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Phase Stability and Ionic Transference Number of a Mn-Zn Spinel Ferrite

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Abstract. The phase stability region of a MnZn ferrite, $\text{Mn}_{0.54}\text{Zn}_{0.35}\text{Fe}_{2.11}\text{O}_4$, has been determined from the isothermal variation of the total conductivity with oxygen partial pressure at elevated temperatures and its mean ionic transference number via Tubandt-type electrotransport experiments in the entire stability range of the ferrite. The ionic transference number increases with increasing oxygen partial pressure in oxidizing atmospheres and with decreasing oxygen partial pressure in reducing atmospheres, which is in accord with the Frenkel disorder as the majority defect type.

1. INTRODUCTION

The information on the ionic partial conductivities of a ferrite is necessary not only for an economic processing of the ferrite but also for the understanding of the defect structure of ferrites.

In the present work, we have measured the mean ionic transference number of MnZn ferrous ferrite, $\text{Mn}_{0.54}\text{Zn}_{0.35}\text{Fe}_{2.11}\text{O}_4$, via a modified Tubandt-like electrotransport technique in the entire stability range of the phase at elevated temperatures. For this purpose, the phase stability range of the ferrite was first located in situ on the basis of the electrical property-phase stability correlations.

2. EXPERIMENTAL

The total electrical conductivity (σ) and the ionic transference number (t_{ion}) were measured against oxygen partial pressure at 1100, 1200 and 1300 °C on single crystalline ferrite $\text{Mn}_{0.54}\text{Zn}_{0.35}\text{Fe}_{2.11}\text{O}_4$ respectively by a four probe d.c. technique and by a Tubandt-like electrotransport technique. The experimental details is referred to Ref. [1].

3. RESULTS AND DISCUSSION

The total conductivity of the ferrite, which is essentially electronic, is as shown in Fig. 1. According to Yoo and Tuller [2,3], the position where a conductivity isotherm abruptly changes its trends against P_{O_2} corresponds to a phase boundary for a ferrous ferrite system. The stability range of the single phase $\text{Mn}_{0.54}\text{Zn}_{0.35}\text{Fe}_{2.11}\text{O}_4$ is thus immediately established as shown in Fig. 2.

The mean ionic transference number of the ferrite as determined from the anodic volume displacement induced by electrotransport is shown in Fig. 3. As P_{O_2} increases, the mean ionic transference number, t_{ion} , first decreases and then increases with a minimum in between, reflecting a change in conduction mechanisms. By combining with the total conductivity in Fig. 1, one can evaluate the ionic partial

conductivity of the ferrite as a function of T and P_{O_2} . Since the total conductivity is very weakly dependent on P_{O_2} as shown in Fig. 1, an ionic-conductivity isotherm varies with P_{O_2} essentially in the same way as t_{ion} . Assuming the ionic mobilities are independent of P_{O_2} , such a V-shaped variation may best be represented as

$$t_{ion} = t_{ion(V)}^0 (P_{O_2}/atm)^{2/3} + t_{ion(I)}^0 (P_{O_2}/atm)^{-2/3} \quad (1)$$

where $t_{ion(V)}^0$ and $t_{ion(I)}^0$ are the transference number of cation vacancies and interstitials corresponding to $P_{O_2}=1atm$, respectively. Eq. (1) is in accord with the Frenkel disorder as the majority defect type of the spinel ferrite. An appreciable deviation of t_{ion} from an ideal $-2/3$ slope in the lower P_{O_2} regime is attributed to an electromigration-induced unmixing of the cations[4].

Fig. 1. Isotherms of total conductivity, σ_{ion} , for a ferrite composition of $Mn_{0.54}Zn_{0.35}Fe_{2.11}O_4$. The P_{O_2} regions bounded by the characteristic points are denoted by the Roman numerals I-III on the 1100°C isotherms as an example.

Fig. 2. Phase stability diagram of a ferrite composition of $Mn_{0.54}Zn_{0.35}Fe_{2.11}O_4$ as derived from Fig. 1.

Fig. 3. Ionic transference number, t_{ion} , of the ferrite spinel $Mn_{0.54}Zn_{0.35}Fe_{2.11}O_4$ against oxygen partial pressure at different temperatures. The solid lines are the best fitted to Eq. (1).

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