## NOTES AND NEW TECHNIQUES

# SYNTHETIC FORSTERITE AND SYNTHETIC PERIDOT

By Kurt Nassau

Large crystals of chromium-containing synthetic forsterite are being commercially manufactured for use as a laser material. Considerable color variation is possible, and some of this material resembles peridot, with which it could be confused. Synthetic peridot has been grown, but only experimentally. This material closely resembles natural peridot and might be difficult to distinguish if it were to appear in the gem market.

Recent research has led to two new products that are of potential interest, and concern, to gemologists: (1) a commercially available synthetic forsterite, MgSiO<sub>4</sub>, which contains chromium as both  $Cr^{3+}$  and  $Cr^{4+}$ ; and (2) a true synthetic peridot,  $(Mg_{0.9}Fe_{0.1})_2SiO_4$ , which currently is grown only on an experimental basis. Both forsterite and peridot are members of the olivine series.

Historically, synthetic gem materials usually emerged either indirectly from studies aimed at understanding mineralogical problems or directly from efforts to achieve the synthetic equivalent of a natural gem for jewelry use. In recent years, however, most new synthetics have been spin-offs of

#### ABOUT THE AUTHOR

Dr. Nassau, retired from his position as Distinguished Scientist at AT&T Bell Laboratories, is now a freelance writer, consultant, and expert witness living in Lebanon, New Jersey.

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Gems & Gemology, Vol. 30, No. 2, pp. 102–108 © 1994 Gemological Institute of America research for solid-state technology, with laser research being the dominant contributor. This is the source of the recently developed synthetic forsterite (Nishide et al., 1985; Verdun et al., 1988), which is being investigated as a host material for a tunable near-infrared laser.

Chromium-doped synthetic forsterite crystals (figure 1) are currently being grown commercially using the Czochralski-pulling technique by K. Yamagishi, at the Ageo City Central Research Laboratory of the Mitsui Mining and Smelting Co., Tokyo. Studies of the optical properties and laser characteristics have been conducted in the Department of Physics and Electrical Engineering, City College of New York (Petricevic et al., 1988b-c, 1989a-c, 1990; Alfano et al., 1989); and by these researchers in cooperation with K. Yamagishi and coworkers (Petricevic et al., 1988a). They have demonstrated that this laser material is synthetic Mg<sub>2</sub>SiO<sub>4</sub>, containing about 0.04 wt.% chromium. Under reducing conditions, all the chromium is Cr<sup>3+</sup>, substituting simultaneously in both octahedral magnesium sites of this orthorhombic structure. When "standard" oxidizing conditions (i.e., ambient air) are used, there is also some Cr<sup>4+</sup> present, substituting for silicon. It is this Cr<sup>4+</sup> that provides the broad infrared fluorescence (680 to 1400 nm) that is used in the laser, which is tunable from 1167 to 1345 nm (note that in some of the



Figure 1. These samples of chromium-doped synthetic forsterite were manufactured by Mitsui Mining and Smelting Co. for laser use: a 2.7-cm-diameter slice, a 0.5-cm cube, and three faceted samples (1.18, 1.07, and 0.83 ct). Photo by N. DelRe.

early reports, the presence of  $Cr^{4+}$  had not yet been recognized). This is indeed the only laser material that uses  $Cr^{4+}$ . This variation in the valence state of chromium, as well as the differences in chromium concentration, combine with the pleochroism of olivine to produce a wide range of colors, including green, blue, pink, and purple. These hues could also be modified by heat treatment in different atmospheres.

According to a recent International Colored Gemstone Association (ICA) Laboratory Alert (Mican, 1992), green, chromium-containing synthetic forsterite is also being marketed for laser and jewelry use inappropriately labeled "chrysolite (olivine)" by Solix Co. of "Minsk, Republic of Byelarus." Mican examined some of this material, but he used the inappropriate designation "synthetic peridot" in his report. The older nomenclature is indeed confusing and is summarized, together with the modern usage, in box A.

## BOX A: THE CHEMISTRY AND NOMENCLATURE OF THE OLIVINE SERIES

Forsterite is a member of the olivine group of minerals, which consists of the fayalite-forsterite solid-solution series with composition  $(100 - x)Mg_2SiO_4$  $xFe_2SiO_4$ , with iron in the divalent state. The designation forsterite applies to the end member  $Mg_2SiO_4$ and traditionally also to the composition range 0 < x< 10 (i.e., with as much as 10 mol.% fayalite), also designated Fo<sub>100</sub> to Fo<sub>90</sub>Fa<sub>10</sub>, where Fo is forsterite and Fa is fayalite. The latter is the other end member, Fe<sub>2</sub>SiO<sub>4</sub>, which has a traditional composition range of 90 < x < 100 or Fo<sub>10</sub>Fa<sub>90</sub> to Fa<sub>100</sub>. Other traditional members of the olivine series are chrysolite, which covers the range 10 < x < 30 or Fo<sub>90</sub>Fa<sub>10</sub> to Fo<sub>70</sub>Fa<sub>30</sub>; hyalosiderite, 30 < x < 50; hortonolite, 50 < x < 70; and ferrohortonolite, 70 < x < 90.

The modern approach is to drop all intermediate names—which, for example, are no longer listed as such in the *Glossary of Mineral Species* (Fleischer and Mandarino, 1991)—and simply to give Fo:Fa percentages. Details of the terminology, chemistry, structure, and other aspects of the olivines have been given by Deer et al. (1962) and by Brown (1982).

The gemologist knows olivine best as peridot, which is usually defined as the transparent to translucent yellowish green to greenish yellow to brownish green gem variety of olivine. The green derives from  $Fe^{2+}$ , whereas the yellow and brown components derive from the presence of some of the iron in the

Fe<sup>3+</sup> state. The typical iron content has been reported as 9% (Bauer, 1904), 10% (Anderson, 1980), and 14% (Hanson et al., 1991), thus ranging in the traditional sense from the end of the forsterite field into the chrysolite field; the range of refractive indexcs reported for peridot also brackets both of these fields (see also Bank, 1986). Thus, peridot is an olivine and belongs to both the iron-rich forsterite and the nowdiscontinued chrysolite mineral species. It does have significant structural iron content, not just at the color-causing impurity level.

The designation by Solix (Mican, 1992) of their chromium-containing forsterite product as "chrysolite (olivine)" is incorrect, because: (1) its composition does not belong to the chrysolite range; (2) even if it did, the term *chrysolite* is no longer used; and (3) while this material is indeed within the olivine series, it is not appropriate to use the series designation when dealing with end-member forsterite. In the opinion of the author, this material should also not be designated "synthetic peridot," as Mican (1992) does, because it contains a different color-causing impurity and also does not contain the necessary 10% or so of structural iron.

Pure (and thus colorless) forsterite has also been grown, both at Mitsui and elsewhere, but it was not available for examination. To a gemologist, such material is simply "colorless synthetic forsterite."



Figure 2. These three inelt-growth techniques have been used to manufacture synthetic forsterite or synthetic peridot. The letters in each diagram refer to the following: M—melt, C—growing crystal, S—sintered ceramic, L—laser beam focused by a mirror and lens system (only partly illustrated), and H—halogen lamp focused by an ellipsoidal reflector. The arrows indicate motion.

True synthetic peridot has been grown as part of a study of the crystal growth of olivines at the Lawrence Livermore National Laboratory (LLNL), Livermore, California, as briefly outlined in box B. Experience has shown that any synthetic material, even if not intended for gem use, is likely to be faceted and would then become a real challenge to the unsuspecting gemologist. Accordingly, both the Mitsui synthetic forsterite and the LLNL synthetic peridot are described here.

## **CRYSTAL SYNTHESIS**

Silicate compounds usually produce too viscous a melt to permit growth by techniques such as Czochralski pulling; rather, they require flux or hydrothermal growth as, for example, with synthetic emerald. However, forsterite and peridot appear to be exceptions, in that melt growth can be used if growth is slow and adequate care is taken.

Three melt-growth techniques have been used to produce laser-quality synthetic forsterite (SF)

and synthetic peridot (SP), as illustrated in figure 2: Czochralski pulling from the melt (for SF; Finch and Clark, 1971; Takei and Kobayashi, 1974; Nishide et al., 1985; also at Union Carbide and at the University of Marburg, Germany, as mentioned by Rager et al., 1991); laser-heated pedestal growth (for SF; Verdun et al., 1988; Jia et al., 1991); and image-furnace floating-zone growth (for SP; Hanson et al., 1991).

The Czochralski technique (figure 2A) is well known, and its use to grow synthetic forsterite is well documented (see, e.g., Peicong et al., 1992). In the pedestal technique (figure 2B), the intense light beam from a laser is used to melt the upper end of a vertical rod of sintered ceramic material; pulling is then performed upward out of this melt. In the floating-zone technique (figure 2C), the radiant energy from two 1.5-kW halogen light bulbs is focused onto a vertical sintered ceramic rod to melt a narrow zone which is then made to traverse the rod. Earlier experiments to produce synthetic forsterite with the Verneuil flame-fusion technique (Shankland and Hemmenway, 1963) and the Bridgeman technique of directional solidification in a crucible (Jordan and Naughton, 1964) were successful, but they did not provide adequate quality or size.

Forsterite crystals over 2.5 cm in diameter and up to 20 cm long have been grown by Czochralski pulling. In North America, the Mitsui synthetic forsterite is marketed for laser use exclusively by Mediscience Technology Corp., Forsterite Division, of New York City. The Solix material (Mican, 1992) reportedly is also made by Czochralski pulling and is available as rods 2.5 cm in diameter and 12 cm long.

### MATERIALS AND METHODS

The synthetic forsterite examined for this study was obtained from Mr. Y. Terashima of Mitsui's New York office. He provided a 15.85-ct slice (0.4 cm thick and 2.7 cm in diameter) and a 2.53-ct Xray oriented cube (0.5 cm) for detailed study, as well as three faceted samples (1.18-ct pale bluegreen, 0.83-ct medium blue, and 1.07-ct dark blue) for brief examination (again, see figure 1). The pleochroic colors seen in the cube are shown in figure 3. Laser-grade material, by its nature, must be of the highest optical quality; the specimens available for study were of lower grade but still adequate for gem use.

A pale greenish yellow crystal of synthetic peridot (figures 4 and 5) was obtained from Dr. F. J. Ryerson of Lawrence Livermore National Laboratory. The 0.79-gram crystal was 0.6 cm in diameter and 1.8 cm long.

The properties given here for synthetic forsterite colored by chromium are based on precision scientific measurements (e.g., on polished prisms) reported by Alfano et al. (1989), Petricevic et al. (1988a–c, 1989a–c, 1990), in the Mitsui sales literature (no author, undated), and in the Solix literature as reproduced by Mican (1992). They are also based on gemological measurements made by the author and by staff members of the GIA Gem Trade Laboratory, New York, on the 15.85-ct slice and 2.53-ct cube.

## BOX B: EXPERIMENTAL SYNTHETIC PERIDOT

True synthetic peridot—that is, a composition in the olivine series containing about 10 mol.% iron-has been produced as part of a research program at LLNL by Hanson, Young, and Ryerson (1991). This group has performed a detailed study on the crystal growth of synthetic olivines ranging from colorless pure synthetic forsterite Mg<sub>2</sub>SiO<sub>4</sub> to a dark green  $Fo_{67}Fa_{33}$  [that is (Mg<sub>0.67</sub>Fe<sub>0.33</sub>)<sub>2</sub>SiO<sub>4</sub>], using the image-furnace floating-zone technique with an atmosphere of mixed carbon monoxide/carbon dioxide and a growth rate of about 0.2 cm per hour. When there was an oxygen leak, a brown peridot resulted, which also sometimes occurs in nature. Both cracking and bubble inclusions were problems, but these could be controlled by adjusting the shape of the crystal-melt interface with an afterheater. Crystals up to 1 cm in diameter and up to 7 cm long were grown without cracks and with only an occasional bubble.

The pale greenish yellow crystal studied was heavily included (see figures 4 and 5). Nevertheless, there were some clear areas. Good-quality and deeper green, higher-iron-composition crystals have been grown, but they were not available for this report as they were needed for technological studies. Although it is possible that such synthetic peridot could enter the market as a lower-cost substitute for the natural material, the low demand for peridot relative to the current production of the natural material makes this scenario unlikely.

Because the clarity of the specimen examined was reduced by the many included gas bubbles, some with tails, only limited gemological data could be determined. A biaxial figure confirmed that the material was, like natural peridot, doubly refractive; other properties are listed in table 1. The pleochroism is light grayish green/light yellow, there was no reaction to U.V. radiation, and the hand spectroscope showed optical absorptions at about 453, 474, and 497 nm. All these data are consistent with values expected for a pale-colored natural peridot, as listed in the literature (leg., Webster, 1983; CIA, 1988).

Since production to date has been experimental only, it is not possible to establish at this point what the distinguishing criteria between natural and a possible future commercial synthetic peridot might be. In view of the limited data available, conventional genoological testing will probably parallel that for many other synthetics, with the presence (or absence) of certain inclusions likely to be the significant distinguishing criterion.



Figure 3. The 0.5-cm cube of chromium-doped synthetic forsterite in figure 1 is illustrated in three different orientations to show the pleochroism for the  $\alpha$ ,  $\beta$ , and  $\gamma$  spectra, respectively. Photos by N. DelRe.

We determined specific gravities by hydrostatic weighing and optical properties using a GIA-GEM Duplex II refractometer, a polariscope, a diffraction-grating hand spectroscope, and a dichroscope. Polarized absorption spectra were obtained from the 0.5-cm cube with a Hitachi U-4001 splitbeam spectrophotometer with an integrating sphere detector.

## GEMOLOGICAL PROPERTIES

The mechanical and optical properties of the slice and cube of synthetic forsterite and the crystal section of synthetic peridot are listed in table 1, together with comparative data for natural forsterite and peridot taken from the literature. Other observations on the synthetic forsterite are described below. The properties of the synthetic peridot specimen, which was not gem quality and was grown for experimental purposes only, are discussed and compared with those of natural peridot in box B. **Color.** Chromium-containing synthetic forsterite varies from pale to deep blue to blue-green, green, pink, and purple. Since the precise pleochroic colors depend on the ratio of  $Cr^{3+}$  to  $Cr^{4+}$  and their concentrations, these colors may vary, including various shades of pale to deep yellow-green, green, blue-green, blue, and reddish purple (again, see figures 1 and 3).

**Fluorescence.** Like natural peridot, chromium-containing synthetic forsterite is inert to both shortand long-wave ultraviolet radiation. The red fluorescence of the chromium R line (present in all  $Cr^{3+}$ -containing materials, such as ruby and emerald) is seen only when the material is cooled to liquid-nitrogen temperature.

**Absorption Spectra.** In the hand spectroscope, there is an intense absorption up to 450 nm; a weak one (which is stronger when the color is intense) from there to 500 nm; a group of three bands at 530, 550,



Figure 4. This 1.8-cm-long synthetic peridot crystal, shown viewed with darkfield illumination, was grown by the Lawrence Livermore National Laboratory for experimental purposes. Photo by N. DelRe. and 580 nm; and a band at 690 nm. This spectrum is quite different from that caused by iron in peridot (GIA, 1988).

The polarized absorption spectra for the cube, shown in figure 6, are essentially the same as those reported by Petricevic et al. (1989a), Alfano et al. (1989), and Rager et al. (1991).

**Inclusions.** Laser-grade forsterite shows no inclusions at  $10 \times$  magnification. The poorer-grade material we examined contained a number of white spicules and thin, thread-like inclusions or gas bubbles. The Solix forsterite was reported by Mican (1992) to contain gas bubbles as well as solid inclusions with tail-like hollow channels attached.

## DISTINCTION OF SYNTHETIC FORSTERITE FROM NATURAL PERIDOT

While the color of chromium-containing synthetic forsterite usually differs from that of peridot, a peridot-like color is possible and there is sufficient overlap in the gemological properties to provide the possibility of confusion. However, both the refractive-index and specific-gravity values for synthetic forsterite are somewhat lower than those recorded for peridot (see table 1). In the absence of a careful specific-gravity determination or a detailed



Figure 5. In this view of a cut and polished surface of the crystal in figure 4, one can see how heavily included it was in some areas. Photo by N. DelRe.

refractive-index study, the best distinction is given by the visible-range spectrum of the synthetic forsterite, which shows chromium-related features not found in natural peridot (or forsterite).

Property	Forsterite			Peridot	
	Synthetic		Natural	Synthetic	Natural
	Literaturea	Measured <sup>b</sup>	Literature	Measuredb	Literatured
Mechanical:					
Mohs hardness Specific gravity Fracture	6 <sup>1</sup> /2-7 3.213-3.217 Conchoidal with vitreous to subvitreous luster	7 3.15 Conchoidal with vitreous to subvitreous luster	7 3.21–3.33 Conchoidal with vitreous to subvitreous luster	7 3.30 Conchoidal with vitreous to subvitreous luster	61/2–7 3.27–3.48 Conchoidal with vitreous to subvitreous luster
Optical:					
Character Refractive index α β γ	Biaxial positive 1.636–1.669 1.6359 1.6507 1.6688	Biaxial 1.63–1.67	Biaxial positive 1.635–1.670 1.635 1.651 1.670	Biaxial 1.65–1.68	Biaxial positive 1.654–1.690 1.654 1.671 1.689

<sup>a</sup>After Alfano et al. (1989), Petricevic et al. (1988a-c, 1989a-c, 1990), the Mitsui sales literature (no author, undated), and the Solix literature reproduced by Mican (1992).

<sup>b</sup>Measurements made by the author and GIA-GTL New York for this study on the five chromium-doped synthetic forsterites and one synthetic peridot described in this article.

After Roberts et al. (1974).

dAfter the Gem Reference Guide (GIA, 1988) and Webster (1983).



Figure 6. These absorption spectra were recorded from the three directions of the synthetic forsterite shown in figure 3: ( $\alpha$ -spectrum E//b) greenish yellow direction, ( $\beta$ -spectrum E//c) bluish green direction, and ( $\gamma$ -spectrum E//a) purple direction.

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#### CONCLUSIONS

Synthetic forsterite colored by chromium, which is being grown from a melt for laser use, is now commercially available in sizes up to 2.5 cm in diameter and 20 cm long. This material can vary somewhat in color because of variable Cr<sup>3+</sup> and Cr<sup>4+</sup> content; it is pleochroic—typically purple, bluish green, and greenish yellow. Although yellowish green to greenish yellow synthetic forsterite might be used as a substitute for natural peridot, the lower R.I. and S.G. values of the synthetic forsterite—due to the absence of a substantial amount of iron—help separate it from gem peridot. In addition, the visible absorption spectrum of the chromium-containing synthetic forsterite is significantly different from that of natural peridot.

The gemological properties of the experimental synthetic peridot examined are essentially the same as those of natural peridot. The only difference noted was in the inclusions.

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