Magnetron sputtering fabrication of α-Al_2O_3:Cr powders and their thermoluminescence properties

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ABSTRACT

For many years doped α-Al_2O_3 has attracted interest as a dosimeter for personal, environment monitoring and food control. The alumina single crystal growth is a difficult process; however, materials in form of powders, ceramics and coating are possible to obtain. In this study for the first time Cr doped α-Al_2O_3 powders were prepared by DC reactive magnetron sputtering followed by milling and oxidation. The morphology and phase analysis was performed; content of residual impurities was determined and thermostimulated glow curves were measured after different x-ray irradiation times (radiation doses). The prepared powder shows the dosimetry properties up to 20 kGy dose.

1. Introduction

Thermoluminescence (TL) phenomena is known for many decades. The theory of phenomena and its applications one can be found in (Chen and McKeever, 1997). TL is used not only in fundamental research mostly in the field of materials science, but also in practical applications as this method is applied to date fossils as well as for determining the radiation dose acquired by the well-defined sample – personal dosimeter. The electrons and/or holes are trapped in trapping centers during excitation of sample by ionizing radiation and by the subsequent heating of the sample the trapped carriers are and recombined at the luminescence centers. The concentration of trapped carriers in some cases is proportional on the excitation dose. This phenomenon underlies TL dosimeters.

Many different compounds and materials exhibit TL in different temperature ranges; however, some specific parameters should be met when evaluating material for the possibility to use it as a personal dosimeter: TL maximum above room temperature, low spontaneous recombination rate (fading), TL intensity or area under glow curve linear response to the absorbed dose as well as radiation stability of the sample. Several standards are established in dosimetry field – all with different dose range and fading amount. One of them is anion-defective α-Al_2O_3:C, abbreviated as TLD-500, with main TSL maximum at 450K (Kortov et al., 2017).

Dosimetry properties of doped α-Al_2O_3 are still being studied as TL properties (dosimetric TL peak position, spectra and dose response) of α-Al_2O_3 depend on dopant type and its concentration. The known dosimeters are Al_2O_3:C (Akselrod et al., 1993) and Al_2O_3:Mg,Y (Ranogajec-Komor and Osvay, 1986). The recombination centers in these materials are charged oxygen vacancies: F-centers (420 nm emission) in Al_2O_3:C and F^+-centers (320 nm) in Al_2O_3:Mg,Y. In doped material the recombination center is dopant ion, for example Tb (Soares et al., 2014) or Cr (Križan et al., 2012).

Search for the efficient TL dosimetry materials including nanostructured materials in accordance with the requirements for dosimeters (radiation resistance, low fading, TL linearity of absorbed doses, tissue equivalence for personal dosimeters etc.) are still very important.

In this paper chromium doped Al_2O_3 powder was successfully prepared by magnetron sputtering technique and the method for powder preparation was described. This method is explored as an alternative method for dosimetry material fabrication. The powder was characterized by XRD, EDAX, SEM, (better to write in open form in the first appearance) radioluminescence (RL) and TL techniques. The TL properties of α-Al_2O_3:Cr powder (glow curves, spectra and irradiation dose

Table 1
Deposition parameters.

Parameters	Numerical value
Target dimensions	Ø 75 mm × 6 mm
Target-to-substrate distance	50 mm
Base pressure	1•10-6 mbar
Working pressure	4.6•10-3 mbar
Argon flow rate	60 sccm (standard cubic centimeter per minute)
Oxygen flow rate	9 sccm
Power density cathode	11.3 W/cm^2
Substrate temperature	Not detected (no external heating)
Deposition time	13 h

dependence) were studied.

2. Sample preparation

Deposition of non-stoichiometric AlO_x doped with Cr was done by DC reactive magnetron sputtering with a cathode of type Leybold PK75 in Aurion vacuum chamber (KIVOS 500). A sintered disk with 99.6 wt% Al and 0.4 wt% Cr was used as a target.

A 2 mm thick aluminum sheet (99.9%) was used as a substrate which was cleaned in an ultrasonic bath prior to deposition of AlO_x. Deposition was carried out in Argon/Oxygen plasma. All process parameters are given in Table 1. Deposition was carried out in the metallic mode and lead to a non-stoichiometric suboxide. Film thickness was measured in situ by an oscillating quartz crystal (Inficon SQM160). After the deposition process, the sputtered material was delaminated by bending the substrate. The average thickness of the peeled off flakes was about 38 μm.

After peeling off the non-stoichiometric Cr-doped alumina material was first crushed in a ceramic mortar to equalize the particle size. This was done to assure a homogeneous oxidation during the post-annealing process. The isothermal annealing was performed in a mixture of Oxygen (5N) and Argon (5N) with a flow rate of 110 cm³/min in a DSC/TG unit (Netzsch STA 409) with batch sizes of approximately 2 g per run for 10 h soak time at 1460 °C in corundum crucibles (3.5 ml, Friatec, Art. No. 209-11000-0064). Heating rate to final temperature was 10 K/min.

Oxidation to stoichiometric alumina was controlled by the measurement of weight gain and the presence/absence of an exothermal enthalpy peak around the melting temperature of pure aluminum. Preliminary annealing trials revealed, that the absence of melt peak in DSC signal does not indicate complete transfer in stoichiometric alumina in a reliable way. Therefore, the process time was set by monitoring the weight increase only. If no further weight gain can be detected, all aluminum sub-oxides have been transferred into alumina.

Note that the non-stoichiometric alumina exhibits a certain metallic luster although the oxygen content is quite high (approximately 80% of the nominal value). After oxidation it is completely white with a certain light red gleam due to the chromium dopant.

3. Experiments

An X ray tube (W target operating at 40 kV, 10 mA) was used as radioluminescence and TL excitation source. The excitation and radioluminescence measurements were conducted at room temperature. Lamp operation mode was 30 kV and 10 mA (500 Gy/min). Andor Shamrock B-303i spectrograph coupled with Andor DU-401A-BV CCD camera and Hamamatsu H8259-02 photon counting head was used for luminescence measurements. In TL experiments, the Cr luminescence was recorded through 700 nm interference filter. For TL measurements, samples were heated to 700 K at a rate of 2K/s. SEM measurements were made on Phenom Pro scanning electron microscope. Cr concentration and concentration of residual impurities was estimate by using X-ray fluorescence analyzer (XRF) EDAX Eagle III XPL. X-ray diffraction spectra for crystalline structure studies were taken using PANalytical X'Pert Pro diffractometer.

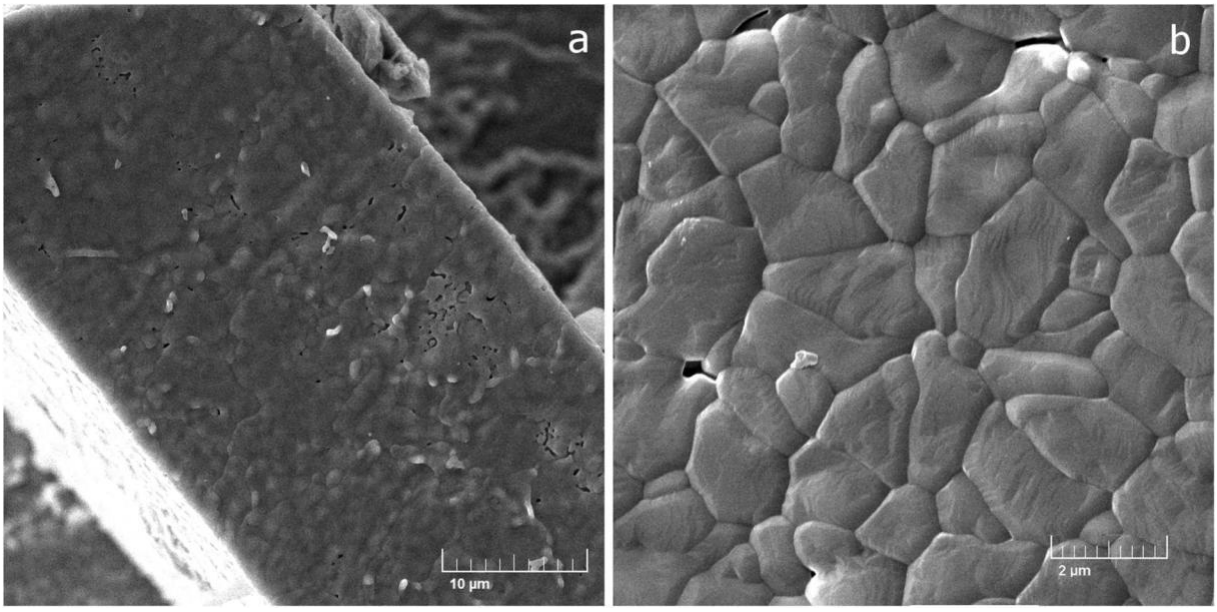

Fig. 1. The SEM images of α-Al_2O_3:Cr grains measured with different magnification (a and b).

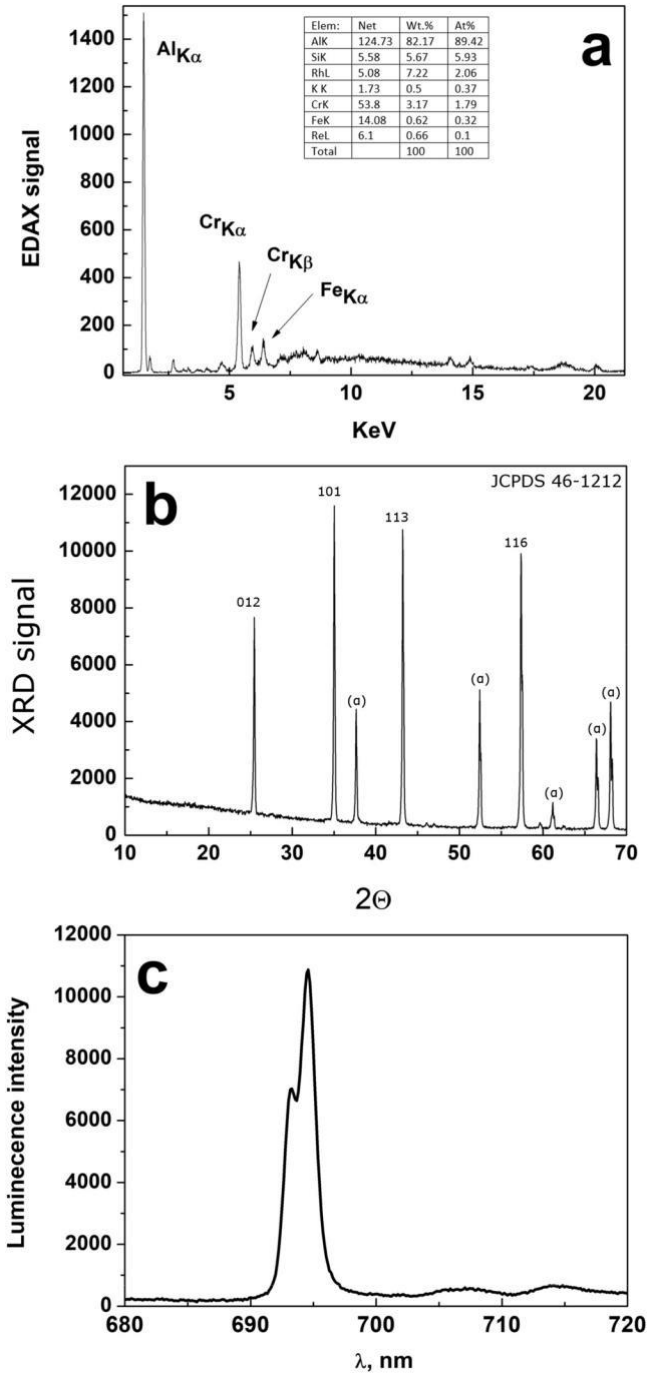

Fig. 2. The EDAX measurement of prepared α-Al_2O_3:Cr powder (a); the XRD analysis for prepared α-Al_2O_3:Cr powder (b); radioluminescence spectrum. The R1 and R2 lines measured with high spectral resolution are shown (c).

4. Results and discussion

In present paper we studied the Al_2O_3:Cr sample with Cr concentration of ~0.3 wt% estimated from energy dispersive X-ray analysis (EDAX) (Fig. 2a). The XRD was used for phase determination. Results are shown in Fig. 2b and according the JCPDS 46–1212 data it is concluded that only α-Al_2O_3 phase exist.

To examine the resulting ceramic sample, scanning electron microscope (SEM) was used. Fig. 1 (a) shows the cross-section of a single flake. The thickness of the flake correlates well with the initial thickness of the coating (30 μm). Slight cavitation is present near the surface of the sample. Fig. 1 (b) shows a zoom in on the surface. A typical ceramic structure is present: irregularly shaped grains with the size of 0.5–2 μm.

Upon excitation with X-rays well known R_1 (694.3 nm) and R_2 (692.8 nm) Cr^{3+} ion luminescence (Patra et al., 2005) bands were observed (Fig. 2c). Long wave bands 707 nm and 714 nm can be associated with structural disorder, or with the presence of Cr^{3+}-Cr^{3+} pair interactions (Derén et al., 1996; Mikenda and Preisinger, 1981). The luminescence of F and F^+ known centers to be present in undoped α-Al_2O_3 were not detected in our experiments with Cr doped α-Al_2O_3. Therefore, only Cr^{3+} ions act as recombination centers in the studied material. We guess the model of TL may be the following; under irradiation electron-hole pairs in the host were created and hole was trapped in Cr^{3+} forming Cr^{4+} centers. Electrons were trapped at anion vacancies complexes and known as the F_2 –type centers (Kuzovkov et al., 2018). These vacancy complexes exist in highly Cr doped α-Al_2O_3. The thermal bleaching of F_2 –type centers (due to ionization of F-type centers) according theoretical study (Kuzovkov et al., 2018) occur at temperatures 500–600K that is close to TL peak in this study. Recombination of Cr^{4+} and electron create excited center of Cr^{3+} and specific Cr lines were observed in TL spectra.

It is known that LiF:Mg, Ti (TLD-100) and Al_2O_3:C (TLD-500) are useful in dose range 10 μGy–10 Gy (Kortov, 2007), therefore are sensitive for low doses and can be used as personal dosimeters. In other study (Salah et al., 2011) the nanoparticles (around 25 nm) of the Al_2O_3:Cr have been prepared using the chemical combustion technique and studied for their TL response (γ-ray sensitivity of 100Gy-20 kGy) for the intended use in dosimetry of food and seeds after radiation sterilization process. Our results confirm that Al_2O_3:Cr prepared by magnetron sputtering technique can be used as a dosimeter for dose range above classical TLD-100 and TLD-500 devices. The samples studied in this work demonstrated dose dependence up until 21 kGy with the linear response range up to 6 kGy (Fig. 3b). The TL peak position slightly shifts with irradiation dose (Fig. 3 a). Three types of F_2 –type centers are known (Kuzovkov et al., 2018) with slightly different thermal bleaching temperatures. Therefore, the dis-tribution of trapping centers is dose dependent and at higher doses the trapping centers with higher activation energies are involved in TL process.

5. Conclusions

In summary, for the first time the powders of chromium doped α-Al_2O_3 were produced by magnetron sputtering. Powder has only α-Al_2O_3 phase. The radioluminescence spectrum and TL spectra show only Cr^{3+} ion luminescence – well known R-lines. The luminescence in spectral region 380–640 nm was under the detection limit and it is confirmed that only Cr^{3+} is the recombination center in TL process. The model of electron-hole processes involving Cr^{4+} (hole trapped on Cr^{3+}) and F-type electron centers were discussed. The prepared powder shows the dosimetric properties and is sensitive in dose range up to 20 kGy with linear response range up to 6 kGy.

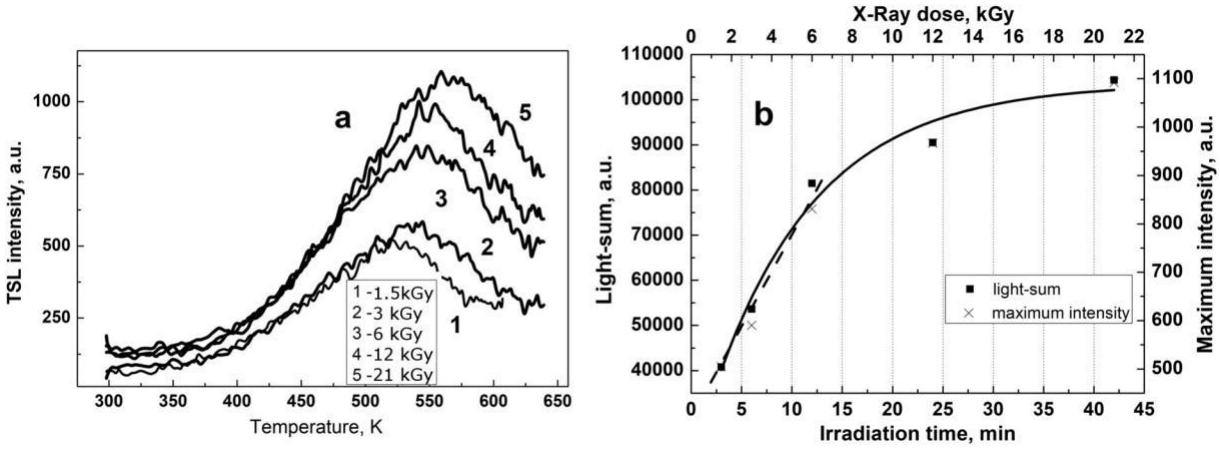

Fig. 3. The TL obtained after irradiation with different irradiation times (doses) (a) and irradiation time (dose) dependence of TL peak maxima and light-sum under TL peak (b).

Acknowledgments

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References

Akselrod, M.S., Kortov, V.S., Gorelova, E.A., 1993. Preparation and properties of α-Al_2O_3 :C. Radiat. Protect. Dosim. 47, 159–164.

Chen, R., McKeever, S.W.,S., 1997. Theory of Thermoluminescence and Related Phenomena. Word Scientific Publishing Ci. Pte.Ltd.

Derén, P.J., Malinowski, M., Strek, W., 1996. Site selection spectroscopy of Cr3+ in $MgAl_2O_4$ green spinel. J. Lumin. 68, 91–103.

Kortov, V., 2007. Materials for thermoluminescent dosimetry: current status and future trends. Radiat. Meas. 42, 576–581.

Kortov, V.S., Zvonarev, S.V., Pustovarov, V.A., 2017. Photoluminescence dose dependences of F and F+-centers in TLD-500 detectors. Radiat. Meas. 106, 52–54.

Križan, J., Možina, J., Bajsić, I., Mazaj, M., 2012. Synthesis and fluorescent properties of chromium-doped aluminate nanopowders. Acta Cim.Slov. 59, 163–168.

Kuzovkov, V.N., Kotomin, E.A., Popov, A.I., 2018. Kinetics of the electronic center annealing in Al_2O_3 crystals. J. Nucl. Mater. 502, 295–300. https://doi.org/10.1016/j.jnucmat.2018.02.022.

Mikenda, W., Preisinger, A., 1981. N-lines in the luminescence spectra of Cr3+ -doped spinels (I) identification of N-lines. J. Lumin. 26, 53–66.

Patra, A., Tallman, R.E., Weinstein, B.A., 2005. Effect of crystal structure and dopant concentration on the luminescence of Cr^{3+} in Al_2O_3 nanocrystals. Opt. Mater. 27, 1396–1401.

Ranogajec-Komor, M., Osvay, M., 1986. Dosimetric characteristics of different TL phos-phors. Radiat. Protect. Dosim. 17 (1–4), 379–384.

Salah, N., Khan, Z.H., Habib, S.S., 2011. Nanoparticles of Al2O3:Cr as a sensitive ther-moluminescent material for high exposures of gamma rays irradiations. Nucl.Insr. and Meth. B 269, 401–404.

Soares, J.V., Gugliotti, C.F., Kawashima, Y.S., Tatumi, S.H., Mittani, J.C.R., 2014. Thermoluminescence and optically stimulated luminescence characteristics of Al_2O_3 doped with Tb. Radiat. Meas. 71, 78–80. https://doi.org/10.1016/j.radmeas.2014. 05.015.

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