Role of some rare earth (RE) ions (RE = La, Pr, Nd, Sm, Gd and Dy) in crystal and mechanical behaviours of sol–gel derived ZrO_2–2 mol% RE_2O_3 spun fibres calcined at 1300°C

M K NASKAR*, M CHATTERJEE and D GANGULI[†]

Sol–Gel Division, Central Glass and Ceramic Research Institute, Kolkata 700 032, India
Present address: Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata 700 032, India

Abstract. Crystal behaviours such as crystallization temperature (amorphous to tetragonal (*t*) zirconia), tendency of phase transformation (tetragonal to monoclinic (*m*) zirconia) and lattice strain were studied with mechanical property e.g. tensile strength of sol–gel derived ZrO_2–2 mol% RE_2O_3 (RE = La, Pr, Nd, Sm, Gd and Dy) spun fibres. Rare earth cations of varying sizes played a significant role in changing the above mentioned properties of ZrO_2–2 mol% RE_2O_3 fibres. It was found that with decreasing the ionic size difference between the zirconium and RE ions, crystallization temperature (amorphous $\rightarrow$ *t*-ZrO_2) decreased, the probability of phase transformation (*t* $\rightarrow$ *m*) decreased, lattice strain which is related to lattice distortion decreased and tensile strength increased.

Keywords. Rare earth; ionic size; crystallization temperature; phase transformation; lattice strain; tensile strength.

1. Introduction

Zirconia fibres have gained importance in recent times for application in high temperature insulation and lately, ceramic–ceramic composites (Hayase *et al* 1988; Hattori and Kurushima 1993). Rare earth ions have been used in the preparation of partially and fully stabilized (PSZ and FSZ) zirconia ceramics (Pyda *et al* 1992; Log *et al* 1993; Naskar and Ganguli 1996). For the stabilization of zirconia, study of its crystal behaviour is becoming important. Ionic size of the dopant cations can influence (i) the particular bonding characteristics of zirconium atom, (ii) the crystallographic nature of the site(s) occupied by zirconium and the dopant and (iii) the interactions among the defects developed with the compositions and temperature (Ho 1982). All the above properties are directly and/or indirectly related to the crystal behaviour of zirconia system. Ionic size of RE ions (Shannon 1976) with respect to that of zirconium with similar oxygen coordination also proved to be a main controlling factor (Naskar and Ganguli 1996) for the crystal behaviour of zirconia fibres.

Measurement of tensile strength of ceramic fibres is essential for assessing the mechanical properties of ceramic–matrix composites (CMC) when such fibres are used as reinforcing media in the composites (Patankar 1991; Chawla 1993). There are two main variables, viz. processing parameters and mechanical/measurement para-

meters, which could affect the tensile strength of a particular fibre. Processing parameters include method of preparation, heating schedule etc of the fibres; mechanical/measurement parameters include gauge length, loading velocity etc of the fibres during their measurement. Mechanical properties of zirconia are influenced by the addition of dopant cations in the ZrO_2 host (Chaim and Brandon 1984) and the point defects generated in presence of the dopant affect the lattice structure of the host (Ho 1982). RE cations of varying ionic sizes affected the tensile strength of zirconia fibres (Naskar and Ganguli 1996).

As there exists a common controlling factor i.e. ionic size of different RE cations, there might have been an interrelationship between crystal and mechanical (tensile strength) behaviours in zirconia fibres. Keeping this view in mind, in this paper, crystal behaviour such as crystallization temperature (amorphous to tetragonal (*t*) ZrO_2 transformation), tendency of phase transformation (tetragonal (*t*) to monoclinic (*m*) ZrO_2) and lattice strain which is related to the lattice distortion effect in the host-dopant system are discussed in relation to their effects on the tensile strength of the fibres.

2. Experimental

2.1 *Preparation of fibres*

Zirconia fibres doped with 2 equivalent mol% of RE_2O_3 (RE = La, Pr, Nd, Sm, Gd and Dy) were prepared by

---

*Author for correspondence

spinning of acetate derived sols followed by calcination of the gel fibres thus obtained at 1300°C with 1 h dwell time (Naskar and Ganguli 1996).

2.2 *Characterization of fibres*

For obtaining the crystallization temperature, the gel fibres were subjected to differential thermal analysis (DTA) on a Netzsch differential thermal analyser (model DTA 404) with a heating rate of 10°C/min in air atmosphere from 30° to 1000°C. The oxide fibres (after calcination at 1300°C/1 h dwell) were characterized by X-ray diffractometry (XRD) using a Philips PW-1730 X-ray unit and Ni-filtered CuKa radiation.

To explain X-ray broadening of the particle, two types of mechanisms are involved (Lipson and Stokes 1943; Smith and Stickley 1943; Hall 1949; Klug and Alexander 1954). One is caused by the small particle size in which the line breadth (b_p) is proportional to l sec q

$$b_p = l/D \cos q, \tag{1}$$

where, l is the wavelength of the radiation (CuK$_a$), q the diffraction angle and D the crystallite size.

The other mechanism is caused by the lattice distortion broadening or stress broadening in which the breadth (b_s) is related with tan q and is independent of l

$$b_s = h \tan q, \tag{2}$$

where, h is the lattice strain.

If both types of broadening are present, the resultant line breadth (b') should be additive

$$b' = b_p + b_s. \tag{3}$$

In this case it can be written as (Lipson and Stokes 1943)

$$b' \cos q/l = 1/D + h \sin q/l. \tag{4}$$

Crystallite size and lattice strain can be determined from (1) and (4), respectively.

The tensile strength of the fibres was measured on an improvised apparatus as used by Kamiya *et al* (1991). Gauge length and loading rate for the measurement were kept at 4 mm and 0·05 g/s, respectively. The fibres with the diameter ranging from 2·5 to 7·5 μm were selected for the measurement of tensile strength. Tensile strength was calculated from the relationship

$$\text{Tensile strength} = \text{Fracture load/fibre cross sectional area.} \tag{5}$$

The effect of random distribution of a single defect on the strength of a solid material was first described by

Weibull (1951). In this paper an attempt has been made to analyse the Weibull distribution among the synthesized fibres.

Mean tensile strength (s), and its standard deviation (S) and coefficient of variation (CV) were calculated from a Weibull plot (Weibull 1951). For Weibull distribution the following relation is applicable (Chawla 1993)

$$\ln[\ln\{(N+1)/(N+1-i)\}] = b \ln s_i + \ln a. \tag{6}$$

In this analysis the tensile strength values were arranged in an increasing order such that the Nth value corresponds to the highest measured strength. In the above equation, b is the Weibull modulus, a the scale parameter and s_i the tensile strength of ith sample.

By plotting $\ln[\ln\{(N+1)/(N+1-i)\}]$ against $\ln s_i$, a straight line is obtained if the tensile strength data follow the Weibull distribution. b and a can be determined from the slope of the line and the intercept the line makes on the X axis, respectively. Knowing a and b, mean tensile strength (s) can be calculated from the relation

$$s = a^{-1/b} \Gamma(1 + 1/b). \tag{7}$$

The standard deviation (S) follows the relation

$$S = a^{-1/b} \{\Gamma(1 + 2/b) - [\Gamma(1 + 1/b)]^2\}^{1/2}. \tag{8}$$

The coefficient of variation (CV) is determined in terms of Weibull mean and standard deviation as

$$\text{CV} = 100 \, (S/s). \tag{9}$$

3. Results and discussion

From the DTA results, crystallization temperatures (amorphous to t-ZrO$_2$ transformation) of RE-doped ZrO$_2$ fibres were obtained from the exothermic peaks above 450°C (Naskar and Ganguli 1998). Table 1 shows that first crystallization temperature of 98ZrO$_2$–2RE$_2$O$_3$ system decreased with decrease in ionic size (Shannon 1976)

Table 1. Change of crystallization temperature of 98ZrO$_2$–2RE$_2$O$_3$ fibres with ionic size (Shannon 1976) difference between RE and Zr ions (Naskar and Ganguli 1998).

Ions (RE–Zr)	Ionic size difference (Å)	Crystallization temperature (°C)
La–Zr	0·320	510
Pr–Zr	0·303	490
Nd–Zr	0·269	485
Sm–Zr	0·239	475
Gd–Zr	0·213	470
Dy–Zr	0·187	465

Note: Ionic radius of Zr^{4+} for 8-fold coordination is 0·084 Å.

difference between Zr and RE ions. Crystalline phase, crystallite size and lattice strain (**h**) of the fibres of composition $98ZrO_2-2RE_2O_3$ developed after heat-treatment in air at 1300°C/1 h are shown in table 2. For large-sized dopant cations La, Pr and Nd mentioned as group A cations, monoclinic (*m*) phase of zirconia appeared; it transformed to tetragonal (*t*) phase with decrease in size of the dopant cations Sm, Gd and Dy mentioned as group B cations (Naskar and Ganguli 1996, 1998). It is apparent from table 2 that crystallite size and lattice strain of $98ZrO_2-2RE_2O_3$ system were in increasing and decreasing

trend, respectively with decrease in the size of the dopant cations.

Koehler and Glushkova (1968) suggested that crystallization temperature was lowered as the size of the RE ion was closer to that of Zr ion. The metastability of *t*-ZrO_2 in RE-doped fibres could be explained on the basis of the lattice distortion (Shi *et al* 1991; Li *et al* 1993) effect in the $ZrO_2-RE_2O_3$ system; because the ionic size difference between the Zr ion and group A cations La, Pr and Nd is higher than that between the Zr ion and group B cations Sm, Gd and Dy, the lattice distortion in the former case is higher than that in the latter (Shi *et al* 1991; Li *et al* 1994). Li *et al* (1993) suggested that $t \to m$ phase transformation required the distortion of both the nearest neighbour Zr–O shell and the next nearest neighbour Zr–Zr shell. Crystallization temperature, amorphous $\to t$-ZrO_2 increased with increase in tendency of phase transformation, t- $\to m$-ZrO_2 (tables 1 and 2). Hence it can be pointed out that crystallization temperature was also related to the lattice distortion in ZrO_2–RE_2O_3 system, i.e. higher the crystallization temperature, higher will be the lattice distortion.

Weibull plots (figures 1–3) were obtained with twenty-five test fibres for each composition of $98ZrO_2-2Sm_2O_3$, $98ZrO_2-2Gd_2O_3$ and $98ZrO_2-2Dy_2O_3$ of group B cations.

Table 2. Phase identification, crystallite size and lattice strain of $ZrO_2-2RE_2O_3$ fibres calcined at 1300°C/1 h by XRD.

Composition (mol%)	Crystalline phase	Crystallite size (nm)	Lattice strain
$98ZrO_2-2La_2O_3$	*m*	33·65	0·95
$98ZrO_2-2Pr_2O_3$	*m*	28·41	1·12
$98ZrO_2-2Nd_2O_3$	*m + t*	28·67	1·04
$98ZrO_2-2Sm_2O_3$	*t*	37·97	0·78
$98ZrO_2-2Gd_2O_3$	*t*	41·51	0·71
$98ZrO_2-2Dy_2O_3$	*t*	38·89	0·76

Note: *t* = tetragonal, *m* = monoclinic.
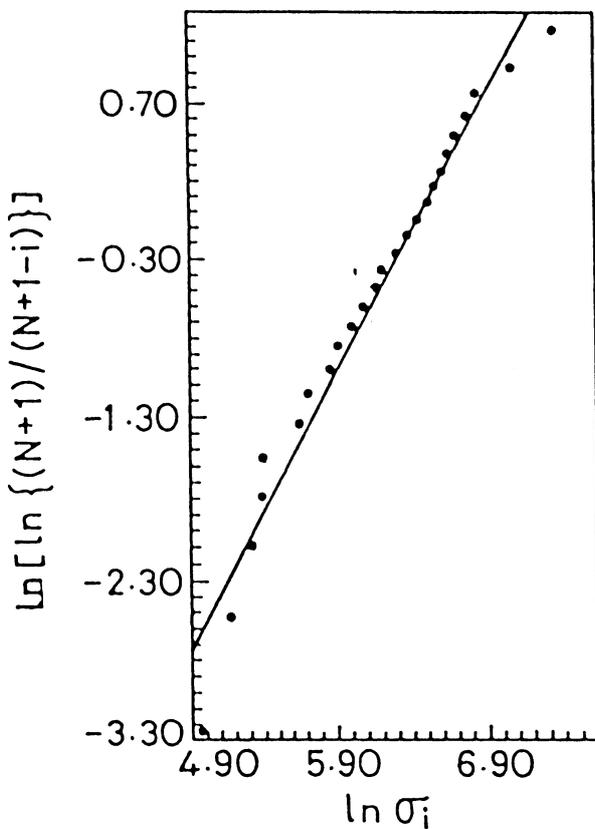
Figure 1. Weibull plot for $98ZrO_2-2Sm_2O_3$ fibres calcined at 1300°C/1 h.
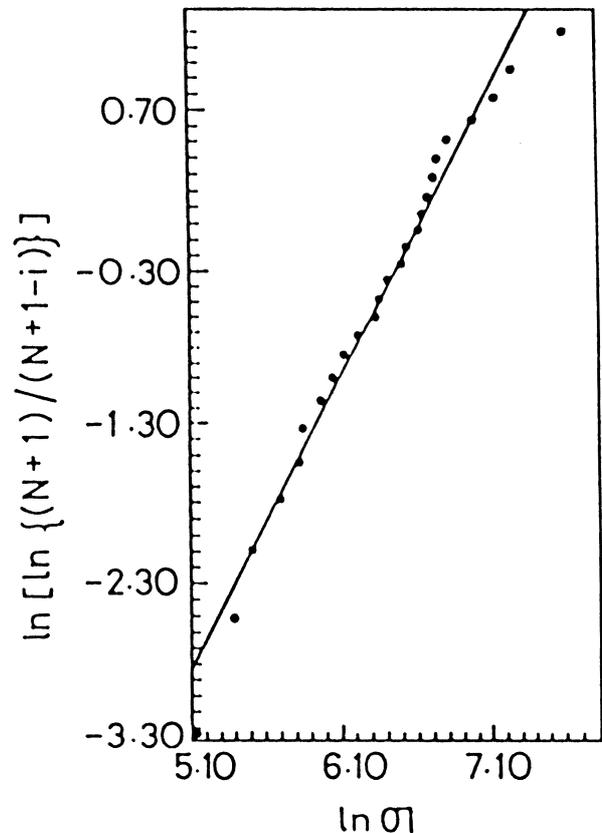
Figure 2. Weibull plot for $98ZrO_2-2Gd_2O_3$ fibres calcined at 1300°C/1 h.

It is to be noted that for the still larger group A cations La, Pr and Nd (Naskar and Ganguli 1996), the fragility of the fibres prevented the measurement of their tensile strength. The fragility of group A fibres is a consequence of the fibres having largely transformed to m-phase (table 2). From the Weibull plots of group B cations, the mean tensile strength (s), scale parameter (a), Weibull modulus (b), standard deviation (S) and coefficient of variation (CV) were calculated (table 3). Of these values, b, the Weibull modulus, is the most important factor for tensile strength distribution (Bergerman 1985; Patankar 1991; Chawla 1993). It signifies the width of the tensile strength distribution, for the high b value, scatter in the
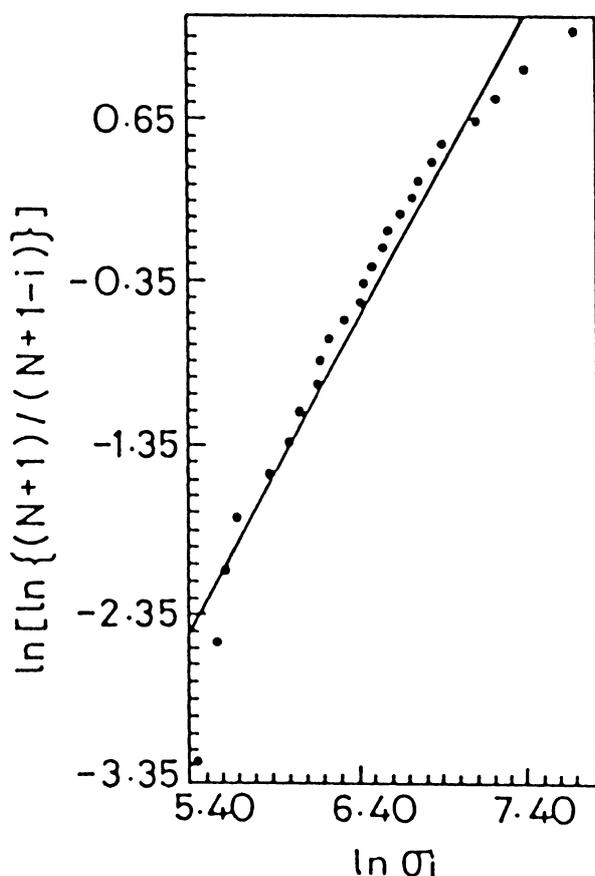
tensile strength data is less, i.e. the tensile strength distribution is narrow. From Weibull plots (figures 1–3), it was found that the Weibull mean strength (s) increased with decreasing size of the dopant: 574·30, 688·58 and 734·69 MPa for Sm^{3+} (1·079 Å), Gd^{3+} (1·053 Å) and Dy^{3+} (1·027 Å), respectively (table 3). It is also clear from table 3 that the values of b decreased with increasing ionic radius of RE ions ($Sm^{3+} > Gd^{3+} > Dy^{3+}$). The increase in mean strength (s) and Weibull modulus (b) with decrease in dopant size is related to increasing ease of the cations to occupy Zr^{4+} sites in t-ZrO_2 (Naskar and Ganguli 1996) and the decreasing structural distortion of zirconia solid solution, however, the former is more effective than the latter in increasing the mean strength (s) and Weibull modulus (b) of the fibres.

In case of the group B cations Sm, Gd and Dy, the maximum Weibull mean strength decreased with increasing size of the dopant cations: 734·69, 688·58 and 574·30 MPa, respectively, for Dy, Gd and Sm. It is apparent from table 2 that lattice strain of $98ZrO_2$–$2RE_2O_3$ system were in decreasing trend with decrease in the size of the dopant cations. Lattice distortion which is related to lattice strain (2) might have also same effect with decrease in the size of the dopant cations. For relatively larger group A cations La, Pr and Nd, the measurement of tensile strength was difficult due to not only the presence of monoclinic (m) phase of ZrO_2 but also having large lattice strain in the system compared to the other group B cations Sm, Gd and Dy (table 2). However, it is to be noted that in increasing the mean strength of the fibres, the metastability of t-ZrO_2 is becoming a very important factor.

From the above investigation a schematic model (figure 4) relating to ionic size difference between zirconium and RE ions, crystallization temperature, tendency of phase transformation ($t \rightarrow m$), lattice strain and tensile strength can be established for RE-doped ZrO_2 fibres. Figure 4 indicates that ionic size difference between the zirconium and RE ions governed the crystallization temperature (amorphous $\rightarrow$ t-ZrO_2), tendency of phase transformation ($t \rightarrow m$), lattice strain which is related to lattice distortion and tensile strength of RE-ion doped ZrO_2 fibres. In the above model (figure 4), the arrows in the same direction ($\leftarrow\leftarrow$) between two parameters indicate that if one increased the other also increased and

Figure 3. Weibull plot for $98ZrO_2$–$2Dy_2O_3$ fibres calcined at 1300°C/1 h.

Table 3. Weibull parameters, mean tensile strength, standard deviation and coefficient of variation of RE ions (Sm^{3+}, Gd^{3+} and Dy^{3+}) doped zirconia fibres calcined at 1300°C/1 h.

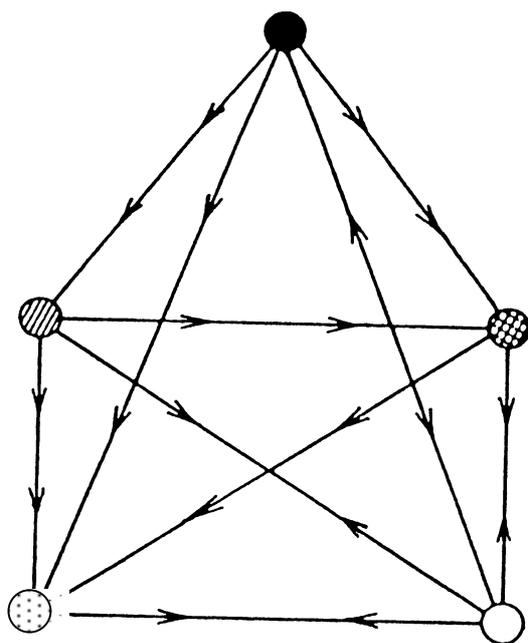| Composition (mol%)	a (MPa^{-b}) × 10^{-6}	b	Mean strength (MPa)	Std. deviation	Coeff. of variation (%)
$98ZrO_2$–$2Sm_2O_3$	10·94	1·76	574·30	268·84	46·81
$98ZrO_2$–$2Gd_2O_3$	4·78	1·84	688·58	301·46	43·78
$98ZrO_2$–$2Dy_2O_3$	3·37	1·87	734·69	407·08	55·41

Figure 4. Schematic model relating to ionic size difference between zirconium and RE ions with the crystal and mechanical (tensile strength) behaviours of RE-doped ZrO_2 fibres. (●, ionic size difference between Zr and RE ions; ⊘, crystallization temperature (amorphous → t-ZrO_2); ⊗, probability of phase transformation ($t \to m$ ZrO_2); ⊙, lattice strain; and ○, tensile strength).

vice versa; on the other hand the arrows in the opposite direction (–↔–) between two parameters indicate that if one increased the other decreased and *vice versa*.

4. Conclusions

From the above investigation it can be concluded that the ionic size difference between the zirconium and RE ions is the main controlling factor to affect/influence the first crystallization temperature (amorphous → t-ZrO_2), the phase transformation ($t \to m$), lattice distortion and tensile strength of the RE-doped ZrO_2 fibres. With decreasing the ionic size difference between the zirconium and RE ions (i) crystallization temperature (amorphous → t-ZrO_2) decreases and *vice versa*, (ii) the probability of phase transformation ($t \to m$) decreases and *vice*

versa, (iii) lattice strain which is related to lattice distortion decreases and *vice versa* and (iv) tensile strength increases and *vice versa*.

References

Bergerman B 1985 *J. Mater. Sci. Lett.* **4** 1143
Chaim R and Brandon D G 1984 in *Adv. in ceramics, Science and technology of zirconia II* (eds) N Claussen, M Ruhle and A H Heuer (Westerville, USA: The Am. Ceram. Soc. Inc.) Vol. **12**, p. 86
Chawla K K 1993 in *Ceramic matrix composite* (London: Chapman & Hall)
Hall W H 1949 *Proc. Phys. Soc. London* **62** 741
Hattori K and Kurushima T 1993 *Ceram. Trans.* **31** 147
Hayase M, Asami H, Asakura H and Saeki T 1988 *Shinagawa Tech. Rep.* **31** 129
Ho S M 1982 *Mater. Sci. Eng.* **54** 23
Kamiya K, Takahashi K, Maeda T, Nasu H and Yoko T 1991 *J. Eur. Ceram. Soc.* **7** 295
Klug H P and Alexander L E 1954 in *X-ray diffraction procedures for polycrystalline and amorphous materials* (New York: Wiley) p. 529
Koehler E K and Glushkova V B 1968 in *Science of ceramics* (Manchester, Great Britain: The Br. Ceram. Soc.) p. 233
Li P, Chen I-W and Penner-Hahn J E 1993 *Phys. Rev.* **B48** 10063,10082
Li P, Chen I-W and Penner-Hahn J E 1994 *J. Am. Ceram. Soc.* **77** 118
Lipson H and Stokes A R 1943 *Nature* **152** 20
Log T, Cutler R A, Jue J F and Virkar A V 1993 *J. Mater. Sci.* **28** 4503
Naskar M K and Ganguli D 1996 *J. Mater. Sci.* **31** 6263
Naskar M K and Ganguli D 1998 *J. Mater. Sci. Lett.* **17** 1971
Patankar S N 1991 *J. Mater. Sci. Lett.* **10** 1176
Pyda W, Haberko K and Zurek Z 1992 *J. Eur. Ceram. Soc.* **10** 453
Shannon R D 1976 *Acta Crystallogr.* **A32** 751
Shi J L, Lin Z-X and Yen T S 1991 *J. Eur. Ceram. Soc.* **8** 117
Smith C S and Stickley E E 1943 *Phys. Rev.* **64** 191
Weibull W 1951 *J. Appl. Mech.* **18** 293