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Synthesis of Lithium-doped Zirconia Nanoceramics of Controlled Oxygen Vacancies

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ABSTRACT

Doping of lithium (Li^+) cations results in stabilised zirconia, especially in tetragonal (t) crystal structure, i.e., Li^+: t-ZrO_2. It is useful to vary oxygen vacancies in Li^+: ZrO_2 powders. The Li^+: t-ZrO_2 powder having 1-5 mol per cent Li^+, are obtained by using a novel chemical method of a polymer precursor, which consists of Li^+ and Zr^{4+} cations capping in polymer molecules of polyvinyl alcohol (PVA) and sucrose. The results are analysed in terms of XRD and microstructure of Li^+: t-ZrO_2 powders prepared under specific conditions of heating the precursor in air at elevated temperatures. The polymer precursor consists of fibrils of average 120 μm length and 0.5–1.0 μm dia. A refined Li^+: t-ZrO_2 powder (15-25 nm crystallite size) occurs after heating the precursor at 500–600 °C for 2 h in air.

Keywords: Stabilised zirconia, ceramics, nanoceramics, microstructure, synthesis, cationic doping

1. INTRODUCTION

Interest in nanocrystalline zirconia (ZrO_2) ceramics, of average diameter in the 2–100 nm range, has increased during recent years, because of their properties (e.g., sintering ability, mechanical toughness, superplastic behaviour) are significantly different from those in a coarse grained structure[1-4]. At atmospheric pressure, pure ZrO_2 exists in three well known polymorphs of P$2_{1/c}$ monoclinic (m), P$4_{2/nmc}$ tetragonal (t), and F $m3m$ cubic fluorite (c) crystal structures, where m-ZrO_2 is the equilibrium bulk structure at low temperatures. Efforts have been made to obtain the high temperature phase t-ZrO_2 or c-ZrO_2 in a thermodynamically stable state at low temperatures using doping of MgO, CaO, Y_2O_3, or other similar oxides[2-4]. Emphasis has been given for the synthesis of such phases either by undersized or oversized cationic doping using hydrothermal processes, and sol-gel processes[5-7].

In this study, synthesis of a nanoceramic t-ZrO_2 powder has been carried out using doping of undersized cations such as Li^+. Murata[8], *et al.* reported that Li^+–modified ZrO_2 offers specific catalytic activity in oxidative coupling of methane to give C_2- hydrocarbon[8]. A forced hydrolysis (by adding NH_4OH) of dispersed Li^+ and Zr^{4+} cations via polymer molecules of polyvinyl alcohol (PVA) and sucrose in water was used to obtain a polymer precursor. For Li^+ limited to 5.0 mol per cent, no Zr^{4+}–Li^+ phase separation encountered during the reaction. Otherwise, Li^+ hardly dissolves in zirconium hydroxides[9]. A reconstructive decomposition follows on heating the polymer gel (dried and pulverised into a powder) in air, forming a refined Li+: t-ZrO_2 powder at temperatures as low as 500–600 °C.

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The results are analysed in terms of XRD and microstructure of the $Li+$: t-ZrO_2 powders.

2. EXPERIMENTAL DETAILS

Separate solutions were obtained for $ZrOCl_2.8H_2O$ in distilled water and Li_2CO_3 in diluted HCl each of 1.0 M concentration. A transparent colourless solution appeared in homogeneous mixing in two components. A similar mixed solution was obtained in 3.0 g/dl PVA and 30.0 g/dl sucrose in distilled water. To form a polymer precursor, the PVA-sucrose solution was added dropwise to the aqueous solution in $ZrOCl_2.8H_2O$ and $LiCl$ (Li_2CO_3 dissolved in HCl) at room temperature. The obtained sample was transferred to a water-cooled bath (Julabo model HD-4) in part to hydrolyse the metal cations by reacting with cold NH_4OH (25 %) at 2–5 °C average temperature. A transparent gel occurred of hydrolysed metal cations as Li^+–doped $ZrO(OH)_2\cdot\alpha H_2O$. As much as 5.0 mol per cent $Li+$ (as per the final $Li+$: ZrO_2 product) could be incorporated in $ZrO(OH)_2\cdot\alpha H_2O$ in a mixed hydroxyl gel (amorphous). Requisite amounts of the reagents used in forming a typical polymer gel (3.0 mol % Li_2O) are given in Table 1. It was observed that, in the solution, the product $Li+:ZrO(OH)_2\cdot\alpha H_2O$ continues to react with the water by polycondensation and polymerisation processes. Average pH at this stage had been reduced to 3.5 as we observed and modelled in the case of a monolithic $ZrO(OH)_2\cdot\alpha H_2O$ gel[10]. Washing in cold water separated byproduct chlorides, resulting in a colorless transparent hydroxyl gel, which was then dried at 90-100 °C over a sand bath (Fig. 1).

The process of forming $Li^+:ZrO(OH)_2\cdot\alpha H_2O$ gel and derived Li^+: t-ZrO_2 powder is summarised in Fig. 1. The Li^+ stabilised t-ZrO_2 occurred of nanoparticles by reconstructive thermal decomposition of *gel* after heating in air at temperatures in the 500–600 °C range. Structures of precursor gels and of those transformed into Li^+: t-ZrO_2 were studied in terms of XRD using Philips P.W.1710 diffractometer with filtered 0.15418 nm CuKα radiation. Microstructures of the samples were studied by scanning electron micrographs using a JEOL model JSM-5800 SEM. Average Li^+: t-ZrO_2 crystallite

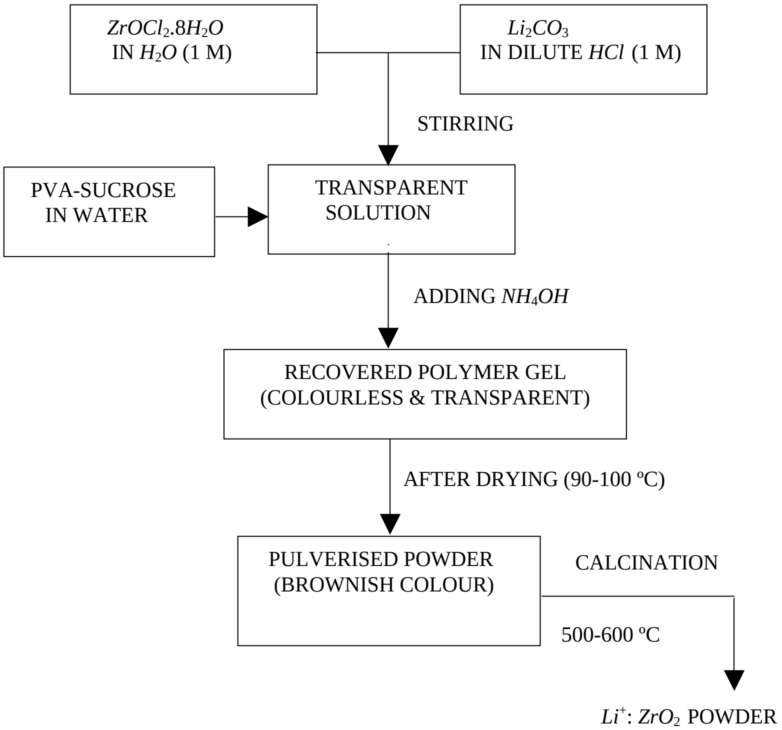

Figure 1. Schematic diagram for preparing a Li^+-modified Zr^{4+} polymer precursor and derived Li^+: ZrO_2 powder.

Table 1. Experimental conditions for forming a polymer precursor of Li^+ -modified Zr^{4+} hydroxyl gel with PVA-sucrose in cold water

Reagents	Solvent	Volume (ml)	Concentration
$ZrOCl_2.8H_2O$	Water	1470	1.0 M
Li_2CO_3	Dil HCl	45	1.0 M
PVA	Water	885	3.0 g/dl
Sucrose	Water	885	30.0 g/dl

A reaction batch of a 100 g sample in a typical $Li_xZr_{1-x}O_{2-1.5x}$ composition, with x = 0.02 or 3.0 mol per cent Li^+.

size (D) was calculated from fwhm-values (full width at half-maximum values) in the diffraction peaks using the Debye-Scherrer relation.

3. RESULTS AND DISCUSSION

3.1 Formation of Hydroxyl Gel and Derived Li^+: $t\text{-}ZrO_2$ Powder

Under favorable conditions of temperature and pH, dispersed Zr^{4+} and Li^+ cations in an aqueous solution undergo hydrolysis reaction with the H_2O molecules. The reaction, especially in the presence of NH_4OH (having a high 12 pH value induces a local chemical potential between the reacting species) in cold condition, can be expressed in this example as follows:

$$xLiCl + xH_2O \rightarrow xLi(OH) + xHCl$$

$$(1\text{-}x)ZrOCl_2 + 2(1\text{-}x)H_2O \rightarrow (1\text{-}x)ZrO(OH)_2 + 2(1\text{-}x)HCl$$

$$(1\text{-}x)ZrOCl_2 + xLiCl + (2\text{-}x)H_2O \rightarrow Li_xZr_{1\text{-}x}\mathrm{O}_{1\text{-}z}(OH)_{2\text{-}x} + (2\text{-}x)HCl \qquad (1)$$

At room temperature, a hydroxyl compound formed in this reaction simultaneously encounters a thermal-induced disintegration as follows:

$$Li_xZr_{1\text{-}x}\mathrm{O}_{1\text{-}x}(OH)_{2\text{-}x} \rightarrow Li_x\mathrm{Zr}_{1\text{-}x}\mathrm{O}_{2\text{-}1.5\,x} + (1\text{-}0.5x)\ H_2O \qquad (2)$$

At low temperature, an interbridging in $Li_xZr_{1\text{-}x}\mathrm{O}_{1\text{-}x}(OH)_{2\text{-}x}$ molecules succeeds in support of mobile H_2O molecules in solution, forming a polymer gel. It plays a crucial role in devising an amorphous gel, which can be expressed as $Li_xZr_{1\text{-}x}\mathrm{O}_{1\text{-}x}(OH)_{2\text{-}x}.\ \varphi H_2O$. A value of φ = 4–5 is estimated from thermogravimetric analysis of a dried sample at reduced pressure (1-5 mbar) at room temperature.

In the gelation process, Li^+ as $Li(OH)$ gets trapped in $ZrO(OH)_2 \cdot \alpha H_2O$, forming a $Li_xZr_{1\text{-}x}\mathrm{O}_{1\text{-}x}(OH)_{2\text{-}x}.\ \varphi H_2O$ glass gel. Notice $ZrO(OH)_2 \cdot \alpha\ H_2O$ is a glass gel former whereas $Li(OH)$, which is an ionic compound, serves as a glass modifier. Presence of the polymer molecules of PVA-sucrose during the hydrolysis templates $ZrO(OH)_2 \cdot \alpha\ H_2O$ in a polymer of extended network over their molecular surfaces. The original sol-gel method involves alkoxides and is expensive one[7]. The present method offers a simple process of hydrolysis type for processing a hydroxyl gel, especially involving the reactions in aqueous medium.

In this method, Li^+-modified $ZrO(OH)_2 \cdot \alpha\ H_2O$ molecules interbridge by means of polycondensation or polymerisation in shape of fibrils (as evidenced from the microstructure in Fig. 2). It is a Li^+: $[ZrO(OH)_2 \cdot \varphi H_2O]_n$ polymer template in support over PVA-sucrose of effectively planar surfaces. In water, sucrose was hydrolysed to fructose and glucose, which was ultimately oxidised to gluconic acid[11]. A metal-ion complex was formed in the reaction with Zr^{4+} and Li^+ cations. It frames a co-branched polymer (planar) with PVA molecules (of otherwise linear structure), offering a multifunctional role in templateing Zr^{4+} and Li^+ in a metal-ion complex over PVA-gluconic acid polymer molecules.

Another advantage of the organic polymer part is that it serves as a dispersoid and an internal fuel in producing Li^+: $t\text{-}ZrO_2$ by autocombusting Li^+:$[ZrO(OH)_2 \cdot \varphi H_2O]_n$ templates at moderate temperatures as low as 500-600 °C in air. Decomposition and *in-situ* combustion of the precursor evolve a plenty of heat of the combustion, which induces reconstructive Li^+: $t\text{-}ZrO_2$ nucleation and growth of limited particle sizes by reaction of small fragmented species of precursor over these temperatures. A high degree of gelation following the hydrolysis of the metal cations in reaction with NH_4OH appears to be an important factor in this example of deriving $Li+$: $t\text{-}ZrO_2$ of nanoparticles at such low temperatures. Virgin $ZrO(OH)_2 \cdot \alpha H_2O$ yields $m\text{-}ZrO_2$ or a mixture

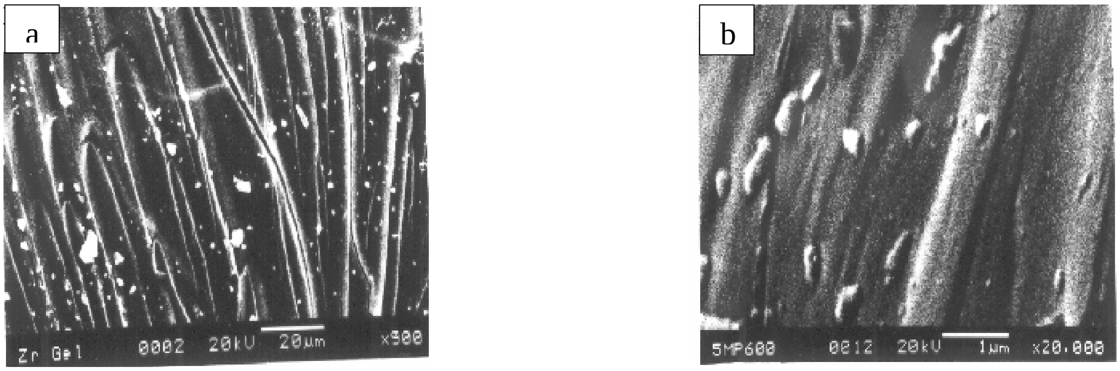

Figure 2. SEM of: (a) $Li_xZr_{1-x}O_{1-x}(OH)_{2-x}\cdot \varphi H_2O$ (x = 0.02) polymer precursor gel and (b) derived Li^+: t-ZrO_2 powder after heating the precursor (dried at room temperature) at 600 °C in air.

with t-ZrO_2[5-9,12,13]. Marote[9], *et al.* reported a t-/m-ZrO_2 mixture by heating $ZrOCl_2$. $8H_2O$ or $ZrCl_4$ in a molten $LiNO_3$ flux at 450 °C. As much Li^+ as 3.4 at per cent incorporates in ZrO_2 in this method. It is not a very viable way for producing Li^+: ZrO_2. Most of Li^+ involved in refluxing evaporates as a byproduct (toxic).

3.2 Microstructure and XRD

Figure 2(a) shows a typical SEM microstructure of polymer precursor gel $Li_xZr_{1-x}O_{1-x}(OH)_{2-x}$. φH_2O (x = 0.02), which has been dried at room temperature. It consists of a peculiar polymeric structure of fibrils or thin layers of average 0.5-1.0 µm dia. As long fibrils as 120 µm are present. These fibrils are developed in directional growth and by polycondensation of $Li_xZr_{1-x}O_{1-x}(OH)_{2-x}$. φH_2O molecules in an interconnected network structure (amorphous) over PVA-sucrose polymer molecules of effectively planar surfaces. This involves formation and *in situ* polycondensation processes of dispersed $Li_xZr_{1-x}O_{1-x}(OH)_{2-x}$. φH_2O in the solution.

On heating, a controlled reconstructive molecular decomposition occurs from the polymer gel of thin fibrils, resulting in a Li^+: t-ZrO_2 powder. A typical micrograph in Fig. 2(b) shows clusters of Li^+: t- ZrO_2 crystallites in derived shapes (100 - 500 nm dia) of precursor of thin fibrils. As can beseen by a close-up of the micrograph in Fig. 2(b), the sample has Li^+: t-ZrO_2 crystallites of rectangular bars (or prisms) of 15-25 nm average dia, which has been correlated to fwhm-values in the XRD peaks in the Debye-Scherer formula (D~20 nm) value. It demonstrates the sample consisting of mostly single crystallites. The final Li^+: t- ZrO_2 size and morphology vary sensitively depending on the Li^+ content and the final calcination temperature.

X-ray diffractogram in Li^+:ZrO_2 powder, after heating the polymer precursor at 500–600 °C in air, has a total of 19 peaks in the 20-100 ° range of the diffraction angle 2θ. A typical diffractogram for 3.0 mol per cent Li^+: t-ZrO_2 powder, heated at 600 °C for 2 h, is given in Fig. 3. As marked by the (*hkl*) values, all the major peaks are indexed in terms of the lattice reflections from the $P4_{2/nmc}$ tetragonal crystal structure as in the monolithic ZrO_2[12]. No diffraction peak is visible in independent Li_2O, confirming the fact that most of the Li^+ used in this reaction is consumed in forming Li^+–doped t-ZrO_2.

In Table 2, the observed values of the interplanar spacings d_{hkl} are fairly reproduced, within a standard deviation of ± 0.0010 nm, assuming average lattice parameters a = 0.3615 nm and c = 0.5201 nm, with volume V = 0.0680 nm^3 and density ρ = 6.01g/cm^3. In comparison to ρ = 6.10 g/cm^3 in monolithic t-ZrO_2[14], a smaller ρ-value observed in this example is according to smaller ionic size of Li^+ relative to the Zr^{4+} value. As can be analysed by intensities in the diffraction peaks, as described earlier[10-12], the sample has a small impurity ~ 5 per cent due to incipient growth of m-ZrO_2.

The diffractogram of the precursor gel powder consists of three halos, as shown in the inset of Fig. 2, at wave vectors 18.7 nm^{-1}, 29.3 nm^{-1} and

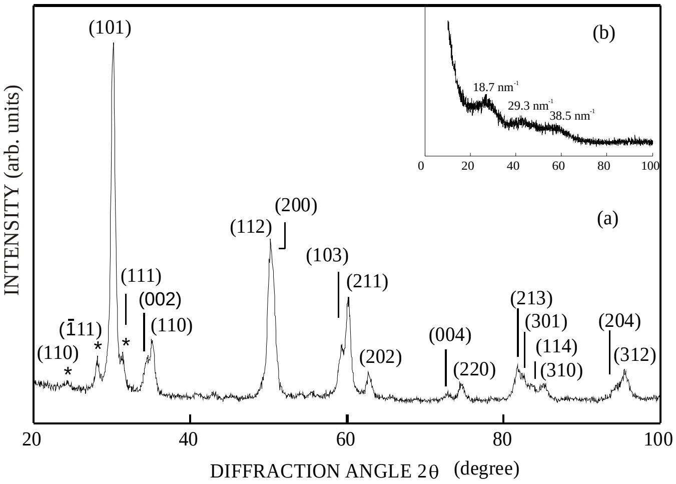

Figure 3. (a) X-ray diffractogram in Li^+: t-ZrO_2 nanopowder after 2 h of heating a precursor {of diffractogram in the inset (b)} at 600 °C in air.

38.3 nm^{-1} in three prominent pair distribution functions in the Zr^{4+} and O^{2-} ions in an amorphous structure, which plays a crucial role in deriving Li^+–doped t-ZrO_2 in this experiment. Otherwise, the precipitate often decomposes to hydrated zirconia $ZrO_2 \cdot \gamma H_2O$, which hardly crystallises into t-ZrO_2.

Table 2. Interplanar spacing (d_{hkl}) and relative peak intensities (I_p) in XRD peaks in 3.0 mol per cent Li^+: t-ZrO_2 powder

d_{hkl} (nm)					
Nanopowder	Bulk	I_p	h	k	l
0.3636*	0.3630	08	1	1	0
0.3160*	0.3156	18	1	1	$\bar{1}$
0.2956	0.2952	100	1	0	1
0.2843*	0.2842	16	1	1	1
0.2600	0.2593	14	0	0	2
0.2540	0.2537	19	1	1	0
0.1790	0.1800	44	1	1	2
0.1810	0.1803	35	2	0	0
0.1560	0.1557	16	1	0	3
0.1540	0.1534	28	2	1	1
0.1481	0.1476	11	2	0	2
0.1305	0.1296	05	0	0	4
0.1272	0.1268	07	2	2	0
0.1178	0.1177	10	2	1	3
0.1168	0.1167	09	3	0	1
0.1547	0.1545	06	1	1	4
0.1372	0.1369	07	3	1	0
0.1053	0.1051	06	2	0	4
0.1045	0.1041	10	3	1	2

The bulk values, with a = 0.3592 nm and c = 0.5168 nm, are reported from literature[14]. *m-ZrO_2.

4. CONCLUSION

A novel chemical method, using hydrolysis of dispersed Zr^{4+} and Li^+ cations via polymer molecules of PVA and sucrose in cold water, is developed and explored to obtain Li^+-doped t-ZrO_2. Adding NH_4OH hydrolyses Zr^{4+} and Li^+ as a hydroxyl compound $Li_xZr_{1-x}O_{1-x}(OH)_{2-x} \cdot \varphi H_2O$, which occurs in shapes of thin fibrils in support over the PVA-sucrose polymer molecules. A Li^+: t-ZrO_2 powder occurs on heating the precursor at temperature as low as 500 °C in air. The PVA-sucrose polymer molecules offer three important functions: (i) a solid dispersoid, (ii) a templateing agent, and (iii) a solid fuel. The sample, having 3-5 mol per cent Li^+, consists of as small crystallites as 10-25 nm, in shape of the tetraoids, unless heating above 600 °C. In comparison to traditional sol-gel process, this is a rather simple method for processing of shape-controlled ceramics such as ZrO_2 and its derivatives.

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REFERENCES

1. Yashimura, M. Phase stability of zirconia. *Am. Ceram. Soc. Bull.*, 1988, **67**, 1950-955.
2. Chen, I. & Xue, L.A. Development of superplastic structural ceramics. *J. Am. Ceram. Soc.*, 1990, **73**(9), 2585-609.
3. Minh, N.Q. Ceramic fuel cells. *J. Am. Ceram. Soc.*, 1993, **76**(3), 563-88.
4. Igawa, N. & Ishii, Y. Crystal structure of metastable tetragonal zirconia at 1472 K. *J. Am. Ceram. Soc.*, 2001, **84**(5) 1169-171.
5. Murase, Y. & Kato, E. Role of water vapour in crystalline growth and tetragonal-monoclinic

transformation of zirconia. *J. Am. Ceram. Soc.*, 1983, **66**(3), 196-200.

6. Ashoka, H. Sol-gel synthesis of crystalline ZrO_2 with partial replacement of zirconium with Al, Nb, Si, and Ta. *Materials Letters*, 1994, **19**, 213-16.

7. Coracoche, M.C.; Ravas, P.C. & Cervera, M.M. Zirconium oxide structure prepared by sol-gel route. *J. Am. Ceram. Soc.*, 2000, **83**(2), 377-84.

8. Murata, K.; Hayakawa, T. & Suzuki, K. Lithium-doped sulphated zirconia catalysts for oxidative coupling of methane to give ethylene and ethane. *Catalysis Today*, 1998, **45**, 41-45.

9. Marote, P.; Durand, B. & Deloume, J.P. Reactions of metal salts and alkali metal nitrates. Role of the metal precursors and alkali metal ions in the resulting phase of zirconia. *J. Solid State Chem.*, 2002, **163**, 202-09.

10. Mondal, A. & Ram, S. Monolithic $t\text{-}ZrO_2$ nanopowder through a $ZrO(OH)_{2.x}\,H_2O$ polymer precursor. *J. Am. Ceram. Soc.*, 2004, **87**, 2187-94.

11. Ram, S. Synthesis and structure and optical properties of metastable ZrO_2 nanoparticles with intergranular Cr^{3+}/Cr^{4+} doping and grain surface modification. *J. Mater. Sci.*, 2003, **38**, 643-55.

12. Mondal, A. & Ram, S. Controlled phase transformation in Al^{3+}-stabilised ZrO_2 nanoparticles via forced hydrolysis of metal cations. *Materials Letters*, 2003, **57**, 1696-706.

13. Hong, J.S.; De la Torre, S.D.; Miyamoto, K.; Miyamoto, H. & Gao, L. Crystallization of Al_2O_3/ZrO_2 solid solution powders prepared by co-precipitation. *Materials Letters*, 1998, **37**, 6.

14. McClume, W.F. Powder diffraction files JCPDS (Joint Committee on Powder Diffraction Standards). *In* International Centre for Diffraction Data, Swarthmore, PA. (a) 24-1164 ($t\text{-}ZrO_2$) and (b) 13-307 ($t\text{-}ZrO_2$).

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