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Short communication

Studies on SnO_2–ZrO_2 solid solution

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Abstract

The solubilities of Sn in ZrO_2 and Zr in SnO_2 are investigated. The X-ray diffraction (XRD) studies show the solubility limit for Sn in zirconia to be 20 mol% whereas Zr in SnO_2 is around 25 mol%. All the compositions were prepared by the coprecipitation method. The average particle size for a typical composition was 25 nm as revealed by the transmission electron microscopy (TEM).

Keywords: B. Electron microscopy; D. ZrO_2; Solid solutions; SnO_2; X-ray diffraction

1. Introduction

Tin dioxide is n-type semiconductor crystallizing in the tetragonal rutile structure. The unit cell parameters are $a = 4.737$ Å and $c = 3.185$ Å and its space group is $P4_2/mmm$. It is very difficult to sinter SnO_2 to high densities without additives due to the condensation–evaporation mechanism operating during sintering. This property of low densification is exploited in the gas and humidity sensing applications. Recently, varistor characteristics were also reported in dense doped SnO_2 [1–5].

Zirconia is a very important engineering ceramic material for a wide variety of applications because of its intrinsic physical properties, such as high hardness, low wear resistance, low coefficient of friction, high elastic modulus, chemical inertness, low thermal conductivity and high melting point [6–12]. It can be used as a transformation toughed material due to its martensitic phase transformation. Zirconia is also used as oxygen gas sensors, as a catalyst support for various kinds of synthesis and has potential as a ceramic-fuel cell electrolyte. Pure ZrO_2 has three polymorphs monoclinic, tetragonal and cubic. While monoclinic is thermodynamically stable at room temperature, the other two phases are unstable. To prepare metastable tetragonal phase various additives, such as yttria, magnesia or calcia are used. Cubic zirconia has fluorite structure in which zirconium has eight-fold coordination.

There are some reports on the solid solution limits in SnO_2–ZrO_2 system [13–15]. Recently, Ray et al. [10] have reported the effect of Sn on polymorphic phases Zirconia. However, they have not studied the unit cell parameter variation of ZrO_2 with SnO_2. Here, we communicate the investigation on the phase range and change in lattice parameter of the solid solution end members of this binary system.

2. Experimental

All the reactants used were of A.R. grade (Loba chimie). Required quantity of $SnCl_4$ is diluted with known amount of ice-cold double distilled water to form $SnOCl_2$ solution and mixed with known quantity of $ZrOCl_2{\cdot}8H_2O$. Standard ammonia solution was added dropwise to the above solution mixture until pH ~ 9 to ensure completion of precipitation. The precipitate was washed free of anions with double distilled water and oven dried at 373 K for overnight. The dried precipitate is calcined at 1373 K for 15 h. The phase contents and lattice parameters were studied using Philips X-ray diffractometer. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the 2θ range of 10–80° for a period of 5 s/step in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to calculate the lattice parameters. The transmission electron microscopy (TEM) picture was recorded with JEOL

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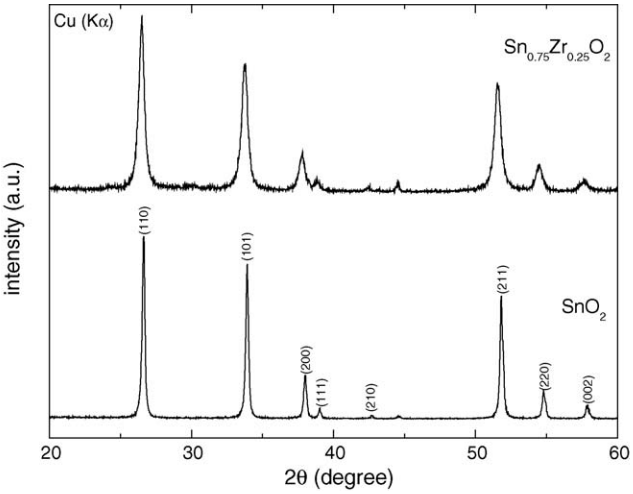

Fig. 1. XRD of pure SnO_2 and $Sn_{0.75}Zr_{0.25}O_2$.

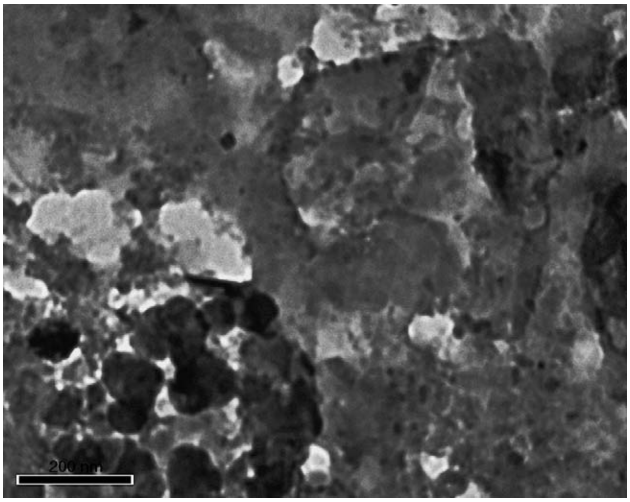

Fig. 3. TEM picture of $Sn_{0.75}Zr_{0.25}O_2$.

model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon-coated TEM copper grid.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) of a Zr-doped SnO_2 sample (calcined at 1373 K). As the concentration of Zr is increased, the peaks shift to lower angle indicating the increase in lattice parameters. The variation of lattice parameter of SnO_2 with Zr incorporation is shown in Fig. 2. The ionic radius of zirconium ion (Zr^{4+}) (0.72 Å) [8] being larger than that of stannic ion (Sn^{4+}) (0.68 Å) [8], the lattice parameter increases accordingly. No second phases are observed upto 25 mol% of zirconium dioxide addition into rutile tin dioxide. The unit cell parameters for the composition, $Sn_{0.75}Zr_{0.25}O_2$ are $a = 4.760$ Å and $c = 3.186$ Å. Above 25 mol% of ZrO_2 addition, peaks corresponding to monoclinic zirconia are seen in the diffractogram. There is some variation in the unit cell parameter observed with literature [13–15] and that may depend on background impurities present in the system. The average dried particle size was found to be 25 nm for $Sn_{0.75}Zr_{0.25}O_2$ powders from TEM studies (Fig. 3). The crystallite size was also calculated using the Scherrer equation, $D = k\lambda/\beta \cos \theta$, where D is the crystallite size, k the constant (=0.9 assuming that the particles are spherical), λ the wavelength of the X-ray radiation, β the line width (obtained after correction for the instrumental broadening) and θ is the angle of diffraction. The average particle size obtained from XRD data is 40 nm. It is to be noted that with zirconia addition, the particle size decreases as compared to end member.

Fig. 4 shows the XRD recorded for $Zr_{0.80}Sn_{0.20}O_2$ powders (calcined at 1373 K) and all the lines can be indexed on monoclinic unit cell parameters, $a = 5.15$ Å, $b = 5.235$ Å, $c = 5.30$ Å and $\beta = 80.10$. There is a small decrease in lattice parameters with tin incorporation in accordance with the reduction in the ionic radius. The major peak of tetragonal zirconia is also seen in trace amounts indicating its formation in

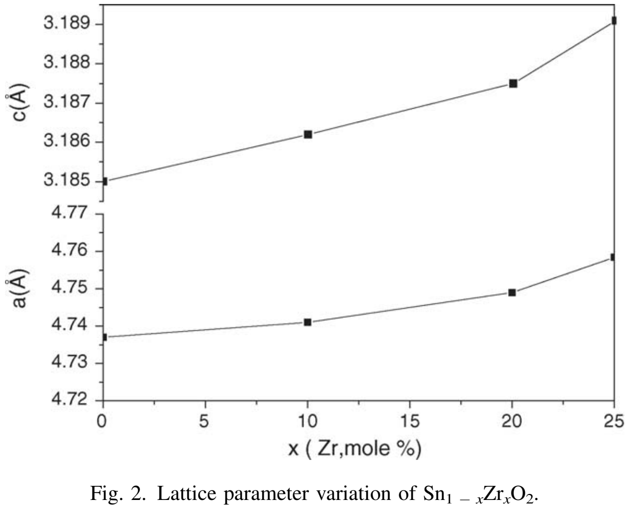

Fig. 2. Lattice parameter variation of $Sn_{1-x}Zr_xO_2$.

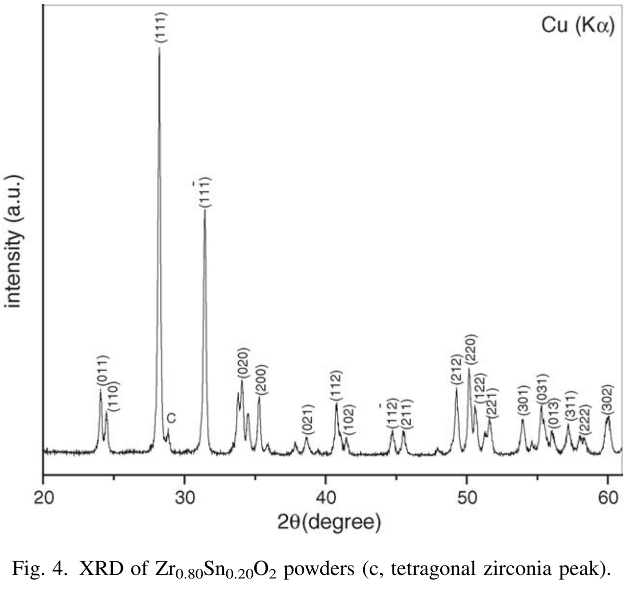

Fig. 4. XRD of $Zr_{0.80}Sn_{0.20}O_2$ powders (c, tetragonal zirconia peak).

the system. The average particle size calculated from XRD data is 70 nm. Above 20 mol% of SnO_2 addition, XRD shows the multiphase composition.

4. Conclusions

The formation of single-phase compositions in the binary system SnO_2–ZrO_2 was investigated. It is found that 20 mol% of SnO_2 can be incorporated in the ZrO_2 without forming second phase whereas 25 mol% of ZrO_2 can be substituted in rutile SnO_2 lattice.

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References

[1] S.R. Dhage, V. Ravi, S.K. Date, Mater. Lett. 57 (2002) 727.
[2] V. Ravi, S.K. Date, Bull. Mater. Sci. 24 (2001) 483.
[3] S.R. Dhage, V. Ravi, Appl. Phys. Lett. 83 (2003) 4539.
[4] S.R. Dhage, V. Choube, V. Ravi, Mater. Sci. Eng. B 110 (2004) 168.
[5] J.G. Fagan, S. Amarakoon, Am. Ceram. Soc. Bull. 72 (1993) 119.
[6] R.C. Garvie, R.H. Hannink, R.T. Pascoe, Nature 258 (1975) 703.
[7] R.H.J. Hannik, P.M. Kelly, B.C. Muddle, J. Am. Ceram. Soc. 83 (2000) 461.
[8] Y.B. Khollam, A.S. Desphande, A.J. Patil, H.S. Potdar, S.B. Desphande, S.K. Date, Mater. Chem. Phys. 71 (2001) 235.
[9] J.C. Ray, R.K. Pati, P. Pramanik, J. Eur. Ceram. Soc. 20 (2000) 1289.
[10] J.C. Ray, R. Saha, P. Pramanik, Mater. Lett. 57 (2003) 2140.
[11] S.K. Saha, P. Pramanik, Br. Ceram. Trans. 94 (1995) 123.
[12] B. Xia, L. Duan, Y. Xie, J. Am. Ceram. Soc. 72 (1989) 467.
[13] A. Deitzel, W. Poch, Radex Rundeschau 4 (1960) 55.
[14] J. Stocker, R. Collongues, Compt. Rend. 244 (1957) 83.
[15] J.F. Collins, I.F. Ferguson, J. Chem. Soc. 1 (1968) 4.