

## CUBIC STABILIZED ZIRCONIAS

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## ABSTRACT

This article contains a short survey on the stability of zirconias and their growth as stable cubic single crystals, followed by physical and crystallographic data on transparent rough and brilliant-cut material. The chemical composition of yttria-stabilized zirconias is verified by means of rarely used formulas. The results of Vickers and Mohs hardness tests on  $(Zr,Y)O_{2-x}$  are compared to the wearing characteristics of other synthetic crystals and diamond, cited in literature. Data of gemmological import are summarized in Table 1 and in Section 5 (Conclusion) which also gives instructions on the positive identification of this efficient new diamond imitation mounted in jewellery.

For the past two decades, the standards for imitating genuine diamonds have been set: their production was successfully achieved by several laboratories. This does not mean that all the other recently grown crystals are essentially less effective 'duplicates'. In general, it can be said that substances with chemical properties similar to those of the diamond (BN,  $B_4C$ , SiC, etc.) and many oxides could be very good diamond imitations (e.g. those of the pyrochlore  $M_2^II M_2^IV O_7$ , and perovskite type  $M^II M^IV O_3$  as well as oxides with garnet structure  $M_3^II M_5^IV O_{12}$ ).

## 1. PROPERTIES OF ZIRCONIA PHASES

In gemmology, cubic stabilized zirconias are new (chemically zirconium dioxides, in ceramics abbreviated as CSZ). Polycrystalline  $ZrO_2$  phases already were known before 1940, single crystals for about ten years. Zirconias have very high melting points and particular ceramic, electrooptical and metallurgical properties (very small expansion coefficients and thermal conductivity). On the other hand, their technical use is limited because of the instability of the non-monoclinic phases. In the chemically pure cubic form, the substance  $ZrO_2$  is stable only at high temperatures. Without the addition of other oxides, it changes into the tetragonal modification below approx.  $2300^\circ C$  and into the monoclinic polymorph below approx.  $1100^\circ C$ , accompanied by considerable decrease in volume. The pure, synthetic material, therefore, exists at room temperature in the same phase as the mineral Baddeleyite, which is

merely stable monoclinic  $\text{ZrO}_2$ . A possible explanation for the existence of cubic zirconia in certain metamict zircons, along with variable proportions of cryptocrystalline  $\text{SiO}_2$  and monoclinic  $\text{ZrO}_2$  (baddeleyite), is the presence of small amounts of impurities (ref. 1, 2).

Improvements in the structural stability are obtained by additions of about 15 mol. % metallic oxide (p,  $\text{MO}_y$ ), usually in the form of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Y}_2\text{O}_3$ , or  $\text{Yb}_2\text{O}_3$ . These stabilized  $(\text{Zr},\text{M})\text{O}_{2-x}$  mixed-crystals remain cubic and single-phased. They display a face-centred crystal structure with 4 formula units in the elementary cell, closely related to the fluorite structure, but with oxygen vacancies in the lattice. The oxygen deficiency,  $x = p(2-y)$ , e.g. amounts to 0.15 O for the divalent metals and decreases to 0.075 O for the trivalent metals. The vacancies are responsible for the efficient electrical conductivity at higher temperatures. The metal ions  $\text{Mn}^{2+}$ ,  $\text{Sc}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Sm}^{3+}$ ;  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$  offer further possibilities of partial  $\text{Zr}^{4+}$  substitution on the lattice sites of  $\text{ZrO}_2$ . It is important that the radius of the metal ion be similar to that of  $\text{Zr}^{4+}$  and that the divalent or trivalent cation be less electronegative than  $\text{Zr}^{4+}$ , thus possessing a more ionic bonding. Foreign radicals such as  $\text{OH}^-$  or  $\text{SO}_4^{2-}$  ions also are conducive to the stabilization of the lattice. Adding two metallic oxides of different valences to the cubic high-temperature modification of zirconia, instead of only one, has the same effect. Thus, through the admixture of titanium-, niobium-, or tantalum-oxide, ternary mixed-crystals develop from binary compounds. They are also stable from room temperature to more than  $2000^\circ\text{C}$  because these metals uniformly fix the eight-, seven- and six-fold oxygen-coordination of  $\text{Zr}^{4+}$  to a coordination number of 8. Some of the aforementioned cubic zirconias, e.g.  $(\text{Zr},\text{Mg})\text{O}_{2-x}$ , become metastable at annealing temperatures as a result of the significant oxygen deficiency which apparently initiates a slow movement of oxygen ions from a disordered, random distribution inside the anion lattice to the ordered lattice sites. Monoclinic  $\text{ZrO}_2$  exsolves. At lower temperatures, the non-stoichiometric, that is the non-integer, composition of the mixed-crystals causes a physical hardening, probably the result of oxygen immobilization (ref. 3, 4, 5, 6).

## 2. THE GROWTH OF STABILIZED $\text{ZrO}_2$ CRYSTALS

Zirconia crystal growth by the known techniques is not



successful. Thus, taking advantage of the difference in electrical conductivity of  $\text{ZrO}_2$  (insulator at room temperature and conductor at high temperatures) by applying the high frequency of an induction coil, the powder can be melted in an open cylindrical crucible. Addition of lower-melting zirconium metal grains and stabilizer powder initiates the process. Simultaneously, a thin layer of the zirconia powder is kept below the melting point at its contact with the wall of the cold crucible, so named because of the palisade of thin water-cooled vertical copper tubes. Upon slowly lowering the temperature, skull or geode shapes crystallize which consist of closely packed, columnar single-crystals measuring  $25 \times 15 \times 10$  mm or more. This process, therefore, is called the skull melting method and has just been presented in detail by Nassau (ref. 7). In his article, he states that the properties of the synthetic material now reaching the market vary with chemical composition and are yet to be investigated.

### 3. THE PHYSICAL PROPERTIES OF STABILIZED $\text{ZrO}_2$

Durafourg & Co., cutters in Lausanne (Switzerland), kindly placed at our disposal rough and brilliant-cut material of yttria-doped zirconia for examination purposes. As expected, it displays small but definite differences from the already characterized zirconia, stabilized with CaO (ref. 8, 9).

#### 3(a) *Inclusions*

The fragment of a columnar crystal, almost 70 ct in weight, consists of a white crust on the base and subconchoidal lateral faces. According to the direction of the breaks, conchoidal faces result, having either a concentric cascade or a radial feather structure. These are accompanied by razor-like edges that will splinter to some extent. The inclusions are confined to the crust, which represents the contact zone of the melting oxide powders in the centre of the crucible and the cold, thermally insulating layer of powder at the innermost wall of the crucible. The polycrystalline crust is terminated by irregular pyramidal surfaces from which run tubelike and dumbbell-shaped cavities toward the centre. These internal growth characteristics continue through the 3 to 4 mm thick crust, becoming subparallel rows of isometric negative crystals. All inclusions are colourless and semitransparent. Their interfaces are lined with  $\text{ZrO}_2$  powder which had been prevented

TABLE 1

## Identification of Cubic Stabilized Zirconias

Properties	(Zr, Y) O <sub>2-x</sub>		(Zr, Ca) O <sub>2-x</sub> (ref. 8)
Cut	round brilliant 32/24		brilliant 32/24(?)
Weight	3.86 ct	1.38 ct	—
Proportions			
Table	58%	60%	
Crown	15 1/2%	14%	
Girdle	6%	6%	
Pavilion	45 1/2%	47%	
Symmetry	good	good	
Polish	medium	insufficient	
Colour	weak	very weak pink	colourless; according to pig-
	yellowish	(almost colourless)	mentation also various hues
			and degrees of saturation
Refractive Index n <sub>D</sub>	2.1712 (±0.0005)	2.1651 (±0.0005)	2.1775 (±0.005)
Dispersion n <sub>F</sub> —n <sub>C</sub>	0.0338	0.0336	(0.0376)
n <sub>G</sub> —n <sub>B</sub>	0.0591	0.0587	0.0653
Reflectivity R <sub>meas.</sub>	13.0% (polish)	12.3% (polish)	—
R <sub>calc.</sub>	13.6%	13.5%	13.7%
Fluorescence			
UV-A	none	vw, reddish	none
UV-C	vw, greenish-yellow	w, greenish-yellow	distinct, yellow
Absorption total	below 370 nm	below 340 nm	below 310 resp. 360 nm
in the VIS	no lines or bands		no lines or bands
Inclusions	parallel rows of small, semitransparent, isometric crystal-like cavities extending into hazy stripes of tiny particles	none	in the experimental stage of growth small gas bubbles and individual large ones; in the new cuttable material no inclusions remain
Spec. Gravity (4°C)	5.950 (±0.005)	5.947 (±0.005)	5.65 (5.60 to 5.71)
Cleavage	none	none	—
Vickers Hardness V (500 g test load)	1250 to 1570 kg/mm <sup>2</sup> (indentation not oriented)		1407 and 1437 kg/mm <sup>2</sup> (oriented?)
Mohs Hardness			
M <sub>det.</sub>	approximately 8 1/4		8 1/2
M <sub>calc.</sub>	approximately 8.2 (8.0 to 8.5)		(8.2 and 8.3)
Brittleness	more brittle than synthetic corundum but less than Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>		analogous
External characteristics	roundish facet edges, percussion marks, small chips		analogous
Magnetism	indifferent (diamagnetic?)		
Conductivity	electrical insulator (room temp.)		

from melting by the insulating action of a liquid or air trapped in the crust. These cavities, therefore, are of two phases, i.e. of the sl- or sg-type (solid, liquid, gaseous, ref. 6).

At the experimental stage of crystal growth, the subparallel rows of isometric negative crystals extended beyond the crust in the



form of hazy stripes. The yellowish brilliant-cut  $(\text{Zr,Y})\text{O}_{2-x}$  of 3.86 ct obviously came from the crust area of a crystal grown in that stage. The new refined material is essentially colourless and the inclusions do not extend into the clear columnar part of the crystal. The 70 ct crystal fragment only possesses a faint orange tinge and is completely transparent. But its surface consists of small, finely chiselled faces which form a weak growth striation parallel to the crust. When compared to each other, the aforementioned striations are perpendicular and leave the impression of 'frozen-in' interference patterns produced by standing mechanical waves.

The crystal fragment rather resembles the smaller brilliant-cut  $(\text{Zr,Y})\text{O}_{2-x}$  in its properties. The specific gravity, 5.966, is actually slightly higher and the fluorescence is somewhat stronger: UV-A weak, orange; UV-C medium, yellow. The scratch hardness is about  $8\frac{1}{4}$ . Material from the crust area manifests specific gravities as low as 5.80.

### 3(b) Scratch Hardness and Indentation Resistances

The investigation on the resistance to mechanical impact is more important when characterizing new synthetics than during subsequent gemmological identification, which in every normal case must be effected with non-destructive techniques. Which hardness test should be relevant is difficult to determine. The Mohs scratch-hardness values, a purely qualitative sequence of numerals, give a picture of the scratching rather than the cutting strength and general stability. A better measure for the velocity of wear of solids is the resistance to penetration, as determined by the Vickers and Knoop tests, both permitting an estimation of the barely measurable brittleness. Other tests deal with cutting or impact resistance qualities. As is to be expected from the atomic bonding, specific for each substance, these properties have a certain relationship to each other. The relationship of Mohs hardness (M) to any indentation hardness (IH) can be expressed by the following empirical, non-linear formula:

$$\log (IH) = 0.2M + 1.5 .$$

With the Vickers test, a square impression is formed by a diamond pyramid with  $136^\circ$  interfacial angle, under a given test load (P) and during a penetration period of normally 30 seconds.

The average diagonal length ( $d$ ) of the square is then measured and used to calculate the Vickers hardness as follows:

$$V = \frac{1.8543 P}{d^2} \left[ \text{kg/mm}^2 \right] .$$

In general, the size of the indentation depends on the test load, the shape of the indenter (sphere, cone; rhomboidal, square or pentagonal pyramid), its crystallographic orientation relative to that of the specimen and the test temperature. Experimentation has proved the Brookes method of indenting hard solids to be the best. Its pentagonal diamond pyramid has a longer life expectancy than other indentors and diminishes the distorting influence of hardness anisotropy on the shape of the impression (ref. 10, 11).

The Vickers hardness of  $(\text{Zr}, \text{Y})\text{O}_{2-x}$ , as measured under the Leitz-Microhardness instrument, lies between 1250 and 1570  $\text{kg/mm}^2$ . Applied to the first formula, these values place the Mohs hardness at 8 to 8.5 which coincides with the actual scratch result of  $8\frac{1}{4}$ . Interestingly, tests with a 1 kg load on a universal indentation apparatus (industrial model OM 250 of Gnehm & Co. in Horgen, Switzerland) resulted in Vickers hardness figures in the same range. The average of 1400  $\text{kg/mm}^2$  is slightly lower than the specifications for  $(\text{Zr}, \text{Ca})\text{O}_{2-x}$ , but this may not be a real difference since the indentations were not oriented (Table 1). Under the same conditions, resistances to penetration were found to be about 1570  $\text{kg/mm}^2$  for  $\text{Y}_3\text{Al}_5\text{O}_{12}$  and 2290  $\text{kg/mm}^2$  for synthetic ruby. These orders of magnitude correspond to the data in the literature (1550  $\text{kg/mm}^2$  for YAG, and 2200  $\text{kg/mm}^2$  for sapphire). Calculated Mohs hardness values are approximately 8.5 and 9.3. So, the new zirconias are not harder than their predecessor, YAG, but less brittle, for they show less tendency to splinter at the edges of the impression produced by the diamond. The synthetic ruby is tougher and considerably harder, though maybe not quite as hard as suggested by the calculation ( $M \approx 9.3$ ). However, for  $M > 9$  the given relation with  $V$  is not quite certain.

The hardness anisotropy of stabilized zirconia samples is possibly a bit higher than indicated, yet in no way extreme. For diamond, hardness differences strongly depend on cleavage directions. Indentation resistances are known to range from 5700 to 10 400  $\text{kg/mm}^2$ , with averages near 9000 to 10 000  $\text{kg/mm}^2$ . These



values illustrate the demands placed on a convincing diamond imitation. With a hardness near 4500 or 4750 kg/mm<sup>2</sup>, cubic boron nitride (BN), among all known substances, comes closest to the diamond in this respect. The great hardness of both materials originates from the same type of strongly covalent, oriented bonding. It differs only in the atomic spacing which measures 1.57Å in boron nitride and 1.545Å in diamond and in the absence of any ionic bonding character of the diamond (ref. 12).

### 3(c) Absorption

The spectral diagram (see Figure 1) reflects the typical course of different nearly colourless synthetic materials and diamond. The relationship among the curves is not real. In each case, however, they display good transparency of the solids in the visible range (VIS) and gradual to steep decrease of transmission (increase of absorption) toward the ultraviolet region. The absence of absorption lines and bands in the VIS causes the weak body colours. The absorption edges of strontium titanate and synthetic rutile have virtually no influence on colour. The human eye is quite insensitive to the violet wavelengths and would not detect their absence. Gadolinium gallium oxide (GGG) demonstrates interesting absorption lines in the UV and emission lines in the VIS, under the stimulation of short-wave UV radiation (medium strong 595 nm and weak 614 nm, not recorded here).

## 4. THE STRUCTURE AND COMPOSITION OF (Zr,Y)O<sub>2-x</sub>

The microprobe analysis showed Zr and Y as metal constituents. Semiquantitatively, proportions of  $\approx 15.8$  mol% YO<sub>3/2</sub> for the crystal fragment and of  $\approx 18.3$  mol% YO<sub>3/2</sub> for the round (Zr,Y)O<sub>2-x</sub>-rough were detected. Ca, Mg, and Ti are not present in these samples. Because of line interferences (even from higher electron orbits), rare earth elements could be ascertained only with considerably refined mathematical corrections. It is very likely that trace elements, e.g. Nd, Ce, Er, cause the very weak pink colour of the small brilliant-cut (Zr,Y)O<sub>2-x</sub>. Hafnium, in the form of hafnia, with its chemical affinity to zirconium, is a permanent companion of zircons (ZrSiO<sub>4</sub>), suppliers of the raw materials. Separation of the two oxides, HfO<sub>2</sub> and ZrO<sub>2</sub>, is both difficult and costly. It is only done for special purposes and for the extraction of hafnia which does not form independent minerals. A HfO<sub>2</sub> content

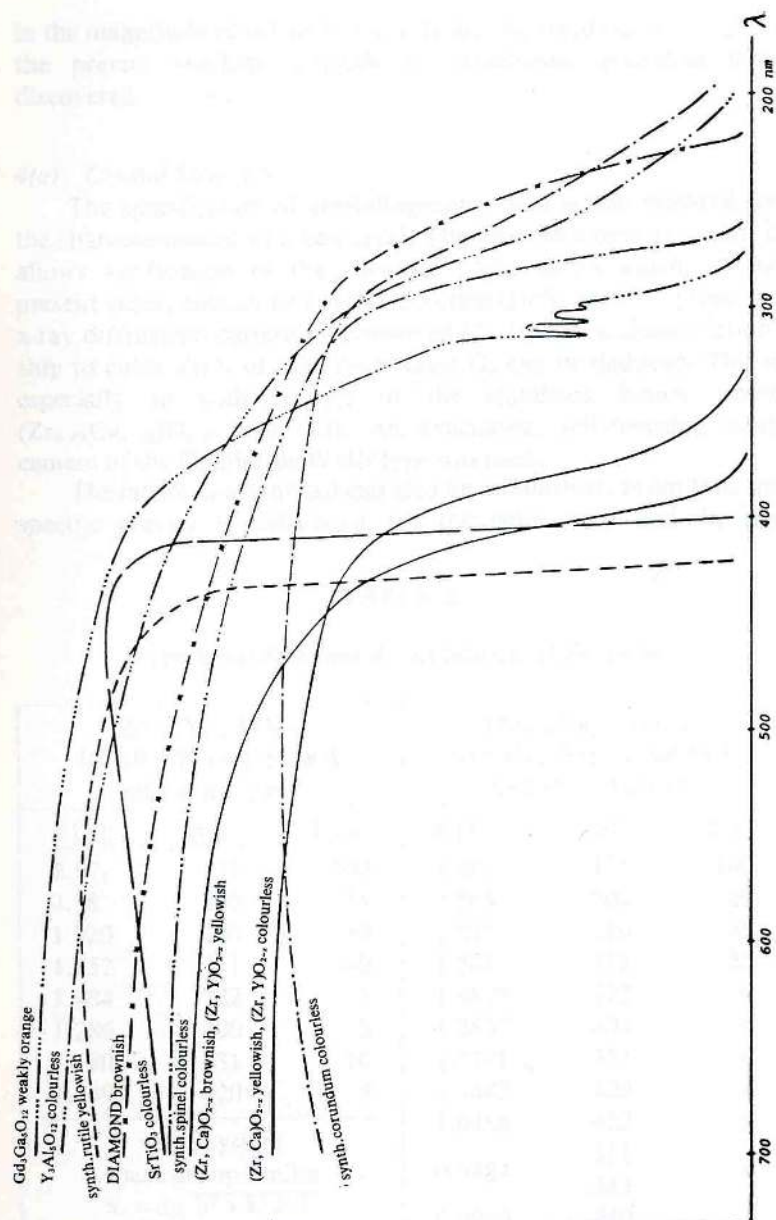


Fig. 1 Schematic presentation of the special transmission behaviour of diamond and its most important imitations at ambient temperatures.



in the magnitude of 0.5 to 1 mol% cannot be ruled out although in the present synthetic crystals no significant quantities were discovered.

#### 4(a) Crystal Structure

The specification of crystallographic data is also required for the characterization of a new solid. Together with optical values, it allows verification of the chemical composition which, in the present cases, cannot be considered completely reliable. From the x-ray diffraction pattern of powdered  $(\text{Zr,Y})\text{O}_{2-x}$ , a close relationship to cubic  $\text{ZrO}_2$  of the crystal-class  $\text{O}_h$  can be deduced. This is especially so with respect to the stabilized binary phase  $(\text{Zr}_{0.85}\text{Ca}_{0.15})\text{O}_{1.85}$  (ref. 13). An evacuated, self-focusing x-ray camera of the Guinier-de Wolff type was used.

The lattice constant ( $a_0$ ) can also be established. From this, the specific gravity is calculated for the cubic case and in the

TABLE 2

*Interplanar Spacings  $d_{hkl}$  of Stabilized Zirconias*

$(\text{Zr}_{0.84}\text{Y}_{0.16})\text{O}_{1.92}$ $\lambda(\text{CuK}\alpha/\text{Ni}) = 1.5418 \text{ \AA}$ silicon standard			$(\text{Zr}_{0.85}\text{Ca}_{0.15})\text{O}_{1.85}$ $\lambda(\text{CuK}\alpha_1/\text{Ni}) = 1.54056 \text{ \AA}$ ASTM card 26-341		
$d [\text{\AA}]$	hkl	$I_{\text{estim.}}$	$d [\text{\AA}]$	hkl	$I/I_1$
2.97 <sub>5</sub>	111	100	2.961	111	100
2.58	200	15	2.565	200	20
1.820	220	50	1.815	220	45
1.552	311	40	1.548	311	25
1.484	222	5	1.4823	222	4
1.286	400	5	1.2837	400	4
1.180	331	10	1.1781	331	6
1.149	420	5	1.1482	420	4
cubic system space group $\text{Fm}\bar{3}\text{m}$ $a_0 = d\sqrt{h^2 + k^2 + l^2}$			1.0484	422	5
			0.9884	511	4
			0.9080	333	1
$a_0 \approx 5.145 \text{ \AA}$ (weighted)			$a_0 = 5.135 \text{ \AA}$ (weighted)		

CGS-system (cm,g,sec) according to the formula:

$$SG = \frac{z M}{N V} = 1.6602 \frac{z M}{(a_0)^3},$$

where  $z$  represents the number of formula units in the elementary cell ( $= 4$  molecules).  $V$  is the unit cell volume and  $M$  the molecular weight of the mixed-crystal.  $N$  represents the Avogadro number of molecules per mole ( $= 6.023 \times 10^{23} \text{ mole}^{-1}$ ; ref. 14).

#### 4(b) Verification of the Chemical Composition

The specific gravity gives a clue to the chemical composition and to impurities such as inclusions and other perturbations of the real crystal. The specific gravity ( $5.966 \pm 0.003$ ) as well as the lattice constant ( $5.145 \pm 0.005 \text{ \AA}$ ) of the crystal fragment are known. So the equation can be resolved for the molecular weight. It follows that  $M = 122.35$ . This coincides with the molecular weight of 122.4 from the analysis, if a trace of hafnium oxide is taken into account. On the basis of 4 (Zr + Y), the approximate non-stoichiometric, that is the non-integer, structural formula can be given as  $(\text{Zr}_{3.37}\text{Y}_{0.63})\text{O}_{7.68}$ . The formula for the round rough approximately is  $(\text{Zr}_{3.27}\text{Y}_{0.73})\text{O}_{7.63}$ . Alternatively, these formulas can be expressed as  $(\text{Zr,Y})\text{O}_{1.92}$  and  $(\text{Zr,Y})\text{O}_{1.91}$  or, in dualistic writing,  $3.37 \text{ ZrO}_2 \cdot 0.63 \text{ Y}_2\text{O}_3$  and  $3.27 \text{ ZrO}_2 \cdot 0.73 \text{ Y}_2\text{O}_3$  (ref. 15).

Gladstone and Dale's rule offers another means of verification. The specific refractivity (or specific refractive power,  $K$ ) of a material is related to its specific gravity ( $SG$ ) and refractive index ( $n$ ) through the following equation:

$$K = \frac{n - 1}{SG}$$

The specific refractivity can be cross-checked with the partial refractive powers ( $k$ ) and weight proportions ( $q$ ) of the constituent oxides by the formula:

$$K = k_1 q_1 + k_2 q_2 + \dots + k_n q_n$$

For most minerals, the two results of  $K$  differ by less than 5% (ref. 16).

The results lie within the expected limits, especially if a small amount of  $\text{HfO}_2$  would be taken into consideration. Calculations with lattice constants from precise x-ray data lead to reliable values for the specific gravity (and molecular weight). This second, physical method is only appropriate for verifying the overall

TABLE 3  
*Verification of the Chemical Compositions*

Specimen	$K = \frac{n-1}{SG}$	$K = k_1q_1 + k_2q_2$
(Zr, Y) <sub>4</sub> O <sub>7.68</sub>	0.197	0.193
(Zr, Y) <sub>4</sub> O <sub>7.63</sub>	0.196	0.191
(Zr, Ca) <sub>4</sub> O <sub>7.44</sub>	0.209	0.203
$k(ZrO_2) = 0.201, k(Y_2O_3) = 0.144, k(CaO) = 0.225, k(HfO_2) = 0.3$		

chemistry because of the relatively uncertain partial refractive power values. A systematic inadequacy of the formula cannot be excluded since it was developed for liquids and gases.

Nevertheless, when the weight proportions of a compound are varied or constituents substituted, the qualitative behaviour of its refractive index and specific gravity can be predicted by means of the two equations for K. Thus, (Zr,Ca)<sub>4</sub>O<sub>7.44</sub> should show a similar refractive index, but a distinctly lower specific gravity than the two (Zr,Y)<sub>4</sub>O<sub>8-4x</sub>. Table 1 confirms this. The partial refractive power of the CaO stabilizer is higher and the molecular weight lower than that of the yttria additive, with lattice constants of the binary zirconias being almost identical (5.07 to 5.15 Å). For cubic stabilized hafnia, theoretically being cuttable material, essentially higher refractive index and specific gravity values must be expected than for each stabilized zirconia, since its lattice constant also is near 5.2 Å (ref. 9, 3).

## 5. CONCLUSION

The stabilized zirconias are the latest products in the jewellery trade. For the time being, they may be considered as the most convincing of medium expensive, highly refractive diamond imitations. The gemmologist has no reason for anxiety if he remains alert and is able to effect a determination of the specific gravity and light refraction, e.g. by the apparent depth method. As many tests have demonstrated, the refractive index ( $n$  = measured depth: apparent depth) can be established, by means of a microscope and competent measurement, with an accuracy better than 1% ( $n$  for (Zr,Y)O<sub>2-x</sub> = 2.17±0.02 to 2.16±0.02). This technique has the advantage of being independent from the quality of the surface



(polish and flatness) and of being more precise than the approximation of  $n$  based on the principle of reflection, e.g. with a Gemeter or micro-spectrophotometer ( $R$  in Table 1).

Usually, not the real but the diamond weight corresponding to the size of the mounted synthetic stone is stated, and this creates additional confusion. It therefore is not possible to determine or estimate the specific gravity of the fake diamond. For positive identification, a value in addition to the refractive index figure would be useful in this case. Here dispersion becomes important. It can be approximated by the microscopic technique mentioned above, applying interference filters. Most likely the differentiation between yttria- and calcia-stabilized zirconias would not be possible. However, this has little significance.

The variations of the gemmologically important values, recently published by Nassau (ref. 7), are: refractive index  $n_D = 2.15$  to  $2.18$ , dispersion  $n_G - n_B = 0.060$  to  $0.063$ , Mohs hardness  $M = 7\frac{1}{2}$  to  $8\frac{1}{2}$  and specific gravity about 6. For jewellery material they have to be slightly altered. The variation of  $n$  remains the same. The dispersion range must be extended to  $\leq 0.059$  for  $(Zr,Y)O_{2-x}$  and to  $\geq 0.065$  for  $(Zr,Ca)O_{2-x}$ . Mohs hardness has not been found inferior to  $M = 8$ . The specific gravity enables the unequivocal separation of  $(Zr,Y)O_{2-x}$  and  $(Zr,Ca)O_{2-x}$ . Their ranges are 5.94 to 5.97, and 5.60 to 5.71 respectively (values for CaO-stabilized zirconia by Gübelin, ref. 8). Stabilized zirconias may be coloured by pigmentation. Almost colourless specimens transmit the visible radiation freely, but absorb totally below about 340 nm. Inclusions are absent in the newest products. At room temperature, zirconias are structurally stable, physically resistant and chemically inert.

It is conceivable that zirconias will appear containing stabilizers other than yttria or calcia. The indicated variations, therefore, may again increase in future.

To verify Mohs hardness values and the chemical composition of solids, rarely used mathematical formulas have been presented. The rule of Gladstone and Dale should be pointed out. It permits a qualitative prediction of the refractive index and specific gravity of materials with identical crystal structure and variable composition. The x-ray data of Table 2 demonstrate that the interplanar spacings and lattice constants, on the other hand, are fairly insensitive to chemical variations.

Reflection patterns of the two brilliant-cut  $(\text{Zr,Y})\text{O}_{2-x}$  with mediocre polish, recorded by means of a Gemprint instrument, did not differ greatly from those of the predecessors  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , synthetic spinel, synthetic rutile, and  $\text{SrTiO}_3$ . The patterns display a limited number of large multipartite black spots on the film negative. They cannot be confused with the configurations of numerous small but intense reflections produced by diamonds and zircons. However, an approximate matching would be possible by improving the polish and reducing the pavilion angle and girdle thickness of the latest diamond imitations.

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[Manuscript received 1st September, 1977.]



Reference to the Department of Health and Social Security, however, has elicited replies from the Health and Safety Executive to the effect that, although experiments have shown that EDB is carcinogenic in rats and mice when large quantities are administered direct to the stomach, there is no evidence to date of any cases of cancer in man following exposure to it. Excessive acute or chronic exposure to EDB, however, can produce toxic effects in man, which can result from skin contact, inhalation of vapour, or, of course, swallowing. Care should therefore be taken in using ethylene dibromide (and also Clerici solution, and indeed any liquids other than clean water) to avoid skin contact or inhalation of vapour, and on no account should any of the liquids used by gemmologists for gem testing be swallowed.

In case of contact with the skin, it should be washed off: if in the eyes, they should be well flushed out with running water: if inhaled, move to fresh air: if swallowed, vomiting should be attempted and medical assistance obtained.

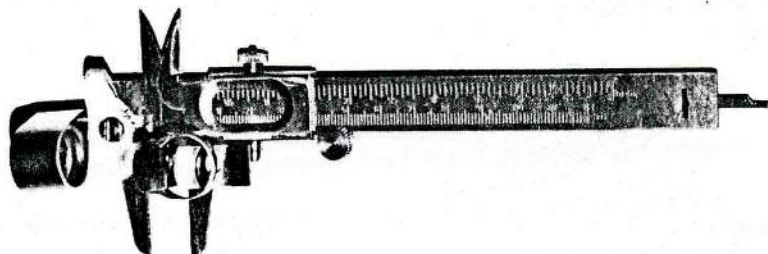
#### **DEUTSCHE GEMMOLOGISCHE GESELLSCHAFT 2nd TECHNICAL CONFERENCE OF 1978**

*(Report received from Mr Peter G. Read, F.G.A.)*

The Second 1978 Technical Conference of the German Gemmological Association was opened by the Association's President, Prof. Dr H. Bank, F.G.A., in the Diamond and Gemstone Bourse in Idar-Oberstein on Saturday, 30th September. This was followed by a talk on 'Methods of Geological Dating' given by Dr Klaus Hellmann, of the Nuclear Research Centre, Karlsruhe. In his talk, Dr Hellmann covered the various techniques of radio-active dating and discussed their relevance to the age determination of rocks and minerals.

This initial talk of the Conference was followed by a series of working and discussion meetings which were held in the well-equipped lecture rooms and laboratories of the new DGemG Gemmological Training Centre.

On Sunday, 1st October, Diplomas were presented to the successful graduates of the DGemG study courses by the President Prof. Dr H. Bank, and by Dr G. Lenzen. Dr Diehl then gave a talk on 'Djevalite, Phianite, Zirconia—what are they?' in which he described the Russian skull melting technique and the methods used to stabilize zirconium oxide in its cubic state. This was followed by talks on 'Automatic Weighing' by P. G. Read and on 'Gemstones of East Africa' by Dr K. Schmetzer.





After these three talks, H. Bartmann demonstrated a novel combination of vernier calliper gauge and hand lens which he had constructed to facilitate the measurement of refractive indices of both mounted and unmounted gemstones by the direct reading method. The illustration shows the device with a ring clipped in a spring holder. The apparent depth of the gemstone in the ring is measured by focusing the lens, via the calliper adjustment, first on the surface of the table facet, and then on the culet, and subtracting the two readings. The actual depth of the stone is measured directly, using, in the case of a mounted stone, an extension anvil fitted to the gauge head.

The final series of talks included short reports by W. Schneider on the 'Slocum Stone' and by D. Schwarz on 'Fluorescent properties of new diamond imitations'.

Among the faceted gem minerals on display were amethysts from Russia and Arizona and morganites from Brazil. Also shown were samples of cubic zirconium oxide crystals and several rock crystal specimens containing large pyrite inclusions.

#### ADDENDA

By way of clarification, Mr G. Bosshart would like to add three notes to his article 'Cubic Stabilized Zirconias' in J. Gemm., XVI, 4, 244-56, namely:

- (1) The following to be added at the end of paragraph 3(c) on page 250 above, viz:  
For obvious reasons a gemmological spectroscope, effective in the wavelength range of 400 to 700 nm, is of little aid in the differentiation between these nearly colourless solids. The yellow type of  $(Zr,Ca)O_{2-x}$  absorbs totally below about 310 nm and the brownish-pink type below about 360 nm, which is roughly inverse to the behaviour of yellowish and faint pink  $(Zr,Y)O_{2-x}$  as indicated in Table 1. For colourless  $(Zr,Ca)O_{2-x}$ , manufactured in Switzerland, total absorption starts near 260 nm as it does for  $(Zr,Y)O_{2-x}$  of the Russian production, this minimum figure being valid for various hues of the faintest saturations (very weakly greenish, bluish, orangy, etc.).
- (2) The label ' $(Zr,Y)O_{2-x}$  colourless' in Fig. 1 on page 251 above to be replaced by ' $(Zr,Y)O_{2-x}$  faint pink'.
- (3) For the interested gemmological reader, the most comprehensive and latest article among modern papers on single crystals of cubic stabilized zirconia and hafnia may be mentioned, namely:

Alexandrov, V. I. *et al.* 1978. 'Synthesis and Crystal Growth of Refractory Materials by Radio-frequency Melting in a Cold Container', in *Current Topics in Materials Science*, vol. 1, pp.421-80. Amsterdam, New York, Oxford: North-Holland Publ. Co.

#### CORRIGENDA

On p.324 above, line 11, for 'The Rubyvale Sapphire Fields' (sub-heading) read 'The Rubyvale and Sapphire Fields'.

On p.331 above, lines 9 and 8 from foot of page, for 'back-how' read 'back-hoe'.

On p.349 above, second column, line 9, for '(Verduyn) Walter, Laetitia' read 'Verduyn-Walter, Laetitia'.