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## Thermoluminescence and sintering of high-purity $\alpha$ -alumina doped by Zr, Th and Ca

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### Abstract

Two parameters were studied upon the thermoluminescence (TL) properties and the sintering behaviour of  $\alpha$ -alumina: the atmosphere during the heat treatment used to transform  $\gamma$ - $\text{Al}_2\text{O}_3$  into  $\alpha$ - $\text{Al}_2\text{O}_3$  and the doping by Zr and Th. It appears that a reducing atmosphere tends to delay the sintering compared with the oxidising atmosphere until 1600°C. Above this temperature, the shrinkage starts again, which is attributed to a change in the mechanism of sintering of  $\alpha$ - $\text{Al}_2\text{O}_3$ .

The concentration of point defects created through charge compensation as the tetravalent dopant integrates into the host material increases until the solubility's limit of the dopant in alumina is reached. Above this concentration, the peaks on the TL glow curves stabilize, and the specific area of the powders stabilizes at its higher value. As a consequence, the final densities obtained for  $\alpha$ - $\text{Al}_2\text{O}_3$ :Th and  $\alpha$ - $\text{Al}_2\text{O}_3$ :Zr are the best when the solubility's limit of the dopant in alumina is reached.

### Keywords:

*$\alpha$ -Alumina; Thermoluminescence; Sintering; Chemical compounds, Alumina, Thorium, Zirconium*

### I. Introduction

The thermoluminescence (TL) properties of alumina have been widely studied since they were suggested for dosimetry applications [1] and [2]. In order to improve  $\text{Al}_2\text{O}_3$  as a thermoluminescent dosimeter material, the mechanisms involved in the TL phenomena have been investigated, particularly the point defects that are the origin of the light emission. In previous papers, the effect of the atmosphere during the heat treatment used to transform  $\gamma$ -alumina into  $\alpha$ -alumina and the doping by thorium were studied from the TL properties [3]. This has allowed the identification of the nature of the point defects involved in the TL peaks observed in our samples [4].

The aim of this work is to go one step further and correlate these structural defects with the reactivity of the powder, especially its sintering behaviour. It will focus chiefly on two parameters: the atmosphere of calcination and the doping by two tetravalent cations:  $\text{Zr}^{4+}$  and  $\text{Th}^{4+}$ .

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## II. Experimental procedure

### II.1. Preparation of the $\alpha$ -alumina powders

The  $\alpha$ -alumina samples studied were prepared using a commercial ultra-pure  $\gamma$ -alumina powder (Baïkowski CR140) obtained by thermal decomposition of ammonium alum ( $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ). The doping is performed through the impregnation of the  $\gamma$ -alumina powder by an alcoholic solution of zirconium or calcium chloride or of thorium nitrate [5]. A further thermal treatment allows decomposition of the solvent and the salts (drying at  $100^\circ\text{C}$  for 24 h) and diffusion of the doping species inside the host material ( $600^\circ\text{C}$  for 24 h). The doped  $\gamma$ -alumina is then transformed into doped  $\alpha$ -alumina by a calcination at  $1450^\circ\text{C}$  for 2 h under a pure gas flow ( $\text{O}_2$  or  $\text{Ar}+2\% \text{H}_2$ ).

### II.2. Characterisation by TL

TL in solids is light emission that takes place during the heating of a solid after absorption of energy from radiation.

The presence of irregularities within the solid (vacant lattice sites, impurities, or other lattice defects) creates structural defects in the host material. These defects, called 'luminescent centers,' create discrete energy states within the forbidden gap of the material, and these new states can be of electron and hole type. The states lying on the top of the valence band possess a greater ability to capture holes (n) whereas those near the bottom of the conduction band will trap electrons (m) (Figure 1a). In the middle of the gap, recombination centers are found (r) where two carriers of opposite sign can recombine releasing energy as photons (luminescence) or phonons (non-radiative recombination) [6] and [7].

The TL phenomenon can be divided in two steps:

- ❖ The irradiation of the solid produces free electrons and holes which can travel through their respective band until they are captured by a trap (Figure 1b); and
- ❖ The heating of the solid gives sufficient energy for the electrons to be released (a). Then they may recombine radiatively or not at a hole-activated luminescent center (b) (Figure 1c).

The light intensity is plotted as a function of the temperature and the resulting graphs are called glow curves. The maxima of those glow curves are functions of various energy level traps.

Since it has been studied,  $\alpha$ -alumina has exhibited 11 peaks which are classified according to their temperature from 105 to 910 K [8]. In this study, we will focus on the D' and E' peaks. The D' peak appears at 470 K and is attributed to an electron trap [4]. The E' peak appears at 630 K and is strongly influenced by its recombination center:  $\text{Cr}^{3+}$  [4].

The TL measurements are obtained with 3 mg of  $\alpha$ -alumina spread on a cupel by sedimentation in acetone. Irradiations are provided by an X-ray generator (Cu anode, 10 mA, 45 kV for 2 min) and the TL measurements are taken for temperatures ranging from room temperature to  $500^\circ\text{C}$  at a heating rate of  $1^\circ\text{C}/\text{s}$ . TL emission is detected by a photomultiplier whose wavelength ranges from 300 to 600 nm. The high-voltage alimentation was 1.1 kV for  $\text{Al}_2\text{O}_3:\text{Zr}$  and 0.65 kV for  $\text{Al}_2\text{O}_3:\text{Th}$ .

### II.3. Other techniques

The dilatometer used for this study is a Setaram TMA 92 and the  $\alpha$ -alumina samples are pressed at 150 MPa for 2 min in a steel die without any binder or lubricant. The specimens are 8 mm diameter and  $\sim 5.5$  mm thick. The sintering is carried out to  $1700^\circ\text{C}$  under a gas flow ( $\text{N}_2+\text{O}_2$ : 80%/20%) at a heating rate of  $2^\circ\text{C}/\text{min}$ .

The specific areas were measured using the BET method with the ASAP 2000 Micromeritics apparatus.

### III. Results

#### III.1. TL

Figure 2 compares the TL intensities obtained for three  $\alpha$ -alumina doped by 25 and 5000 ppm of thorium, and by 5000 ppm of zirconium. Each measurement was conducted using the same high-voltage alimentation: 0.65 kV. The light emission is the most intense for thorium, whereas the zirconium exhibits a TL intensity weaker than the sample doped with the lowest concentration of thorium (25 ppm). The  $\alpha$ -alumina doped at 5000 ppm of  $\text{Th}^{4+}$  is 15 times greater than for the  $\alpha$ -alumina doped at 5000 ppm of  $\text{Zr}^{4+}$ . So, it can be concluded that the concentration in point defects is higher for the doping by thorium than for the doping by zirconium.

Figure 3 and Figure 4 show the TL intensities *vs.* concentration in thorium or zirconium for the two peaks revealed in the glow curves. For both dopants, the intensity of the D' peak is always greater than the E' peaks' intensity. It must be noted that the doped  $\alpha$ -alumina in this example is calcined under reducing atmosphere. As already mentioned, the intensity of the E' peak strongly depends on its recombination center. But under a pure gas flow of Ar+2%  $\text{H}_2$ ,  $\text{Cr}^{3+}$  ions are reduced most likely to  $\text{Cr}^{2+}$  ions, which explains the decrease of the E' peak's intensity [4].

The evolutions of the intensities are different for the two dopants. In the case of zirconium, the evolution is almost the same for the two peaks. First, they increase to reach a maximum for 500 ppm of  $\text{Zr}^{4+}$ , and then they decrease a little and then stabilize. Considering now  $\text{Th}^{4+}$ , the two peaks increase as the amount of thorium increases up to a value between 500 and 1500 ppm. But above 1500 ppm, the E' peak stabilises whereas the D' peak's intensity still increases slowly. TL is a very sensitive technique for analysing defect structure in solids, even at low concentrations. So any variation of a TL peak implies a variation in the concentration of point defects in the host material. Assuming this, it can be concluded that the zirconium integrates into  $\alpha\text{-Al}_2\text{O}_3$  until 500 ppm. Above this concentration, it does not integrate any more into alumina; instead, it precipitates into the baddeleyite form  $\text{ZrO}_2$  as shown through RX diffractometry. This explanation is still valid for the E' peak of the alumina doped by thorium because at 1500 ppm, RX diffractometry shows a second phase in the solid: the thorianite  $\text{ThO}_2$ . The increase of the D' peak above 1500 ppm suggests that a small part of thorium still inserts into  $\alpha$ -alumina and creates  $V_{Al}^{\prime\prime\prime}$  through charge compensation, which is assumed to be the trap for this peak in  $\alpha$ -alumina [4].

#### III.2. Dilatometry: effect of the atmosphere

Figure 5 and Figure 6 show the rate of shrinkage during the dilatometry measurements for undoped aluminas and for  $\alpha$ -aluminas doped by 250 ppm of zirconium, each calcined under oxidizing or reducing conditions.

Two observations are valid for the two atmospheres: First, the process for doping the samples is disadvantageous to the sintering; and secondly, the doping by zirconium accelerates it after 1500°C. A delay of 200°C at the beginning of shrinkage between the undoped and doped aluminas for each calcination condition has indeed been observed. This is explained through the agglomeration phenomenon that occurs after the impregnation with an alcoholic solution [9], [10] and [11]. But as the temperature increases, the rate of shrinkage becomes higher for the doped alumina, which is attributed to the doping with 250 ppm of  $\text{Zr}^{4+}$ .

Considering only the undoped aluminas now, a reducing atmosphere during the calcination delays the maximum shrinkage's rate by 50°C. But while the rate of shrinkage decreases for the alumina calcined under oxidizing atmosphere, a second peak of shrinkage appears for the reducing atmosphere. This second peak is attributed to a change in the mechanism of sintering of  $\alpha\text{-Al}_2\text{O}_3$  and is still being studied. But it can be concluded that reducing conditions during the transformation from  $\gamma\text{-Al}_2\text{O}_3$  to  $\alpha\text{-Al}_2\text{O}_3$  hinders shrinkage until 1600°C, where above this temperature, the shrinkage starts again. The only difference between the two undoped alumina powders is the concentration of point defects caused through the atmosphere during the calcination. The main differences observed on the glow curves of those alumina concern the B peak whose recombination centers are oxygen vacancies [3]: its

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intensity increases with the reducing character of the calcination's atmosphere, *i.e.* with the concentration in VO. Comparing this evolution with the second peak observed during the sintering of these samples, it is assumed that the VO created in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> under reducing conditions plays an important part in the second stage of sintering.

### III.3. Dilatometry: effect of the dopants

Figure 7 and Figure 8 show the green densities and the final densities vs. concentration of zirconium or thorium for the doped  $\alpha$ -alumina calcined under reducing atmosphere. It is clear that the green densities are, to some extent, influenced by the concentration of dopants, whereas the final densities strongly increase initially before reaching a maximum at 500 ppm for Zr<sup>4+</sup> and 500 ppm for Th<sup>4+</sup>. This evolution is identical with the one obtained as the specific area reported vs. the dopant's concentrations in Figure 9. It is concluded that the point defects created through the doping by both tetravalent dopants stabilise the specific area of  $\alpha$ -alumina, and the higher it is, the better shrinkage obtained. Thereafter, the second phase precipitates: ZrO<sub>2</sub> for the doping by 500 ppm of zirconium and ThO<sub>2</sub> for the doping around 1000 ppm of thorium. So for those two aluminas, the evolution of the TL peaks is limited by the solubility of the dopant in the structure of  $\alpha$ -alumina.

It can also be mentioned that the final densities are greater for the doping by thorium. This can be explained through the TL intensity for the doped alumina: the peak's intensity is higher for the doping by thorium compared with the doping by zirconium. It means that the point defects created are in a higher concentration in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:Th<sup>4+</sup>; so, the stabilization of the specific area appears at a higher value. As a consequence, the final densities are greater for the doping by thorium than by zirconium.

## IV. Conclusion

The atmosphere during the calcination to transform  $\gamma$ -alumina into  $\alpha$ -alumina influences the presence of point defects in the structure and the reactivity of  $\alpha$ -alumina. So a reducing atmosphere first delays the sintering compared with oxidising conditions; but above 1600°C, the mechanism of sintering changes and the shrinkage begins again.

Th<sup>4+</sup> and Zr<sup>4+</sup> give rise to the same peaks on the glow curves, but the intensity is higher for Th<sup>4+</sup>. It means that the point defects involved in the TL phenomena are the same, but not of the same concentrations. It is astonishing to observe for both dopants that the doping promotes shrinkage in the case of very low concentrations, in fact, until the cation integrates into the host material. Thereafter, the TL intensity stabilises as do the specific area and the final density.

Some other experiments are still being conducted in our laboratory concerning the doping of alumina by calcium chloride. The conclusions relating to the TL phenomena are very different from those from the tetravalent dopants; but as the hibbonite precipitates (the CA6 form), a new peak appears, which can be attributed to CA6. The sintering behaviour of the  $\alpha$ -alumina doped by calcium is more difficult to explain than that observed for the doping by tetravalent dopants. Nevertheless, it is supposed that a liquid phase appears during the sintering, which cannot be connected to the point defects seen through the TL technique.

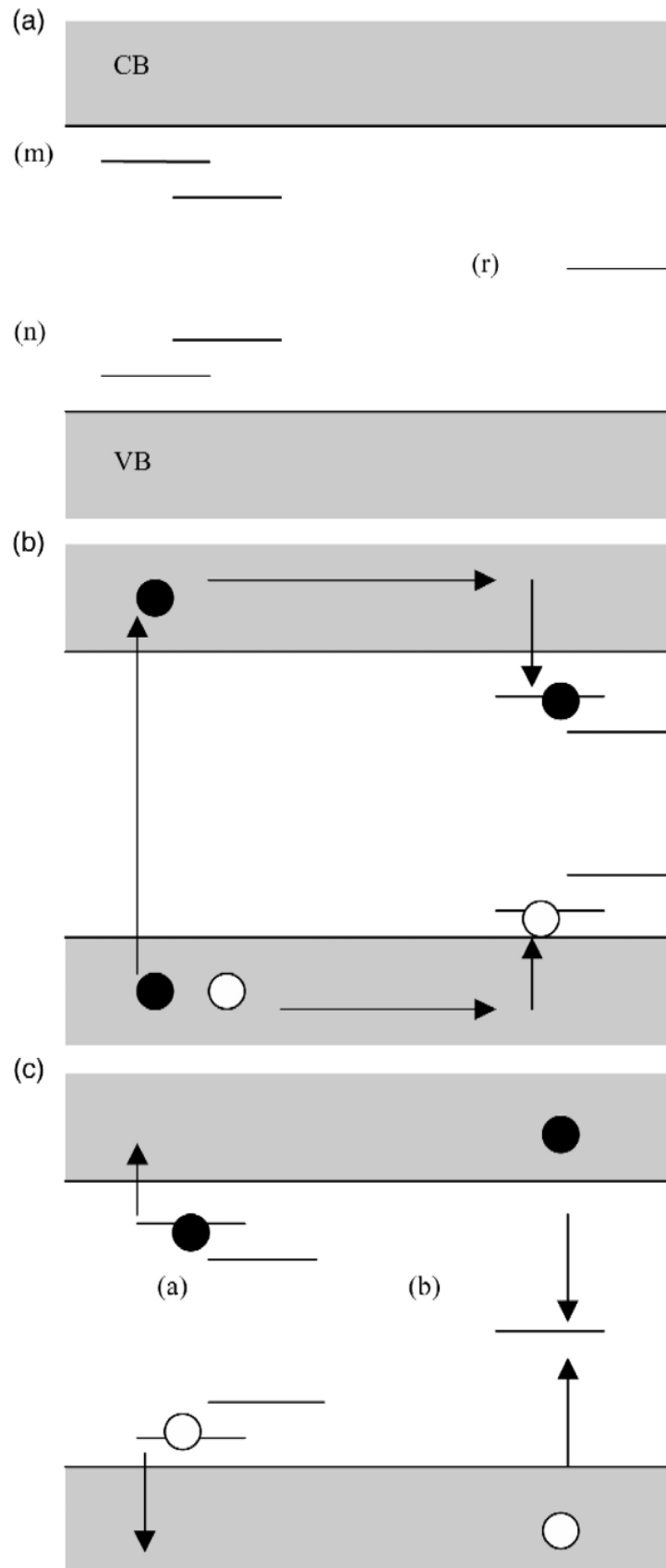
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**Figures**



*Figure 1: (a) Point defects involved in the theory of the TL. (b) First step of theory of the TL. (c) Second step of the theory of the TL.*

TL intensity (a.u.)

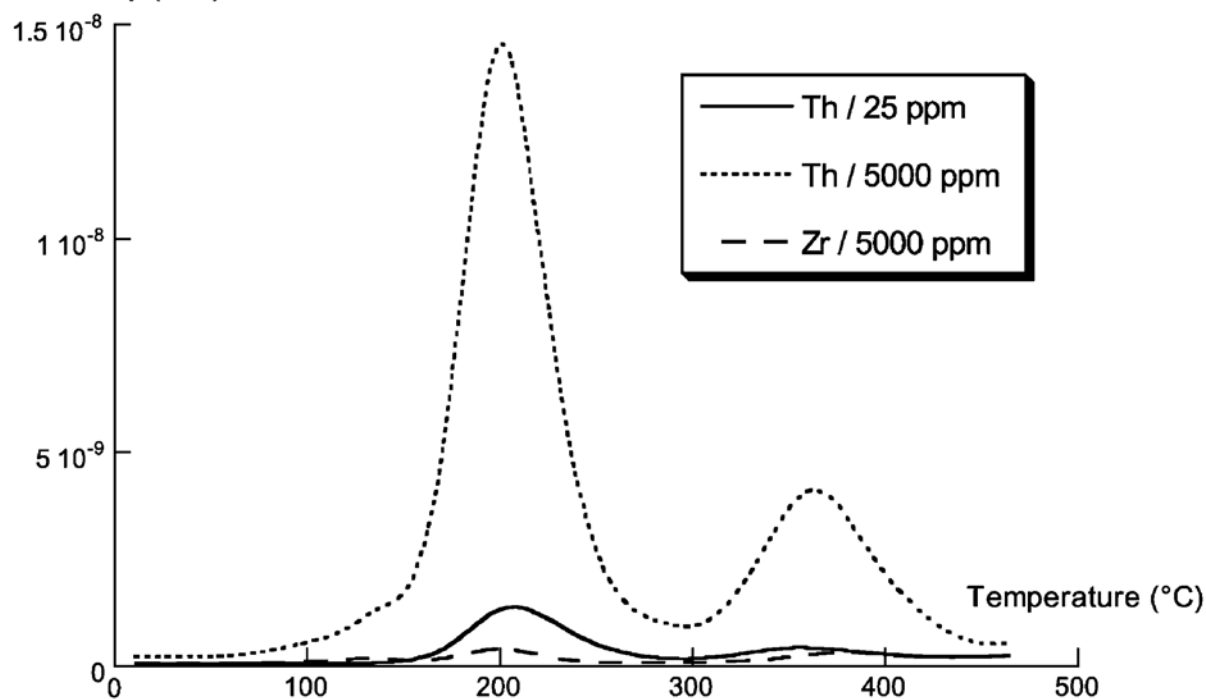


Figure 2: TL intensity for three doped  $\alpha$ -alumina calcined under reducing conditions ( $\text{Ar}+2\% \text{H}_2$ ).

TL intensity (a.u.)

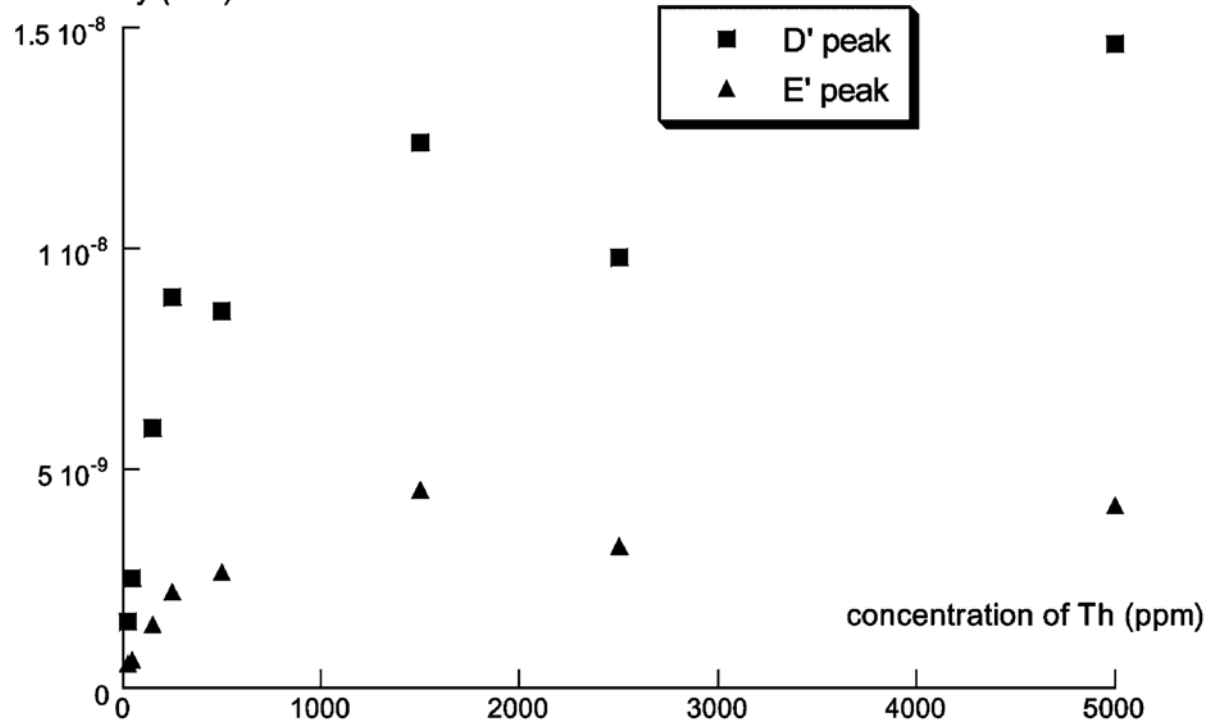


Figure 3: TL intensity vs. the concentration of thorium. Samples calcined under  $\text{Ar}+2\% \text{H}_2$ .



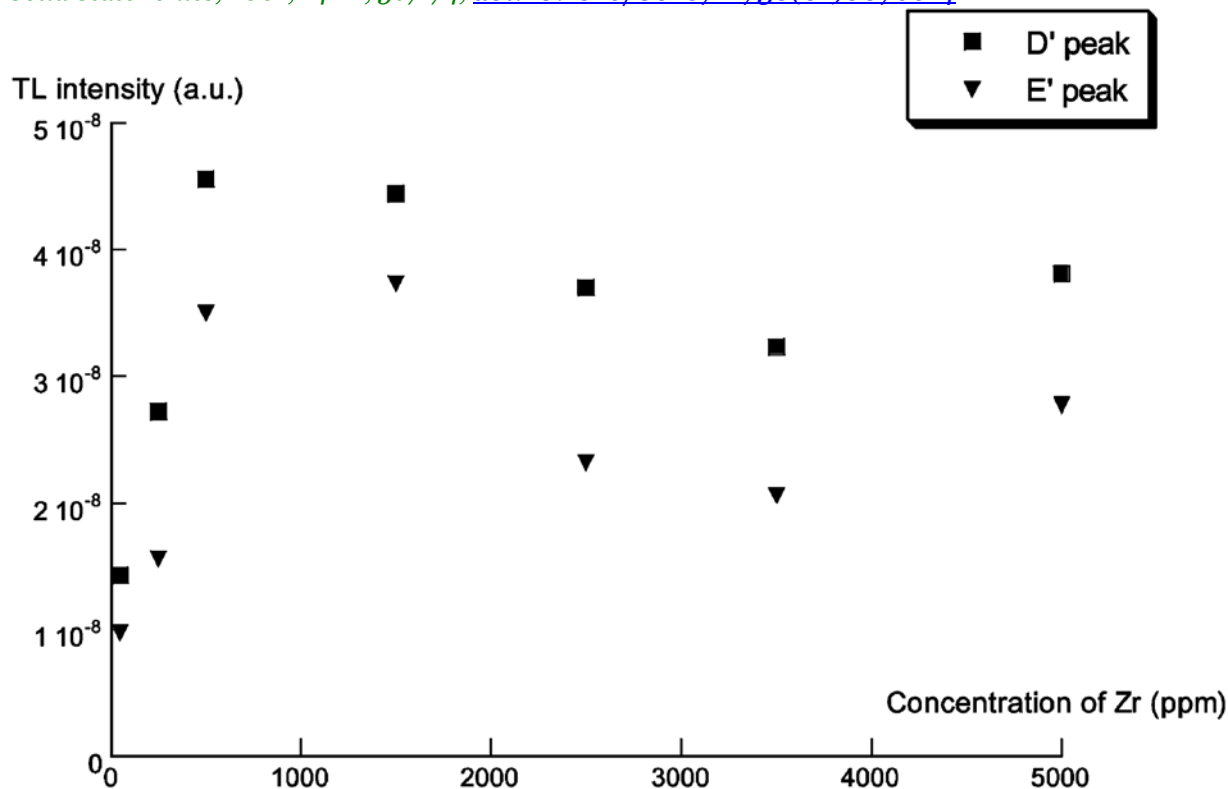


Figure 4: TL intensity vs. the concentration of zirconium. Samples calcined under Ar+2% H<sub>2</sub>.

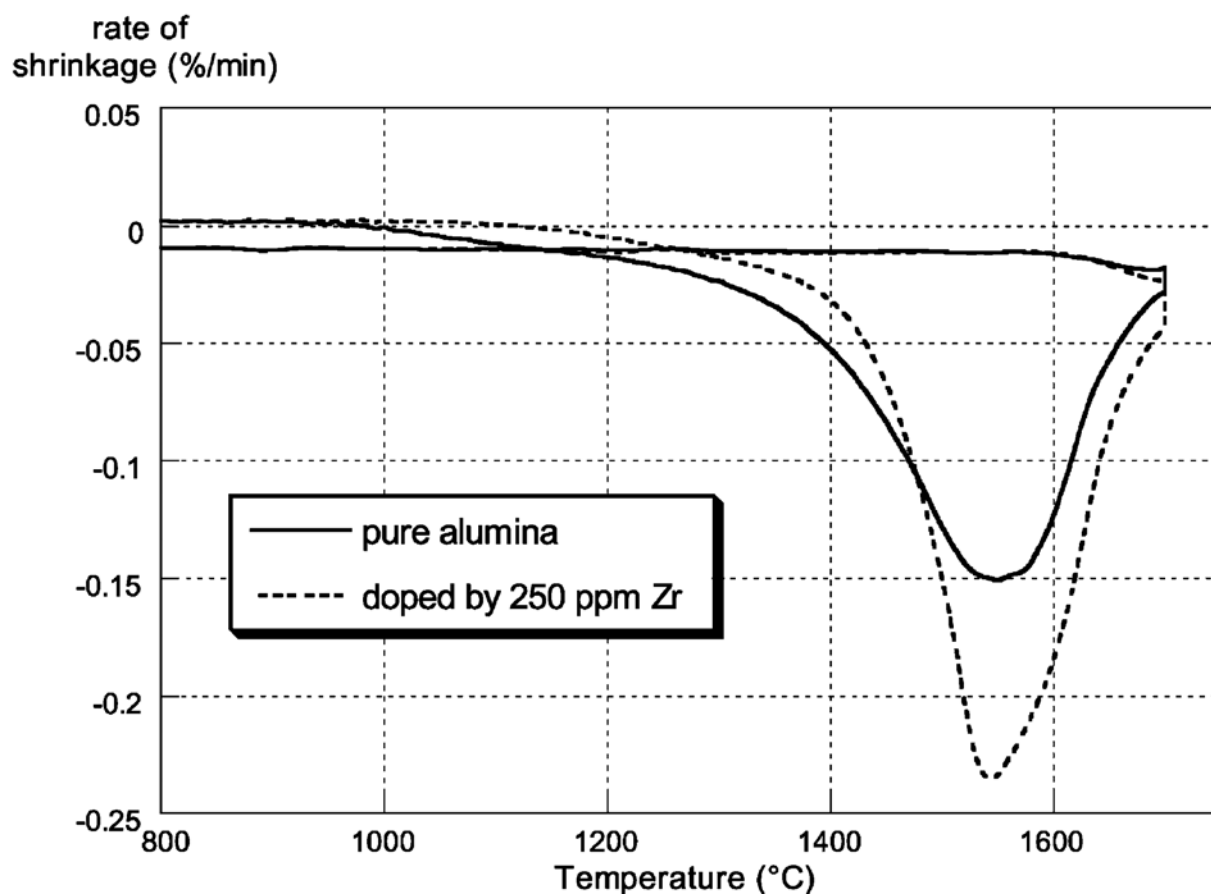


Figure 5: Rate of shrinkage of pure alumina and alumina doped with 250 ppm of zirconium. Samples calcined under O<sub>2</sub>.

rate of  
shrinkage (%/min)

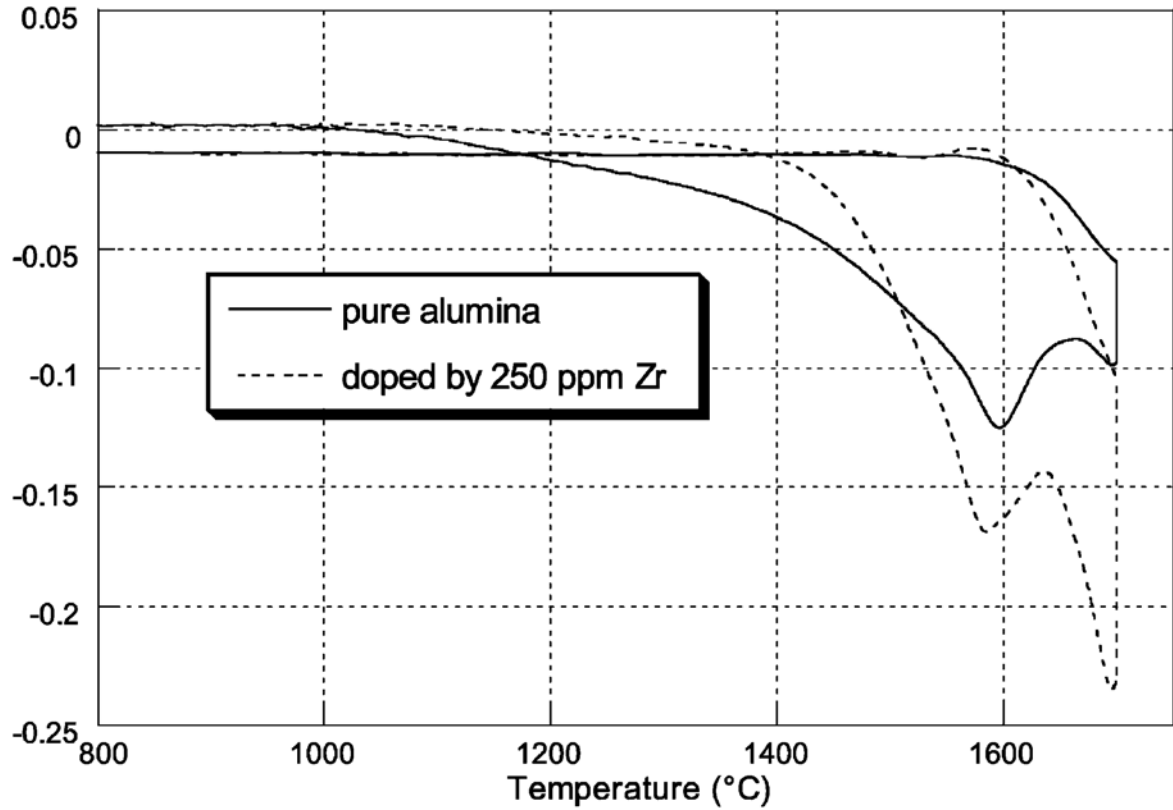


Figure 6: Rate of shrinkage of pure alumina and alumina doped with 250 ppm of zirconium. Samples calcined under Ar+2% H<sub>2</sub>.

Density (%)

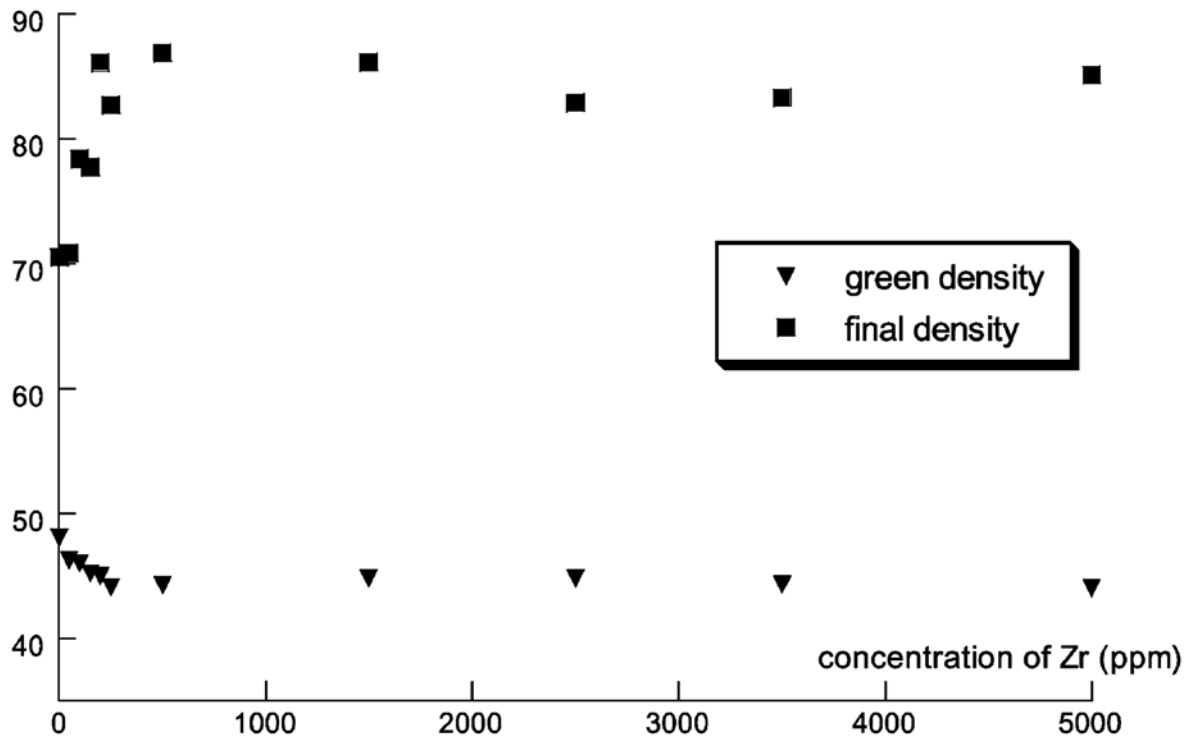


Figure 7: Green and final densities of zirconium-doped  $\alpha$ -alumina. Samples calcined under Ar+2% H<sub>2</sub>.

Density (%)

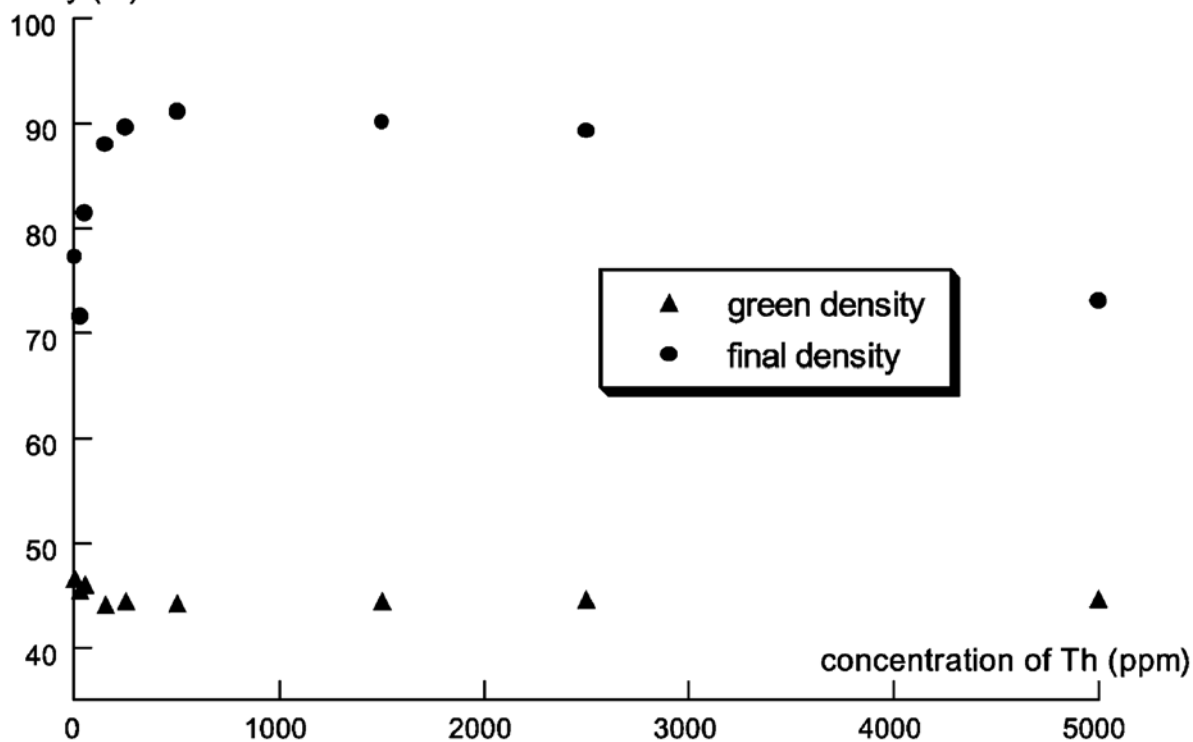


Figure 8: Green and final densities of thorium-doped  $\alpha$ -alumina. Samples calcined under Ar+2%  $H_2$ .

specific area ( $m^2/g$ )

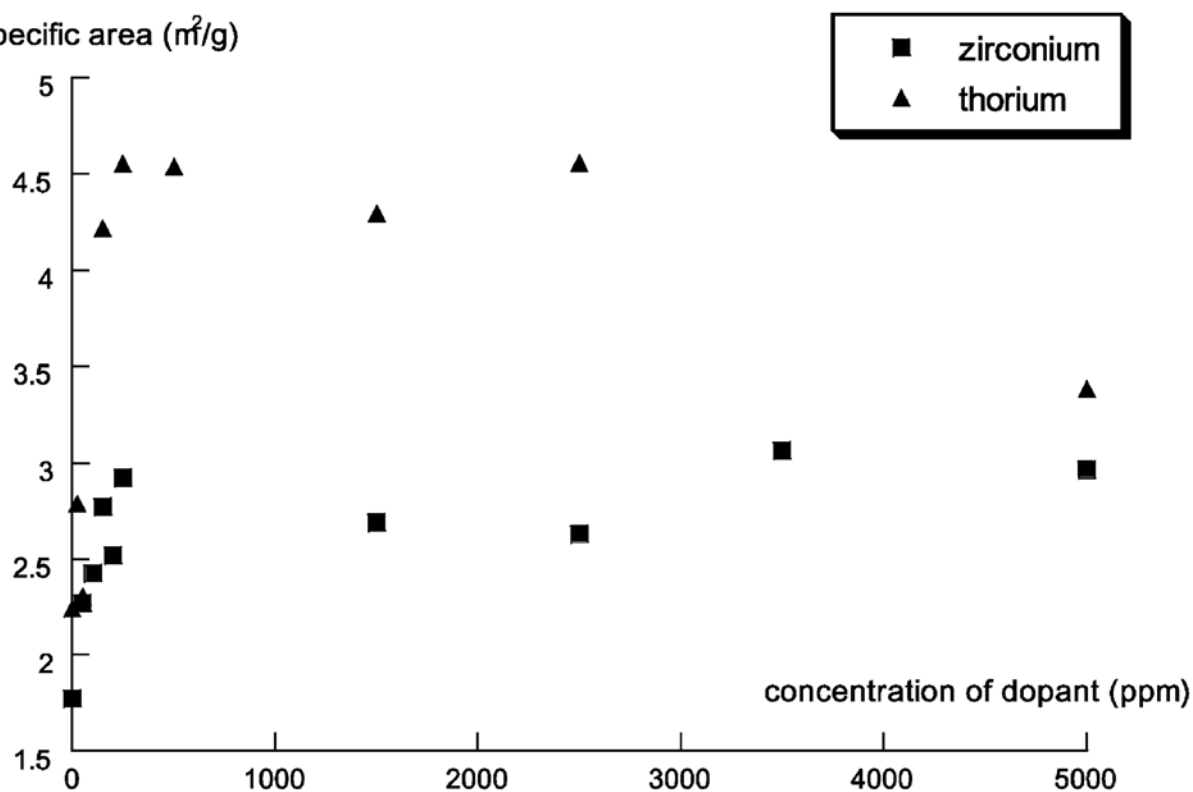


Figure 9: Specific area vs. the concentration in Zr or Th. Samples calcined under Ar+2%  $H_2$ .