Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Pergamon

Materials Research Bulletin 38 (2003) 1713–1724

Materials Research Bulletin

www.elsevier.com/locate/matresbu

Rietveld refinement study of nanocrystalline copper doped zirconia

Mahesh Bhagwat[a], A.V. Ramaswamy[a], A.K. Tyagi[b], Veda Ramaswamy[a,*]

[a]Catalysis Division, National Chemical Laboratory, Pune 411008, India
[b]Solid State Chemistry Section, Applied Chemistry Division, Bhabha Atomic Research Center, Mumbai 400085, India

Received 2 January 2003; received in revised form 7 July 2003; accepted 18 July 2003

Abstract

Structural studies of Cu-doped zirconia samples with varying Cu content have been carried out. Copper–zirconia samples containing 2–20 mol% Cu were prepared by the co-precipitation technique using tetramethylammonium hydroxide as the precipitating agent and calcined at 773 K in air. The powder XRD data following Rietveld refinement revealed stabilization of zirconia in both tetragonal and cubic phases for all the samples with some monoclinic impurity phase. A decrease in the unit cell parameters of the cubic and tetragonal phase indicates incorporation of copper in the zirconia lattice of both the phases. An increase in the copper concentration (up to 20 mol%) stabilizes zirconia into the cubic phase at the expense of the tetragonal phase, with a decrease in the crystallite size (6–8 nm). Rietveld refinement of the high temperature XRD data reveals that both cubic and tetragonal phases exist up to 723 K with the cubic phase dominating (80% at 723 K). At temperature higher than 723 K, cubic phase gets transformed into the tetragonal phase, which further transforms into the monoclinic phase at 1173 K. At 1173 K, copper comes out of the cubic zirconia lattice forming a separate copper oxide phase and only the tetragonal and monoclinic polymorphs of zirconia exist.

Keywords: A. Nanostructure; B. Chemical synthesis; C. X-ray diffraction; D. Crystal structure; D. Phase transitions

1. Introduction

The discrepancies in the research reports of zirconia and the inconsistencies in the zirconia literature are mainly with reference to the structural properties of zirconia, which alter as a function of temperature or doping of other metal atoms in the lattice [1]. Among the three well-defined polymorphs, the monoclinic phase is stable up to 1447 K. It then transforms into the tetragonal phase,

---

[*] Corresponding author. Tel.: +91-20-393300; fax: +91-20-393761.
E-mail address: veda@cata.ncl.res.in (V. Ramaswamy).

0025-5408/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0025-5408(03)00201-0

which further goes into the cubic phase at 2643 K. The cubic phase is stable up to the melting point (2953 K) of zirconia. The nature of the phase governs the physical properties of zirconia. The properties of zirconia, namely, high hardness, low wear resistance, low coefficient of friction, high elastic modulus, chemical inertness, low thermal conductivity, and high melting temperature make the material interesting for applications as advanced ceramics such as refractories, piezoelectric devices, ceramic condensers, and oxygen sensors [2]. High thermal stability, high BET surface area and amphoteric nature make zirconia a good catalyst support [3]. As a catalyst, while sulfated zirconia is used as a super-acid [4], zirconia doped with other metal oxides has been explored for redox reactions. Earlier ZrO_2 doped with alkaline and rare earth metal oxides like CaO, MgO, Y_2O_3, La_2O_3, and Ce_2O_3 [5–9] have been studied. Later, the transition metal oxides, like CuO, Cr_2O_3, Fe_2O_3, MnO_2, and NiO were used with a view to exploit the redox properties of these multivalent metals that could be well dispersed in the zirconia lattice [10–14]. The main aim of using these metal oxides as dopents is to obtain zirconia in the cubic phase (at low temperatures) with a high surface area. Formation of the low temperature stable or meta-stable cubic or tetragonal phase and the corresponding phase transformations with the change in temperature has been explained by various theories [15–19]. The metal ions used as dopents are generally of smaller size and lower valence (than Zr^{4+} ions) that may result in a decrease in the unit cell volume and generation of positive holes with lattice defects (oxygen vacancies). It is proposed that these defects in the zirconia lattice play a major role in stabilizing the system in a cubic phase. While several studies reported the stabilization of zirconia in the cubic phase [20–23], some reports point to the formation of a pseudo-tetragonal phase [24,25] on metal doping. Reports are also available where low temperature tetragonal phase is formed even without adding any dopent [26]. These stabilized or partially stabilized zirconia phases have been exploited for a number of catalytic reactions, as oxygen pumps and as gas sensors where these properties of zirconia are structure dependent.

In the present work, we have prepared copper stabilized zirconia samples with different concentrations of copper by co-precipitation technique to study the effect of Cu doping on phase stabilization. The samples were characterized by HTXRD from room temperature (303 K) to 1173 K to find the changes in the phase composition as a function of temperature. Since it becomes difficult to distinguish the three closely related phases of zirconia, Rietveld refinement technique [27,28] has been used to overcome the problem arising due to overlapping of reflections of the three polymorphs. The concentration of the three phases was determined by the Rietveld refinement technique for samples with different concentrations of copper and at different temperatures.

2. Experimental

2.1. Synthesis of copper–zirconia solid solutions

The copper–zirconia samples were prepared by co-precipitation technique. Zirconium oxynitrate and copper nitrate were used as the starting materials. Aqueous solutions of both the salts were mixed in the required ratio and stirred continuously for 1 h. Copper and zirconium were co-precipitated as hydroxides by adding tetramethylammonium hydroxide drop-wise to the above mixture till the pH was adjusted to 9. The hydroxide precipitate was filtered, washed with de-ionized water and then calcined in a muffle furnace in air at 773 K for 9 h. Zirconia samples with 2, 5, 10, and 20 mol% Cu were prepared by this technique and labeled as $CuZr_2$, $CuZr_5$, $CuZr_{10}$, and $CuZr_{20}$.

2.2. Powder XRD studies

The polycrystalline zirconia samples were analyzed on a Philips Powder X-ray diffractometer, Model PW 1729, using monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å). High temperature diffraction studies were carried out using a Philips X'pert Pro XRD unit equipped with Anton Paar HTK attachment. A small amount of sample was mounted on a Pt stage-cum-heating element. A Pt/Pt–13%Rh thermocouple spot-welded to the bottom of the stage was used for measuring the temperature. The XRD patterns were recorded in the range 20–80° 2θ with a step of 0.02° and at a scan rate of 1 min^{-1} from room temperature (303 K) to 1173 K, at a regular interval of 150 K, in air atmosphere. The Si and Pt were used to calibrate the diffractometer. The Rietveld Refinement studies of the powder XRD profiles were performed using the DBWS Rietveld refinement program with a Cerius-2 interface.

3. Results and discussion

3.1. Effect of Cu concentration

Fig. 1 shows multiple plot of the powder XRD patterns of samples $CuZr_2$, $CuZr_5$, $CuZr_{10}$, and $CuZr_{20}$. The patterns show cubic zirconia as the major phase with small concentrations of monoclinic phase. There was a great difficulty in distinguishing between the tetragonal and the cubic phase because of the overlapping reflections. Further, the splitting of the 0 4 0 reflection of the cubic phase into 4 0 0 and 0 0 4 reflections of the tetragonal phase, which is a useful tool to distinguish between the two phases is masked by the broad nature of the peaks. Hence, the Rietveld refinement technique was used to analyze the XRD patterns. Rietveld refinement of powder X-ray diffraction data are reported to

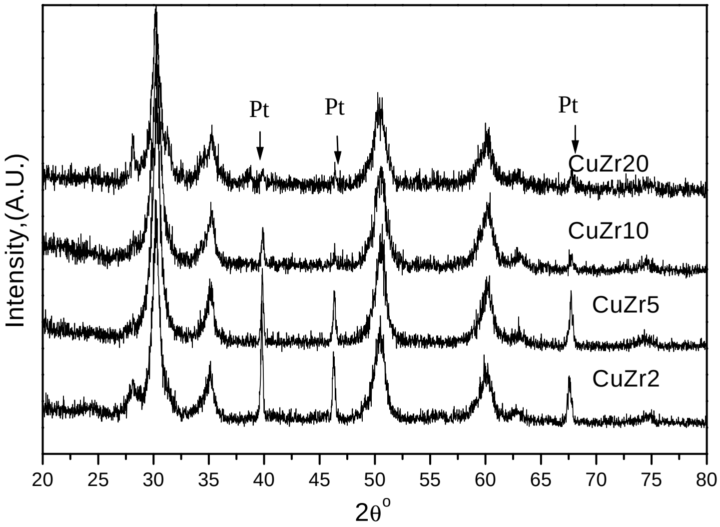

Fig. 1. Multiple plots of the powder XRD patterns of the zirconia samples containing 2, 5, 10, and 20 mol% copper, respectively. Reflections from Pt are indicated.

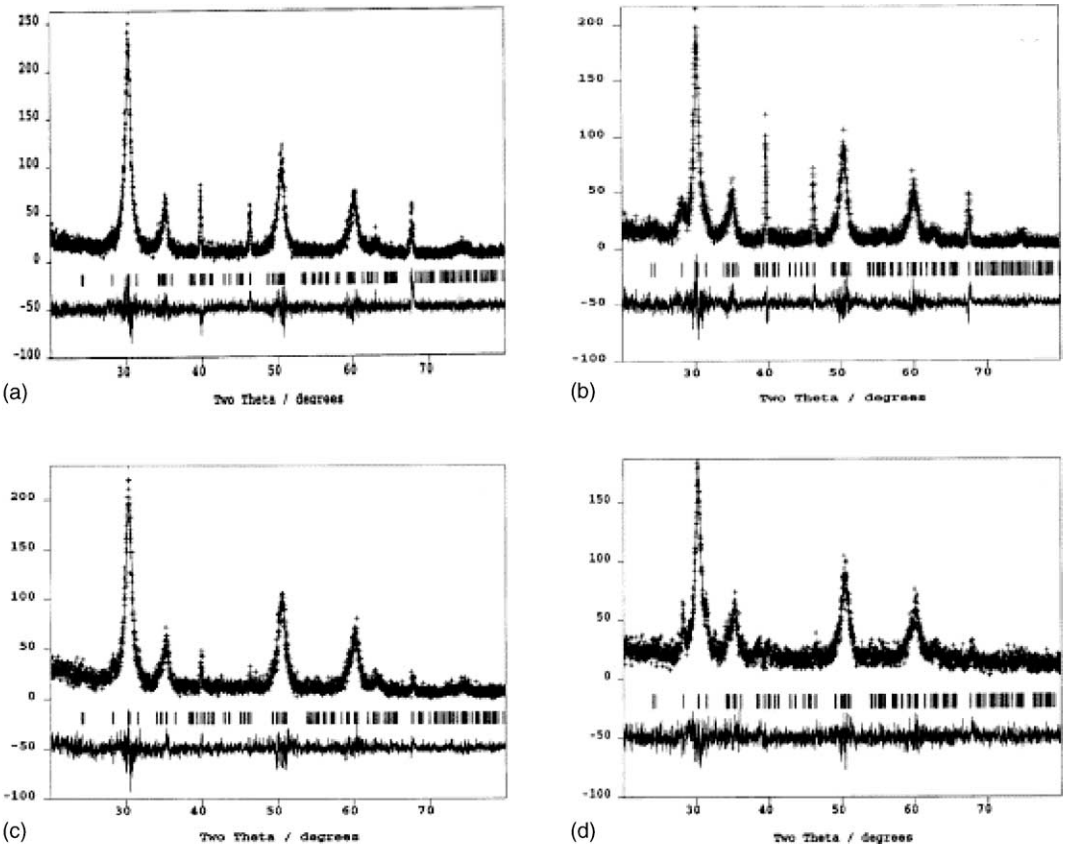

Fig. 2. Rietveld refinement plots (a) $CuZr_2$, (b) $CuZr_5$, (c) $CuZr_{10}$, (d) $CuZr_{20}$ samples scanned at 303 K.

distinguish between the cubic phase and the metastable tetragonal phase of Y stabilized zirconia [29]. The presence of cubic phase is reported in the copper stabilized zirconia prepared by sol–gel procedure [23] where the overlapping peaks of cubic and tetragonal zirconia could not be distinguished. Fig. 2a–d shows the Rietveld refinement plots of $CuZr_2$, $CuZr_5$, $CuZr_{10}$, and $CuZr_{20}$, respectively. The combination of the cubic (space group Fm3m) and the monoclinic (space group $P2_1/c$) phases was used as the starting models for refining a typical sample, $CuZr_2$. It was observed that the lattice parameters could not be refined and refinement did not progress. Then the tetragonal phase with space group $P4_2/nmc$ and the monoclinic phases were studied with no improvement in the refinement as well. Finally, all the three phases were introduced as the starting models. The background was refined using a polynomial with six refinable coefficients. The peak shape was refined using a Pseudo–Voigt function. The peak width (FWHM) was determined using the equation, $\mathrm{FWHM} = \sqrt{(u + v\tan\theta + w\tan^2\theta)}$ and then the crystallite size (L) was determined using the Scherrer equation [30]. As the refinement progressed, the relative percentage of the tetragonal phase decreased while that of the cubic phase increased. Similarly, the powder XRD patterns $CuZr_5$, $CuZr_{10}$, and $CuZr_{20}$ were refined. The various R factors obtained from the refinement results are listed in Table 1. The higher R_{EXP} (and hence higher R_{WP}) is due to the counting statistics being poor with a HTXRD fast scan, but the goodness of fit (G.O.F. given by R_{WP}/R_{EXP}) justifies a very good refinement. All the three phases were observed in all

Table 1
R factors obtained from the Rietveld refinement results of the powder XRD patterns of the copper substituted zirconia samples

R factors	$CuZr_2$	$CuZr_5$	$CuZr_{10}$	$CuZr_{20}$
R_P	19.54	18.19	16.50	16.00
R_{WP}	27.13	25.20	23.08	21.10
R_{EXP}	23.88	22.21	21.32	19.69
G.O.F., S	1.14	1.13	1.08	1.07
D-WD	1.75	1.74	1.82	1.86

the samples, with monoclinic phase in small concentration (about 2 wt.%) and the concentration of tetragonal and cubic phases varying with the copper content.

The Rietveld refinement results infer that zirconia is stabilized partially into tetragonal phase and partially into the cubic phase. Changes in the relative phase concentrations with the copper content are shown in Fig. 3. The percentage of the cubic phase seems to increase at the expense of the tetragonal phase as the copper concentration increases indicating that higher concentrations of copper is required for stabilizing zirconia in the cubic phase. Fig. 4 shows the change in unit cell volume of the cubic phase as a function of the copper concentration. A decrease in the unit cell volume of the cubic phase with an increase in copper concentration indicates substitution of copper in the zirconia lattice. A similar decrease in the unit cell volume of the tetragonal phase indicates substitution of some copper in the tetragonal lattice as well. Studies on copper stabilized zirconia by sol–gel procedure revealed that only about one half of the input copper probably goes into the lattice and the remainder stays as extra

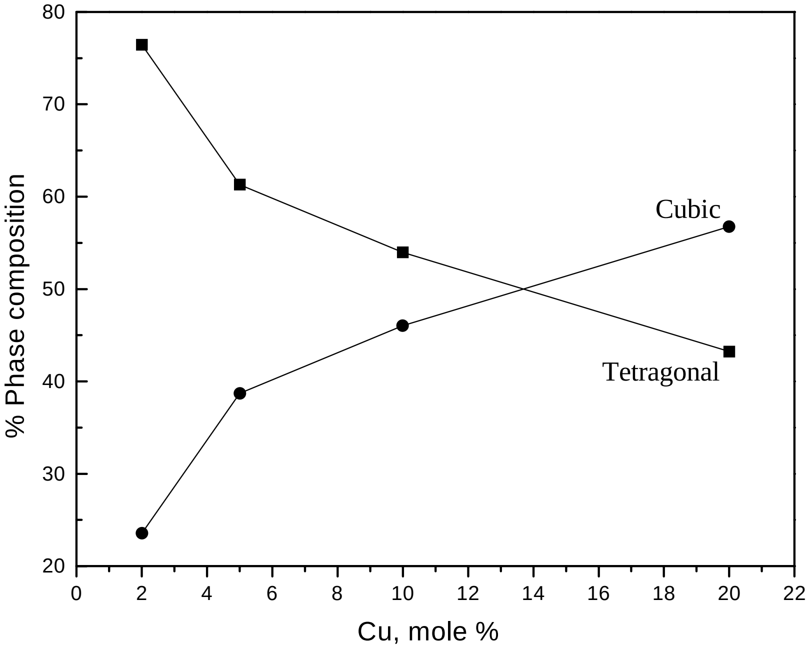

Fig. 3. Change in the relative concentration of the tetragonal and cubic phases as a function of copper concentration in zirconia. (■) Tetragonal; (●) cubic.

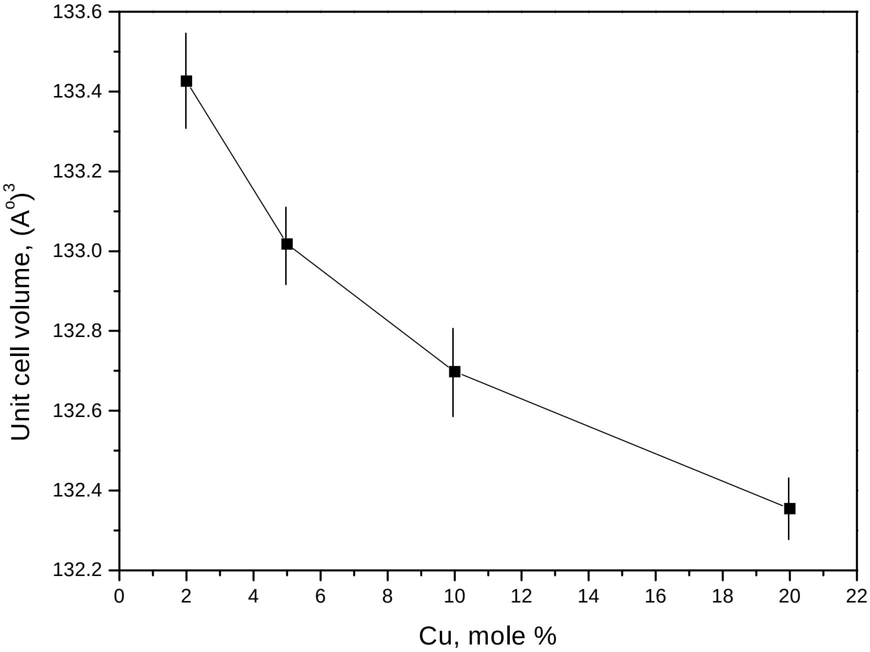

Fig. 4. Change in the unit cell volume of the cubic phase as a function of the copper concentration.

lattice copper [23]. This conclusion was drawn on the basis of comparison of lattice parameters calculated using the ionic radii of copper and zirconium with the experimental value. On the basis of our results from the Rietveld refinement of similar type of samples prepared by a different technique, it can be argued that the extra lattice copper could be in the tetragonal phase, which could not be detected by the authors in the absence of refinement studies. Fig. 5 shows the change in crystallite size and relative amount of the cubic phase with the varying copper content. It can be observed that the crystallite size of the cubic phase decreases continuously from 26 nm to about 8 nm with the increasing copper content from 2 to 20 mol%, respectively. Thus, zirconia seems to stabilize in the cubic phase at smaller crystallite size and higher copper content. Recently, Wang and Caruso [31] have reported formation of only tetragonal zirconia by doping copper using the same co-precipitation technique, whose crystallite size was of the order of 14–16 nm. Our results indicate stabilization of zirconia into both cubic and tetragonal phases with smaller crystallite size at similar copper loading.

3.2. HTXRD studies and effect of temperature

All the copper–zirconia samples were studied by HTXRD to determine the changes taking place in the samples as a function of temperature. Fig. 6a shows the multiple plots of the powder XRD patterns of the $CuZr_{20}$ sample scanned at various temperatures. The multiple plots of the various samples scanned at 1173 K are given in Fig. 6b. The *R* factors obtained from the refinements of the HTXRD patterns of the $CuZr_{20}$ sample are given in Table 2. Fig. 7 shows Rietveld refinement plot of HTXRD pattern at 1173 K of $CuZr_{20}$ sample. The changes in the relative phase compositions of the samples with the increasing temperature are plotted in Fig. 8. The refinement studies of the $CuZr_{20}$ indicate the

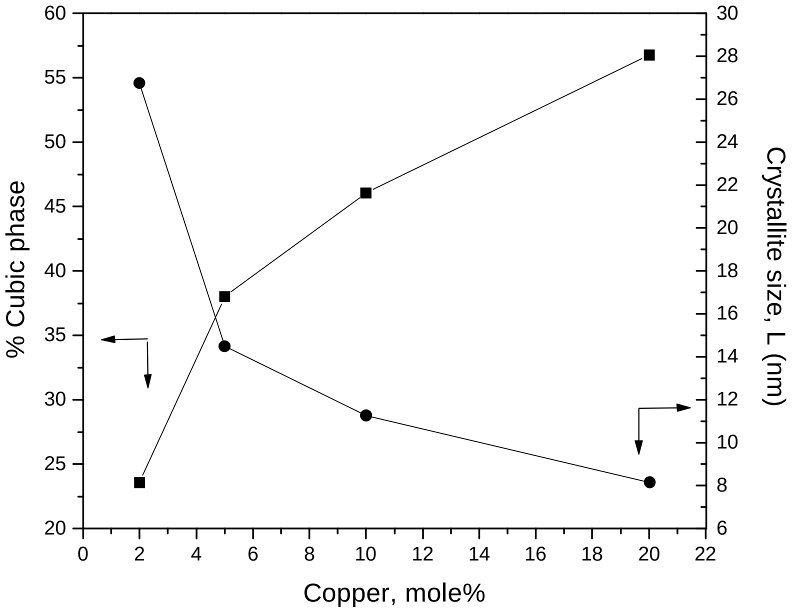

Fig. 5. Change in the crystallite size and the relative percentage of the cubic phase with varying copper content. (■) Percent of cubic phase; (●) crystallite size.

presence of all the three zirconia polymorphs up till a temperature of 1023 K. It can be observed that the relative percent of the cubic phase increases from room temperature to 723 K and then it starts decreasing as the temperature increases to 1023 K. At 1173 K, the cubic phase vanishes completely. However, the amount of the tetragonal phase seems to decrease with the temperature up to 723 K, after which there is an increase till 1023 K. It can be observed that the relative amount of the cubic and the tetragonal phases increases or decreases at the expense of each other. There seems to be a continuous and steady increase in the relative amount of the monoclinic phase from room temperature up till 1023 K. At 1173 K there is a sudden rise in the amount of the monoclinic phase where the remaining phases seem to vanish. This indicates the conversion of the cubic and tetragonal phases into the monoclinic phase at higher temperature (>1173 K). The zirconia sample at 1173 K contains monoclinic copper oxide as an additional phase indicating loss of copper from the zirconia lattice. The copper oxide formed is a nanocrystalline material with the average crystallite size of about 18 nm. No reflections for the copper oxide phase could be observed at lower temperatures indicating the stability

Table 2
The R factors obtained from the Rietveld refinement results of the HTXRD data of the $CuZr_{20}$ sample

R factors	303 K	423 K	573 K	723 K	873 K	1023 K	1173 K
R_P	16.00	16.20	16.65	16.80	17.35	17.27	19.32
R_{WP}	21.10	21.62	22.61	22.68	22.95	23.46	25.33
R_{EXP}	19.69	19.71	19.96	19.96	19.86	20.00	20.01
G.O.F., S	1.07	1.08	1.13	1.14	1.16	1.17	1.27
D-WD	1.86	1.77	1.85	1.82	1.67	1.55	1.26

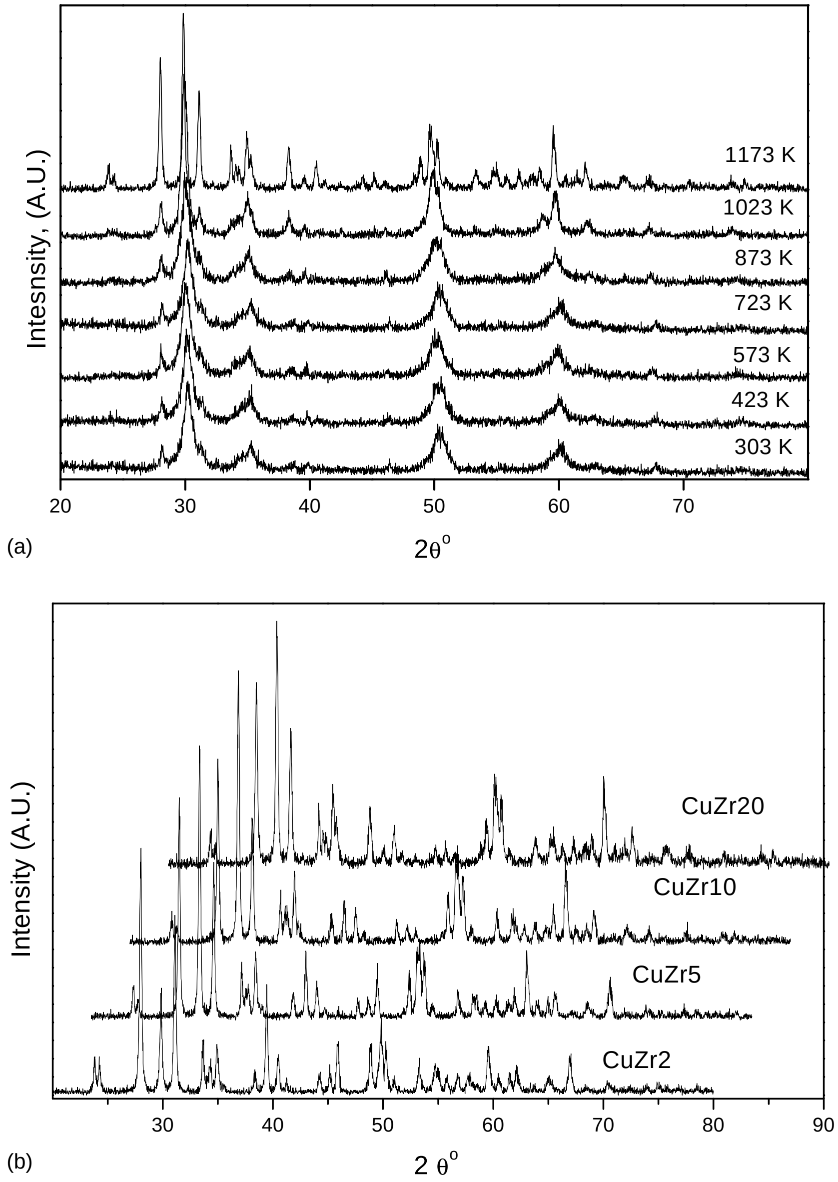

Fig. 6. (a) Multiple plots of the powder XRD patterns of the $CuZr_{20}$ sample scanned at various temperatures. (b) Multiple plots of the $CuZr_2$, $CuZr_5$, $CuZr_{10}$, and $CuZr_{20}$ samples scanned at 1173 K.

of the copper–zirconia solid solutions up to 1023 K by our HTXRD studies. Wang and Caruso [31] have reported, on the other hand, formation of copper oxide as an impurity even at a lower temperature (723 K). The change in the percentage of the cubic phase and the crystallite size has been plotted as a function of temperature in Fig. 9. The crystallite size of the cubic phase remained constant within the experimental errors till 723 K. Above 723 K, a sudden increase in the crystallite size can be seen. An increase in the relative percentage of the cubic phase can be seen till 723 K. Above 723 K the increase

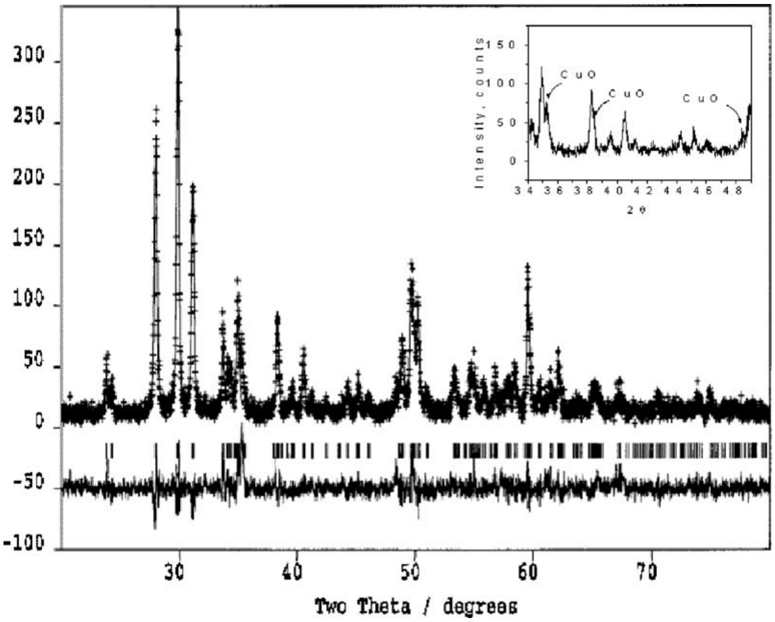

Fig. 7. Rietveld refinement of $CuZr_{20}$ sample scanned at 1173 K.

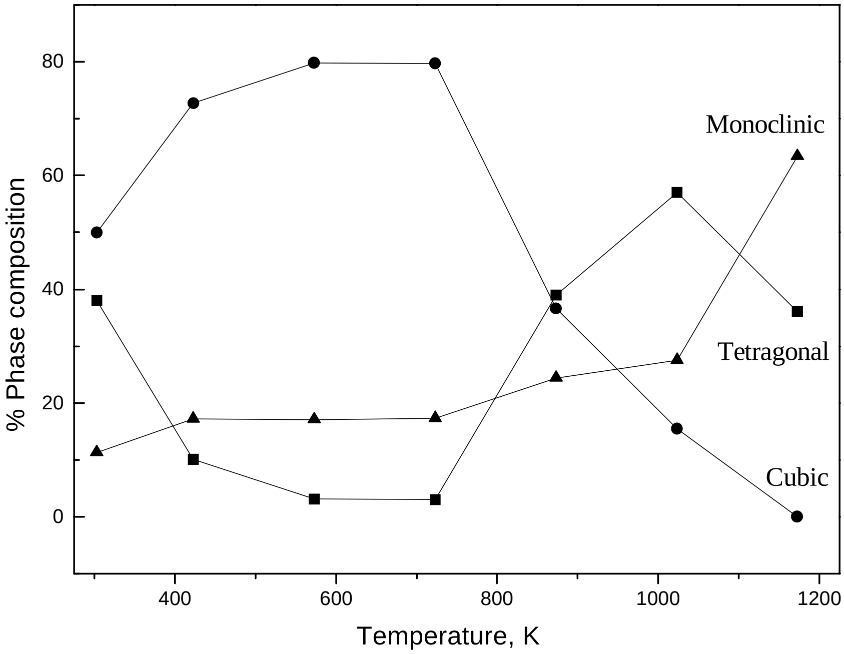

Fig. 8. Changes in the relative phase compositions of the samples with the increasing temperature. (■) Tetragonal; (●) cubic; (▲) monoclinic.

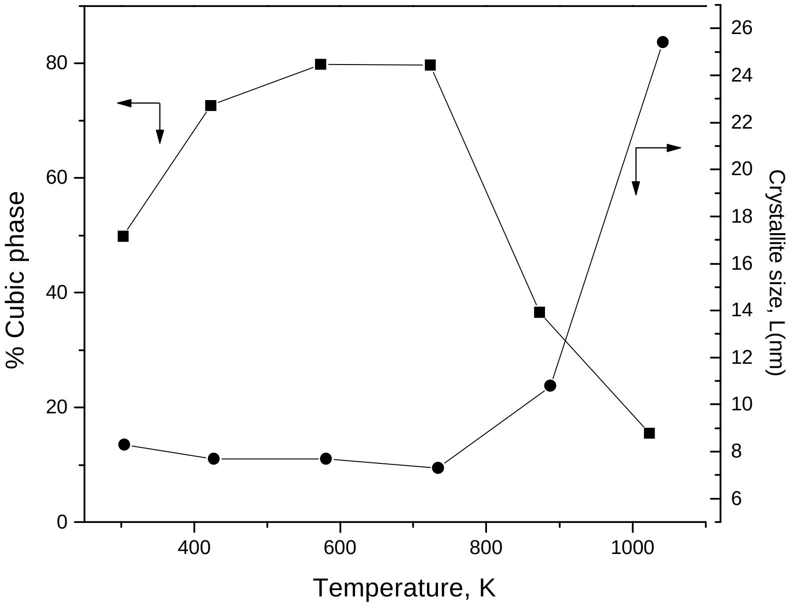

Fig. 9. Change in the percentage of the cubic phase and the crystallite size as a function of temperature. (■) Percent of cubic phase; (●) crystallite size.

in crystallite size is accompanied by a decrease in the percentage of the cubic phase. The tetragonal phase is a mixture containing sintered crystals, which are already present, and those formed because of the cubic to tetragonal transformation. All these crystallites contribute to the average crystallite size of the phase. Hence, no particular trend can be observed for the change in the crystallite size of the tetragonal phase. There is a continuous increase in the crystallite size of the monoclinic phase and an increase in the amount of the phase in the polymorph mixture. Similarly, the HTXRD patterns of the

Table 3
Percent phase composition of the copper–zirconia samples obtained from the Rietveld refinement of the HTXRD patterns

Sample	Phase	303 K	423 K	573 K	723 K	873 K	1023 K	1173 K
$CuZr_2$	C	31	35	37	38	28	21	0
	T	64	42	37	37	46	54	19
	M	5	21	26	25	26	26	81
$CuZr_5$	C	36	45	46	48	30	18	0
	T	59	45	43	42	52	53	28
	M	5	10	11	10	18	29	72
$CuZr_{10}$	C	45	52	53	53	27	12	0
	T	49	40	33	34	52	63	32
	M	6	8	14	13	21	25	68
$CuZr_{20}$	C	50	73	80	81	37	16	0
	T	38	10	3	3	39	57	37
	M	11	17	17	17	24	27	63

C: cubic; T: tetragonal; M: monoclinic.

$CuZr_2$, $CuZr_5$, and $CuZr_{10}$ samples were analyzed by Rietveld refinement. The changes in the phase composition of the samples as a function of temperature are given in Table 3. It can be observed that all the samples follow the same trend, with the relative amount of the cubic phase increasing with the increase in temperature till 873 K followed by a decrease in the concentration of the cubic phase. Simultaneously, a steady increase in the concentration of the monoclinic phase can be seen. The cubic phase vanishes at 1173 K for all the samples with formation of copper oxide in small concentrations. This indicates stability of the copper–zirconia solid solutions till 1023 K.

4. Conclusions

From the Rietveld refinement studies it is clear that in ZrO_2–Cu samples zirconia has not been stabilized into the cubic phase alone and is a mixture of both cubic and tetragonal phases. The relative amount of the cubic phase increases with the increasing copper concentration and a reduction in the unit cell volume confirms substitution of copper into the zirconia lattice. There is an increase in the percentage of the cubic phase at the expense of the tetragonal phase till 723 K with a steady decrease in the crystallite size of the cubic phase. Between 723 and 1023 K, the amount of the tetragonal phase increases along with an increase in the crystallite size. Above 1023 K, the increase in the crystallite size is related to a decrease in the concentration of the tetragonal phase with corresponding increase in concentration of the monoclinic phase. Higher concentration of dopent copper and smaller crystallite size are the governing factors in the stabilization of zirconia into cubic phase. The poor counting statistics due to the low crystallinity of the samples and a fast HTXRD scan yielded higher R_{WP} values. In spite of this, the reliability of the refinement is very good.

Acknowledgements

The authors acknowledge the financial support of DST, New Delhi for this work. One of the authors (M.B.) is grateful to CSIR, New Delhi, for a fellowship.

References

[1] B.C. Weber, J. Am. Ceram. Soc. 45 (12) (1962) 614.
[2] R. Stevens, An Introduction to Zirconia, 2nd ed., Magnesium Electron Ltd., 1986.
[3] T. Yamaguchi, Catal. Today 20 (1994) 199.
[4] K. Arata, Adv. Catal. 37 (1990) 165.
[5] S.K. Saha, P. Pramanik, Br. Ceram. Trans. 94 (1995) 123.
[6] C.F. Grain, J. Am. Ceram. Soc. 50 (6) (1967) 288.
[7] R.P. Ingel, D. Lewis III, J. Am. Ceram. Soc. 69 (4) (1986) 325.
[8] H. Ishizawa, O. Sakurai, N. Mizutani, M. Kato, Am. Ceram. Soc. Bull. 65 (1986) 1399.
[9] A.M. George, N.C. Mishra, N.C. Jayadevan, J. Mater. Sci. Lett. 11 (1992) 404.
[10] R.X. Zhou, X.Y. Jiang, J.X. Mao, X.M. Zheng, Appl. Catal. A 162 (1997) 213.
[11] J.C. Ray, P. Pramanik, S. Ram, Mater. Lett. 48 (2001) 281.
[12] T.H. Etsell, S.N. Flengas, Chem. Rev. 70 (1970) 1970.
[13] A. Keshavaraja, A.V. Ramaswamy, J. Mater. Res. 9 (1994) 837.

[14] M. Hoch, M. Mathur, J. Am. Ceram. Soc. 45 (1962) 373.

[15] R.C. Garvie, J. Phys. Chem. 69 (4) (1965) 1238.

[16] R.C. Garvie, J. Phys. Chem. 82 (4) (1978) 218.

[17] V.S. Stubican, J.R. Hellman, in: Advance Ceramics, III, Science and Technology of Zirconia, 1981, 25 pp.

[18] M. Yashima, S. Sasuki, M. Kakihana, Y. Yamaguchi, H. Arashi, M. Yoshimura, Acta. Cryst. B 14 (1995) 381.

[19] A. Clearfield, J. Mater. Res. 5 (1) (1990) 161.

[20] L.E. Depero, P. Levrangi, J. Solid State Chem. 110 (1994) 190.

[21] G. Pang, S. Chen, Y. Zhu, O. Palchik, Y. Koltypin, A. Zaban, A. Gedanken, J. Phys. Chem. B 105 (2001) 4647.

[22] F. Tietz, W. Jungen, P. Lersch, Chem. Mater. 14 (2002) 2252.

[23] M.K. Dongare, V. Ramaswamy, C.S. Gopinath, A.V. Ramaswamy, S. Scheurell, M. Brueckner, E. Kemnitz, J. Catal. 199 (2001) 209.

[24] D.G. Lamas, N.E. Walsue De Reca, J. Mater. Sci. 35 (2) (2000) 5563.

[25] G.E. Lascalea, D.G. Lamas, E. Djurado, N.E. Walsue De Reca, in: Proceedings of the Twenty Second International Symposium on Materials Science, Denmark, 2001, 313 pp.

[26] J.A. Wang, M.A. Valenzuela, J. Salmones, A. Vazguez, A. Garcia Ruiz, X. Bokhimi, Catal. Today 68 (2001) 21.

[27] H.M. Rietveld, Acta. Crystallogr. 20 (1996) 508.

[28] R.A. Young, The Rietveld Method, International Union of Crystallography, University Press, Oxford, 1993.

[29] D.G. Lamas, N.E. Walsue De Reca, Mater. Lett. 41 (1999) 204.

[30] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, John Wiley and Sons, New York, 1974, 618 pp.

[31] Y. Wang, R.C. Caruso, J. Mater. Chem. 12 (2002) 1442.