

# Low temperature heat capacities of zirconia and yttria-doped zirconia $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ ( $x = 0, 0.0200, 0.0396$ )<sup>1</sup>

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## Abstract

Heat capacity measurements were performed on zirconia and yttria-doped zirconia,  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  ( $x = 0, 0.0200, 0.0396$ ), between 13 and 300 K by adiabatic calorimetry. Powder X-ray diffraction and Raman spectra showed that the structure of the samples with  $x = 0$  and 0.0396 was monoclinic and tetragonal, respectively, while the sample with  $x = 0.0200$  was a mixture of the two phases. The heat capacity of the sample of  $x = 0.0200$  was not estimated on the basis of the additivity rule from the values of the other two samples ( $x = 0, 0.0396$ ). A broad hump was found around 20 K in the heat capacity curve of  $C_p T^{-3}$  versus  $T$  of the sample of  $x = 0.0396$ .

**Keywords:** Heat capacity; Zirconia; Yttria-doped zirconia; Low energy excitations

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## 1. Introduction

Yttria-doped zirconia has long been attracting much attention because of its potential in a variety of industrial applications. In particular, the mechanism of the high ionic oxygen conductivity has been studied extensively. Yttria doping leads to replacement of  $\text{Zr}^{4+}$  by  $\text{Y}^{3+}$ , and to formation of vacancies at the oxygen sites caused by the restriction of electrical neutrality. The oxygen mobility is facilitated by such defects randomly distributed in the crystal, and thus the oxygen conductivity increases with increasing yttria

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doping up to 8 mol%. However, further doping results in a decrease in oxygen conductivity. Some interactions among the defects might cause the decrease in the oxygen conductivity. Recently, studies have been extended to the low temperature region, where the defects cause excess heat capacity due to so-called “low-energy excitation” in the crystal [1–5] similar to that in amorphous solids [6]. Although a number of studies have been made on such phenomena in yttria-doped zirconia, the detailed mechanism is still an open question. Thermodynamic studies have been very few [7,8], and the present authors started thermodynamic studies on this compound [9,10]. In the present investigation, heat capacity measurements have been performed on zirconia and yttria-doped zirconia  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  ( $x = 0, 0.0200, 0.0396$ ). The results are given and discussed in detail.

## 2. Experimental

Fine powders of  $\text{Y}_2\text{O}_3\text{--ZrO}_2$  containing different amounts of  $\text{Y}_2\text{O}_3$  were prepared by a hydrolysis technique using a solution of  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  (Tosoh Corporation) and  $\text{YCl}_3$  (commercial grade). The procedure of the preparation was described in detail elsewhere [10]. The average particle size of the products was about  $0.45\ \mu\text{m}$  as estimated by SEM observations. Elemental analysis [10] gave values for the corresponding oxides;  $\text{Y}_2\text{O}_3 = 0, 3.61, 7.03$ ,  $\text{SiO}_2 = 0.005, 0.009, 0.007$ ,  $\text{Fe}_2\text{O}_3 = 0.005, 0.004, 0$ ,  $\text{Na}_2\text{O} = 0.007, 0.018, 0.03$ ,  $\text{I}_g\ \text{loss} = 0.61, 0.90, 0.66$ ,  $\text{ZrO}_2 = 99.373, 95.459, 92.273\ \text{wt}\%$  which led to  $x = 0, 0.0200, 0.0396$ , respectively, in the chemical formula  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ . The samples were identified and characterized by powder X-ray diffractometry with graphite monochromatized  $\text{CuK}\alpha$  radiation (model MXP18HF, MAC Science Co., Ltd.), and by Raman scattering spectroscopy with an argon ion laser of 488 nm wavelength (model NR-1100, JASCO).

The heat capacities of the samples were measured between 13 and 300 K using a laboratory-made adiabatic calorimeter [11]. The amount of the samples of  $x = 0, 0.0200, 0.0396$  loaded in the calorimeter vessel was 15.0278 g (0.12196 mol), 16.7682 g (0.13385 mol) and 17.2482 g (0.13550 mol), respectively. The calorimeter vessel was then evacuated and a small amount of He gas (about 10 kPa at room temperature) was introduced to promote thermal equilibration within the calorimeter vessel. After the addition of He gas, the calorimeter vessel was sealed with Wood's alloy. The temperature scale of the platinum resistance thermometer (type 5187L, H. Tinsley and Co. Ltd.) mounted on the calorimeter vessel had been calibrated at the National Physical Laboratory in England on the basis of the International Temperature Scale of 1990 (ITS-90) between 13 and 303 K.

## 3. Results and discussion

The results of the powder X-ray diffractometry on the three samples are shown in Fig. 1. The diffraction pattern of the sample of  $x = 0$  is in fair agreement with that of the JCPDS No. 37-1484 for monoclinic  $\text{ZrO}_2$ . The sample of  $x = 0.0396$  is similar to the JCPDS No. 30-1468 for cubic  $92\text{ZrO}_2\cdot 8\text{Y}_2\text{O}_3$  except for the peaks of (2 0 0) and (3 1 1)

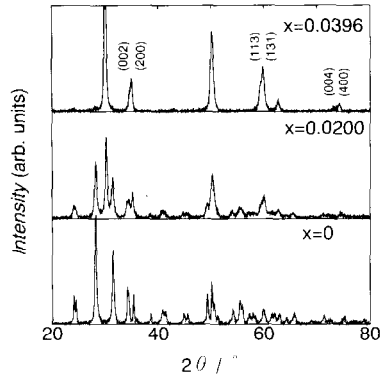


Fig. 1. Results of the powder X-ray diffractometry on the three samples of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  ( $x = 0, 0.0200, 0.0396$ ).

which split into two peaks. These results indicate that the structure of the sample of  $x = 0$  is monoclinic and that of  $x = 0.0396$  is tetragonal. However, the diffraction pattern of the sample of  $x = 0.0200$  is a superposition of those of the other two samples ( $x = 0, 0.0396$ ). Raman spectra of the three samples are shown in Fig. 2, where the superposition of the spectra of the two samples of  $x = 0, 0.0396$  also gives the spectrum of the sample of  $x = 0.0200$ . Therefore the sample of  $x = 0.0200$  is considered to be a mixture of monoclinic and tetragonal crystals.

During the heat capacity measurements, no abnormal hysteresis and/or thermal relaxation phenomena were observed, and the experiments were carried out in the ordinary manner [11]. The measured molar heat capacities of the three samples of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  ( $x = 0, 0.0200$  and  $0.0396$ ) are shown in Fig. 3. It seems that the value of the heat capacity increases with increasing yttria doping content, and thus the sample of  $x = 0.0396$  has the largest values of heat capacity. However, the number of atoms in  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  increases with increasing value of  $x$ ;  $(3 \times 1)N$ ,  $(3 \times 0.98 + 5 \times 0.02)N$

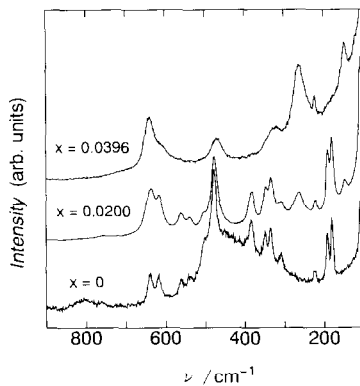


Fig. 2. Raman spectra of the three samples of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  ( $x = 0, 0.0200, 0.0396$ ).

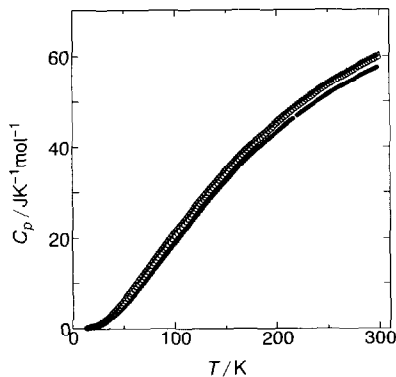


Fig. 3. Measured molar heat capacities of the three samples of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  ( $\bullet$ ,  $x = 0$ ;  $\circ$ ,  $x = 0.0200$ ;  $\Delta$ ,  $x = 0.0396$ ).

and  $(3 \times 0.9604 + 5 \times 0.0396)N$  for the sample of  $x = 0, 0.0200$  and  $0.0396$ , respectively. Therefore, the value of the molar heat capacity  $C_p$  of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  must be normalized for the purpose of quantitative comparison, and thus the normalized heat capacity  $C_p^*$  is defined as  $C_p^* = 3C_p/(3 + 2x)$ .

The Debye characteristic temperatures corresponding to the normalized heat capacities are shown in Fig. 4, in which each atom is assumed to have 3 degrees of freedom. The  $\Theta_D$  value of the sample of  $x = 0$  is the highest compared with the other two samples, and the yttria doping is found to soften the crystal lattice. In contrast to Fig. 3, Fig. 4 shows that the curves of the samples of  $x = 0.0200$  and  $0.0396$  intersect each other at about 260 K. Thus, it turns out that the heat capacity of the sample of  $x = 0.0200$  is not estimated on the basis of the additivity rule from the values of the other two samples ( $x = 0, 0.0396$ ), although the sample of  $x = 0.0200$  is considered to be a mixture of the two phases as indicated by the X-ray diffractions and Raman spectra.

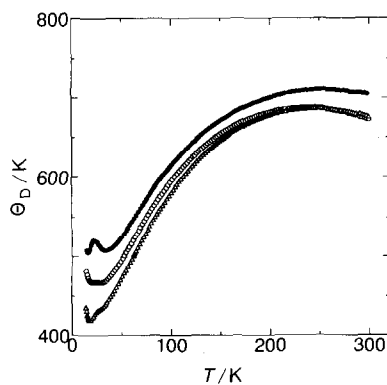


Fig. 4. Debye characteristic temperatures of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ , assuming 3 degrees of freedom per atom ( $\bullet$ ,  $x = 0$ ;  $\circ$ ,  $x = 0.0200$ ;  $\Delta$ ,  $x = 0.0396$ ).

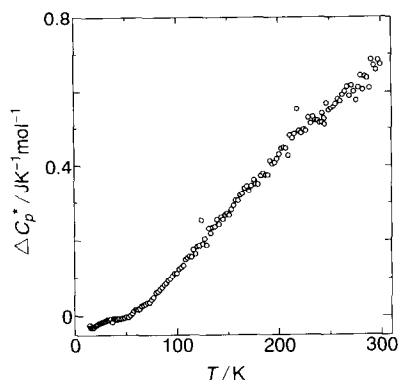


Fig. 5. Excess heat capacity of the sample with  $x = 0.0200$ .

The excess heat capacity  $\Delta C_p^*$  of the sample of  $x = 0.0200$  is obtained by subtracting the heat capacity calculated on the basis of the additivity rule assuming that the sample of  $x = 0.0200$  is a mixture of the pure monoclinic sample of  $x = 0$  and the tetragonal sample of  $x = 0.0396$  from the measured and normalized value  $C_p^*$  of the sample of  $x = 0.0200$  as follows:

$$\Delta C_p^* = C_{p(x=0.0200)}^* - \left(1 - \frac{0.0200}{0.0396}\right) \times C_{p(x=0)}^* - \frac{0.0200}{0.0396} \times C_{p(x=0.0396)}^* \quad (1)$$

The result of the calculation is shown in Fig. 5, where the value of the excess heat capacity is too large to be attributed to the effects of any chemical impurities existing in the samples. This discrepancy should be clarified by further studies taking into account the mixing mechanism, surface energy and so on. A heat capacity measurement is also re-

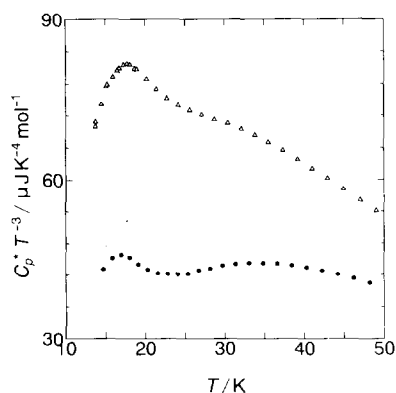


Fig. 6. Normalized heat capacities of  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$  in the low temperature region (●,  $x = 0$ ; Δ,  $x = 0.0396$ ).

quired on some sintered samples to see the particle-size effects; such a study is under way [12].

In the lowest temperature region in Fig. 4, the curves of the Debye characteristic temperatures show a rather large depression, which implies an additional contribution of some modes due to low energy excitations. In this region, the normalized heat capacities of the samples of  $x = 0$  and 0.0396 are given by the plots of  $C_p^* T^{-3}$  versus  $T$  in Fig. 6, where the sample of  $x = 0.0396$  shows a large hump with a maximum at about 18 K. The sample of  $x = 0$  shows a small broad hollow at about 23 K and a hump at about 17 K, which should be ascribed to van Hove singularity. The large hump found in the curve of the sample of  $x = 0.0396$  resembles that of amorphous solids which have been recently known to have some additional excitations besides that caused by the so-called two-level system [13–15], and have been explained on the basis of a soft anharmonic potential model [16–18]. Yttria doping into zirconia causes substitution of  $Y^{3+}$  for  $Zr^{4+}$  and thus formation of vacancies at oxygen sites which form double minimum potentials in the crystal. The randomly distributed vacancies lead to the two-level system which results in a glass-like linear  $T$  term in the low temperature heat capacity. The soft potential might also exist where the barrier height between the double minima is too low to form the tunneling state. Further detailed investigations are in progress [12].

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## References

- [1] W.N. Lawless, *Phys. Rev. B*, 21 (1980) 585.
- [2] W.N. Lawless, *Phys. Rev. B*, 22 (1980) 3122.
- [3] D.A. Ackerman, D. Moy, R.C. Potter, A.C. Anderson and W.N. Lawless, *Phys. Rev. B*, 23 (1981) 3886.
- [4] W.N. Lawless and T.K. Gupta, *Phys. Rev. B*, 28 (1983) 5507.
- [5] F.J. Walker and A.C. Anderson, *Phys. Rev. B*, 29 (1984) 5881.
- [6] P.W. Anderson, B.I. Halperin and C.M. Varma, *Philos. Mag.*, 25 (1972) 1.
- [7] K.K. Kelley, *Ind. Eng. Chem.*, 36 (1944) 377.
- [8] M.V. Nevitt, Y. Fang and S.-K. Chan, *J. Am. Ceram. Soc.*, 73 (1990) 2502.
- [9] T. Tojo, T. Shirakami and T. Atake, *Report Res. Lab. Eng. Mater.*, Tokyo Inst. Technol., 20 (1995) 43.
- [10] T. Shirakami, T. Atake, T. Mori and H. Yamamura, *Solid State Ionics*, 79 (1995) 143.
- [11] T. Atake, H. Kawaji, A. Hamano and Y. Saito, *Report Res. Lab. Eng. Mater.*, Tokyo Inst. Technol., 15 (1990) 13.
- [12] T. Atake, T. Shirakami, T. Tojo, T. Mori and H. Yamamura, unpublished.
- [13] U. Buchenau, N. Nucker and A.J. Dianoux, *Phys. Rev. Lett.*, 53 (1984) 2316.
- [14] R.O. Pohl and E.T. Swartz, *J. Non-Cryst. Solids*, 76 (1985) 117.
- [15] U. Buchenau, M. Prager, N. Nucker, A.J. Dianoux, N. Ahmad and W.A. Phillips, *Phys. Rev. B*, 34 (1986) 5665.
- [16] V.G. Karpov, M.I. Klinger and F.N. Ignat'ev, *Soviet Phys. JETP*, 57 (1983) 439.
- [17] M.A. Il'in, V.G. Karpov and D.A. Parshin, *Soviet Phys. JETP*, 65 (1987) 165.
- [18] U. Buchenau, Yu. M. Galperin, V.L. Gurevich, D.A. Parshin, M.A. Ramos and H.R. Schober, *Phys. Rev. B*, 46 (1992) 2798.