CRYOGENICS, AN AID TO GEMSTONE TESTING

By Stephen C. Hofer and D. Vincent Manson

Cooling of gemstones to low temperatures provides for enhanced detail in the absorption spectra. This article identifies some simple techniques for cooling gems that are available to the jeweler-gemologist and offers a detailed description of the procedures used in the research laboratory for automatic recording of spectra at low temperatures. Examples of the differences observed between spectra recorded on stones held at room temperature and those recorded for the same stones at significantly lower temperatures are presented for diamond, emerald, and synthetic alexandrite.

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The ability to measure the detailed transmission or absorption spectra of gemstones in the ultraviolet, visible, and infrared portions of the electromagnetic spectrum is a necessity for the modern gemological research laboratory. Accurate data on the occurrence of absorption lines can be invaluable in the identification of some gemstones. When used by the informed gemologist, spectra can also aid in distinguishing natural from synthetic, treated, or imitation gemstones as well as in determining the cause of the color in certain gemstones (Liddicoat, 1977).

In recent years, technological advances in spectroscopy have provided the gemologist with new and interesting possibilities. The specially designed optical spectroscopy equipment assembled in the Department of Research of the Gemological Institute of America has proved invaluable in applying some of these advances, enabling the research gemologist to record, file, photograph, display, manipulate, and store spectral data for comparison in future identifications.

Recently the application of cryogenics (i.e., the use of very low temperatures) to the system has played an important role in extending the usefulness of spectroscopy in gem testing. The chapter on atomic motion in Holden (1965) describes the phenomenon whereby the thermal vibrations of atoms modify the transmission characteristics of light passing through a material. Essentially, atomic vibrations in the crystalline lattice "diffuse" the energies at which absorption occurs and make the absorption lines broad and elusive at room temperature. Cooling the gems to low temperatures enhances the detail with which the absorption lines appear by slowing down the atomic vibrations in the crystalline lattice.

This article discusses some techniques of cooling gemstones that are accessible to the jeweler-gemologist who is familiar with a hand spectroscope, as well as

methods and equipment used in the more sophisticated research laboratory. To illustrate the usefulness of cryogenics in gemology, details of spectra recorded for diamond, emerald, and synthetic alexandrite are also given.

LOW-TEMPERATURE SPECTROSCOPY FOR THE JEWELER-GEMOLOGIST

There are several methods by which gems can be cooled to provide enhanced spectra for the gemologist using a hand spectroscope unit. Spectroscope units that provide a gemstone holder are preferred, since the holder minimizes the need for handling and thus prematurely warming the cold specimen. If the unit does not have a built-in heat filter, one should be added to protect the gemstone from lamp heat.

One useful cooling agent is refrigerant gas, which is commercially available in disposable cans. Refrigerant aerosol products are marketed under a variety of names (e.g., Quik-Freeze MS-240, manufactured by Miller-Stephenson Chemical Co.); all provide effective cooling of gemstones to temperatures of approximately −45°C/−50°F. Such temperatures are usually recorded in the scientific literature on the Kelvin scale. See table 1 for temperature conversions between Fahrenheit, Celsius, and Kelvin.

An alternative coolant might be ice or, preferably, "dry ice" (solid carbon dioxide). A less satisfactory cooling method, but one that is still of value with some stones, is to leave the stone in a pair of tweezers in a food freezer for a short period of time (approximately 15 minutes) before examining it with the spectroscope.

With some practice, in most cases the gemologist will be able to see a sharpening of spectral lines on the cooled stone, and thus will observe more detailed spectra. Additional information on other spectroscopic techniques for improving spectral observations can be found in Webster (1975). An excellent series of articles on techniques useful to the spectroscopist have been published by Anderson (1953).

While there are some advantages to be gained with the methods of cooling described above, they are not entirely satisfactory. First, the gem will absorb heat rapidly from the surrounding air, so spectral examinations must be done quickly to ensure the most satisfactory results. Second, some gemstones, because of inclusions present, are susceptible to damage when subjected to abrupt temperature changes (Koivula, 1980). Great care should be taken not to "thermally shock" the stone. We recommend that cooling with refrigerant gas or dry ice be avoided when testing highly included gems.

TABLE 1. Temperature conversions for degrees Fahrenheit, degrees Celsius, and Kelvin units.

Degrees Fahrenheit (°F)	=	9/5 (°C) + 32
Degrees Celsius[a] (°C)	=	5/9 (°F − 32)
Kelvin (K)	=	°C + 273.16

[a]Previously Centigrade.

LOW-TEMPERATURE SPECTROSCOPY WITH LIQUID NITROGEN

In order to cool gems gradually and observe spectra at cryogenic temperatures on a routine basis, the GIA research department recently constructed an optical bench spectroscopy unit similar to the one described by Scarratt (1976). This design for an apparatus to lower the temperature of gems during a spectroscopic examination was proposed by Dr. A. T. Collins of King's College, London, for use in the London Chamber of Commerce Gem Testing Laboratory.

While the optical bench arrangement does not readily provide a permanent record of the observed spectrum, it is very practical and relatively inexpensive compared to the more sophisticated equipment used in the research laboratory. By boiling off liquid nitrogen (available from suppliers of industrial gases) and passing the vapor through a tube protected by an evacuated annular sleeve (see figure 1), the gemologist can easily achieve a temperature of 120 K and maintain it for an extended testing period relative to the abbreviated period available with the previously mentioned cooling methods. The windows in the tube are made of silica glass to extend the light transmission into the ultraviolet and near infrared regions of the spectrum.

A unique feature of the GIA system results from the design of the tube system to enable the testing of as many as seven stones during a single cooling cycle. The mounting plate has apertures to accommodate gemstones of various sizes, and is connected to a rod for positioning the gem in the focused light beam. This metal rod also serves as a thermocouple probe which provides for a display of the gemstone's temperature. The light

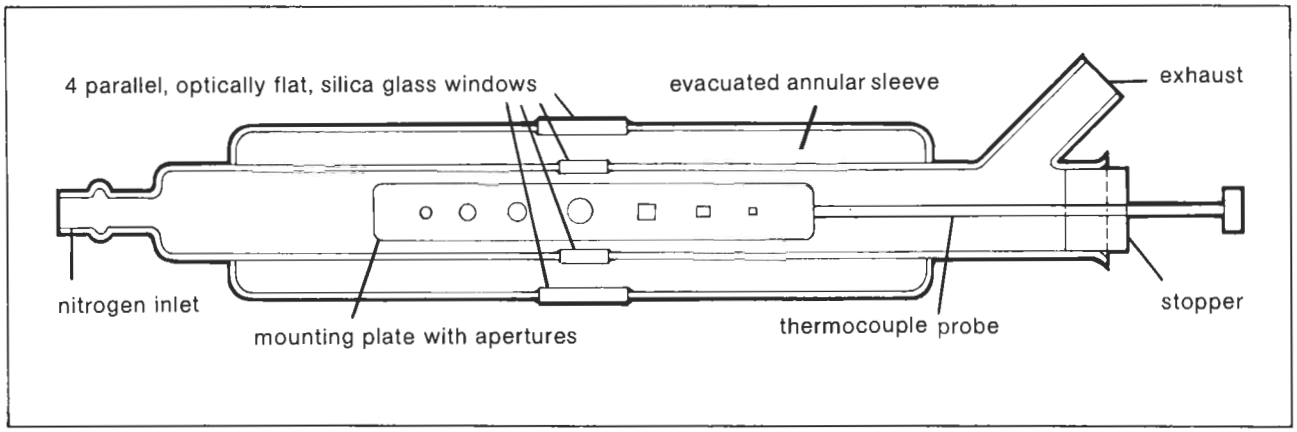


Figure 1. Diagram of a glass tube with evacuated annular sleeve and mounting plate for use with liquid nitrogen on an optical bench.

beam, after it passes through the cooled gem, is collimated and focused with lenses onto the slit of a direct-vision spectroscope for analysis. Cooling the gem for spectral analysis by this system has proved useful in the lab and provides a dramatic view of the sharpening effect that cooling has on spectra. For more detailed analysis of gem spectra, a recording capability is desirable.

THE RECORDING SPECTROPHOTOMETER

The Zeiss PMQ_3 spectrophotometer used at GIA is suitable for studying the absorption of radiation by gemstones in the ultraviolet, visible, and near infrared regions of the electromagnetic spectrum from 2000 Å (angstroms) to 25,000 Å. The essential equipment to complete such a spectrophotometry system includes a light source, a monochromator, a sample compartment, a detector, and recording devices (figure 2). The monochromator is used to select the electromagnetic radiation of a single frequency from a beam of radiation that covers a wide range. The Zeiss PMQ_3 single-beam monochromator is equipped with an automatic wavelength drive assembly, which makes a spectral scan between any two wavelengths in the ultraviolet, visible, and near infrared regions possible.

The wavelength drive is equipped with a remote-control start/stop switch operated by a computer that is programmed to record an absorption spectrum and store it in computer memory automatically. As many as 150 different spectra may be stored on one "floppy" data disc. Later comparison and manipulation of the stored spectra is possible with display of the spectral transmission curve on a cathode ray tube screen or on a chart recorder. These displays enable the operator to assess the character of the spectral scan rapidly and to measure the wavelength of the absorption bands precisely.

The absorption lines and bands may be measured directly at the wavelength at which they occur (in angstroms) or may be converted into units of electron volts that correspond to the energy associated with that wavelength, wavenumbers, or into any other desired unit (Nassau, 1976).

With the addition of the custom-designed cryogenic system to the spectrophotometer, transmission spectra may be collected on faceted gemstones held at temperatures as low as 50 K. The Air Products and Chemicals Corporation model CS-1003 cryogenic compressor is a closed-cycle cooling system with a cooling range to 40 K (−233°C). The unit consists of a compressor module that is connected to a high-pressure valve assembly which provides a flow of research-grade helium to the "cold tip," a displacer/expander cooling assembly. The system gives fast (less than 30 minutes) cool down and temperature stability at 40 K. The ease of operation and small size of the CS-1003 make it suitable for use with the Zeiss PMQ_3 spectrophotometer.

To control the transfer of convective heat and to provide a moisture-free environment for the stone, a high-vacuum sample cell was fabricated. The cell has optically flat silica glass windows for transmission of the light beam. With this apparatus, a vacuum of 1×10^{-3} torr is maintained for

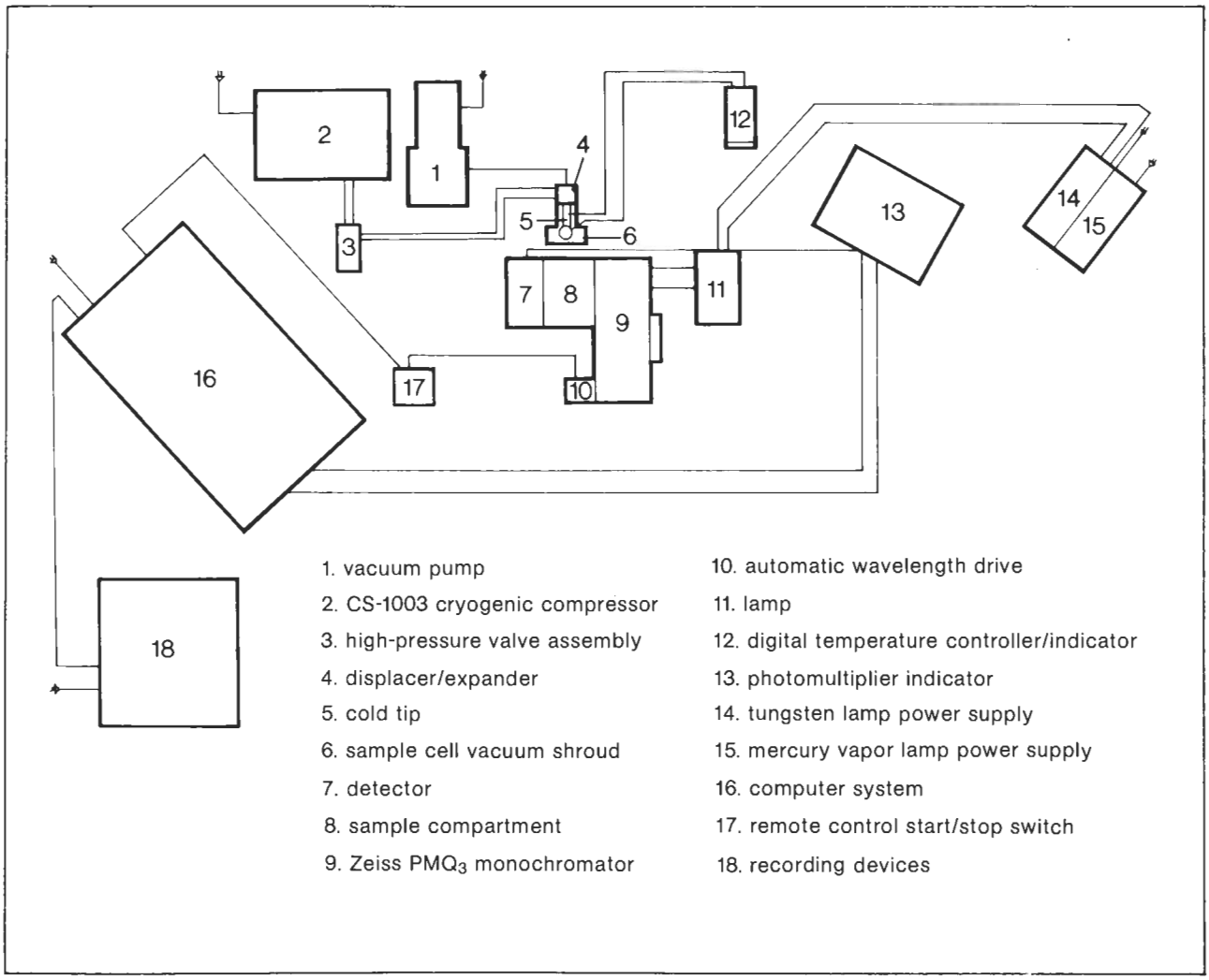


Figure 2. Schematic diagram of the automatic recording spectrophotometer and cryogenic system used at the Gemological Institute of America.

extended periods during a cryogenic spectroscopic examination.

Collecting the scattered transmittal light signal that results when the collimated light beam is passed through a small faceted gemstone poses a problem that has also been solved with this system. A set of truncated parabolic reflectors with known focal lengths are positioned back to back with the gemstone at the common focal point. This allows examination of gems of any shape from 0.5 mm to a maximum of approximately 20 mm in any dimension (figure 3).

With the addition of an ADP-B temperature indicator/controller, the system can monitor the temperature of samples to a stability of ±1 K over a range of 40 K to 300 K. The cool-down time is less than 30 minutes, and the addition of a heater circuit at the tip enables the rapid return of the cold head to room temperature. Two iron-doped gold vs. Chromel thermocouples are connected to the temperature indicator/controller, one for the cold tip and the second for the sample mount to determine the temperature gradient, if any, between the cold head and the actual sample.

The present arrangement of a single-stone sample cell has proved invaluable to linking the cryogenic capability with gemstone spectroscopy in the research laboratory. To extend these capabilities, a new sample cell has now been designed with a vacuum shroud that will accommodate up to five samples for examination during a one-hour cool-down period.

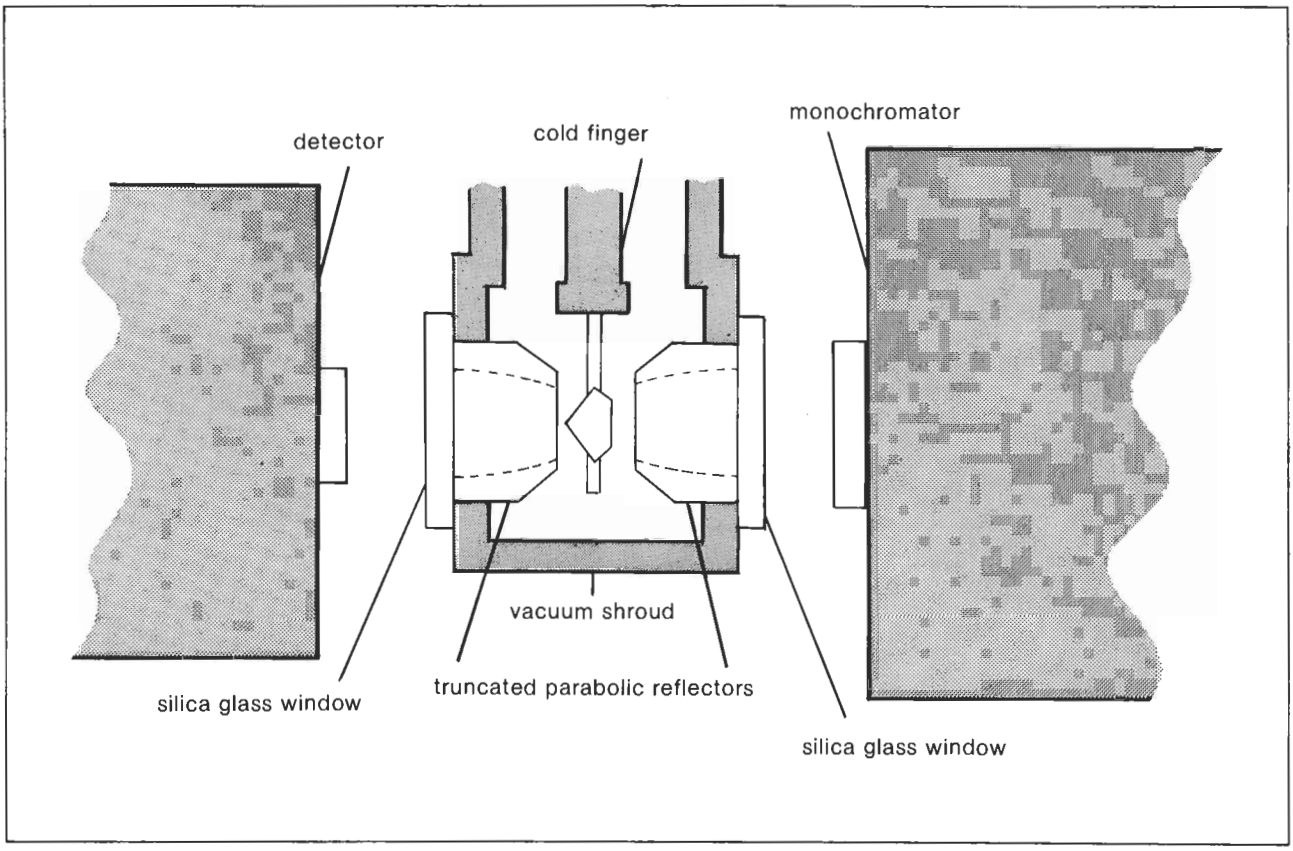


Figure 3. Schematic diagram illustrating the use of truncated parabolic reflectors in a cryogenic sample compartment.

EXAMPLES OF CRYOGENIC SPECTROSCOPY

Three examples of how the spectral absorption lines observed in gemstones cooled to very low temperatures can show more detail than those observed in the same stones at room temperature are presented here. Two visible-region spectra were recorded for an irradiated diamond, an emerald, and a synthetic alexandrite for the wavelength range from 4000 Å to 8000 Å, as shown in figure 4. In each section of this figure, the upper spectrum plot is recorded at room temperature, the lower at 55 K (−218°C), on the Zeiss PMQ_3 spectrophotometer. The absorption "lines" appear here as sharp depressions in the continuous transmission curve. In figure 5, the same spectra are shown as they would be observed on the hand spectroscope used by most gemologists.

Diamond. Some of the principal features of the optical absorption spectra of an irradiated diamond are displayed in section A of figure 4. A natural diamond containing nitrogen impurities (evident from the line at 4155 Å) has been irradiated and heat treated to enhance its color. The key to the history of this stone was found through spectral examination at a very low temperature. The 4960 Å/5040 Å pair is barely discernible at room temperature (upper plot), and the 5920 Å line is questionable because of its elusive nature. On the spectral absorption plot produced when the stone was cooled to 55 K, the enhancement of the 5920 Å and other absorption lines proves the irradiation history of this stone.

Emerald. Cooling of an emerald, as represented in section B of figure 4, provides the spectroscopist with a classic representation of the absorption pattern of emeralds. The sharp line at 4770 Å, which is not often seen in light-colored emeralds, is clearly evident at 55 K. The general appearance of the chromium lines in the red area improved after cooling. There are three main lines, at 6352 Å, 6593 Å, and 6830 Å; under close inspection, the 6830 Å line is seen to be a doublet of lines at 6802 Å and 6843 Å.

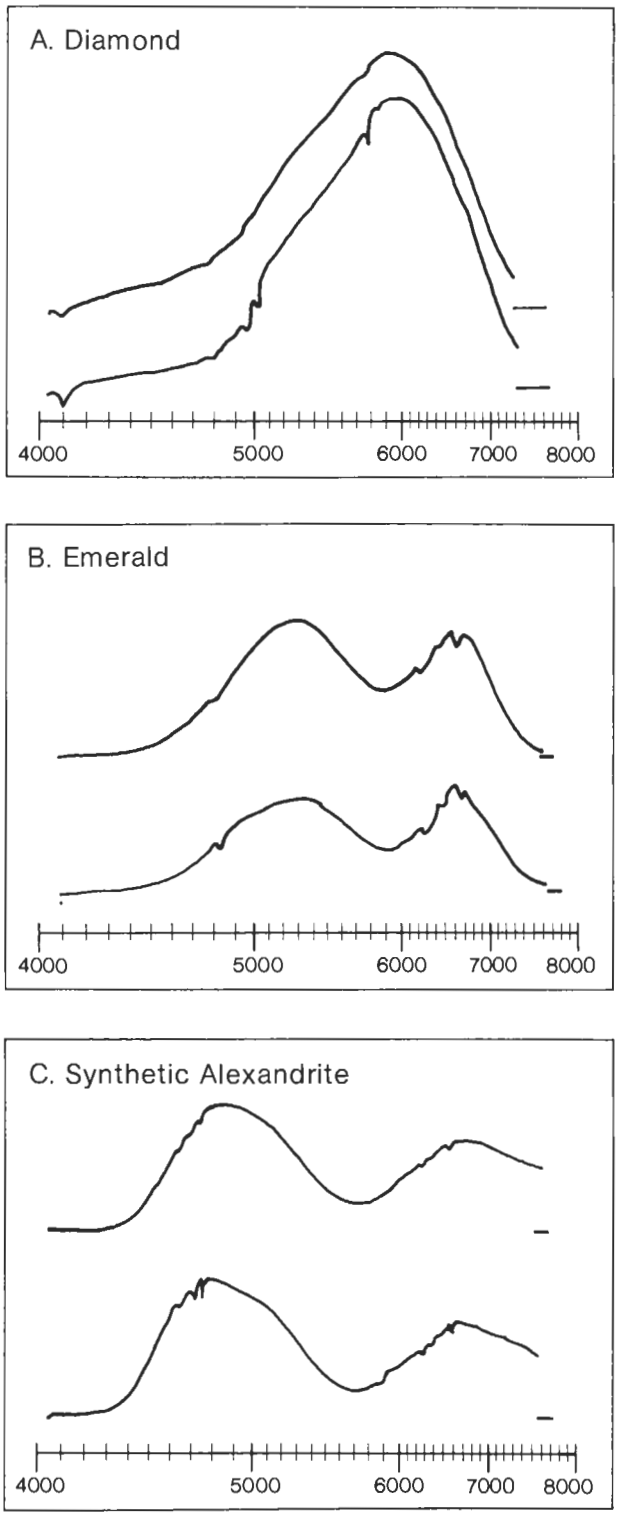


Figure 4. Visible-light spectral transmission curves for (A) diamond, (B) emerald, and (C) synthetic alexandrite, as documented by the automatic recording spectrophotometer at room temperature (upper curve) and at 55 K (lower curve).

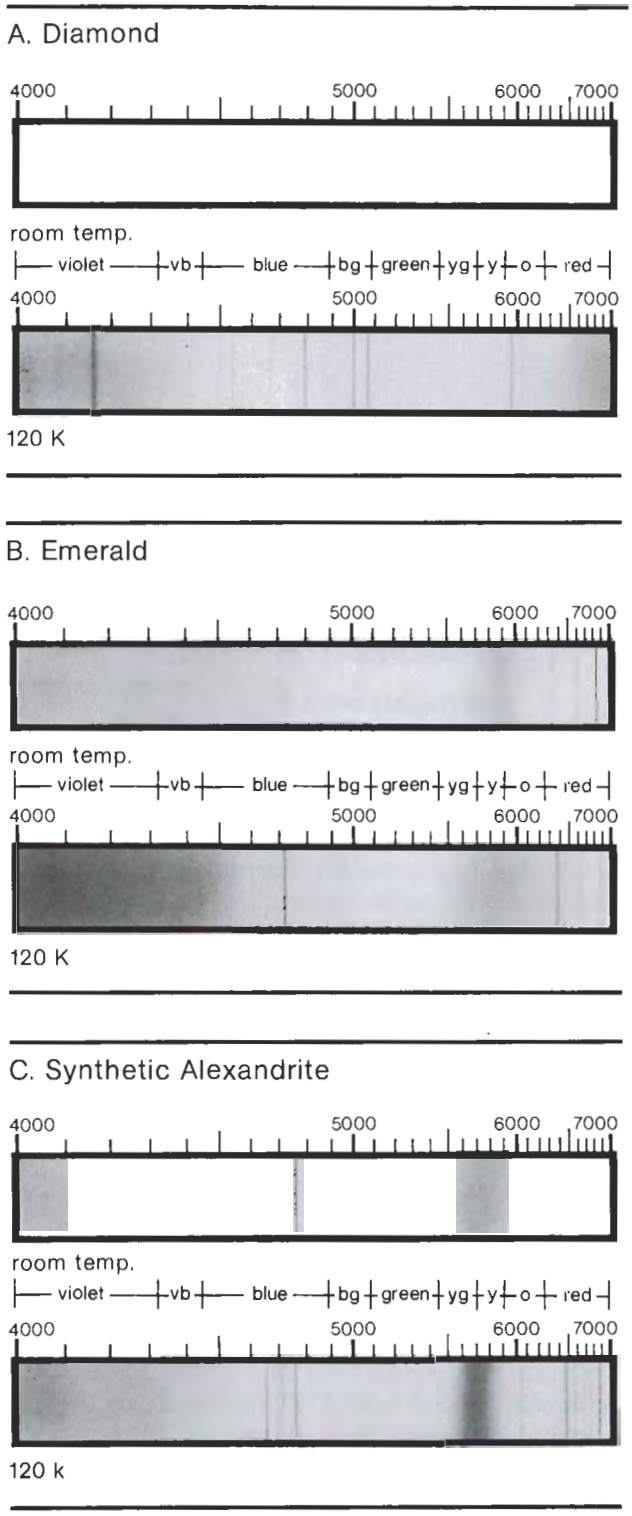


Figure 5. Drawings of absorption spectra for (A) diamond, (B) emerald, and (C) synthetic alexandrite, as observed on a direct-vision spectroscope before (at room temperature) and after the stones were cooled with liquid nitrogen.

Synthetic Alexandrite. Part C of figure 4 shows the spectra recorded for a synthetic, flux-grown alexandrite. Cooling to 55 K provided for a most interesting enhancement of the spectrum seen at room temperature. A fine structure of absorption lines extends from the 6830 Å line toward the green, and the two weak absorption lines in the blue region at room temperature resolve into four lines with separate energies at 55 K.

CONCLUSION

Cooling of gemstones to low temperatures during spectroscopic examination provides for enhanced detail in the spectra observed. The jeweler-gemologist who uses the simple methods for cooling gems described here will, with a little practice, find that he or she can obtain better spectral information on many gemstone species. The spectroscopist is advised, however, to exercise caution to avoid thermal shock and possible damage to the gemstones.

The use of more sophisticated equipment allows for the controlled and gradual change of temperature, which greatly reduces the danger of damage and provides for longer observation at low temperatures. Results obtained on the automatic recording instrumentation used in the GIA research laboratory have demonstrated the advantages of using cryogenic temperatures in the spectroscopic observation of gemstones.

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