

NATURALLY-COLOURED AND TREATED YELLOW AND ORANGE-BROWN SAPPHIRES

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ABSTRACT

Natural yellow, orange and orange-brown sapphires owe their colour to colour centres and/or to trace elements (Fe^{3+} , Ti^{3+} , Cr^{3+}). Similar colorations can be achieved in synthetic corundums by Ni^{2+} and Cr^{3+} as well as by an additional annealing procedure. With colourless or pale yellow natural corundums, comparable hues can be obtained by irradiation or by annealing. Both types of treatment (irradiation or annealing) generate colour centres which cause a continuous increase of light absorption from orange to the blue end of the visible spectrum. They also produce a broad absorption band at approximately $21\,500\text{ cm}^{-1}$ (465 nm). These treated natural corundums appear in intense yellow to orange-brown colours. While the colour centres, artificially induced by irradiation, are extremely unstable, the colour centres created by annealing do not heal out on further heating up to $1000\text{ }^{\circ}\text{C}$. For use in jewellery annealed stones can thus be considered colour-stable.

With regard to absorption, the irradiated or heated corundums differ little from naturally-coloured light yellow sapphires from Sri Lanka, apart from the generally stronger absorption in the violet and ultraviolet regions. On the contrary, intensely yellow to yellow-brown sapphires exhibit a pronounced iron or iron-chromium spectrum and synthetic yellow to orange corundums show a nickel or nickel-chromium spectrum. The inclusions of annealed golden yellow sapphires present the same modified characteristics as those encountered in heated corundums of the other hues.

In practical gemmology, the problem of identifying irradiated as well as synthetic yellow and orange-brown corundums has repeatedly been a matter of discussion (Oughton, 1970; McColl, 1970; McColl & Oughton, 1971; Schiffmann, 1981). The present study compares the results of an investigation on a *new type of golden-yellow corundums* (on one side) with the well-known natural and synthetic yellow and brown sapphires (on the other side). These new stones have been on the gem market for some time, occasionally offered by the dealers as corundums of 'treated' yellow to orange-brown colour. Colorations similar to these treated ones are shown by untreated natural yellow corundums known to originate from Sri Lanka, Thailand, Tanzania and Australia and

TABLE 1. Causes of coloration of yellow, orange and orange-brown corundums

	Colour	Colour causes	Colour after heating to 500 °C	Colour after irradiation with x-rays
untreated natural corundum	pale yellow ^a	colour-centres $\pm \text{Fe}^{3+}$	colourless*	more intensely yellow-orange
	pink-orange ^a (padparadshah)	colour-centres $+ \text{Cr}^{3+} \pm \text{Fe}^{3+}$	pink (pale ruby)	
	intensely yellow ^{b,c,d}	$\text{Fe}^{3+} + \text{Ti}^{3+}$ $\text{Fe}^{3+} + \text{Cr}^{3+}$ $\text{Fe}^{3+} + \text{Ti}^{3+} + \text{Cr}^{3+}$	unchanged	
	yellow-orange to orange-brown ^d	$\text{Fe}^{3+} + \text{Cr}^{3+}$	unchanged	
annealed natural corundum	intensely yellow, yellow-orange or orange-brown	colour centres	unchanged	more intensely yellow, orange or brown
irradiated natural corundum	intensely yellow, yellow-orange or orange-brown	colour centres	colourless*	intensely yellow, yellow-orange or orange-brown
synthetic corundum, in part annealed, doped with Ni \pm Mg, Fe, Ca Cr \pm Mg, Fe, Ca Ni + Cr \pm Mg, Fe, Ca	yellow or yellow-orange [†]	Ni^{3+} or Cr^{3+} or $\text{Ni}^{3+} + \text{Cr}^{3+}$ \pm colour-centres (produced by annealing)		

Sources: a Sri Lanka, b Australia, c Thailand, d Tanzania

*Occasionally a residual pale yellow coloration is visible (Fe^{2+}).

†Further possibilities of yellow coloration of synthetic corundums are conceivable. In a yellow-orange specimen of Verneuil corundum Ca and V were detected experimentally (in the absence of Ni and Cr).

TABLE 2. Chemical data for natural and synthetic yellow and orange sapphires, in weight %
(atomic absorption spectroscopy*)

Source	Colour	Mg	Cr	Mn	Fe	Ni	Spectrum
Sri Lanka	pale yellow	0.008	0.004	0.002	0.05	0.011	Fig. 1c
Sri Lanka	pale yellow	0.010	0.005	0.002	0.11	0.004	Fig. 1b
Anakie, Australia	intensely yellow	0.008	0.004	0.002	0.75	0.007	Fig. 4b
Umba, Tanzania	intensely yellow	0.015	0.008	0.004	0.50	0.006	Fig. 5a
Umba, Tanzania	intensely yellow	0.007	0.012	0.003	0.42	0.003	Fig. 5b
synthetic sapphire, Verneuil (annealed?)	light yellow	0.010	0.013	0.004	0.04	0.011	Fig. 7a
synthetic sapphire, Verneuil (annealed?)	orange	0.006	0.016	0.003	0.02	0.007	Fig. 7b

*Ti < 0.05; V < 0.005; Ca < 0.05 (in all specimens); the vanadium contents of the samples are near the limit of detectability of the method used; in small concentrations vanadium reinforces the colour due to Cr³⁺ (Schmetzer & Bank, 1981).

by the padparadshah variety from Sri Lanka. The golden-yellow colours also are comparable to those of artificially irradiated yellow to orange-brown sapphires as well as to the coloration of synthetic yellow to orange-brown corundums by Verneuil, produced by the addition of nickel or nickel plus chromium (Recker, 1973). The colours of the latter can be intensified by an additional heat treatment. A compilation of the various types of natural and synthetic yellow, orange and orange-brown corundum and of the origin of their colours is presented in Table 1 (cf. Schmetzer & Bank 1980, 1981). New analytical data are given in Table 2.

Natural pale yellow corundums are coloured by colour centres and so far are known to the authors to originate only from Sri

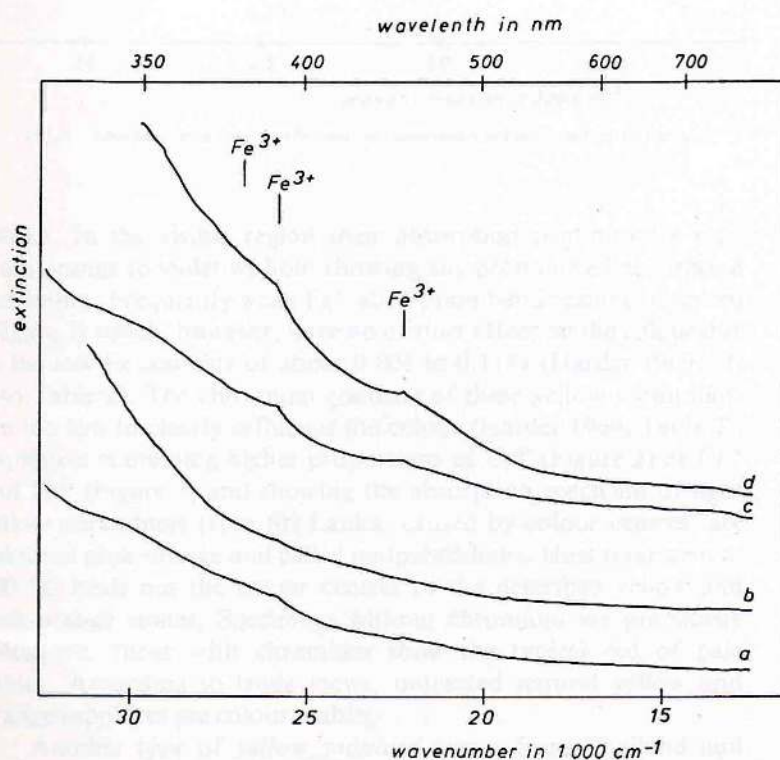


FIG. 1. Absorption spectra of pale yellow naturally-coloured corundums from Sri Lanka.

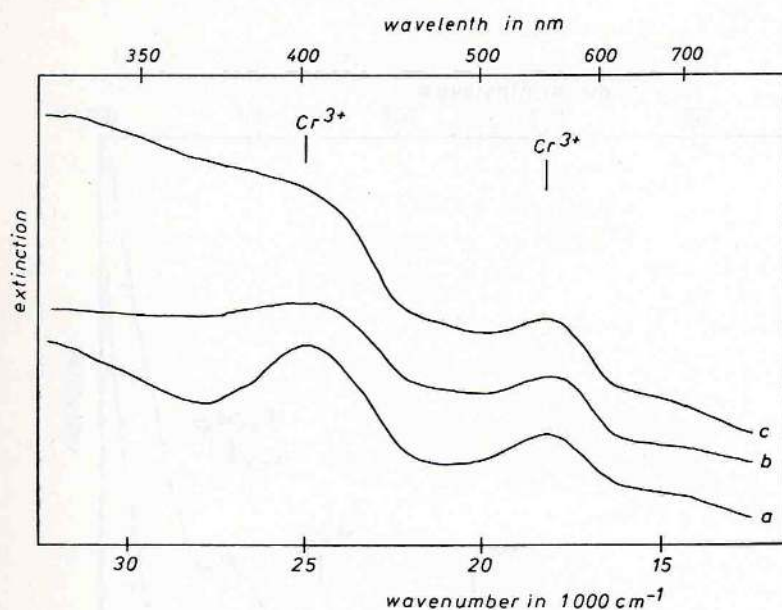


FIG. 2. Absorption spectra of the pink-orange corundum variety padparadshah from Sri Lanka.

Lanka. In the visible region their absorption continuously rises from orange to violet without showing any pronounced absorption maximum. Frequently weak Fe^{3+} absorption bands can be observed (Figure 1) which, however, have no distinct effect on the colour due to the low Fe contents of about 0.005 to 0.11% (Harder 1969, cf. also Table 2). The chromium contents of these yellow corundums are too low to clearly influence the colour (Harder 1969; Table 2). Sapphires containing higher proportions of Cr^{3+} (Figure 2) or Cr^{3+} and Fe^{3+} (Figure 3) and showing the absorption spectrum of light yellow corundums from Sri Lanka, caused by colour centres, are coloured pink-orange and called padparadshahs. Heat treatment at 500 °C heals out the colour centres of the described yellow and pink-orange stones. Specimens without chromium are practically colourless, those with chromium show the typical red of pale rubies. According to trade views, untreated natural yellow and orange sapphires are colour-stable.

Another type of *yellow sapphire* comes from Thailand and Australia. Stones from these sources show iron contents between

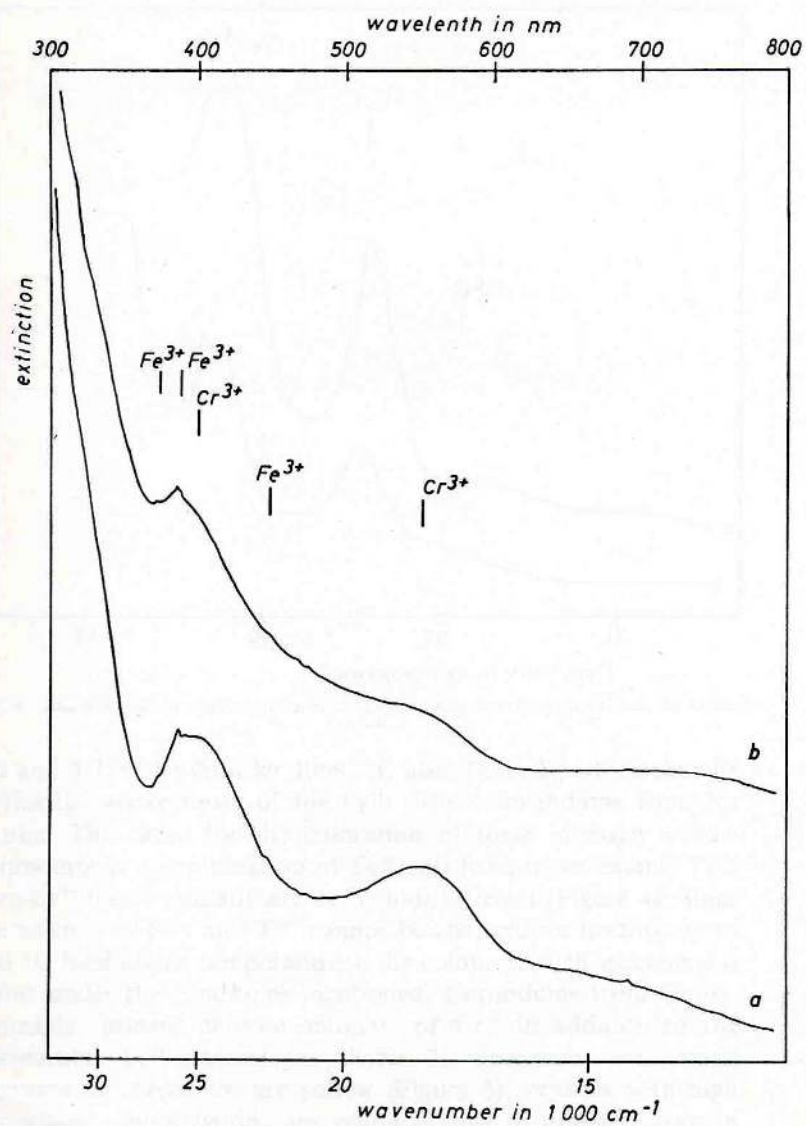


FIG. 3. Absorption spectra of the pink-orange corundum variety padparadshah from Sri Lanka.

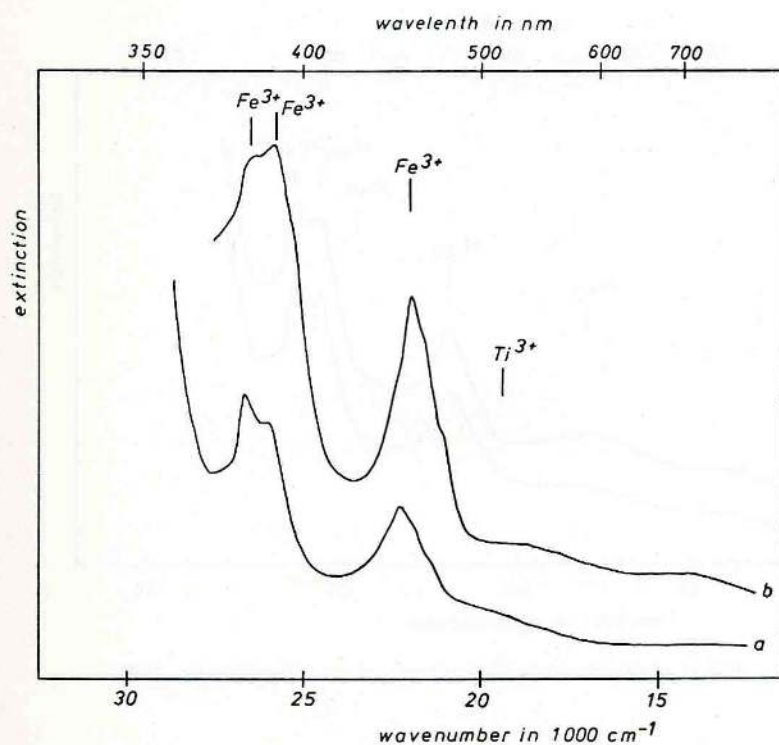


FIG. 4. Absorption spectra of golden yellow naturally-coloured sapphires from (a) Thailand, (b) Anakie, Australia.

0.5 and 0.75% Fe (Harder 1969, cf. also Table 2), which thus lie distinctly above those of the light yellow corundums from Sri Lanka. The cause for the coloration of these intensely yellow corundums is a combination of Fe^{3+} and (to a lesser extent) Ti^{3+} ; here Cr^{3+} traces virtually are not colour-efficient (Figure 4). Since the valence of Fe^{3+} and Ti^{3+} cannot be changed on heating up to 500 °C (and higher temperatures), the colour of such specimens is stable under the conditions mentioned. Corundums from Umba, Tanzania, present definite amounts of Cr^{3+} in addition to the comparable Fe^{3+} percentages (Table 2). Specimens with small amounts of chromium are yellow (Figure 5), crystals with high chromium concentrations are yellow-orange to orange-brown in colour (Figure 6). As yet sapphires of this type have been noted only from Umba, Tanzania. Heating up to 500 °C does not alter the described colours.

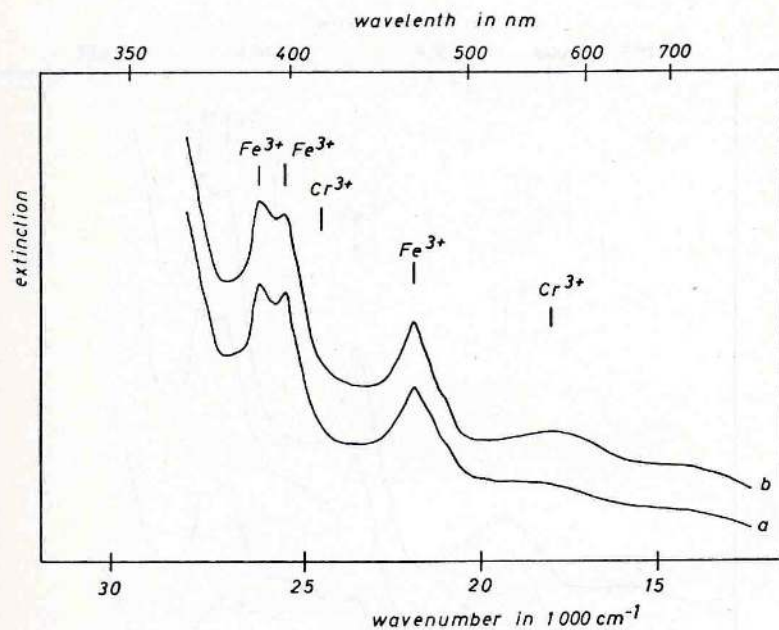


FIG. 5. Absorption spectra of yellow naturally-coloured sapphires from Umba, Tanzania.

Synthetic sapphires exhibit similar hues to those of natural sapphires although the latter mostly have other causes of coloration. The yellow colours of Verneuil synthetics are produced by Ni^{3+} , while orange hues are brought about by Cr^{3+} and Ni^{3+} (Figure 7, Table 2). By the addition of divalent cations (Mg^{2+} , Fe^{2+} , Ca^{2+}) and by subsequent annealing the colours of the commercially grown synthetic stones can be intensified, according to information on hand (cf. Table 1).

It has been known for quite some time that x- or γ -rays produce bright yellow and yellow-orange hues with originally pale yellow or almost colourless sapphires from Sri Lanka. The improved colours, however, become unstable when exposed to daylight (Pough & Rogers, 1947). Similarly after short-term heating to 500°C the colour centres created by irradiation can be healed out too: the heated stones ordinarily turn completely colourless. Therefore the finding came as a surprise that the colour of the new type of 'treated' sapphire, which is indistinguishable

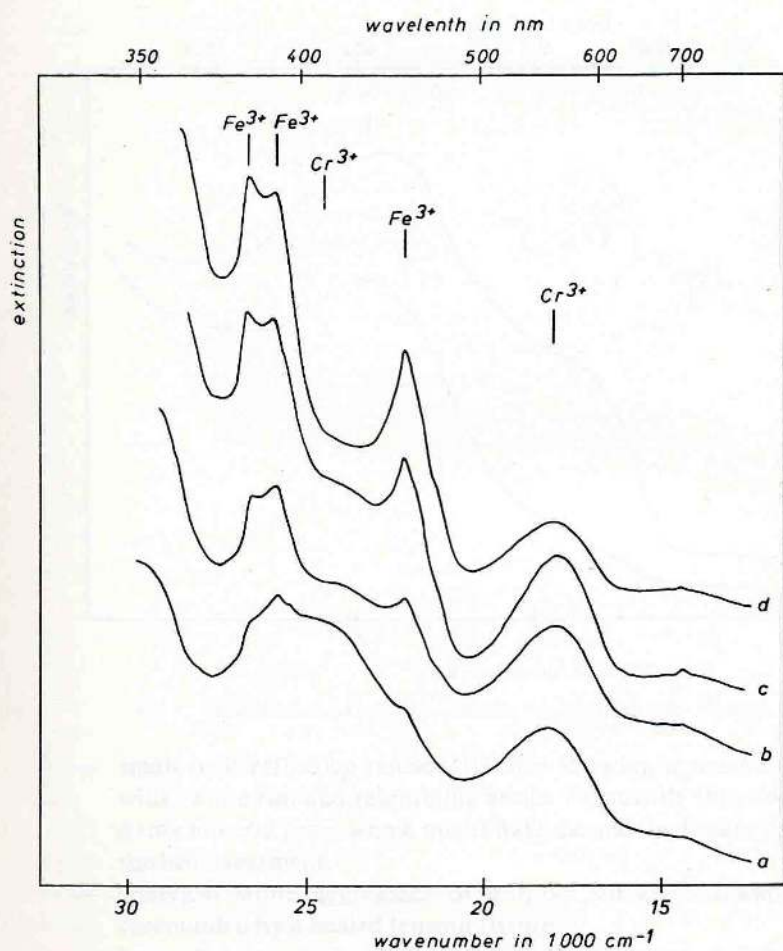


FIG.6. Absorption spectra of orange-brown naturally-coloured sapphires from Umba, Tanzania.

from the irradiated one in terms of colour, remained stable on heating at 500 °C and even up to 1000 °C. An irradiation could thus not be the cause of the strong yellow or orange coloration.

The examination of the *inclusions* of some rough and cut stones which in part stemmed directly from the corundum cookery in Thailand produced the following results (Figures 8 to 11):

- clouds of tiny inclusions mostly concentrated in certain zones and of turbid appearance under the microscope.

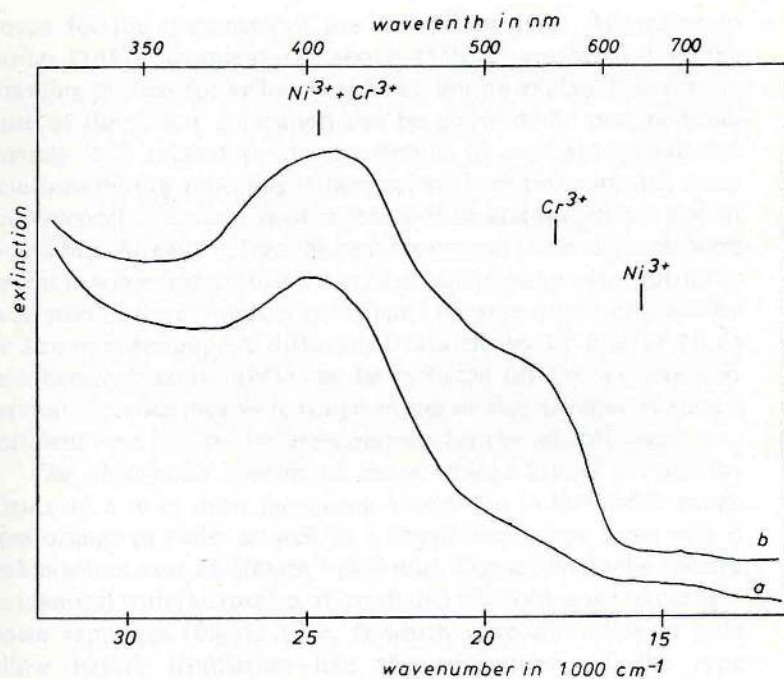


FIG. 7. Absorption spectra of synthetic corundums by Verneuil, (a) light yellow, (b) orange.

- small oval reflective tension fissures showing a more or less wide, white rim and resembling atolls. Frequently they contain a tiny mineral grain which might have caused the fissure during the heat treatment.
- spherical white aggregates of a spiky surface, occasionally surrounded by a healed tension fissure.
- larger healing cracks (feathers) with drop-shaped to tube-like cavities.
- altered fibre-like zonal structures with oriented inclusions (rutile, hollow tubes?).

The inclusions of these golden-yellow corundums thus exhibited the characteristics of the types of inclusion found in annealed natural corundums (Nassau, 1981; Crowningshield & Nassau, 1981; Hänni, 1982). A heat treatment as described recently in several articles (Gunaratne, 1981; Nassau, 1981; Crowningshield & Nassau, 1981; Harder, 1982) therefore can also be considered

proven for the specimens of the new yellow type. According to Harder (1982), temperatures above 1550 °C are applied in the annealing process for yellow sapphires, but no explanation for the cause of the yellow coloration can be given at the present time. Possibly it is related to the resorption of pre-existent mineral inclusions during annealing. Chemical analyses (microprobe, x-ray fluorescence) indicate limited contents of Fe and sometimes also of Cr and Mg. Already before the heat treatment, these elements were present in some form inside the crystal (as inclusion constituents or on Al sites of the corundum lattice) and became colour-efficient by the strong annealing. A diffusion treatment by Cr and/or Ni as described by Nassau (1981) can be excluded for the specimens at disposal, because they were rough stones or else no signs of such a treatment were observed microscopically for the cut specimens.

The absorption spectra of burnt orange-brown corundums (Figure 12 a to c) show increasing absorption in the visible range from orange to violet as well as a broad absorption band with a peak position near $21\,500\text{ cm}^{-1}$ (465 nm). Consequently the spectra are identical with the spectra of irradiated vividly orange to orange-brown sapphires (Figure 12 e, f) which were colourless or pale yellow before irradiation like the corundums of the type represented in Figure 1. The absorption spectra of annealed or irradiated yellow to orange-brown corundums thereby differ clearly from the Fe-Cr spectra of natural yellow, orange or orange-brown sapphires (Figure 2 to 6). By subsequent additional irradiation of the annealed yellow corundums, their coloration can be reinforced. The absorption spectra of such heated and irradiated corundums exhibit the same characteristics as the spectra of solely annealed or solely irradiated sapphires (Figure 12 d). A second heat-treatment heals out the colour centres additionally produced by the irradiation. The coloration and the intensity of the absorption bands correspond to the status before irradiation (after the first annealing), which means that the stones still are yellow-orange to orange-brown in colour.

The influence of the various *colour centres* on the optical properties of rubies and sapphires as well as the methods of their creation in synthetic corundums have been discussed in a considerable number of papers. While formerly synthetic chromiferous corundums (rubies) were of primary interest due to their importance for laser techniques (e.g. Flowers & Jenney, 1963;



FIG. 8. Clouds of tiny inclusions and reflective, marginally structured tension fissures in an annealed yellow corundum; 40 x.



FIG. 9. Plate-like tension fissure resembling an atoll, in an annealed yellow corundum; 30 x.



FIG. 10. Healing fissure of drop-shaped and tubular cavities in an annealed yellow corundum; 40 x.



FIG. 11. Fibre-like altered, oriented inclusions and plate-like tension cracks in an annealed yellow corundum; 10 x.

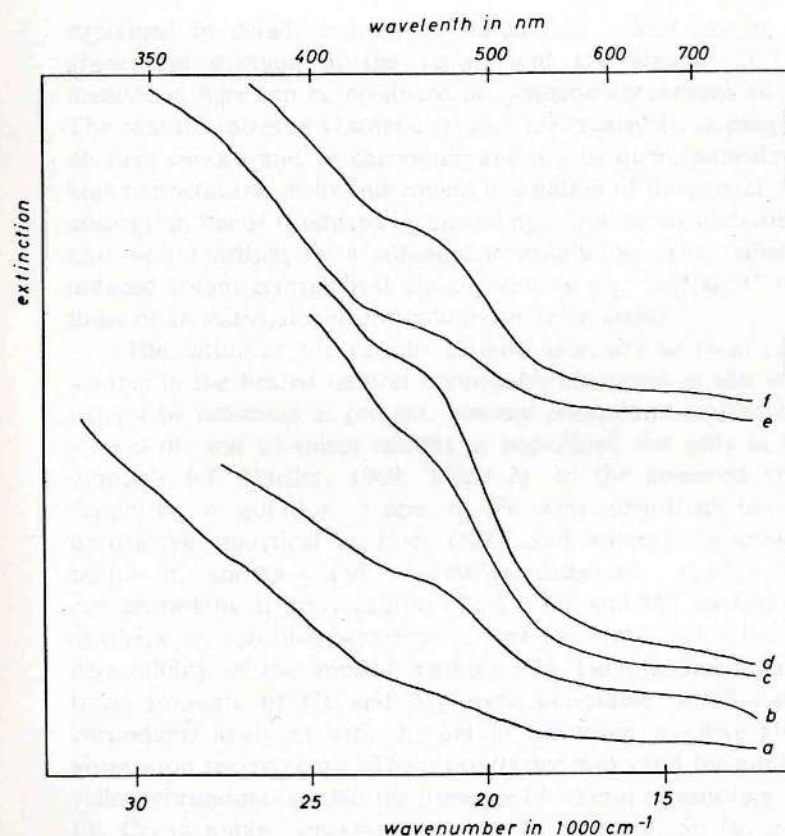


FIG. 12. Absorption spectra of treated yellow, yellow-orange and orange-brown sapphires: (a,b,c) annealed corundums, (d) sample b additionally irradiated, (e,f) originally pale yellow, irradiated corundums from Sri Lanka.

Schultz, 1964; Hoskins & Soffer, 1964; Standley & Vaughan, 1965; Arkhangelskii *et al.*, 1967, 1969; Sviridov, 1968; Borer *et al.*, 1970; Sidorova *et al.*, 1972, 1973; Sandreyev *et al.*, 1973; Bessonova *et al.*, 1974; Kvapil *et al.*, 1981), more recently a series of studies deals with the optical properties of undoped corundums following heat-treatment and/or irradiation as well as of corundums doped with divalent cations, e.g. Fe^{2+} , Mg^{2+} , Ca^{2+} , Be^{2+} (Gamble *et al.*, 1964; Bartram *et al.*, 1965; Gorban' & Kondratenko, 1972; Kvapil *et al.*, 1972, 1973; Govinda, 1976; Lee *et al.*, 1977; Lee & Crawford, 1978; Kulis *et al.*, 1979, 1981). Without specifying the nature of the colour centres, described in the various articles but not yet entirely

explained in detail, it may be stated that colour centres with absorption maxima in the visible and UV similar to those mentioned here can be produced in synthetic corundums as well. The colour centres in synthetic crystals are created by doping with divalent cations and/or chromium and a subsequent annealing at high temperatures or by subsequent irradiation of the crystals. The absorption bands produced by annealing synthetic corundums can also be intensified by a subsequent irradiation. The radiation-induced colour centres heal out on heating e.g. to 500 °C while those of annealed, doped corundums are fairly stable.

The cation or the various cations necessary to form colour centres in the heated natural corundums examined in this study, cannot be indicated at present. Natural corundums usually show several di- and tri-valent cations as impurities, but only in trace amounts (cf. Harder, 1969; Table 2). In the annealed yellow sapphires in question, traces of Fe were identified by non-destructive analytical methods (XRF and microprobe analyses, both in energy- and wavelength-dispersive mode). The concentrations of other cations like Cr, Ni, and Mg used to dope synthetic crystals only occasionally were found within the limits of detectability of the applied methods. As Table 2 demonstrates, trace amounts of Cr and Mg were detectable in all natural corundums analysed with the aid of the more sensitive atomic absorption spectroscopy. These results are also valid for annealed yellow corundums so that the presence of several cations (e.g. Mg, Fe, Cr) in minor concentrations can be assumed. So far it is a matter of uncertainty, if the colour centres are created during the annealing process by a divalent cation like Fe^{2+} or Mg^{2+} , by a trivalent cation like Cr^{3+} or Fe^{3+} or by several di- and tri-valent cations.

The *distinction* of annealed or irradiated natural corundums from yellow to orange-brown corundums and synthetic corundums is possible on the basis of their spectroscopic and microscopic characteristics compiled in Figures 1 to 12. A diffusion treatment is discernible by optical examination (Hänni, 1982).

The annealing of pale yellow corundums leads to stable colorations. According to CIBJO *nomenclature* this treatment is a practice tolerated by the trade and has not to be declared explicitly. This stands in contrast to the diffusion-treatment of corundums, which must be indicated without exception.

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