AN EXAMINATION OF NONTRANSPARENT "CZ" FROM RUSSIA

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White, pink, and black nontransparent synthetic "cubic zirconia" is currently being manufactured in Russia and marketed primarily in cabochon and bead form. These unusual materials are potentially useful as substitutes for such gem materials as pearl, dyed black chalcedony ("onyx"), and even black diamond. The authors provide a detailed description of these new products, including the chemistry and probable manufacturing techniques. These products can be readily identified by standard gemological tests.

Synthetic cubic zirconia (CZ) is best known as a transparent, essentially colorless diamond simulant. Few would argue that, to date, it is the most effective imitator of that important gem. Annual production now exceeds one billion carats (Nassau, 1990). In 1989 alone, Thailand exported 13,256 kg (66,280,000 ct) of fashioned CZ ("Thais cut more CZ," 1990).

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Over the past several years, CZ has also become available in a wide variety of colors, including some that make effective imitations of fancy-color diamonds (see, e.g., Nassau, 1981; Crowningshield, 1985; Hargett, 1990) and others that imitate various other gems (see, e.g., Nassau, 1981; Read, 1981, 1989; Fryer et al., 1983).

Until recently, virtually all CZ has been essentially transparent. In the Fall of 1991, however, we learned that nontransparent "cubic zirconia" was being manufactured in Russia and marketed in the United States by the firm of Kyle Christianson Ltd., Sylvania, Ohio. One type, produced in both white and pink, is marketed as "Pearl CZ" (Weldon, 1991) because of its resemblance to the organic gem material. In subsequent discussions with employees of the Christianson firm, we learned that they also sell a black CZ.

According to Kyle Kisseberth of the Christianson firm (pers. comm., 1991), all three types are produced in Novosibirsk, Russia. The Christianson firm first marketed them in early to mid-1991. Both rough and fashioned (white and pink, primarily cut en cabochon; black, faceted or as beads)

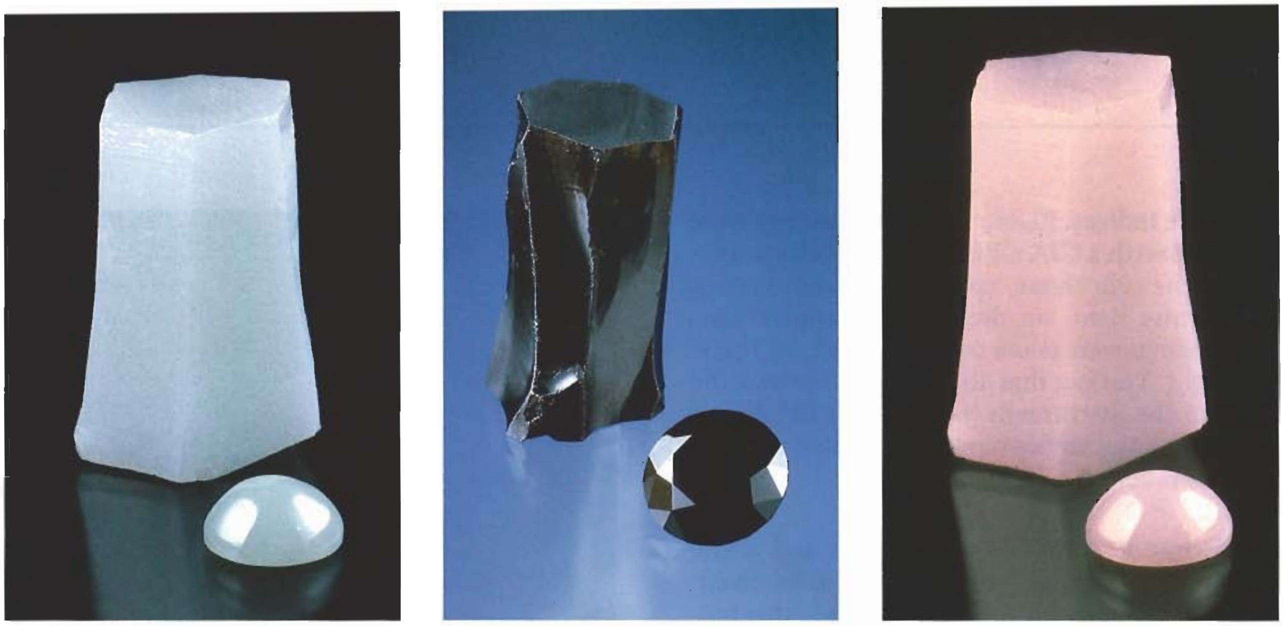


Figure 1. These samples are representative of the material examined in this study (from left to right): white "Pearl CZ" (98.62 ct and 8.03 ct), black CZ (65.09 ct and 6.60 ct), and pink "Pearl CZ" (141.85 ct and 7.14 ct). Photos by Shane F. McClure.

materials are sold, with the fashioning done in Bangkok. As of late November 1991, over 1,000 kg each of the white and pink materials, and almost 1,000 kg of the black, had been sold.

In terms of the materials' jewelry use, Mr. Kisseberth indicated that the white and pink cabochons have found their most obvious application as a reasonably priced simulant for Mabe pearls. The black material has been marketed to date as a substitute for (dyed) "black onyx" (chalcedony), having the advantage of greater scratch resistance. To establish the properties of these three materials and determine the cause of their unusual appearance, we examined several samples of each and submitted them to a number of testing procedures. The results are reported below.

SAMPLES STUDIED

The authors obtained the following samples from the Christianson firm: five cabochons (4.39-8.03 ct) and one "crystal" (98.62 ct) of the white; five cabochons (3.75-7.83 ct) and one "crystal" of the pink; and three faceted (0.57-6.60 ct) and three "crystals" (65.09-87.47 ct) of the black. All of the cabochons had slightly convex bases. Representative samples of these materials are shown in figure 1.

PROPERTIES

The properties determined on these samples are summarized in table 1 and discussed below.

Visual Appearance. The white "Pearl CZ" has a uniform, milky white body color while the pink "Pearl CZ" has a uniform, medium pink body color. When examined with moderately intense direct transmitted lighting, all the cabochons appeared translucent. With more intense lighting, however, all the cabochons showed subtle variations in translucency with a somewhat banded, striped, or striated distribution. Where this was most noticeable, as in two of the pink cabochons (figure 2), the appearance was somewhat reminiscent of the striped effect noted when bead-nucleated cultured pearls are examined in intense transmitted light, a technique known as "candling" (see, e.g., Webster, 1983, p. 541; Liddicoat, 1989, p. 123). Nassau (1980) described and illustrated a similar effect that occurs occasionally in transparent colorless CZ.

In reflected light, the black material appears to have a uniform coloration. When placed over the end of a fiber-optic light pipe, the larger samples remain essentially opaque, transmitting no light. The smaller pieces, however, appear semitranslucent and exhibit a dark brownish red transmission reminiscent of the body color of almandite garnet (figure 3); a thin (approximately 1.75 mm) slice of one of the larger rough specimens exhibited the same transmission color.

The luster of all the polished samples was notably high. The luster of the black material is best described as adamantine, as the faceted samples resemble some black diamonds. Using the GIA cultured pearl grading system (GIA, 1984), as the white and pink materials are marketed as pearl simulants, the luster of the "Pearl CZ" would be classified as very high.

Refractive Indices. Refractive index readings were measured with a GIA GEM Duplex II refractometer. On the cabochons, spot readings were taken using white light; on the faceted samples, flat-facet readings were taken using near-sodium equivalent light. The fact that all readings were over the limits of the instrument (i.e., above 1.81) is consistent with the values reported for cubic zirconia (see e.g., Liddicoat, 1989).

Polariscope Reaction. Both the pink and white cabochons transmitted enough light to be examined between crossed polars; in all cases this produced an aggregate-type reaction. All the black specimens appeared opaque in the polariscope, so no optic character could be determined for this material.

Ultraviolet Luminescence. The white material was essentially inert to long-wave U.V. radiation. This material fluoresced a very weak light pink to

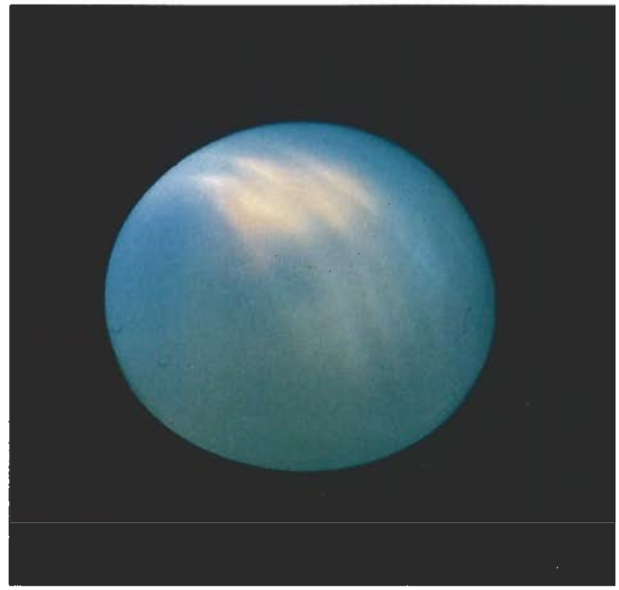


Figure 2. In strong transmitted light, this 7.83-ct pink "Pearl CZ" exhibits a characteristic striped appearance. Photo by Maha Smith.

TABLE 1. Gemological properties of nontransparent white, pink, and black "CZ."

Properties	White	Pink	Black
Visual appearance			
Reflected light	Uniform milky white	Uniform pink	Uniform black
Transmitted light	Somewhat banded, striped, or striated	Somewhat banded, striped, or striated	Dark brownish red transmission color
Diaphaneity	Translucent	Translucent	Semitranslucent to opaque
Polish luster	Very high	Very high	Very high (adamantine)
Refractive index	OTL[a]	OTL[a]	OTL[a]
Polariscope reaction	Aggregate	Aggregate	N/A[b]
Ultraviolet luminescence			
Long-wave	Inert	Strong yellow-green	Inert
Short-wave	Very weak light pink	Weak to moderate chalky light yellow-green	Inert
Absorption spectrum[c]	No detectable features	Fine lines at approx. 440, 449, 541, 543, 546, 644, 646, 650, 653, 655, and 656 nm; wider bands at 486, 515, and 523 nm	No detectable features
Chelsea filter reaction	Yellowish green	Yellowish green	Dark red
Thermal conductivity reaction[d]	—	—	Simulant
Specific gravity[e]	6.11-6.12	6.14-6.16	5.93-5.94

[a] *Over the limits of the conventional refractometer (1.81+).*
[b] *All black specimens appeared opaque in the polariscope.*
[c] *Visible range (400-700 nm), as determined using both prism and diffraction-grating type desk-model spectroscopes.*
[d] *Test not performed on pearl simulants; reaction of black material typical of that observed with other colors of CZ.*
[e] *Determined by hydrostatic weighing method.*

short-wave U.V. There was no phosphorescence to either wavelength.

The pink material fluoresced a strong yellow-green to long-wave U.V. and a weak to moderate chalky light yellow-green to short-wave U.V. Again, there was no phosphorescence. This response resembles the fluorescence reaction of transparent pink CZ (Read, 1981).

The black material was inert to both wavelengths.

Chemistry. All three types of material were analyzed using a Tracor Spectrace 5000 energy dispersive X-ray fluorescence (EDXRF) spectrometer, and all were found to contain zirconium, hafnium, and yttrium. Yttrium is a common stabilizer used in the production of CZ, while hafnium is an impurity associated with zirconium (Bosshart, 1978). The relative proportions of zirconium and yttrium found in the spectra of the "Pearl CZ" differ from those measured for a transparent, colorless, yttrium-stabilized CZ sample run for comparison. Normalizing the peak heights for zirconium in the chemical spectra of the opaque and transparent CZ samples reveals an yttrium peak height for the transparent CZ that is approximately four times greater than that of either the white or pink translucent materials. In other words, the yttrium stabilizer concentration is approximately four times greater in the transparent CZ studied than in the nontransparent material. The pink samples were also found to contain erbium (chemical symbol: Er), a rare-earth element. The chemistry of the black CZ was found to be very similar to that of the transparent, colorless CZ. In some samples (of all colors), we found traces of iron, calcium, and manganese, which are common trace elements in colorless CZ.

Spectroscopy. All samples were examined using GIA GEM desk-model spectroscopes, both prism and diffraction-grating types (the latter with an LCD digital readout). Neither the white nor black materials exhibited any detectable absorption features.

The pink specimens, however, exhibited a strong absorption pattern of the type associated with gem materials that contain rare-earth elements. The most prominent features were fine lines at approximately 440, 449, 541, 543, 546, 644, 646, 650, 653, 655, and 656 nm, with wider bands at 486, 515, and 523 nm. Where lines are tightly spaced (for example, the four between 650 and 656 nm), they may appear as a single, broad line. The spectrum is similar to that noted by the authors in some transparent pink CZ and attributed by Read (1981) to doping with erbium oxide (Er_2O_3); Nassau (1981) also reports erbium (as well as europium and holmium) as a dopant used to produce pink CZ. This is consistent with the results of the chemical analysis described above.

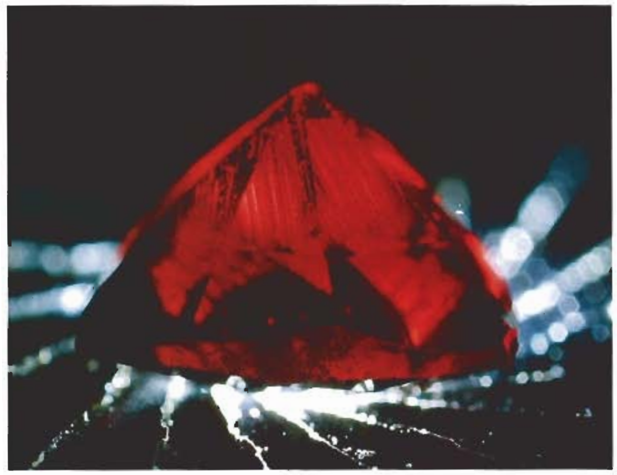


Figure 3. Thin edges and smaller faceted pieces of the black CZ, like this 0.57-ct triangular brilliant, appear brownish red when examined in strong transmitted light. Photo © GIA and Tino Hammid.

The ultraviolet, visible, and near-infrared absorption spectra of the pink and white materials were also measured using a Hitachi U-4001 U.V.-visible spectrophotometer (figure 4). The white material does not show any absorption in the visible range, which is consistent with its color appearance. It does, however, exhibit some very weak, broad absorptions in the near-infrared between 1700 nm (5880 cm^{-1}) and 2500 nm (4350 cm^{-1}).

By contrast, the pink samples show a series of very sharp absorptions in the visible range. The strong absorptions located between 480 and 550 nm result in the pink color. It is interesting to note that these features are accompanied by broader ones at about 900 and 1500 nm in the infrared, as well as the much weaker set of broad absorptions already observed for the white material.

The near-infrared and visible absorption spectra of the pink material arise from the presence of the erbium ion Er^{3+}. Except for the features

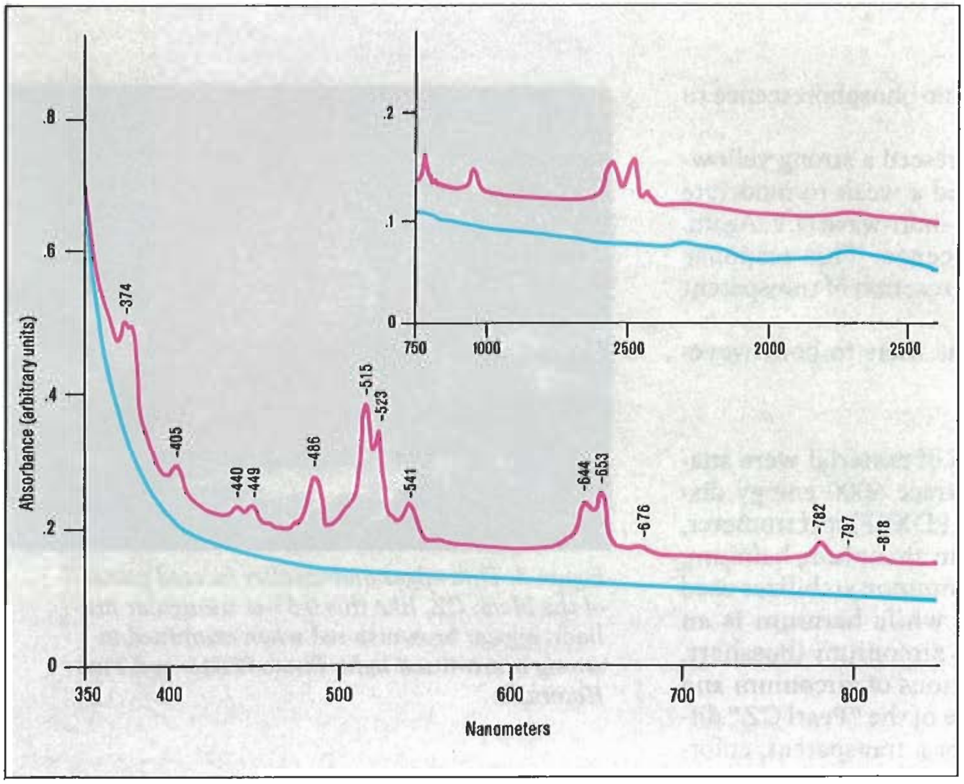


Figure 4. The ultraviolet-visible absorption spectra of white (lower curve) and pink (upper curve) "Pearl CZ" are shown here. The near-infrared absorption spectra of the same samples appear in the box (the axes of the box have the same units of measure as the larger spectra).

between 1700 and 2300 nm, the various groups of sharp absorptions from the ultraviolet to the near-infrared can be attributed to the various energy levels of the Er^{3+} ion observed by Dieke (1968, p. 134) in the $LaCl_3$ structure.

Because the pink material exhibits such a strong luminescence to long-wave U.V. radiation, we also examined the emission spectrum with a desk-model prism spectroscope. This revealed two sharp lines in the green, at approximately 540 and 550 nm, that correspond to the 541-nm absorption (and its very weak 550-nm companion) of the Er^{3+} ion (figure 5). Therefore, the U.V. luminescence is due to this dopant.

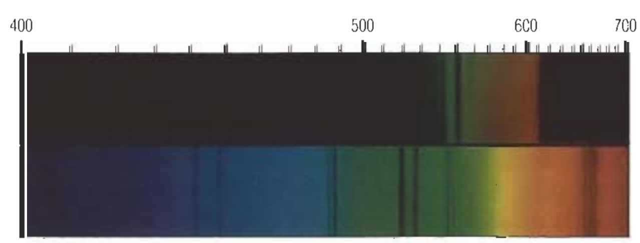
Chelsea Filter Reaction. The white and pink samples were viewed through a Chelsea filter while illuminated in the strong transmitted light provided by the base lighting system of a GIA GEM spectroscope, as were the smaller faceted black specimens and extremely thin edges of the black rough samples. Both white and pink types appeared yellowish green. As for the black samples, all areas that transmitted light appeared dark red.

Thermal Conductivity. Because the black "CZ" could be visually confused with some black diamonds (its over-the-limits R.I. could add to such confusion), it was tested with a thermal conductivity probe. All of the samples revealed a typical "simulant" reaction.

Specific Gravity. S.G. was determined by the hydrostatic method with a Mettler AM100 electronic scale. Three separate determinations were made for each sample so tested. The white material gave values of 6.11-6.12, the pink produced values of 6.14-6.16, and three of the black specimens (the larger ones) gave values of 5.93-5.94.

The values for the white and pink materials are somewhat higher than those generally reported

Figure 5. Comparison of the yellow-green long-wave U.V. fluorescence spectrum (upper) with the optical absorption spectrum of the pink material demonstrates that this luminescence originates mostly from the Er^{3+} ion.



for cubic zirconia (see, e.g., Nassau, 1981; Liddicoat, 1989). However, Read (1981; 1989) points out that both refractive index and specific gravity of CZ can vary with the amount and nature of stabilizer used. The values for the black material are within the range described in the literature for transparent, colorless CZ (e.g., Nassau, 1980; Liddicoat, 1989).

Magnification. Observation of the samples with a standard binocular microscope revealed no additional distinctive features. In surface-reflected light, the "Pearl CZ" showed an essentially smooth surface (in contrast to the contoured platelet structure of pearls).

DISCUSSION

Cubic zirconia is produced commercially by a technique known as skull melting, in which crystals are grown at high temperatures in a self-contained melt or cold crucible of powdered zirconium oxide (for a more complete description of the technique, see Nassau, 1980).

Of particular relevance to this discussion is the fact that a stabilizer—normally yttrium oxide or calcium oxide—must be used if the end result is to be a stable product crystallized in the isometric (cubic) crystal system. When yttrium oxide (Y_2O_3) is used, the amount might typically be on the order of 15 wt.%, although a cubic product can be produced with up to about 65 wt.% (J. Wenckus, pers. comm., 1991). One of the early patents filed is for cubic zirconia stabilized with 10 to 30 mol.% (16-44 wt.%) yttrium oxide (Nassau, 1980).

The amount of stabilizer is of particular interest here, as it appears from the following that the reduced transparency in both the white and pink materials results from the intentional use of insufficient stabilizer. According to Mr. Joseph Wenckus of Ceres Corp., a major U.S. manufacturer of CZ, inadequate amounts of stabilizer (for example, 5-6 wt.% yttrium) result in a material that consists of a multitude of tetragonal zirconia needles (ZrO_2) contained within a cubic zirconia matrix. Under very high magnification, Ingel (1982) observed a "tweed-like" structure in a thin section of material containing 5 wt.% yttrium oxide. The reduced transparency is the result of light scattering from these tetragonal needles. Mr. Wenckus also volunteered that, with respect to nomenclature, these products are not cubic zirconia but rather partially stabilized zirconia (PSZ).

Ceres Corp., under contract with the Naval Research Laboratory in Washington, DC, has grown a wide variety of PSZ crystals over the past 10 years, some of which have been marketed in small quantities to the gem trade (J. Wenckus, pers. comm., 1991). The authors examined a 144.66-ct white specimen, produced this past year, that was virtually identical in appearance to the white material produced in the Soviet Union. EDXRF analysis by the authors confirmed that it had yttrium and zirconium concentrations similar to those of the white "Pearl CZ."

R. P. Ingel (1982) provides further quantitative data relating yttrium content to the crystal transparency of CZ and related materials. At 3 and 4 wt.% Y_2O_3, the crystals are white and essentially opaque; at 5 wt.%, they are semitranslucent; and at 12-20 wt.%, they are transparent and colorless. This is consistent with results of the semi-quantitative chemical analyses obtained for this study.

The authors believe that the light scattering described herein alone accounts for the body color of the white material, as this material did not appear to contain a color-producing dopant. Furthermore, the striped appearance seen when the white and pink "Pearl CZ" is illuminated in strong transmitted light can be accounted for by the inhomogeneous nature of these materials.

The fact that the black samples showed no major chemical difference from the colorless reference samples indicates that their color is not due to the presence of trace elements.

Mr. Wenckus has also volunteered an explanation for the appearance of the black CZ, which Ceres Corp. has also grown in small quantities for customers in the gem trade. Such material can be produced by growing CZ under neutral and/or reducing conditions. (Alternatively, transparent CZ crystals can be "blackened" by post-growth annealing under the same atmospheric conditions [i.e., neutral or reducing] at temperatures above 1400°C). In either case, the resulting product contains color centers that absorb so much light as to cause the black color. Heating such material in an oxidizing atmosphere eliminates color centers, resulting in transparent, colorless CZ. In fact, Mr. Wenckus noted, jewelry repair operations, such as the retipping of prongs with the material still in the mounting, have had the undesired effect of turning the material colorless.

To confirm this report, the authors had a cross-

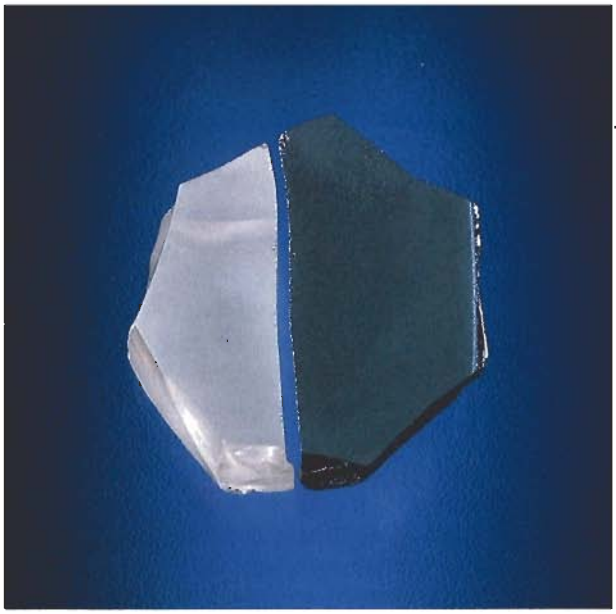


Figure 6. Heating to a red heat with a jeweler's torch caused the 6.02-ct piece of black CZ on the right to become transparent and essentially colorless. The 8.37-ct piece on the left was cut from the same original rough. Photo by Shane F. McClure.

sectional piece sawn from one of the samples of black rough and subsequently had it cut into two pieces. The larger (8.37 ct) piece was retained as a control while the smaller (6.02 ct) piece was heated on a charcoal block to a red heat with a jeweler's torch. Upon cooling, the smaller piece became transparent and essentially colorless (figure 6). A similar heating procedure performed on a 5.20-ct white cabochon and a 7.10-ct pink cabochon produced a temporary color change at high temperature, but both stones reverted to their original appearance on cooling.

CONCLUSION

The white and pink "Pearl CZ" investigated for this report appear to be partially stabilized zirconia (PSZ), which lacks sufficient stabilizer to produce a homogeneous cubic structure. Although the materials exhibit neither overtone nor orient (two components of pearl color), they are attractive and do make relatively effective pearl imitations in some jewelry applications. Their significantly higher density (6+ vs. less than 3 for natural and cultured pearls), over-the-limits R.I.'s, and smooth surface should serve to separate them easily from natural and cultured pearls. Care must be exercised, however, not to mistake their appearance in strong transmitted light for the "candling" effect seen in some bead-nucleated cultured pearls. It is interesting to note that because the reduced transparency of the PSZ is not connected to the colorant used, one may assume that any of the other colors of CZ could be similarly produced in a translucent to opaque form.

With its high luster, the black, partially reduced CZ could make an effective simulant for a number of black gems, including black diamond. A "diamond probe" should serve to separate this material quickly from either natural-color or artificially irradiated black diamonds. In addition, the brownish red transmission color noted in small samples and thin sections of this simulant differs from the light gray or brown to colorless appearance of transparent areas of natural-color black diamonds or the green transmitted color of irradiated "black" diamonds (Kammerling et al., 1990).

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