>>**Entry Name: Zirconium(*IV*) oxide (ZrO_2),** 11Cl
Synonym(s): Zirconium dioxide. Zirconia

CAS Registry Number: 1314-23-4
Related CAS Registry Numbers(s): 12164-98-6
Extra CAS Registry Numbers(s): 53801-45-9

ZrO_2

Molecular Formula: O_2Zr
Molecular Weight: 123.223
Accurate Mass: 121.894533
Percentage Composition: O 25.97%; Zr 74.03%

is not pressure sensitive at r.t. Phase changes from monoclinic << >> tetragonal << >> cubic (CaF_2 struct.) occur at 1100 and 2300° respectively. Sol-gel material has amorphous struct. below 300°; annealing at higher temps leads to nanophases cont. both tetragonal (main) and monoclinic forms, with similar crystallite sizes; further annealing results in irreversible transformation of tetragonal into monoclinic phase. Morphology of aerogels dependent on preparative conditions
Source/Synthesis: Synth. of ZrO_2 and 10% Cu-ZrO_2 by forming gels from $ZrO(NO_3)_2$ or $ZrO(NO_3)_2$ and $Cu(NO_3)_2$ and drying supercritically at 533K and 8.1 MPa. Redn. at 575K yields the catalyst: Cu is reduced preferentially. Commercial material may be synth. by hydrol. of any Zr^{IV} compd. Cryst. may be grown by flux methods. Mesoporous, high-surface-area zirconia synth. by controlled heating of surfactant/ZrO_2composite; latter obt. by reaction of $Zr(OCH_2CH_2CH_3)_4$ or $ZrOCl_2$ with e.g. alkyltrimethylammonium halides, dodecyl phosphate or sulfate, or hexadecyl sulfonate. Nanocrystalline zirconia can be prepared by the sol-gel technique, e.g. reaction of $Zr[O(CH_2)_3CH_3]$ with hydrol. catalyst such as HCl, H_2SO_4, $C_2H_4O_2$ and NH_4OH. Europium-doped crystalline powders can be produced by heating mixt. of co-precipitated hydrated Eu and Zr oxides
Use/Importance: Used in ceramics, enamels and electrical devices. Tends to crack on thermal cycling because of the phase change at 1100°. The cubic form is stabilised by adding MgO or CaO leading to cubic zirconia as a gemstone substit. for diamond. In fibrous form may be used as an insulator. A semiconductor sol, synth. by hydrol. of $ZrO(C_2O_4)$ in water at 90° for 48h , is a sensitiser for uv cleavage of water. Monoclinic form is used as additive to hydroxyapatite as a toughening agent to form a composite for prosthetic applications. Interesting new catalyst systems. Materials had surface areas >250m^2 g^{-1}. After redn. ZrO_2 hydrogenated CO to form 2-propanol with high selectivity. The Cu-ZrO_2 system is a better MeOH catalyst than Cu-ZnO. Can be used as thermal shield. Doped material finds applications in sensor devices (e.g. for O_2) and in fabrication of fuel cells
Physical Description: White or colourless solid
Melting Point: Mp *ca.* 2710°
Other Data: Ionic conductor when doped with divalent or trivalent cations. Low thermal conductivity at high temps. Porosity and surface area of aerogels dependent on preparative conditions. Luminescent material produced by doping with $Eu^{3(+)}$

Aldrich: 23069-3
Fluka: 96596
Sigma: Z2500

>>**Variant:** Mineral-form
Synonym(s): Baddeleyite (ZrO_2)

CAS Registry Number: 12036-23-6
Molecular Formula: O_2Zr
Molecular Weight: 123.223
Accurate Mass: 121.894533
Percentage Composition: O 25.97%; Zr 74.03%
Source/Synthesis: Widespread occurrence
Physical Description: May be almost any colour depending on impurities; dark submetallic cryst.

References:

Palache *et al.*, *Dana's System of Mineralogy*, 7th Ed., 1944, **1**, 608, *(baddeleyite)*
Ono, A.*, Mineral. J.*, 1972, **6**, 442, *(monoclinic and tetrag cryst)*
Ushio, M. *et al.*, *Nippon Kagaku Kaishi*, 1973, 2295, *(growth large crysts from flux)*
Anthony, A.M.*, Ind. Ceram. (Paris)*, 1975, **686**, 483, *(rev, struct, props)*
Kirk-Othmer Encycl. Chem. Technol., 3rd edn., Wiley, 1978, **20**, 65, *(use)*
Stubican, V.S.*, Ceramica (Florence)*, 1983, **36**, 46, *(rev, ceramics)*
Poletaev, I.F. *et al.*, *Tsvetn. Met. (Moscow)*, 1983, 67; *CA*, **99**, 197305b, *(manuf from zircon)*
Hann, R.E. *et al.*, *J. Am. Ceram. Soc.*, 1985, **68**, C285, *(cryst struct, monoclinic form)*
Suyama, R. *et al.*, *J. Am. Ceram. Soc.*, 1985, **68**, C314, *(orthorhombic cryst)*
Kudoh, Y. *et al.*, *Phys. Chem. Miner.*, 1986, **13**, 233, *(cryst struct at high pressure)*
Ganguly, K.M. *et al.*, *Chem. Comm.*, 1993, 682, *(synth, photocleavage)*
Sun, Y. *et al.*, *Chem. Comm.*, 1993, 1242, *(synth, use, catalysis)*
Nagarajan, V.S. *et al.*, *J. Mater. Chem.*, 1993, **3**, 43, *(monoclinic form, use)*
Knowles, J.A. *et al.*, *Chem. Comm.*, 1995, 2083-2086, *(mesoporous form, synth, powder struct, dta, tg, surface area)*
Pacheco, G. *et al.*, *J. Mater. Chem.*, 1998, **8**, 219-226, *(mesoporous form, synth, powder struct, sem, tem, mas P-31 nmr, surface area)*
Stocker, C. *et al.*, *J. Non-Cryst. Solids*, 1998, **223**, 165-178, *(aerogel, synth, surface area, powder struct, tem, sem, thermal anal)*
Gutzov, S. *et al.*, *J. Phys. Chem. Solids*, 1998, **59**, 69-74, *($Eu^{3(+)}$-doping, powder struct, luminescence spectra)*
Bokhimi, X. *et al.*, *J. Solid State Chem.*, 1998, **135**, 28-35, *(aerogel, synth, powder struct, ir, dta, tg)*