Ionic and Electronic Conductivity in CaTi$_{1-x}$Fe$_x$O$_{3-y}$ (x = 0.1-0.3)

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Abstract. Electrical conductivity measurements on CaTi$_{1-x}$Fe$_x$O$_{3-y}$ (x = 0.1, 0.2, 0.3) were performed on polycrystalline pressed and sintered tablets using the van der Pauw four point method in controlled atmospheres. The results were interpreted to reflect n-type, ionic and p-type conductivity at different oxygen partial pressures. An increasing iron content increases the number of oxygen vacancies and increases the ionic conductivity at high temperatures, but also increases the tendency of ordering, which suppresses the ionic conductivity at more moderate temperatures. These findings are in accordance with the phase diagram of the system CaTiO$_3$-CaFeO$_2$$_3$ based on X-ray and Mössbauer studies.

1. Introduction

Perovskites, oxides with the general formula ABO$_3$, are being considered for use as electrodes in solid-oxide electrochemical reactors and as oxygen separators. They are also of geophysical importance, as the Earth's lower mantle is composed of Fe-containing MgSiO$_3$ perovskite. The effect of oxygen vacancies on phase transitions, microstructure development and mechanical properties in these perovskite type structures is therefore important in order to understand the geophysical properties of the lower mantle. As MgSiO$_3$ is stable in the perovskite structure only under extreme pressures, Fe-containing CaTiO$_3$ serves as a suitable model substance. It is stable over a large range of temperature and oxygen activity and exhibits interesting conduction behaviours. Point defects in single crystal CaTiO$_3$ were already studied by George and Grace [1] and conductivities in undoped, donor-doped and acceptor-doped polycrystalline CaTiO$_3$ were measured by Balachandran et al. [2]. Iwahara et al. reported high conductivities and oxygen ion transport numbers in air for iron-substituted calcium titanate [3]. Sutija et al. [4] and Dunyushkina et al. [5] reported conductivity measurements in the CaTi$_{1-x}$Fe$_x$O$_{3-y}$ (0 ≤ x ≤ 0.5) system and Xie et al. [6] measured conductivities in the CaTi$_{0.5}$Fe$_{0.2}$O$_{3-y}$ system at different temperatures.

The structural properties of the CaTi$_{1-x}$Fe$_x$O$_{3-y}$ system, reported by Grenier et al. [7], are determined by the ability of iron ions to accept both octahedral and tetrahedral coordination of oxygen. The pure CaTiO$_3$ (x = 0) has at room temperature a perovskite type orthorhombic structure with corner-sharing TiO$_6$ octahedra. In the x = 1 end member CaFeO$_2$$_3$ one perovskite layer of the corner-sharing FeO$_6$ octahedra o alternates with one layer of FeO$_4$ tetrahedra t, forming the otot ordered structure of brownmillerite. This compound can be considered as a non-stoichiometric perovskite AMO$_{3y}$ (A = Ca, M = Fe) corresponding to y = 0.5 and its structure is derived from the cubic perovskite structure, assuming that the oxygen vacancies (one per six anionic sites) are ordered along [101] rows in each second (0k0) plane. For intermediate compositions (0 < y < 0.5), a sequence of (n-l) perovskite-like sheets of MO$_6$ octahedra alternates with one sheet consisting of parallel chains of MO$_4$ tetrahedra. The general formula of such phases is A$_n$M$_{3n-1}$O$_{3n}$ (n ≥ 2, y = 1/n).

A phase diagram of the system CaTiO$_3$-CaFeO$_2$$_3$ (Fig. 1) has recently been published [8] showing, that disordered CaTi$_{1-x}$Fe$_x$O$_{3-y}$ phases exist at high temperatures and iron...
contents $0.1 < x < 0.4$ where oxygen vacancies are randomly distributed in the structure, i.e., five coordinated iron can be observed. The transition between ordered and disordered phases has influence on the concentration and the mobility of mobile defects and can therefore affect the electrical conductivity.

2. Defect Chemistry

Iron substitution in CaTiO$_3$ may be written in terms of Kröger-Vink notation as

$$2\text{CaO} + \text{Fe}_2\text{O}_3 \rightarrow 2\text{CaFeO}_2 + 2\text{Fe}^{2+} + 5\text{O}_2 + V_{O}^{**}.$$  (1)

Considering this equation it is assumed that the electroneutrality condition may be approximated by

$$c_{\text{Fe}^{2+}} = 2c_{V_{O}^{**}} = \text{constant.}.$$  (2)

Oxygen vacancies are in equilibrium with oxygen gas, electron holes $h^*$ and electrons $e^-$:

$$\frac{1}{2}O_2 + V_{O}^{**} = O_{O}^X + 2h^*$$

$$K_3 = \left[ \frac{[V_{O}^{**}}{[O_{O}^X]} \right]^{1/2} p(O_2)^{-1/2}.$$  (3)

$$O_{O}^X = 2e^- + V_{O}^{**} + \frac{1}{2}O_2$$

$$K_4 = \left[ \frac{[e^-]^2}{[V_{O}^{**}}[O_{O}^X]} \right]^{-1}.$$  (4)

To take the entropy appropriately into consideration, we here use site fractions or occupancies instead of concentrations; $[i]$ represents the occupancy of a species $i$ as the concentration $c_i$ divided by the density of sites (or states).

Assuming small defect concentrations, electron hole and defect electron concentrations are obtained as:

$$[h^*] = \left( K_3 [V_{O}^{**}] \right)^{1/2} p(O_2)^{1/4}$$  (5)

$$[e^-] = \left( K_4 [V_{O}^{**}]^{-1} \right)^{1/2} p(O_2)^{-1/4}.$$  (6)

The equilibrium constants $K_i$ can be calculated using the enthalpy and entropy of the reactions:

$$K_i = \exp \left( -\frac{\Delta H_i}{kT} + \frac{\Delta S_i}{k} \right).$$  (6.1)

The total conductivity $\sigma_{\text{tot}}$ is given by the sum of electronic and ionic conductivity

$$\sigma_{\text{tot}} = \sigma_{\text{ion}} + \sigma_{h} + \sigma_{e}.$$  (7)

The conductivity of each particle of type $i$ in an electric field can be expressed by its mobility $\mu_i$ and its concentration $c_i$,

$$\sigma_i = z_i e c_i \mu_i,$$  (8)

where $z_i$ is the charge of the particle and $e$ the elementary charge. The concentrations can be received from the site fractions calculated with eqs. (5) and (6) by multiplying them with the density of sites.

Combining eqs. (7) and (8) with (5) and (6) we get the following equation for the conductivity as a function of the oxygen partial pressure:

$$\sigma_{\text{tot}} = e c_{\text{Fe}^{2+}} \mu_{\text{Fe}^{2+}} + e \left( \frac{1}{2} K_3 c_{\text{Fe}^{2+}} \right)^{1/2} p(O_2)^{1/4} \mu_h$$

$$+ e \left( 2 K_4 c_{\text{Fe}^{2+}}^{-1} \right)^{1/2} p(O_2)^{-1/4} \mu_e.$$  (9)

The equilibrium of generation and recombination of electronic defects

$$n \times p = K_i(T) = K_i^0 \exp\left( -E_g/kT \right),$$  (11)

where $n$ and $p$ are the concentrations of electrons and holes.

![Phase diagram CaTiO$_3$-CaFeO$_2$]