STRUCTURE AND CONDUCTIVITY OF PYROCHLORE AND FLUORITE TYPE SOLID SOLUTIONS

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High oxygen conductivities can be achieved in cation ordered $\text{Ln}_x\text{Zr}_{1-x}\text{O}_{2-\frac{1}{2}x}$ ($\text{Ln}=\text{Gd}, \text{Nd}$) solid solutions with pyrochlore (P) structure. High values of the pre-exponential factor σ_0 are correlated with the degree of anion disorder in the 8b oxygen sublattice (neutron diffraction). The activation energy ΔH is lowered by cation ordering (F-P transition; effect of x) due to the occurrence of a preferential diffusion path. Maximum oxygen conductivity is achieved in $(1-x)\text{Bi}_2\text{O}_3-x\text{Ln}_2\text{O}_3$ solid solutions with fluorite related $\delta\text{-Bi}_2\text{O}_3$ structure for $\text{Ln} = \text{Er}$ and $x = 0.20$. Neutron diffraction measurements indicate the occurrence of short range ordering in "Er-O units" with relative small interatomic distances at $T < 820 \text{ K}$. This leads to an increased activation energy.

1. INTRODUCTION

Defect fluorite type solid solutions in $\text{Ln}_x\text{Zr}_{1-x}\text{O}_{2-\frac{1}{2}x}$ show the well known maximum in the ionic conductivity σ for $x \approx 0.18$ and a fractional oxygen vacancy concentration $V_O'' \approx 0.045$ [1]. Depending on the ionic radius of Ln, at a given (higher) value of x the disordered defect fluorite (F) is transformed at least partially [2,4] to the pyrochlore (P) structure $\text{A}_2\text{B}_2\text{O}_6\text{O}'$ which can be considered as a skeleton structure with 3 different O sites [3]. Literature results of σ for $x > 0.30$ are scarce and conflicting [4]. In our opinion this is due to different degrees of order resulting from different preparation conditions. The interesting features of the P structure are the use of the skeleton character of this structure and the occurrence of preferential diffusion paths. These can be used for the optimization of σ [4]. This will be discussed in this paper. Solid solutions of $\text{Bi}_2\text{O}_3\text{-Ln}_2\text{O}_3$ can be stabilised [5,6] to the cubic $\delta\text{-Bi}_2\text{O}_3$ (fluorite) structure and are excellent oxygen ion conductors [7]. Systematic investigation of the optimization of σ has been described [6]. Correlation of σ with structural features was reported previously [8] and is discussed now.

2. STRUCTURE OF $\text{Ln}_x\text{Zr}_{1-x}\text{O}_{2-\frac{1}{2}x}$ SOLID SOLUTIONS

For $x \approx 0.5$ solid solutions with $\text{Ln} = \text{Nd}, \text{Gd}$ have the P structure (space group $\text{Fd}3\text{m}$) with general composition $\text{A}_2\text{B}_2\text{O}_6\text{O}$. Three different (O) sites occur called 48f ($\equiv 48$ sites per unit cell), 8a and 8b sites respectively. In fully cation ordered stoichiometric $\text{Ln}_2\text{Zr}_2\text{O}_7$ the 8b sites are empty. The $\text{ZrO}_2\text{-Gd}_2\text{O}_3$ (ZG) system has special characteristics. The P phase field of it is bell-shaped within a defect fluorite phase field and has a maximum P-F transition temperature T_c of 1550°C for $\text{Gd}_2\text{Zr}_2\text{O}_7$. A combination of quenching (yields F) and annealing yields hybrid and P phases with different degrees of order. Refinement of neutron diffraction data [4,9] of non-stoichiometric ($x \neq 0.5$) $\text{ZrO}_2\text{-Nd}_2\text{O}_3$ (ZN)

show a temperature independent excess²⁾ occupation of 8b sites of 16%. The concentration of these "interstitial" $\text{O}_i(8\text{b})$ ions originate from the 48f sublattice, the vacancy concentration V_O'' in this lattice equals that of $\text{O}_i(8\text{b})$ and is of the same magnitude as V_O'' values before the maximum conductivity at $x \approx 0.18$.

2.1 Conductivity of $\text{Ln}_x\text{Zr}_{1-x}\text{O}_{2-\frac{1}{2}x}$ solid solutions

The (high) ionic conductivity σ plotted as a function of x shows a maximum (Gd) or a minimum (Nd) for $x = 0.5$. Curves of x versus activation enthalpy ΔH and pre-exponential factor σ_0 in the expression $\sigma T = \sigma_0 \exp(-\Delta H/RT)$ have similar shapes [10]. The same type of curves are achieved for Gd and Nd (fig. 1). Characteristic points of the σ versus x curves are tabulated in table 1.

system	x	$\sigma (\Omega^{-1}\text{m}^{-1})$ ($T=1000\text{K}$)	$\sigma_0 (\Omega^{-1}\text{m}^{-1}\text{K})$	$\Delta H \text{ kJ}(\text{mol})^{-1}$
ZrGd(P)	0.5	0.41	1.0×10^7	84
ZrGd(F)	0.35	0.094	2.5×10^8	123
ZrNd(P)	0.5	0.0027	2.0×10^8	74
ZrNd(P)	0.35	0.36	$\sim 2 \times 10^8$	110

Table 1: Characteristic conductivity data for $\text{Ln}_x\text{Zr}_{1-x}\text{O}_{2-\frac{1}{2}x}$

Figure 1: Characteristic shape of ΔH and σ_0 as a function of x in $\text{Ln}_x\text{Zr}_{1-x}\text{O}_{2-\frac{1}{2}x}$

At the composition where the P-F transition is situated no discontinuity occurs in the curves of σ , σ_0 and ΔH versus x .

2.2 Description of the conductivity with a structural model

By combination of neutron diffraction [9] and conductivity data [10] the shape of ΔH and σ_0 versus x curves and the decrease of ΔH with increasing cation order can be calculated qualitatively [4]. Values of σ_0 are calculated assuming that in this concentration regions $[V_O^{\bullet}]$ versus x curves reflect σ_0 versus x curves and vice versa. With $[V_O^{\bullet}]$ equals excess $[O_i^{2-}]$ (8b) the calculated values of σ_0 show a good fit with experimental σ_0 values and indicate considerable anion disorder in $Gd_2Zr_2O_7$. Consequently relatively high σ_0 values are achieved for this composition.

Figure 2: Total strain energy (activation energy) for:

- a two step 48f $\rightarrow$ 48f jump through a type B and a type C tetrahedron plane in the P structure
- a two step jump through cation tetrahedra with the average mesh width in the defect F structure

The expression for ΔH contains different terms. In the present model it is assumed that the dominant variable term as a function of x and ordering degree is the strain energy involved during the passage of oxygen through cation tetrahedra planes surrounding this oxygen. The effective mesh width (TMW) of a certain tetrahedron plane is determined by the actual occupation of its corners with small or large cations (fig. 3, e.g. plane ACD). In the P phase a preferential diffusion path can be constructed through cation tetrahedra around 48f sites, characterised by jumps through one plane with a relative large

TMW of type B (2 small Zr and 1 large Ln ion) in combination with one plane of type C (2 large Ln and 1 small Zr ion). See fig. 3.

Figure 3: A two step jump between adjacent oxygen sites M_1 and M_2 (tetrahedron centres) through planes ACD (type B) and CDE (type C). (A,D) = Zr; (C,E) = Ln.

Calculation of the strain energy term E_s as a $f(x)$ with equations:

$$E_s = A r_{tm} (r_{tm} - r_{O2-})^2 \quad (1)$$

and

$$r_{tm} = \frac{a}{\sqrt{6}} - \bar{r}_c \quad (2)$$

with A = constant, a = unit cell dimension, r_{tm} = tetrahedron mesh width and $\bar{r}_c$ = average cation radius, yields fig. 2. It can be concluded that i) E_s is always smaller for P than for F phases for a given value of x and ii) going from F phase ($x = 0.35$) to (100%) P phase ($x = 0.5$) the curve of E_s versus x must pass through a minimum at $x = 0.5$. This can be easily seen by considering that at $x = 0.35$ a fluorite phase exists with a high E_s while at $x = 0.5$ a pyrochlore phase is present with a much lower value of E_s . Intermediate compositions must "step over" from the F curve (at $x = 0.35$) to the P curve (at $x = 0.5$) and this yields the observed extrema. The absence of any discontinuity in σ , σ_0 and ΔH across the P-F phase boundary indicate the gradual development of a hybrid crystal around this phase boundary with E and σ_0 values intermediate between those of the pure P and F phases.

3. STRUCTURE AND CONDUCTIVITY OF $(1-x) Bi_2O_3-xLn_2O_3$ SOLID SOLUTIONS

Maximum conductivity is achieved with the minimum Ln concentration (x_m) which is necessary

for stabilisation of the δ - Bi_2O_3 structure. The value of x_m is dependent on the Ln ionic radius and exhibits a minimum for Er^{3+} ions. A maximum value of $\sigma = 40 \Omega^{-1}\text{m}^{-1}$ (1000K) is achieved for $x = 0.2$ Er [6,8]. Materials with Ln concentrations somewhat larger than x_m show a bend in the activation enthalpy ΔH versus $1/T$ curves for $T > 820\text{K}$ and consequently exhibit a lower, but concentration dependent, ΔH (fig. 4).

Figure 4: The activation energy ΔH for low ($< 820\text{K}$) and high temperatures ($> 900\text{K}$) as a function of composition
 ∇ : Ln = Er; $\square$ = Gd; Δ = Dy; $\circ$ = Y

At $T > 820\text{K}$ neither an indication of a phase change nor long range ordering could be observed by X ray and neutron diffraction, however the expansion coefficient and the Debye Waller factor change. The value of $\sigma_0 \approx 10^5 \Omega^{-1}\text{m}^{-1}$ is independent of x . At $T < 820\text{K}$ the value of σ_0 decreases from $\sigma_0 \approx 10^8 \Omega^{-1}\text{m}^{-1}$ ($x = 0.2$) to $\sigma_0 \approx 10^6 \Omega^{-1}\text{m}^{-1}$ ($x = 0.4$). Preliminary neutron diffraction experiments show a strong modulation in the diffuse background at $2\theta \approx 70^\circ$ ($\lambda = 2.590\text{\AA}$). At $T \approx 770\text{K}$ this peak is split up in two peaks whereas above $T \approx 820\text{K}$ its total intensity decreases strongly (fig. 5). Using a simplified radial distribution function¹⁾ we obtained the distance r_{ij} between pairs of atoms. This result is interpreted in terms of short range ordering in "Er(Ln)-O coordination units" in the solid solution. This is schematically represented in fig. 6 for a small domain. In this domain the Ln ions are ordered and the oxygen ions are displaced towards the Ln ions. The experimentally observed distances of $2.68\text{\AA}$ and $2.90\text{\AA}$ (from the double peak) are identified with the short O-O distances within the "Er-O" unit and the long O-O distances between oxygen belonging to different units respectively (see fig. 6).

Figure 5: Diffuse "peaks" in the neutron diffractogram of $0.8 \text{Bi}_2\text{O}_3-0.2 \text{Er}_2\text{O}_3$

Figure 6: Ordering model for $0.75 \text{Bi}_2\text{O}_3-0.25 \text{Ln}_2\text{O}_3$

- O ions in the (100) plane at $Z = 3/4$
- $\square$ (Bi), $\blacksquare$ (Ln) below respectively above the (100) plane

The average O-O distance in the solid solution equals $2.77\text{\AA}$ (from the single peak). The observed changes of ΔH and σ_0 as a function of T and x can be explained now easily [11] making the following assumptions. ΔH is mainly determined by the bond length and the bond energy of the Ln-O bond whereas the energy necessary to migrate through tetrahedron planes may play some role (high temperatures). In the low temperature region only oxygen in (Bi_3, Ln) tetrahedra is

mobile and determines σ_O . At $T > 820\text{K}$ and x just above the minimum concentration which is necessary to stabilize the fcc phase, short range order and the short Ln-O bond disappears and consequently ΔH decreases compared with its value at low temperature (fig. 4). For $x \geq 0.30$ and low temperatures Ln_2Bi_2 tetrahedra are formed which immobilise the oxygen connected to it, the concentration of mobile oxygen decreases and σ_O is lowered but ΔH is not changed and it is determined by the situation in the (Bi_3Ln) tetrahedra. The variation of ΔH with Ln concentration at high temperature is less straight forward and a combination of larger bond length (larger unit cell) and larger polarisability of the tetrahedraplanes (Bi ions) with decreasing x play a role [11], both leading to smaller ΔH values.

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Note 1: $\rho(r) = r^{-1} \sum s \star i(s) \sin(rs)\Delta s$
 $\rho(r)$ = atomic density as a f(r)
 $s = 4\pi(\sin\theta)/\lambda$, $i(s)$ = normalised intensity corrected for the scattering of the average cell.

Note 2: Excess means: in excess with respect to the occupation which has to be expected on basis of the (Zr rich) composition with formula $\text{Ln}_{2-y}\text{Zr}_{2+y}\text{O}_{7+0.5y}$