyls of 1.46 to 1.78 ct in weight from the Ilakaka mining area, Madagascar, in daylight. The sample in the centre weighs 1.62 ct and measures 7.9 x 6.9 mm.
Photo by K. Schmetzer

Fig. 10 Example of a faceted alexandrite of 1.25 ct in weight originating from the secondary deposit in the Ilakaka area, Madagascar in daylight (left) and incandescent light (right). Size 13 x 12 mm.
Photo by A.-K. Malsy

Chrysoberyls and alexandrites from the Ilakaka mining area, Madagascar

The large secondary deposit in the area of Ilakaka, Madagascar, has supplied different varieties of chrysoberyl including chrysoberyl cat's-eyes and alexandrites (Hänni, 1999; Milisenda et al., 2001). Yellowish green and green chrysoberyls from this area were described by Schmetzer et al. (2002).

The yellow to green chrysoberyls and alexandrites examined (Figs 9, 10) mostly show a very complex pattern of internal growth planes (Fig. 11a, b), similar to the internal growth structures seen in alexandrites from Sri Lanka. However, in rare cases, a growth structure consisting of several irregularly curved grain boundaries, which reveal a characteristic interference pattern under crossed polarisers, was also observed (Fig. 12). This pattern is comparable to the internal growth structure observed in the alexandrite sample of 1.10 ct described above (see again Figs 1-3).

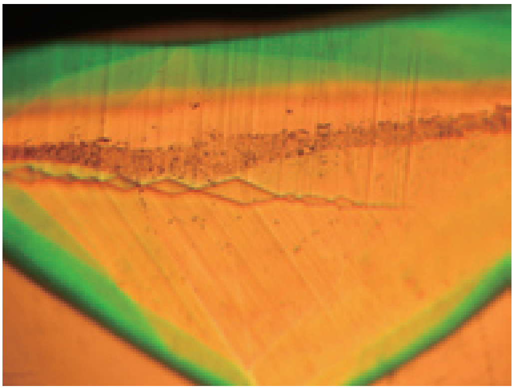

Fig. 11a

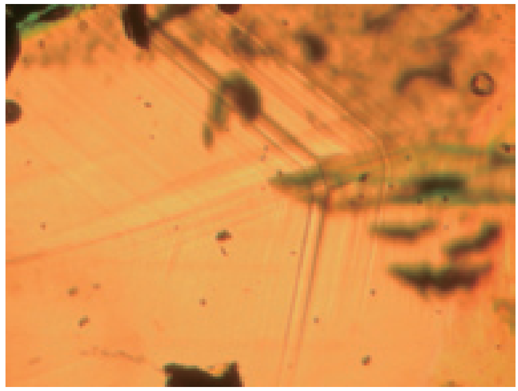

Fig. 11b

Fig. 11 a,b The microscopic examination of greenish yellow or yellowish green chrysoberyls as well as colour-change alexandrites from Ilakaka, Madagascar, shows a complex growth pattern consisting of different series of growth planes. Two examples are given for a greenish yellow chrysoberyl (a) and a colour-change alexandrite (b) Immersion, 30X (a), 60X (b).
Photos by K. Schmetzer

Table 1. Ranges of colour causing trace element contents in selected natural and synthetic alexandrites (in wt%)

Samples	**Remarks**	**V_2O_3**	**Cr_2O_3**	**Fe_2O_3**
Rough alexandrite, Mananjary, 70.74 ct	Fig. 8	0.013-0.022	0.07-0.23	1.35-1.67
Faceted alexandrite, 1.10 ct	Fig. 1	0.014-0.018	0.18-0.22	0.92-1.23
Alexandrites, Ilakaka	Fig. 10	0.006-0.052	0.06-0.20	0.73-1.90
Greenish yellow chrysoberyls, Ilakaka	Fig. 9	0.004-0.026	0.02-0.03	1.25-1.51
Synthetic alexandrites grown by Seiko	Fig. 4	below detection limit	0.14-0.26	0.38-0.78

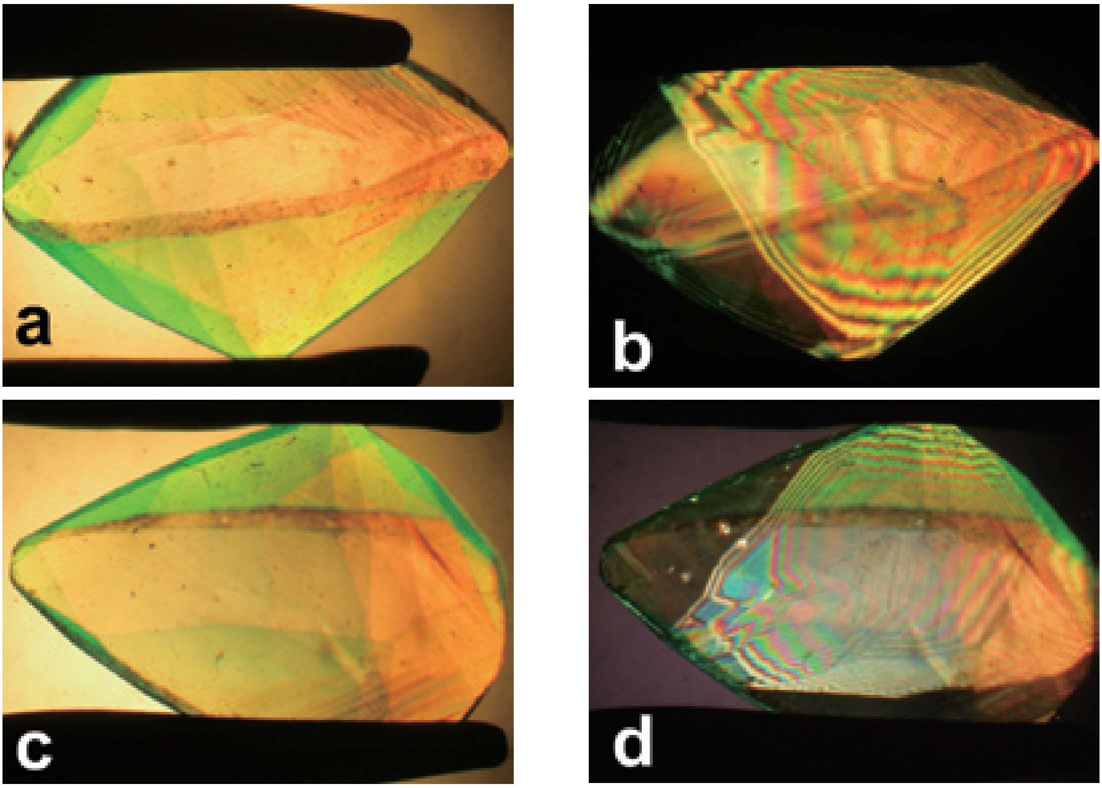

Fig. 12 Interference figures and irregularly curved grain boundaries in natural greenish yellow chrysoberyl of 1.46 ct in weight, size 7.3 x 7.2 mm (see Fig. 9, left sample) in two different orientations (upper and lower row). The photos were taken in plane polarised light (a, c) and under crossed polarisers (b, d). *Photos by K. Schmetzer*

Trace element chemistry

In addition to the microscopic examination, trace element chemistry was performed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS); details of the technique are given by Malsy (2010).

Concentrations of colour causing trace elements, i.e. vanadium, chromium, and iron contents are summarised in Table 1 and shown graphically in Figure 13. Chromium contents in the larger sample of 70.74 ct rough from Mananjary were quite variable (from 0.07 to 0.23 wt% Cr_2O_3), which reflects the varying colour intensity observed in different parts of this large crystal. Alexandrites from the large mining area of Ilakaka reveal similar chromium contents in the range of 0.06 to 0.20 wt% Cr_2O_3. The two samples described by Schmetzer et al. (2002) contained chromium contents in the same range of 0.06 or 0.12 wt% Cr_2O_3, respectively. The alexandrite of 1.10 ct was in the upper part of this range measured for Madagascar samples. In contrast, some greenish yellow samples from Ilakaka examined recently by the authors (Fig. 9) showed distinctly lower chromium contents of 0.02 to 0.03 wt.% Cr_2O_3. Please note that a detailed discussion about the separation of alexandrite from the green of yellowish green chrysoberyl is beyond the scope of this paper.

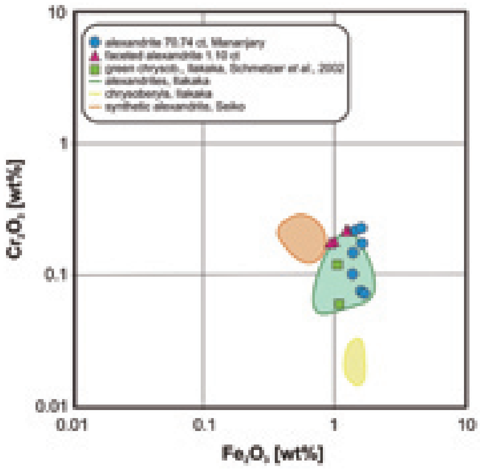

Fig. 13 Fe_2O_3/Cr_2O_3 binary diagram showing the variability of these two colour-causing trace elements in alexandrite and green to yellow chrysoberyl from Madagascar compared to the trace element contents of synthetic alexandrite grown by Seiko in Japan.

The chromium content of the synthetic alexandrite material from Seiko varies from 0.14 to 0.26 wt% Cr_2O_3 and, thus, was found to overlap with the chromium values of the samples from Madagascar. Only slightly lower iron contents were detected in the synthetic alexandrite crystals from Seiko.

Binary and ternary graphs of different trace elements are applied for locality determination (Malsy, 2010), but can also be applied for the separation of natural and synthetic alexandrites. One example is depicted in Figure 14. The binary graph shows the variability of magnesium versus tin in natural samples from Madagascar and synthetic alexandrites grown by Seiko. The different trace element contents in both groups of samples are obvious. Another possible graph which clearly shows different population fields for natural and synthetic samples is a plot of boron versus gallium contents. The trace element pattern of the faceted sample with irregularly curved growth boundaries (Fig. 1) is comparable with the analytical data measured for natural samples.

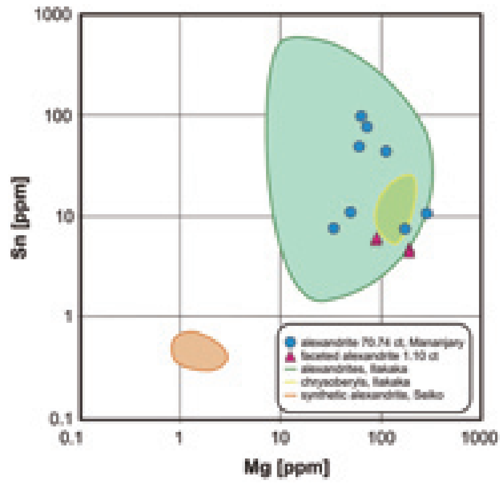

Fig. 14 Binary diagram showing the variability of magnesium and tin (given as parts per million by weight) in synthetic alexandrites grown by the floating zone technique by Seiko and different natural alexandrites reportedly originating from Madagascar. Synthetic alexandrites, in general, contain smaller amounts of trace elements than natural chrysoberyl and alexandrite.

Conclusions

Although the faceted sample with irregular growth boundaries described in this paper shows a pattern which is typically observed is synthetic alexandrite grown by the floating zone technique, the alexandrite also reveals several properties which would allow this gemstone to be determined as natural. First, the plane growth structures associated with colour zoning have not yet been observed in any synthetic alexandrite grown by the floating zone technique. In addition, the trace element pattern is distinct from that of Seiko synthetics and similar to the pattern of natural alexandrite unearthed from the primary emerald deposits in Madagascar or from the large secondary gem field of Ilakaka. Finally, the infrared spectrum shows the characteristic absorption band of natural chrysoberyl.

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