Point defects in alumina studied by thermoluminescence

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POINT DEFECTS IN ALUMINA STUDIED BY THERMOLUMINESCENCE

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ABSTRACT

α-alumina powders have been produced by thermal treatment under controlled atmosphere of highly pure γ-alumina. The influence of the atmosphere and the addition of dopants (Mg^{2+}, Cr^{3+}, Th^{4+}) were studied by thermoluminescence (TL). TL is a technique which gives information about point defects. It allowed to reveal the presence of oxygen and aluminium vacancies. The sintering of undoped powders prepared under different atmosphere was investigated by dilatometry. Powders prepared under oxygen densify more rapidly (at least below 1600°C). It is suggested that a higher aluminium vacancy content improves aluminium diffusion.

INTRODUCTION

Point defects are involved in many aspects of research on solids. They act for example as colour centres in optical phenomenon, they are implicated in diffusion mechanisms to help atoms to migrate...Electrical conductivity is widely used to characterise point defects. The aim of our work is to develop a process in order to produce alumina for dosimetry applications. This led us to study point defects by thermoluminescence (TL). In this paper we describe the TL technique, and we report results obtained for pure and doped α-alumina powders. The sintering behaviour of pure alumina powders is interpreted in term of point defects.

EXPERIMENTAL PROCEDURE

γ-alumina is transformed in α-alumina powder by a thermal treatment at 1450°C under controlled atmosphere (oxygen, nitrogen or hydrogenated argon). γ-alumina is a commercial powder (supplied by Baikowski Chimie, France) synthesised by thermal decomposition of ammonium alum ($NH_4Al(SO_4)_2.12H_2O$), a process used in industry to produce highly pure alumina (>99.98% Al_2O_3). Doped α-alumina are also produced by impregnation of the γ-alumina followed by the same thermal treatment as for pure powders.

Powders are analysed by thermoluminescence (TL). TL[1,2] is a physical property existing in insulators and semi-conductors. These solids are capable of emitting light in the visible range when they are heated to an appropriate temperature after having been pre-excited by some suitable radiation (UV, γ, X-ray). The emitted light is due to point defects usually called colour centres. Figure 1 describes this phenomenon. The introduction of defects and impurities creates energy levels within the energy gap of the host material. Absorption of light during irradiation will excite electrons and holes that can be trapped to

the defect states. The detrapping of electrons from the occupied traps is possible by supplying thermal energy. These carriers then move in the conduction band to a recombination centre resulting in the emission of light. The plot of luminescence intensity as a function of the rising temperature exhibits one or more peaks. The temperature of one peak depends on the potential barrier E of the trap, so on the defect involved.

The powder is deposited in a holder; possibly cooled down to liquid nitrogen temperature, irradiated (X-ray radiation, λ=1.5406Å, 18 Gy) and heated while measuring the emitted light. TL measurements are taken either for temperatures ranging from -190°C to 100°C with a heating rate of 0.5°C/s, or from room temperature to 500°C with a heating rate of 1°C/s. TL emission is detected by a photomultiplier.

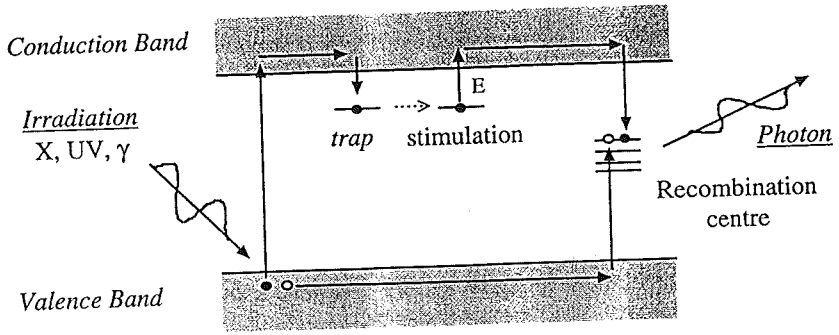

Figure 1 : Schematic diagram of thermoluminescence mechanism.

The sintering behaviour is investigated by dilatometry. Samples are compacted by unidirectional pressing (40 MPa). No additive is used. The green density is determined by weighing and measuring the dimensions. The dilatometric analysis are performed in an Adamel DI-24 dilatometer, under flowing nitrogen for all samples. The sintering atmosphere does not change. Samples are sintered at 1600°C for 15 minutes at the rate of 2°C/min.

RESULTS and DISCUSSION

From -190°C to 500°C, five TL peaks are observed at -40 (A), -5 (B), 190 (C), 270 (D) and 360°C (E). The presence and the intensity of these peaks depend strongly on the synthesis conditions.

Atmosphere effect :

The influence of the thermal treatment atmosphere on undoped alumina is very important, as can be seen in figures 2 and 3. The peaks A and B intensity increases for a reducing atmosphere, whereas peak E is sensitive to an oxidising atmosphere. Peak D was not detected in this case. A spectral analysis revealed that the emission is due to F (420 nm) and F^+ (310 nm) centres for A and B, to Cr^{3+} ions (695 nm) for the others. These three recombination centres are well known in alumina[3]. F and F^+ are respectively oxygen vacancies which caught two electrons and oxygen vacancies which caught one electron. Cr^{3+} is known for the laser effect in ruby.

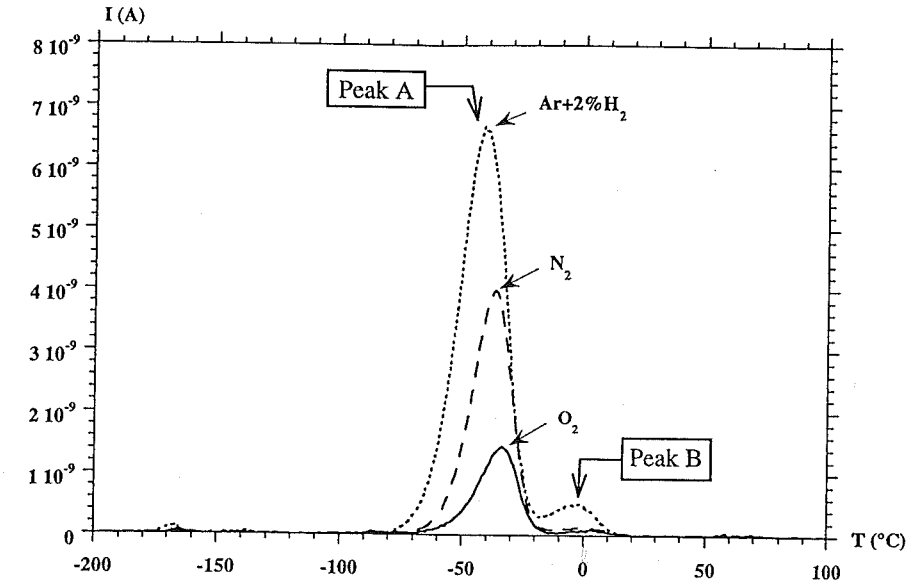

Figure 2 : Thermoluminescence curves after X irradiation at -190°C. Influence of the synthesis atmosphere.

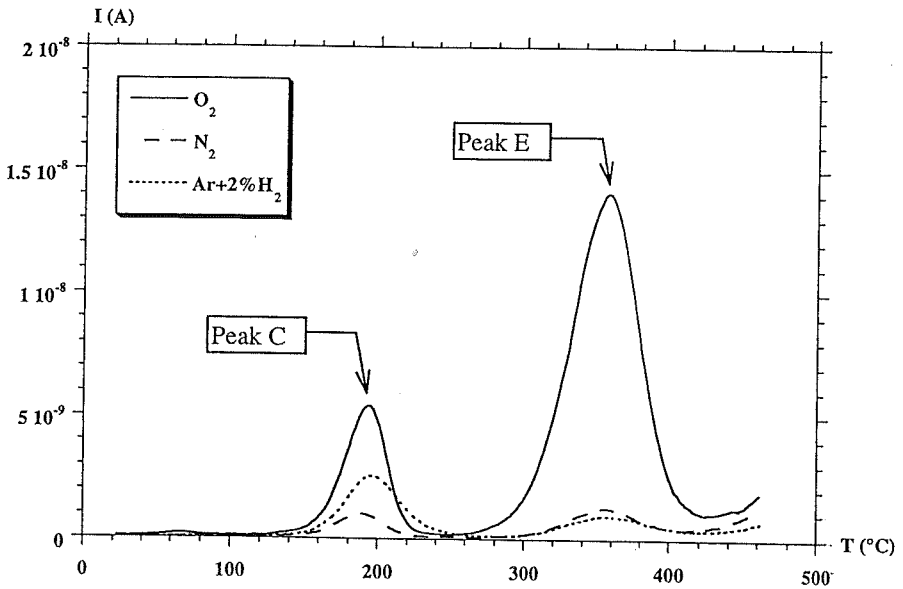

Figure 3 : Thermoluminescence curves after X irradiation at 20°C. Influence of the synthesis atmosphere.

Doping effect :

The introduction of chromium increases peak E intensity (figure 3). The evolution of this peak as a function of Cr^{3+} concentration is shown in figure 4. It first grows, reaches a step for 100 ppm, and start to decline for 500 ppm. The spectral emission is at 695 nm in the red region, due to Cr^{3+} ions. Doping with Cr^{3+} adds recombination centres and so intensifies the emission at 360°C. The intensity decrease for high concentration is attributed to an optical effect that occurs when another emitting ion is located within a certain radius of another. The emission is absorbed by the neighbouring chromium by energy transfer provoking the luminescence quenching.

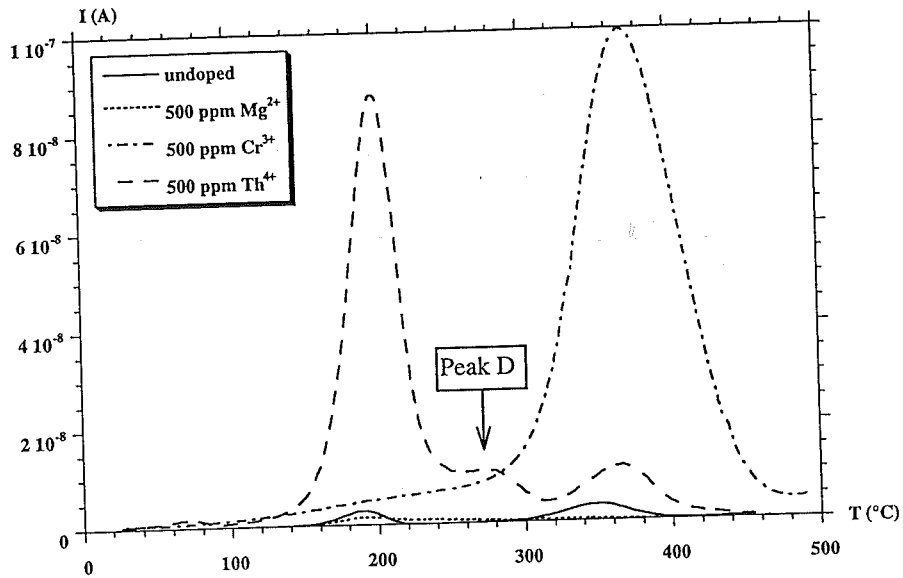

Figure 3 : Doping effect on thermoluminescence after X irradiation at room temperature of α-alumina powders prepared under oxygen.

Mg^{2+} and Th^{4+} have been chosen to act on trap centres. These species enter as cation substitutionals, and modify the defect structure by charge compensation. The doping effect is illustrated in figure 3. TL response of Mg-doped alumina has almost disappeared whereas Th^{4+} intensifies significantly peaks C and E and creates a new peak (D). The recombination centre of C, D and E is still Cr^{3+}. It is then supposed that TL intensity variations are linked to trap defects.

The intensity of peaks C, D and E are plotted versus thorium concentration (figure 5). The saturation that starts around 500 ppm probably represents the solubility limit of thorium in alumina. Beyond this point, we suppose that Th^{4+} does not enter the lattice, and so do not create new defects.

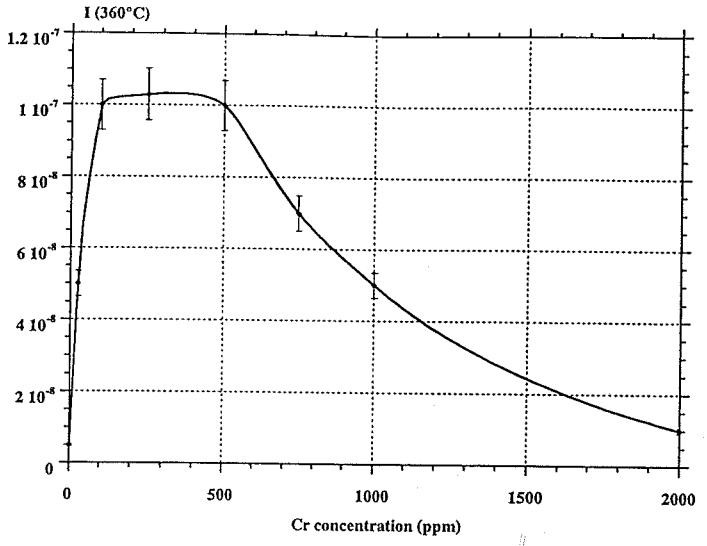

Figure 4 : Intensity of peak E as a function of chromium concentration.

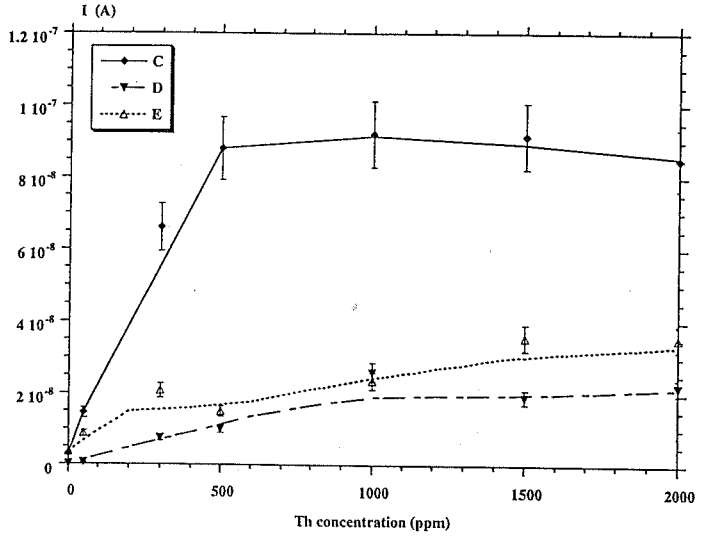

Figure 5 : Intensity of peaks C, D, E as a function of thorium concentration.

Defects involved in TL :

Each peak involves at least two defects : a trap centre and one or more recombination centres, and of course they can both evolve. For this reason, interpretations

are quite difficult. Kortov *et al.*[4] proposed a model explaining the luminescence at -40°C. He suggested that magnesium impurities are trap centres for peak A, F and F^+ the recombination centres. This is in agreement with our results on undoped samples (figure 2), since a reducing atmosphere is supposed to create oxygen vacancies and so F/F^+ centres. Peak A intensity would then be a function of oxygen vacancies, since magnesium concentration is fixed.

High temperature peaks (C, D, E) are sensitive to oxidising atmosphere and Th^{4+} doping. This suggests that aluminium vacancies are involved in these peaks. Firstly, Alumina reacting with oxygen can be written as follow :

$$\frac{3}{2} O_{2\ (gas)} \Leftrightarrow 2V_{Al}^{'''} + 3O_O + 6h^{\cdot}$$

Two aluminium vacancies (that then diffuse in the lattice) and three oxygen ions (coming from the gas) form an Al_2O_3 unit. Secondly, Th^{4+} substitutes Al^{3+} forming the defect $Th_{Al}^{\cdot}$. The positive charge will be compensated by the creation of aluminium vacancies $V_{Al}^{'''}$. Oxygen interstitials $O_i^{''}$ are rarely considered because of their high heat of formation. The high temperature peaks would then be linked to aluminium vacancies.

Supposing that defects are submitted to the Schottky equilibrium :

$$2\,V_{Al}^{'''} + 3\,V_O^{\cdot\cdot} = 0 \qquad K_S = [V_{Al}^{'''}]^2[V_O^{\cdot\cdot}]^3$$

the increase of one of these two concentrations implies the decrease of the other. The inverted behaviour of peaks A and E could be explained in this way, as well as the reduction of peaks C, D, E when Mg is added. $Mg_{Al}^{'}$ can be compensated by $V_O^{\cdot\cdot}$ or $Al_i^{\cdot\cdot\cdot}$. The formation of $V_O^{\cdot\cdot}$ is expected to eliminate some $V_{Al}^{'''}$. So TL peaks C, D and E are much less intense when Mg is added.

One can notice that aluminium vacancies $V_{Al}^{'''}$ can be the trap of only one peak. But if they are ionised ($V_{Al}^{''}$, $V_{Al}^{'}$, V_{Al}^{x}) their energy levels change and several peaks can be observed.

Sintering behaviour :

The dilatometric curves of undoped powders allow us to observe in all cases that shrinkage starts around 1000°C but that the rate is then dependent on the atmosphere employed for the synthesis of the powder. The more oxidising the atmosphere is, the faster the densification is (figure 6).

This results in an evolution of the final density. Powders prepared under Ar+2%H_2 attain 79% of the theoretical density whereas those prepared under oxygen attain 86% (For a sintering at 1600°C for 15 minutes). It is important to note that green density is the same for all samples. The final density evolution is only due to differences in the sintering rate.

All these powders have exactly the same microstructural characteristics. No change of the particle size, particle shape, specific surface area (1.85 m^2/g) and crystallography has been measured. Oxidising atmosphere is favourable to create aluminium vacancies, whereas oxygen vacancies concentration decreases. It is so suggested that powders prepared under oxygen densify more rapidly because of their higher aluminium vacancy content, that improves aluminium diffusion. This would mean that the sintering of our alumina powders is limited by aluminium diffusion in the temperature range studied.

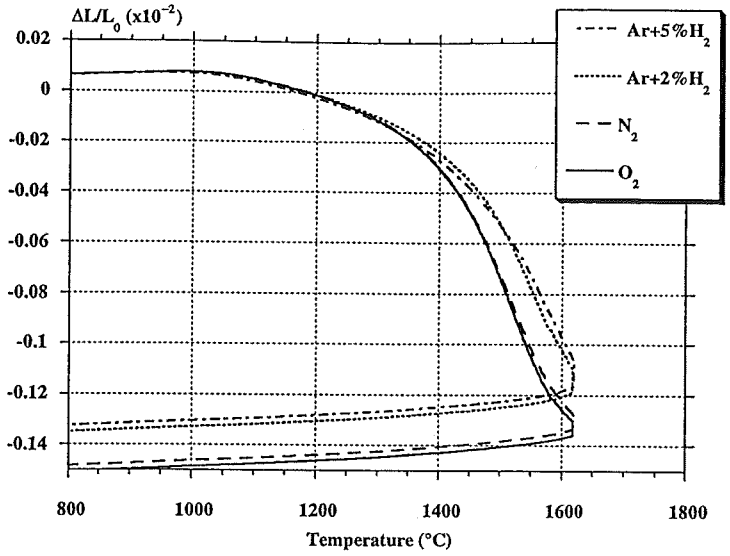

Figure 6 : Shrinkage as a function of temperature. Influence of the powder synthesis atmosphere.

CONCLUSION

Thermoluminescence analysis can provide interesting information on point defects. Low temperature peaks (A and B) are dependent on oxygen vacancies and high temperature peaks (C, D and E) seem to be linked to aluminium vacancies. Further work is necessary to get more details from this technique. Interpretations of the results are quite difficult because of optical interactions and because several point defects are at the origin of one peak. As all defect concentrations vary when we change a parameter of the process, it is not easy to explain an intensity change.

Despite a constant microstructure, undoped alumina sintering behaviour is dependent on the powder synthesis atmosphere. « Oxidised » powders sinter more rapidly up to 1600°C. The densities obtained are quite low, we are now studying the sintering at higher temperature.

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