

The Effect of Lattice Stresses in Ion Conducting Fluorites and Perovskites

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In a solid oxide fuel cell (SOFC) the electrolyte and the electrodes are composed of oxide ion conducting materials, which usually have either fluorite or perovskite type of structure. In the fluorites, MO_2 , M is a relatively large four-valent cation like Zr^{4+} and Ce^{4+} . In the perovskites, ABO_3 , A is a large ion like La^{3+} or Sr^{2+} , and B is a small ion like Ga^{3+} , Co^{3+} , Mn^{4+} or Ti^{4+} . The species to be transported is oxide ions, or equivalently, oxide ion vacancies. The vacancies are introduced by doping with lower valent cations.

Several structural and thermodynamic parameters such as the critical radius of the bottleneck, which the moving oxide ion must pass, free lattice volume and average metal-oxide bond energy, have been claimed to be determining for the oxide ion conductivity. In this paper we explore the relations among such parameters for fluorite and perovskite oxides by considering their sensitivities to the individual ionic radii. The volume and stability of the oxide ion vacancies is also discussed in terms of ionic radii and lattice stresses.

Previous analyses by van Gool¹, and Pouchard and Hagenmuller² have outlined conditions that should favour high ionic conductivity. They are in short for fluorites and perovskites: 1) high concentration of mobile charge carriers, i.e. oxide vacancies, 2) equal or only slightly different energy of the oxide sites, 3) weak bonding energy resulting in a relatively low melting point, and 4) open paths between oxide ion sites.

Sammells et al.³ claimed that oxide ion conductivity in perovskites could be predicted by: 1) The size of the smallest dimension of the pathway of the oxide ion movement, the critical radius, r_c , as defined by Kilner and Brook⁴, 2) The Goldschmidt tolerance factor⁵, $G_t = (r_A + r_O)/(\sqrt{2}(r_B + r_O))$, 3) The lattice free volume, V_f , defined as the unit cell volume minus the volumes of all constituent ions, and 4) The lattice energy or average metal-oxygen bond energy, E_b , derived via a Born-Haber cycle. We expect a degree of redundancy among these four parameters as argued previously⁶.

We have found by analysing literature data that the most important parameter is the lattice stress due to mismatch between dopant and host cation size. It was pointed out for fluorites by Kilner⁷ and Kim⁸ that matching is important. The matching radius is slightly larger than the host cation. For perovskites we define two matching radii, one for the A-site ion, which is equal to the radius of the oxide ion (1.4 Å) and one for the B-site ion which is estimated to 0.64 Å, slightly bigger than the octahedral holes (the B-sites) in the perovskite lattice⁹. Collected empirical data, which support our conclusion, are given in tables 1 and 2 for fluorites and perovskites, respectively. For fluorites optimised using matching dopants the other parameters seem less important. In the perovskite case the only parameter, which correlates well with the conductivity, is $\Delta r_{m,B} = r_B - r_{m,B}$, where r_B is the radius of the host B-ion, and $r_{m,B}$ is the matching radius on the B-site, estimated to be 0.64 Å.

Table 1. A collection of values relevant to the oxide ion conductivity of $\text{Mh}_{0.8}\text{Md}_{0.2}\text{O}_{1.9}$ at 800°C in mS/cm.

Host Mh^{4+}	Zr^{4+}	Ce^{4+}	Hf^{4+}	Th^{4+}
r of Mh^{4+} , Å	0.84	0.97	0.83	1.05
r_m , Å, Md^{3+}	0.95	1.04	0.94	1.10
Near match Md^{3+} , r in Å	Yb^{3+} 0.99	Gd^{3+} 1.05	Yb^{3+} 0.99	Nd^{3+} 1.11
E_b , MJ/mol O	5.4	5.1	5.6	5.3
M_p MhO_2 , °C	2680	2750	2770	3390
Conductivity ^a	40 ¹⁰	40 ¹¹	30 ¹²	

^a Including the extra resistance from grain boundaries

Table 2. Properties of the B-site ions and parameters that might determine the ionic conductivity in $\text{La}_{0.9}\text{Sr}_{0.1}\text{B}_{0.9}\text{Mg}_{0.1}\text{O}_{2.9}$ and measured ionic conductivities at 800°C in mS/cm. For further details, see Lybye^{13,14,15}.

B Ion	Al^{3+}	Ga^{3+}	Sc^{3+}	In^{3+}
r_B , Å	0.54	0.62	0.75	0.80
$\Delta r_{m,B}$, Å ^a	- 0.10	-0.02	0.11	0.16
r_c , Å ^b	0.897	0.929	1.010	1.046
M_p , °C ^b	2077	1550	2290	
E_b , MJ/mol O ^b	4.7	4.7	4.4	3.9
G_t	1.002	0.964	0.914	0.893
V_f , Å ³	9.7	14.4	20.9	22.8
Conductivity ^c	0.2	95	1.2	0.9

^a $r_{m,B}$ is estimated to be 0.64 Å. ^b for LaBO_3 . ^c incl. gr. br.

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