PRESSURE-INDUCED DEFECTS IN ZIRCONATES

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Defects, *e.g.* vacancies and interstitials, play an important role on the physical properties of oxides, especially on their ionic transport. Those defects in oxides are generally controlled and analyzed as functions of dopant concentration, *c*, temperature, *T*, and oxygen chemical potential, μ_{O2}, but not of total pressure, *P*. This is not surprising given that a molar volume, V_m, of solids is much smaller than that of gas phase by a factor of ≈1/1000. Meanwhile, under high pressure such as several GPa, the effect of total pressure on free energy, *i.e.* $V_m P$, reaches 20~100 kJ/mol, which is high enough to affect the defect formation and migration in solids. In fact, pressure-induced phenomena are recently of great interest in solid state ionics. In this study, we focus on the pressure effects on the defect formation in some stabilized ZrO_2 and acceptor-doped $BaZrO_3$.
For Y-stabilized ZrO_2, reduction was found to be enhanced under high pressure. Figure 1 shows the lattice constant of 8YSZ electrochemically reduced under high pressure as a function of oxygen deficiency introduced. Under high pressure such as 1 to 6 GPa, 8YSZ was easily reduced even at $3V_{DC}$ at 500°C. The oxygen deficiency reaches δ = 0.05. Unlike reduced CeO_2 which shows lattice expansion, the reduced 8YSZ shows 0.5% smaller lattice constant. The lattice shrinkage was also confirmed by DFT calculations. This supports that applying high pressure, which in general enhances a reaction with negative volume change, enhances the reducing reaction of cubic ZrO_2. Figure 2 shows the temperature dependence of electrical conductivity of reduced 8YSZ. The reduced 8YSZ appears to show mixed ionic and electronic conduction; major carrier is electrons. Acceptor-doped $BaZrO_3$ was also subjected to high pressure on the order of GPa. Their defect equilibrium and proton conductivity will be also discussed.

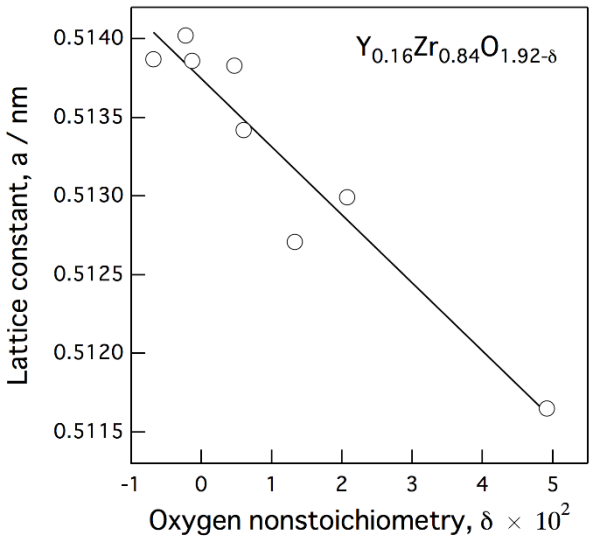

Figure 1 – Lattice constant of 8YSZ reduced under high pressure as a function of oxygen deficiency.

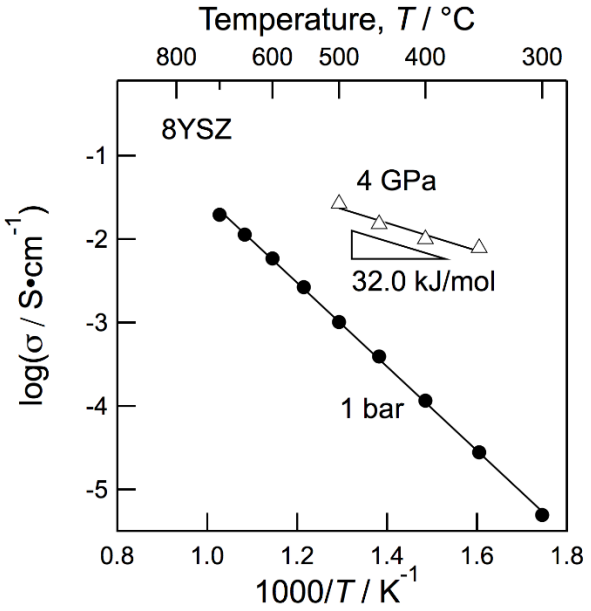

Figure 2 – Electrical conductivity of 8YSZ reduced under high pressure.