

Luminescence properties of Ti-doped gem-grade zirconia powders

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Abstract. A detailed investigation on luminescence properties of gem-grade zirconia (NFC) as a function of Ti doping is presented. The effect of various parameters such as Ti concentration, environment of heat treatment and temperature was studied in detail and the optimum conditions for producing zirconia with luminescence properties comparable to standard material determined.

Keywords. Zirconia; gem-grade; luminescence.

1. Introduction

Gemstones are certain minerals which are highly valued because of their beauty, durability and scarcity. In general, any stone which can fetch a high price if attractively mounted in jewellery is considered as gemstone. Diamond (allotropic form of carbon) is the supreme colourless gemstone. The most popular substitutes for diamond in the past were zircon and colourless sapphire. However, in recent years, cubic zirconia (zirconium dioxide, ZrO_2) has emerged as the sole alternative to diamond due to the closeness in the properties of diamond and cubic zirconia (except specific gravity). The properties of some of the diamond substitutes are given in table 1.

India has a well-established zirconium industry and has excellent prospects of becoming one of the most important producers and exporters of gem-grade zirconia. Efforts are under way at the Nuclear Fuel Complex (NFC), Hyderabad, to produce gem-grade ZrO_2 . In view of this, the present work was undertaken to assess the utility of luminescence studies in the fabrication of proper raw material for gem-grade zirconia.

1.1 Zirconium dioxide (ZrO_2 , zirconia)

Zirconium is a member of group IV of the periodic table. Baddeleyite (ZrO_2) and zircon (zirconium orthosilicate, $ZrSiO_4$) are at present the main sources for industrial zirconium.

Zirconia is produced by ignition of zirconium hydroxide or other zirconium salts, viz. sulphates and nitrates, obtained during the extraction of zirconium from the minerals. Commercial zirconia is always associated with hafnium as major impurity due to closeness in their crystal radii (Zr^{4+} 0.79 Å, Hf^{4+} 0.78 Å). Besides Hf, commercial zirconia also contains Fe and Ti as major impurities. Zirconia is very stable and refractory and has a high melting point ($> 2700^\circ C$). Zirconia displays polymorphism and normally exists in monoclinic form at room temperature, and on heating changes to tetragonal ($1250^\circ C$), hexagonal ($1900^\circ C$) and cubic ($\sim 2300^\circ C$), and upon cooling reverts to monoclinic (Elwell 1979). The cubic form of zirconia is stabilized by addition of CaO, MgO or Y_2O_3 and finds a variety of applications

Table 1. Properties of some diamond substitutes.

Material	Chemical formula	Hardness (Mohs scale)	Refractive index	Birefringence	Dispersion	Sp. gravity
Diamond	C	10.0	2.42	0	0.044	3.52
Cubic zirconia	ZrO ₂	8.0	2.16	0	0.060	6.00
Zircon	ZrSiO ₄	7.5	1.92	0.059	0.039	4.69
Strontium titanate	SrTiO ₃	5.6	2.41	0	0.190	5.15

(Elwell 1979)

such as protective coatings and solid-state electrolyte, apart from a substitute for diamond.

1.2 Optical properties of zirconia

Optical properties of cubic zirconia are largely governed by stoichiometric oxygen vacancies and presence of dopants such as rare earths, nickel, chromium, titanium, iron, etc. Weakly reduced cubic zirconia exhibits yellow coloration due to loss of oxygen without any change in structure (Aleksandrov *et al* 1978; Bonola *et al* 1991). Black crystals of zirconia are produced on vacuum annealing at 2000°C and rapid cooling; blackness is due to partial oxygen loss and the formation of colour centres. On heating in air at 1200°C, zirconia regains its original colour (Aleksandrov *et al* 1978). Single-crystal yttria-stabilized cubic zirconia in the as-grown state is reported to be a transparent pale yellow or brown material without any strong absorption in the visible region of the spectrum (Wright *et al* 1973). Doping with Ce or Cr gives orange or red crystals respectively.

The vacancies in ZrO₂ crystal may also be created by electroreduction at relatively low temperatures and applied voltages (Bonola *et al* 1991).

Commercial samples of monoclinic zirconia are reported to exhibit blue-white luminescence with a long persistence when excited by ultraviolet light or cathode rays. However, high-purity zirconia does not respond to ultraviolet or cathode-ray excitation (Sarver 1966). The observed luminescence was believed to be due to the presence of an impurity which works as primary activator and was identified as Ti. Studies on luminescence properties of Ti-doped high-purity zirconia have been reported. Presence of Fe impurity appears to be detrimental to Ti emission. Purity and Ti concentration appear to play an important role in governing the luminescence properties of Ti-doped zirconia (Sarver 1966).

1.3 Luminescence studies on zirconia

Zirconia powders from three sources, viz. (i) imported (China) (IC), (ii) MEL (UK) (MEL) and (iii) synthesized indigenously at NFC, Hyderabad, were used for luminescence studies. Detailed luminescence studies were conducted with NFC powders. MEL sample was used as a standard for comparison. In table 2, spectrographic analysis of the above mentioned three samples is given. It is evident that the IC

Table 2. Analysis of ZrO₂ samples*.

Element	Concentration in ppm on Zr basis		
	IC	MEL	NFC
Al	< 10	15	
B	< 0.5	< 0.5	< 0.5
Bi	< 25	< 25	< 25
Ca	500	< 50	< 50
Co	< 5	< 5	< 10
Cr	< 10	< 10	< 25
Cu	< 25	< 25	< 25
Fe	< 10	< 10	< 20
Hf	—	1.9%	—
Mg	< 25	< 25	< 25
Mn	< 5	< 5	< 5
Mo	< 25	< 25	< 25
Ni	< 5	< 5	< 5
Pb	< 25	< 25	< 25
Sb	< 25	< 25	< 25
Si		10	
Sn	< 10	< 10	< 10
Ti	> 500 (~ 2000)	> 500 (1500)	150
U	< 1	< 1	~ 5
V	< 10	< 10	< 10
W	< 25	< 25	< 25

* Analysis supplied by NFC, Hyderabad.

sample contains higher Ti whereas MEL sample contains higher Hf and Ti values compared to NFC zirconia. Fe content of NFC sample is high compared to the other two samples.

It is interesting to note that with 307 nm excitation of these zirconia samples MEL ZrO₂ exhibited strong luminescence with a wide emission band extending below 400 nm to above 650 nm with a peak emission at ~ 473 nm; whereas IC ZrO₂ exhibited relatively weak luminescence. The NFC sample showed weakest luminescence which could be slightly improved by annealing in oxygen for a long time. The very weak luminescence exhibited by NFC sample may be attributed to low Ti content, viz. 150 ppm.

1.4 Improvement of luminescence properties of NFC zirconia

In view of the above, it was of interest to study (i) the feasibility of improving the optical properties of NFC zirconia by Ti doping, (ii) to determine the optimum Ti content to yield zirconia with luminescence comparable to that of MEL, and (iii) the role of oxygen/argon annealing of zirconia if any.

In the present work data on Ti doping of NFC ZrO₂ and its effect on luminescence properties of the powders is presented.

2. Preparation of Ti-doped ZrO₂ samples

Gem-grade ZrO₂ sample received from a particular batch of NFC, was used as such without further purification. Ti was doped in ZrO₂ sample in concentrations from 0.1 to 1 wt%. Required amount of Ti sulphate solution and 0.5 g ZrO₂ were mixed to form a slurry and evaporated to dryness on a sand bath. The dried product was mixed by grinding and heated in a platinum crucible at 1000°C for 1 h in air, quenched, followed by grinding and further heating to 1100°C for 30 min. The cooled product (A) was further annealed in oxygen (B) or argon (C) at 1000°C for 1 h.

All the above samples gave blue-white emission on 307 nm excitation. The excitation and emission spectra were recorded using a Hitachi F-4010 spectrofluorimeter fitted with Hamamatsu R-928 F photomultiplier tube. All the luminescence measurements were done with front surface geometry. The powdered samples were packed in a special holder, the front face of which is made of a quartz glass plate. The thickness of the materials packed in the holder was about 0.3 mm for all the measurements.

The optical properties for the samples A, B and C are summarized in table 3. Data on IC and MEL ZrO₂ samples are also included for comparison.

X-ray diffraction patterns were recorded for stock and Ti-doped ZrO₂ powders with Ni-filtered Cu-K α radiation on a Philips pw 1710 diffractometer. The X-ray diffraction patterns agreed well with that of monoclinic ZrO₂ pattern reported in the literature (Smith and Newkirk 1965).

3. Results

3.1 Luminescence studies on zirconia

With 307 nm excitation IC, MEL and NFC ZrO₂ samples received as such and Ti-doped NFC ZrO₂ samples exhibit a wide emission band extending from below 400 nm to above 650 nm with a peak emission intensity at 473 nm. Figure 1 shows

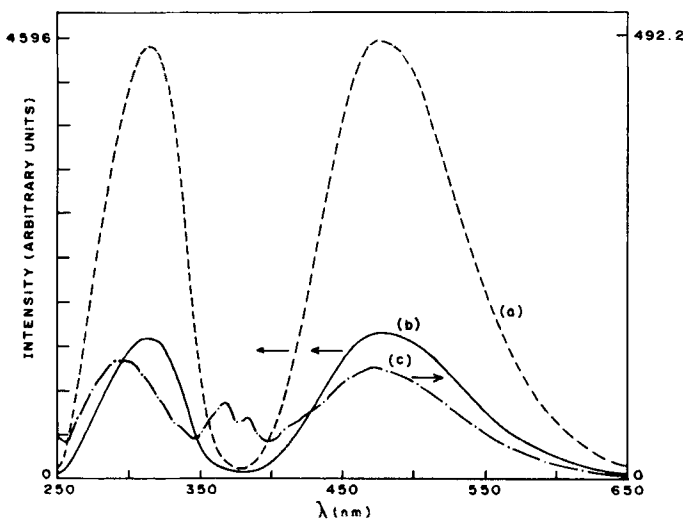


Figure 1. Excitation and emission spectra of ZrO₂: (a) MEL, (b) IC and (c) NFC.

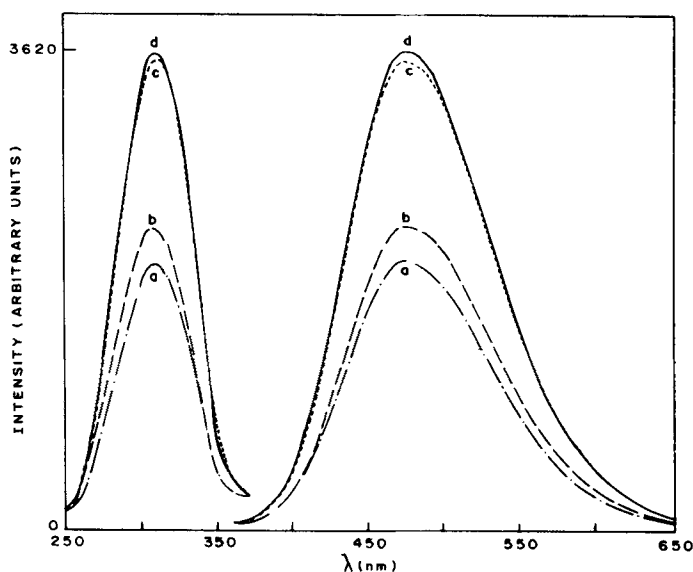


Figure 2. Excitation and emission spectra of Ti-doped NFC ZrO_2 : (a) 0.2, (b) 0.125, (c) 0.175 and (d) 0.15% Ti.

excitation and emission spectra for IC, MEL and NFC ZrO_2 samples received as such. Figure 2 shows the excitation and emission spectra for Ti-doped NFC ZrO_2 . The emission spectra are similar to that reported in the literature (Sarver 1966) for Ti-doped ZrO_2 .

3.2 Effect of Ti doping

Emission properties of NFC samples were studied as a function of Ti doping. Table 3 shows the intensity of maximum luminescence (I_{max}) at 473 nm when excited at 307 nm as a function of Ti content and environment of annealing. From the data in table 3 (column A), it can be seen that I_{max} increases initially with increase in Ti content, attains a maximum value at 0.15 wt% Ti (1500 ppm) in ZrO_2 (sample no. 3), and then decreases with increase in Ti doping. The I_{max} value for NFC ZrO_2 (sample no. 3) is slightly lower compared to MEL ZrO_2 containing ~ 1500 ppm Ti (sample no. 13). The lower value for NFC ZrO_2 may be attributed to presence of more Fe content, viz. 20 compared to < 10 ppm, in MEL sample.

3.3 Effect of heat treatment environment on emission intensity

From table 3, it appears that the environment used for ZrO_2 powders plays a significant role in determining luminescence properties of Ti-doped ZrO_2 . Comparison of the data given in table 3 columns A and B, and columns A and C brings out remarkable differences in the behaviour of ZrO_2 powders containing optimum/near-optimum concentrations of Ti (sample nos. 2 to 4) and samples with non-optimum concentration of Ti (sample nos. 1 and 5–10) when subjected to oxygen and argon annealing at

Table 3. Effect of Ti concentration and environment on emission intensity for gem-grade ZrO₂ (NFC) (A: air, B: oxygen, C: argon).

Ti (wt%)	Emission intensity (relative counts)			Remarks
	A	B	C	
0.1	495	1940	489	NFC
0.125	2301	2206	2779	NFC
0.150	3620	3330	2806	NFC
0.175	3554	3121	2749	NFC
0.200	670	2043	1986	NFC
0.300	550	1669	492	NFC
0.400	426	1585	482	NFC
0.500	362	1557	439	NFC
0.600	286	1001	397	NFC
1.000	234	310	273	NFC
0.015	125	715	275	NFC
0.20	1503	1331	1566	IC
0.150	4567	4443	4596	MEL

1000°C. With the oxygen annealing of the air-heated (A) sample nos. 2 to 4, a slight decrease in I_{\max} is observed. However, on argon annealing of these samples the decrease in I_{\max} is more pronounced compared to oxygen-annealed samples.

Oxygen annealing of the air-heated (A) sample nos. 1 and 5–10, containing non-optimum concentrations of Ti, produced a three to four fold increase in I_{\max} , whereas Ar annealing has hardly any significant effect on I_{\max} .

Behaviour of NFC and MEL samples both containing ~1500 ppm Ti (sample nos. 3 and 13) on oxygen annealing is comparable.

Comparison of NFC and IC samples both containing 2000 ppm Ti reveals that NFC sample (no. 5) has better luminescence properties than the IC sample no. 12, in spite of higher Fe content.

NFC and MEL ZrO₂ containing ~1500 ppm Ti on further annealing in oxygen at 1300°C showed further decrease in I_{\max} .

4. Conclusions

Luminescence properties of zirconia along with elemental analysis compared with standard give valuable information on role of impurities, Ti doping, environment used in heat treatment and temperature for annealing in the synthesis of gem-grade zirconia and help in the selection of raw material.

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