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# Rare earth oxide doping in oxide cathodes

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## Abstract

The effect on life performance and poisoning with $O_2$ by doping oxide cathodes with rare earth oxides and pseudo rare earth oxides, notably yttria, is qualitatively explained in terms of electrolysis of BaO during emission of electrons. Doped cathodes show less electrolysis and consume therefore less Ba during life: consequently, doped cathodes have a better life performance. However, the lower Ba-production makes doped cathodes more sensitive to oxygen poisoning. The experimentally found relation between conductivity and yttria concentration was the motive to propose a new model for the crystal imperfections in BaO. In this new imperfection model most $Y^{3+}$-ions will combine with barium vacancies, therefore, the increase of the conductivity is modest and also the effect on the position of the Fermi level is modest. By assuming a combination of bulk and surface conductivity, the agreement between experiment and theory can be improved further.

*Keywords:* BaO; Yttria; Electrolysis; Electron emission; Crystal imperfection; Schottky defect

## 1. Introduction

New technologies, such as invar shadow mask material and improved oxide cathodes have enabled a considerable improvement of the picture quality of CRTs in the 1980s and 1990s. Doping of the emitter material of oxide cathodes with rare earth oxides was a major improvement, since it allowed the application of higher cathode loads [1–4].

The improvement of the life performance of oxide cathodes by mixing $(Ba,Sr)CO_3$ powder with scandia powder has been described for the first time by Saito et al. [1,2]. They noticed a substantial reduction of the interfacial layer between cathode nickel and oxide coating. This finding was quite unexpected, since Gorman had not found any improvement of the initial emission by doping of (Ba,Sr)O with rare earth oxides in concentrations of 100–500 ppm [5]. Gorman expected that rare earth dopes were shallow donors and would lower the work function for electron emission. That is not the case. Also Zalm [6] indicated that impurities, which give rise to donor centers in (Ba,Sr)O, are detrimental for good emission. Based on a model of crystal imperfections in BaO he recommended dopes, such as alkali metals to promote p-type conduction. Neither Gorman nor Zalm have described life tests with oxide cathodes, doped with trivalent ions.

Derks [3] showed that by decreasing the grain size of the added rare earth oxides best lifetime results were obtained by using smaller amounts of these materials. These findings led to the idea that only a small amount of rare earth oxide (yttria, scandia, europia and other oxides) dissolves in the (Ba,Sr)O-grains during decomposition of the carbonates and subsequent cathode activation and that doping (dissolving rare earth ions in the (Ba,Sr)O lattice) is enhanced by reducing the rare earth oxide grain sizes. Indeed, it was found that only very small molecular concentrations of rare earth oxides in the (Ba,Sr)O led already to significantly improved life-test results [3]. Moreover, Derks observed that oxide cathodes doped with either yttria or europia showed about two times lower Ba evaporation rate during life tests [7].

Hayashida et al. [4] reported good lifetime results with group III, IV and V dopants, indicating that the positive effect of doping is not exclusively connected to pseudo rare earth (Sc and Y) and rare earth oxides. They also found a positive correlation between electron emission and conductivity after life tests.

Kobayashi and Nakagawa [8] conducted life tests with $Eu_2O_3$-doped and non-doped cathodes without drawing current. They showed that under these conditions doped cathodes performed

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better. They explained their results in terms of a two-step process: Mg from the base metal is first reducing the rare earth oxide and in the next step the rare earth metal is reducing BaO to yield Ba. Although this model could be thermodynamically allowed for Eu, it is not for yttria, since Mg from the cathode nickel cannot reduce yttria at 1000 K or higher temperatures, because of a positive ΔG for the reaction $Y_2O_3 + 3Mg \rightarrow 3\ MgO + 2Y$. So, we have to reject the Kobayashi–Nakagawa model, because it is not including the pseudo rare earth elements.

Recently, we have suggested that the positive effect of rare earth oxide doping is caused by the increased electronic conductivity of (Ba,Sr)O [9,10]. The idea is that a high electronic conductivity of the emitter layer reduces the electrolysis of BaO. This has a positive effect on the life performance; however, at the same time it increases the sensitivity for poisoning with oxygen. It is the purpose of this study to adjust the imperfection model of (Ba,Sr)O in such a way that it could explain the experimentally observed relationship between conductivity and dopant concentration.

## 2. Effect of doping

Fig. 1 shows the conductivity of a (Ba,Sr)O layer after 24 and 1500 h of operation as a function of the square root of the of the $Y_2O_3$ concentration [10]. This figure shows that the relation between conductivity σ and the concentration of yttrium [Y] in (Ba,Sr)O can be written as:

$$\sigma = \sigma_0 + C_1[\mathrm{Y}]^n, \qquad (1)$$

where $\sigma_0$ is the conductivity of non-doped (Ba,Sr)O, the exponent $n = 0.5$, being slightly smaller than 0.5 for larger concentrations and $C_1$ is a proportionality constant.

Gaertner et al. [11] have shown that doping of (Ba,Sr)O with yttria increases the sensitivity for poisoning with $O_2$. The results of their poisoning experiments are represented in Fig. 2. The vertical axis in this figure indicates the ratio between the current $I$ after oxygen admission, and the initial current $I_0$ before poisoning. It can be seen that the larger the dope concentration, the larger the sensitivity for poisoning.

The same observation was made for scandia doped oxide cathodes by Chou et al. [12]. These results contrast to some extent with the improved lifetime of the oxide cathode by increasing the dope concentration.

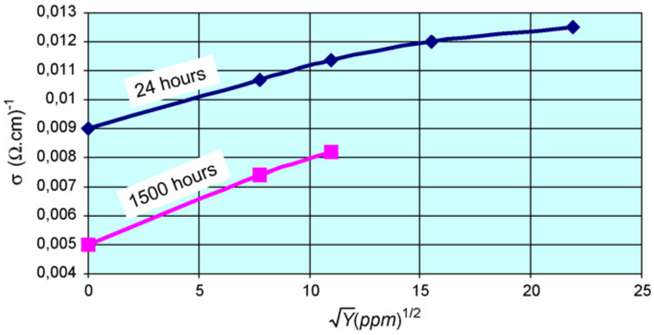

Fig. 1. Electronic conductivity of the oxide coating at 1050 K as a function of square root of yttria concentration($\sqrt{\mathrm{Y}}$)after 24 and 1500 h.

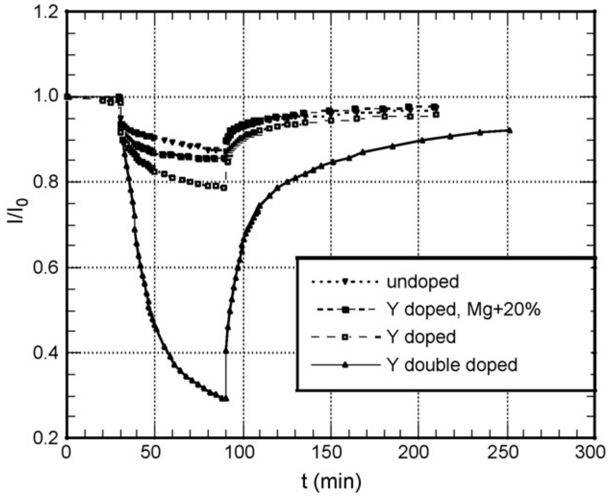

Fig. 2. Poisoning of the emission by oxygen. The vertical axis in this figure indicates the ratio between the actual emission-current $I$ after oxygen admission and the initial emission $I_0$ before poisoning.

A new explanation for the effect of $O_2$ on doped oxide cathodes has been presented in Ref. [9]. The underlying idea is to consider the cathode as an electrochemical cell with (Ba,Sr)O as an electrolyte, which exhibits both electronic and ionic conductivity. Although, the electronic conductivity is at least six orders of magnitude larger than the ionic conductivity, the mere existence of the latter is the cause for electrolysis. Electrolysis of BaO can only occur if the voltage difference $V_O$ over the oxide layer, as shown in Fig. 3, is larger than the decomposition voltage of BaO, being 2.3 V at 1050 K.

In non-doped oxide cathodes $V_O$ will be larger than in doped cathodes, hence, electrolysis in non-doped cathodes will be larger than in doped cathodes. When electrolysis occurs, the generation of Ba is larger than when Ba is only formed by the exchange reaction from the activators in the cathode nickel. This model explains why doped cathodes have a longer endurance, i.e. show less exhaustion of Ba during life and allow slightly larger cathode loads during life.

However, since electrolysis is suppressed in doped cathodes and less Ba is generated during current drawing, the sensitivity for poisoning with $O_2$ increases.

Figs. 1 and 3 also explain the life tests of Kobayashi and Nakagawa [8] in a qualitative way. If $Eu_2O_3$ behaves in the

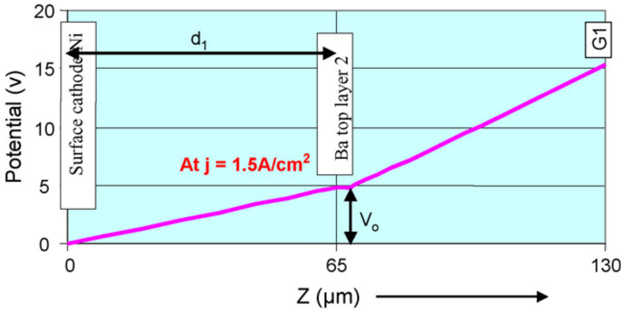

Fig. 3. Voltage difference $V_O$ over the oxide layer due to current drawing.