DETECTION OF FOREIGN PHASES IN DOPED α-ALUMINA POWDERS BY THERMOLUMINESCENCE

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Abstract

The thermoluminescence (TL) after excitation by UV or X-rays radiation of doped α-alumina powders is investigated. In the case of zirconia, the alumina-zirconia composites present five of the characteristic peaks of zirconia at –170, –145, –90, 0 and 95°C. After a thermal treatment of mixed oxides, a new peak is observed at –35°C in TL. This peak reveals the presence of stabilized tetragonal zirconia in the material. In the case of calcium, the TL curves of α-alumina doped by calcium present a double peak around 110 and 130°C which can be attributed to the presence of the hibonite phase: $CaAl_{12}O_{19}$.

Moreover, in the case of zirconia, by comparing this analysis with those realised by X-rays diffraction (XRD), it can be shown that the TL has one better limit of detection than the XRD.

Keywords: Al_2O_3, $CaAl_{12}O_{19}$, calcium, composites, defects, thermoluminescence, ZrO_2

Introduction

The objective of this work is to show that the thermoluminescence (TL) allows the detection of foreign phases in the alumina matrix. The thermoluminescence (TL) is a technique used to study the fine structure of crystals by revealing the point defects. The purpose of this paper is to give two examples of foreign phases detected in alumina.

The TL of monoclinic zirconia has already been studied [1–3]. Six peaks were found at –170, –140, –85, –30, 10 and 110°C [3], (for a measurement at 30°C min^{-1}) and one of them (–30°C) was attributed to the presence of tetragonal zirconia, which is present as foreign phase in the sample of monoclinic zirconia [3–4].

The $Al_2O_3 \cdot CaO$ system was studied a lot according to its importance in metallurgy, ceramics or cements. The low limit of solubility of calcium in alumina (according to the system binary diagram) leads to the presence of the hibonite phase in the alumina matrix [5]. The optical properties of alumina are then changed.

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Experimental procedure

The mixture preparation

α-Al$_2$O$_3$–ZrO$_2$ mixed powders

The γ-alumina used in this study is a highly pure (>99.99% Al$_2$O$_3$) commercial pow-
der (Baikowski A125) obtained by thermal decomposition of ammonium alum
(NH$_4$Al(SO$_4$)$_2$·12H$_2$O). Then α-alumina is obtained by a thermal treatment of γ-alu-
mina at 1400°C under controlled atmosphere (oxygen). The zirconia is a commercial
powder (supplied by Rhône-Alpes Chimie, France) and its purity is higher than 99%.
XRD analysis shows that this zirconia powder exists in the form of monoclinic phase
(baddeleyite).

The mixtures of oxides, α-Al$_2$O$_3$ and ZrO$_2$, were wet ground in an organic sol-
vent (acetone), with continuous stirring. Various mixtures are used: 1, 5, 10…mass%
of ZrO$_2$. 5 g of each mixture were prepared.

Then half part of these mixtures undergoes a thermal treatment under controlled
atmosphere (oxygen), in order to reveal and study, by the techniques of X-rays dif-
fraction and thermoluminescence, the effect of doping by zirconia on the alumina
crystalline structure.

This treatment is conducted by the procedure described in Fig. 1.
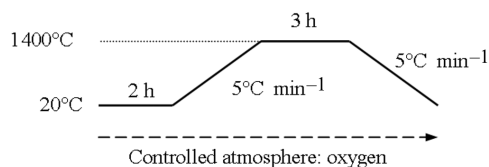
Fig. 1 Thermal cycle for the treatment of the α-Al$_2$O$_3$–ZrO$_2$ mixtures

α-Al$_2$O$_3$:Ca samples

The α-alumina doped by calcium samples are prepared using a commercial ultra-pure
γ-alumina powder (Baïkowski CR140) obtained by thermal decomposition of ammo-
nium alum (NH$_4$Al(SO$_4$)$_2$·12H$_2$O). The doping is performed through the impregna-
tion of the γ-alumina powder by an alcoholic solution of calcium chloride [6]. All the
doping concentrations (in ppm) are calculated on the basis of a mole ratio of Ca/Al. A
further thermal treatment allows the decomposition of the solvent and the salt, and the
diffusion of the calcium inside the host material (drying at 100 and 600°C for 24 h).
The doped γ-alumina is then transformed into doped α-alumina by a thermal treat-
ment at 1450°C for 2 h under a pure gas flow (O$_2$ or Ar+2%H$_2$).

The doping by Ca^{2+} was performed for concentrations in calcium ranging from 0
to 10000 ppm.

The experimental techniques

The X-ray diffraction (XRD) experiments have been performed with a Siemens D5000 diffractometer using CuK$_\alpha$ radiation (λ_{K_α} =0.15406 nm) in a $\theta/2\theta$ configuration. A database on CD-ROM is used for searching and retrieving X-ray powder diffraction patterns.

The TL emission is detected by a photomultiplier Hamamatsu R562 with a spectral response between 160 and 850 nm. For semiconducting or insulating solid crystals, the valence and the conduction bands are separated by an energy gap (Fig. 2). When the crystal is submitted to ionising radiation (UV, X-ray, γ…), an electron-hole pair is formed in the valence band. The electron is free to travel through the conduction band and to fall into an electron trap. While, the hole travels through the valence band and falls into a hole trap.
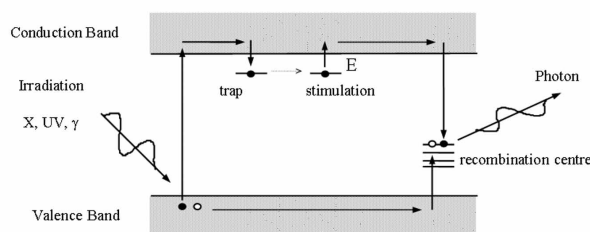

Fig. 2 Schematic diagram of thermoluminescence mechanism

After irradiation, the trapped charges may escape if the temperature of the crystal is raised and may recombine together on a centre, which de-excites by photon emission. If the heating rate of the sample is constant and if the emitted luminous intensity is measured using a photomultiplier tube (PMT) linked to a pico-ammeter, some peaks are observed, their temperature position being characteristic of the trap nature and their intensity depending on concentrations of both the traps and the recombination centres.

For the irradiation, we expose the samples one minute under an UV lamp (λ=253.7 nm), or five minutes under a W-target (45 kV, 2 mA), at –190°C, and then we keep the samples two minutes in the dark.

The samples are then heated at 60°C min^{-1} in the case of UV exposure, and at 30°C min^{-1} in the case of X-ray irradiation.

Experimental results

The case of tetragonal zirconia

Pure oxides (monoclinic zirconia and α-alumina) were studied by low temperature TL after UV irradiation, before and after the thermal treatment at 1400°C under oxygen. The studied α-alumina presents no peak after UV irradiation. The monoclinic

zirconia, which is used in this study, presents 6 TL peaks after UV irradiation situated at –170, –145, –90, –35, 0 and 95°C, but the peak at –35°C disappears when the powder undergoes the thermal treatment.

In the case of alumina-zirconia mixtures (before thermal treatment), we observe the same peaks as for pure zirconia, except the one at –35°C which doesn't appear. On the other hand (after thermal treatment), the peak at –35°C appears on the TL glow curve (Fig. 3).
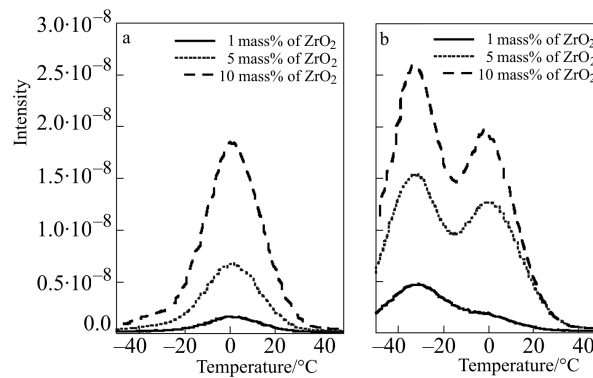
Fig. 3 Thermoluminescence after UV irradiation of mixtures before and after the thermal treatment (for 1wt%, 5wt% and 10wt% of ZrO_2)

Above 1170°C, the stable phase of zirconia is the tetragonal one [7]. The presence of tetragonal zirconia in the powder is detected by XRD, but only for mixtures realised with a zirconia amount higher or equal to 10 mass% and treated at 1400°C (Fig. 4): XRD being not sensitive enough to detect tetragonal zirconia for lower amount of zirconia in the mixtures.
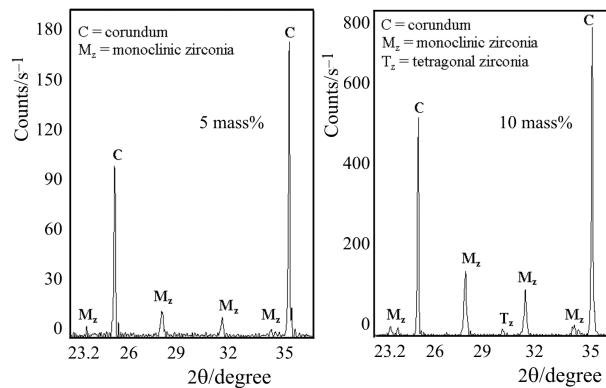

Fig. 4 X-rays diffraction at room temperature of mixtures after the thermal treatment for amount of 5wt% and 10wt% of ZrO_2

In Al_2O_3–ZrO_2 composites, the tetragonal phase is stable at room temperature only if the zirconia grain size lies between two critical values (from about 0.1 up to 0.5 μm) [8].

So, in order to verify that the peak at –35°C is due to the presence of the tetragonal phase, we have studied a commercial mixture (containing 10 vol% of m-ZrO_2), allowing the stabilisation of zirconia in tetragonal form after sintering. This mixture is prepared in the following manner: an alumina powder (purity>99.9% Al_2O_3) is homogeneously mixed with a monoclinic zirconia (purity>99.9% ZrO_2) in distilled water, with a conventional mixing-milling technique. Subsequently, they are spray-dried. The final size of the grains in the mixture was measured between 0.33 and 0.40 μm.

This mixture was characterised by TL and XRD, before and after the thermal treatment (at 1400°C under oxygen). Before the thermal treatment, we observe by TL (Fig. 5) an intense peak at –145°C, a peak towards –50°C, and a peak at 0°C which is probably the characteristic peak of monoclinic zirconia at 0°C. After thermal treatment, the peaks at –50 and 0°C disappear, the one at –145°C decreases and a peak at –35°C appears.
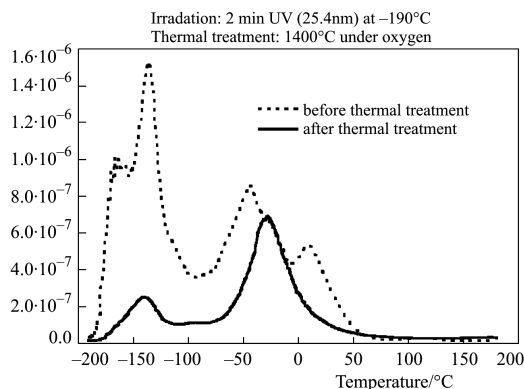

Fig. 5 Thermoluminescence after UV irradiation of a commercial mixture (allowing the stabilisation of zirconia in tetragonal form after sintering), containing 10 vol% of ZrO_2, before and after the thermal treatment

By X-ray diffraction, the presence of the monoclinic phase is observed in the mixture. But after the thermal treatment, almost all the monoclinic zirconia disappears and we observe a strong prevalence of the tetragonal zirconia (Fig. 6).

After complementary experiments carried out by low temperature TL under X-rays irradiation, it is reasonable to attribute the appearance of the TL peak at –35°C to the presence of tetragonal zirconia stabilised by the alumina.

The case of hibonite (Ca)

The study of high temperature thermoluminescence (TL) on non-doped alumina reveals the presence of three peaks called C' (around 70°C), D' (200°C) and E' (360°C) (Fig. 7). These are well known TL peaks in alumina [9].
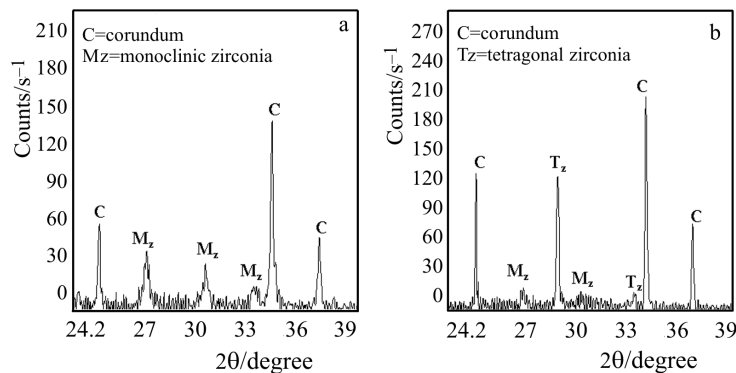
**Fig. 6** X-rays diffraction of the commercial mixture (10 vol% of ZrO$_2$) before and after the thermal treatment
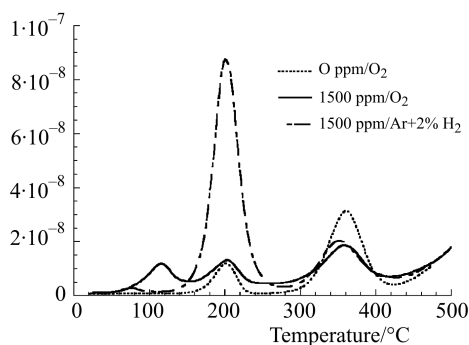
Fig. 7 TL curves of α-Al$_2$O$_3$ doped by Ca^{2+}, prepared by a thermal treatment under O$_2$ or Ar + 2% H$_2$

When we analyse, by thermoluminescence, the effect of both doping alumina by Ca^{2+} and an oxidizing atmosphere of samples calcination, for a dopant amount of 1500 ppm, we still observe the presence of D' and E' peaks, but the C' peak seems to be moved forward from 70 to 110°C.

But in the case of a reducing atmosphere of doped alumina calcination, for the same amount of dopant, the C' peak does not move.

In that case, TL's intensity of the C' peak is represented according to the amount of calcium in the Fig. 8. For weak amount of dopant, the intensity strongly increases until a 1500 ppm concentration of Ca^{2+}; beyond, TL's signal rapidly decreases. This peak, which seems rather unstable by its intensity as much as by its position in temperature, presents the phenomenon of quenching by concentration. The more the amount of a defect is important in the lattice, the more the distance between two defects is weak. In case these defects intervene as centre of recombination, they are susceptible to re-absorb emitted photons during TL's analysis by a point defect of the
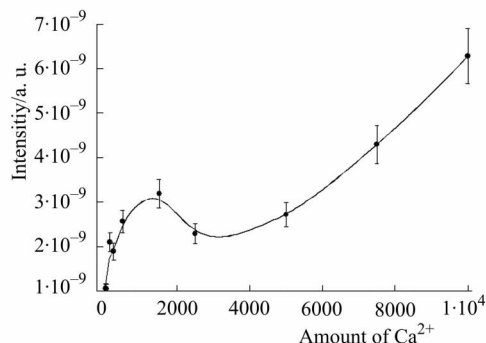
Fig. 8 Evolution in function of the amount of dopant, of the TL intensity of the peak situated between 70°C and 110°C for α-Al$_2$O$_3$ doped by Ca^{2+}, prepared by a thermal treatment under Ar + 2% H$_2$

same nature situated in its neighbourhood. The extinction by concentration was already observed for example by Daviller in α-Al$_2$O$_3$:Cr [10].

Beyond 2500 ppm amount of Ca^{2+}, TL's intensity of the C' peak increases linearly with the concentration of dopant (Fig. 8). We supposed so that the second part of this curve reports really the evolution of the thermoluminescence of a peak of another phase than the alumina. This new peak takes place at 110°C.

An analysis by X-rays diffraction, for both atmospheres of calcination, showed the presence of a second phase, the calcium hexaluminate CaAl$_{12}$O$_{19}$, so called up hibonite or CA6 phase.

We can summarize the amount of calcium from which the CA6 phase is discovered by X-rays diffraction, according to the atmosphere:

– Calcination under oxygen: 2500 ppm

– Calcination under Ar+H$_2$ (2%): 5000 ppm

In order to characterize its thermoluminescence, the hibonite was synthesised from a mixture of α-alumina [5] and calcium carbonate CaCO$_3$ in the isopropanol.

The high temperature thermoluminescence of the hibonite presents at least six peaks, as one can see on the DSC curve of the Fig. 9: a double peak between 90 and 130°C, three less intense peaks at 230, 345 and 415°C and a very weak intense peak around 280°C.

We have then compared the TL of the hibonite and the TL of alumina doped by 5000 ppm of calcium with a calcination atmosphere of O$_2$ (Fig. 9). For the doped sample, one finds the peak around 100°C, as well as a less intense one at 130°C, which characterise the presence of the CA6 phase. In the case of the oxidizing atmosphere, there is no uncertainty as regards the allocation of peaks, because the C' peak of alumina is not visible.

The linear increase of C' peak intensity with the amount of calcium under reducing atmosphere (Fig. 7) can be attributed to the double peak of the hibonite.
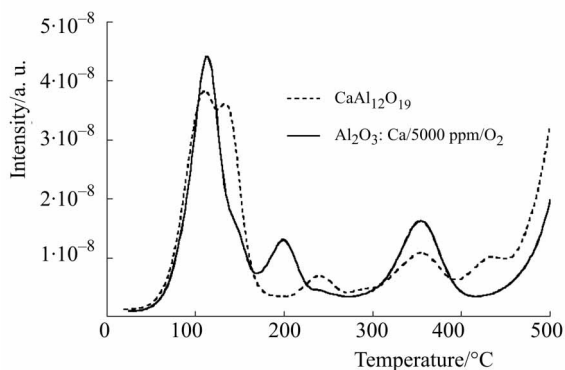
Fig. 9 TL curves of the hibonite phase and of α-Al$_2$O$_3$ doped by 5000 ppm of Ca^{2+}, prepared by a thermal treatment under O$_2$

There is however an ambiguity in the case of the reducing atmosphere: why is the double peak of the hibonite discovered at the same temperature as the C' peak, around 70°C ?

The answer probably lies in the instability of the thermoluminescence of the CA6 phase. Indeed, several analyses of thermoluminescence were realized successively on the same sample of alumina doped by 5000 ppm of calcium with a calcination atmosphere of Ar+2% H$_2$ (Fig. 10). We observe then very clearly that the C' peak of alumina moves forward to the highest temperatures under the successive irradiations influence, until it corresponds to the double peak of the hibonite.
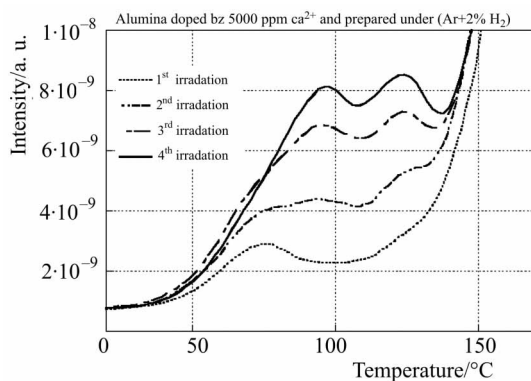
Fig. 10 Effect of successive irradiations on the TL peak of the hibonite phase

Finally, it is necessary to note that the thermoluminescence of the hibonite is more intense than that of the α-alumina. This observation allows to explain that we can detect the CA6 phase even when it is in very small quantity in alumina.

Conclusions

The presence of zirconia tetragonal phase stabilized by alumina can be detected in alumina–zirconia composites by the thermoluminescence technique.

Moreover, the detection limit of this technique is appreciably better than with the X-rays diffraction technique. Indeed, for an amount of zirconia lower than 10 mass% in the composite, XRD does not allow to detect the presence of tetragonal zirconia, while the peak at –35°C is still appearing for only 1 mass% of zirconia by TL method.

In the same way, the thermoluminescence is a valid technique to detect the presence of the hibonite phase in an alumina lattice.

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