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THE EPR MEASUREMENTS OF AL_2O_3 POWDERS AND MULLITES USED IN AEROSPACE INDUSTRY FOR CORES AND SHAPES

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In this work the electron paramagnetic resonance (EPR) spectra of Al_2O_3 powders were measured for different sizes of grains (# 200, # 325) as well as the mullites (0.007 and 0.012). The measurements were performed at room temperature and in the temperature range from 140 K up to 380 K. The main purpose of this work was to investigate the possible relationships between EPR spectra and the size of powder grains as well as the identification of EPR spectra in view of potential application of EPR technique as a fingerprinting method.

INTRODUCTION

The ceramic nano-powders are widely used in various industries, including aerospace industry. The polymer nanocomposites stiffened by ceramic nano-filling are characterized by very high hardness and resistance for abrasion in comparison with composites in micrometric scale (Jurczyk, Jakubowicz, 2004; Jurczyk, 2001). The annealing of Al_2O_3 powders in temperatures 350, 600, 900°C do not influence the size of particles of the investigated powders.

The heating in temperature 1200 ° C leads to the 30% growth of the average size of grains (due to the fritting processes) and at the same time the growth of crystalinity degree of alumina and the phase transition δ, γ, η, ε-Al_2O_3 → α-Al_2O_3 take place (Zawada, Boczkowska, Ziemkowska, Kunicki, Pietrzykowski, Olszyna, 2006). The conditions of synthesis of the precursor as well as usage of its modifier significantly influence the Al_2O_3 morphology (Sołgała, Kunicki, Olszyna,2008). Also important is the reaction of environment in which the homogenization of both Al_2O_3 and nanometric ZrO_2 powders take place. The environment, in which particles of both powders have the same electric charge signs, leads to the forming of the mechanically resistant agglomerates. This is detrimental for the condensation of material during fritting. In the sintering process, the cracks with sizes about of hundreds of micrometers as well as inhomogeneity of packing in individual micrometers scale are created (Zych, Haberko, Bućko, Rutkowski, Trybalska, Piekarczyk, Lach, 2008). The aim of this work is to investigate by EPR methods the role of cores and shapes of basic Al_2O_3 materials used for industrial applications. The motivation for this study comes from the need to solve the problem of fractures of shape.

EXPERIMENTAL DETAILS

For the experiment the samples of corundum with different size and incorporating a second phase were used (see Table 1). The samples of mullite with a size of grains in the range 0.007 - 0.012 were also studied. For the EPR measurements the standard X-band (~ 9 GHz) spectrometer, produced in Wroclaw, with digital registration of the spectra was used. The temperature measurements were done using the digital temperature control system (BRUKER ER 4131VT), which allows the temperature range from 100K to 500K.

Table 1. The specification of the corundum samples.

No	Sample	Qualitative analysis of phase composition by X-ray diffraction methods
1	Al_2O_3 #200	α Al_2O_3 – corundum 93,9±0,1 [%] $NaAl_{11}O_{17}$ – β-Al_2O_3 6,1±0,1 [%]
2	Al_2O_3 #325	α Al_2O_3 – corundum 95,5±0,1 [%] $NaAl_{11}O_{17}$ – β-Al_2O_3 4,5±0,1 [%]

RESULTS AND DISCUSSION

The obtained EPR spectra are presented in Figs 1 to 4. In the case of Al_2O_3 powders, we observed one wide EPR line with several considerably narrower lines superimposed characterized by the peak to peak width of

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bout 3-4 mT for sample # 200, whereas of few mT for sample # 325. The EPR spectra for both mullites are very similar and the differences appear only in the line intensity for the line with g = 4.29. The EPR spectra of Al_2O_3 powders reveal some differences in the line intensity and their positions. For sample # 200, a new line appears in the magnetic field equal to 300mT.

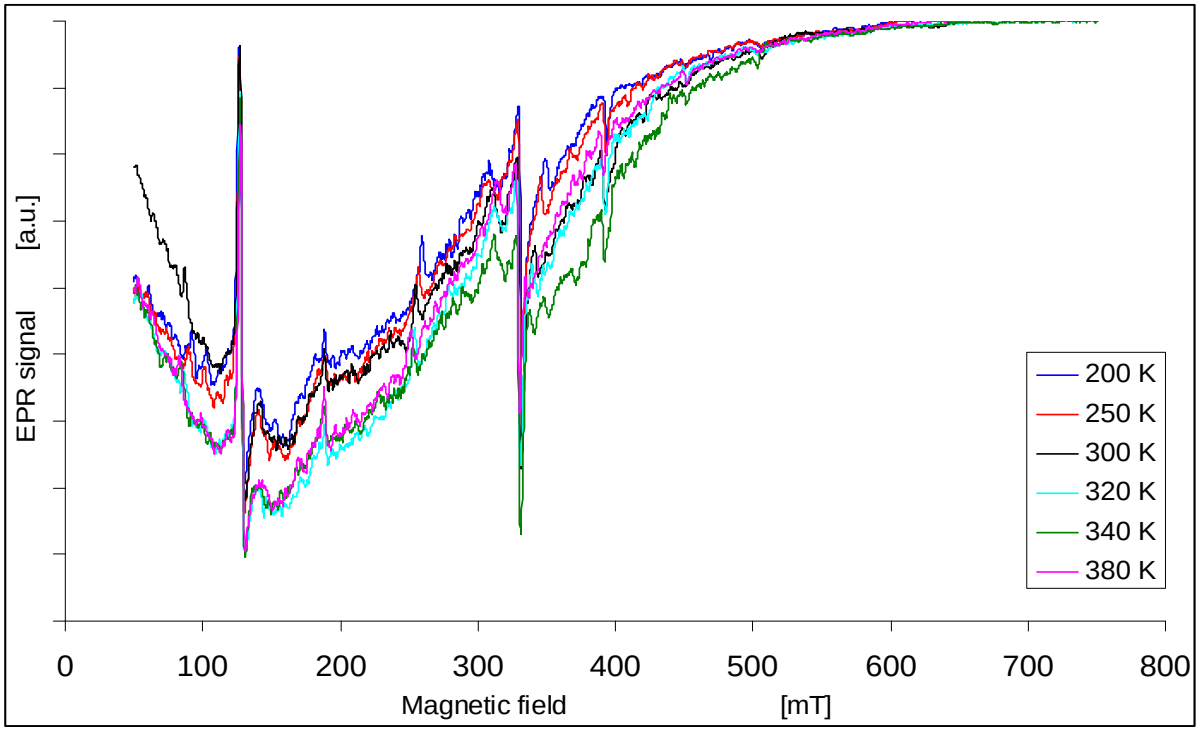

Fig.1. The EPR spectra of Al_2O_3 powder sample #200 at different temperatures.

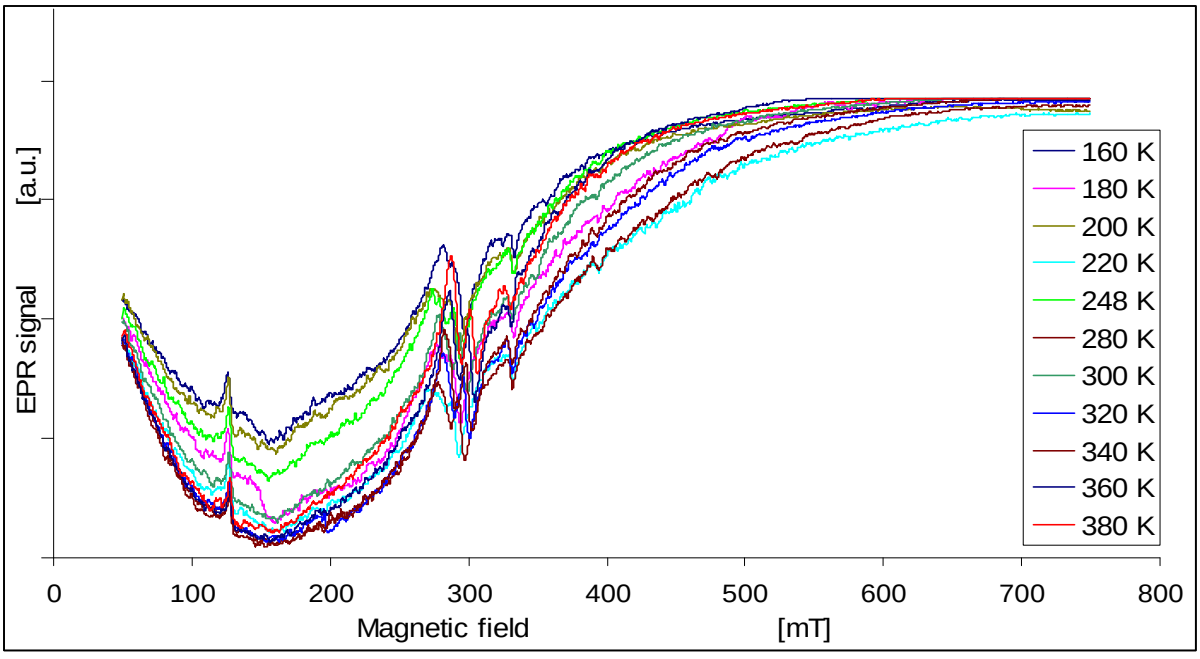

Fig. 2. The EPR spectra of Al_2O_3 powder sample #325 at different temperatures.

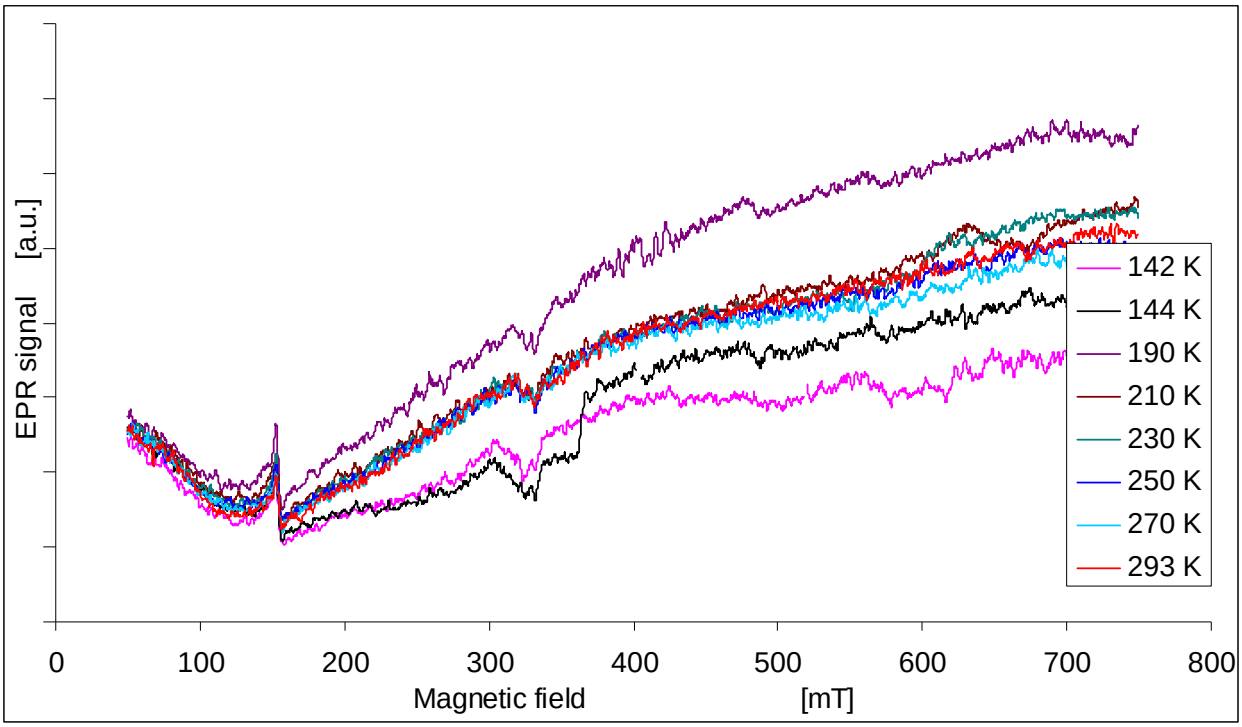

Fig. 3. The EPR spectra of mullites 0,007 at different temperatures.

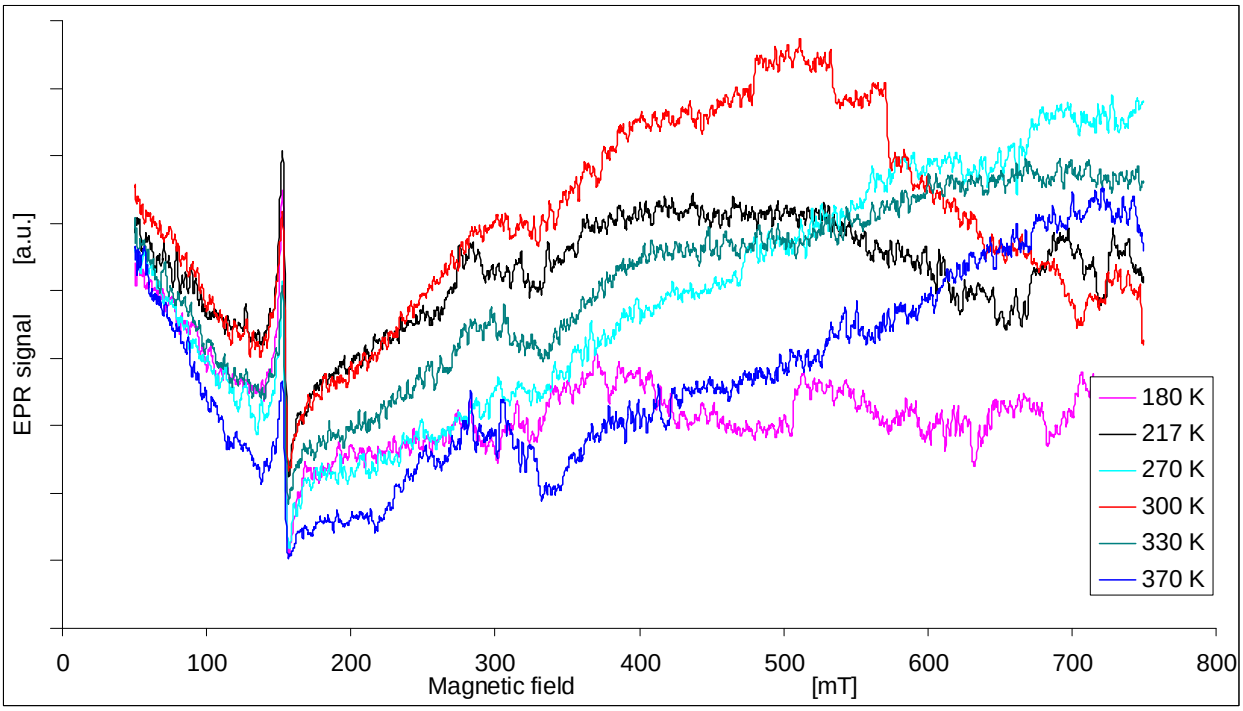

Fig. 4. The EPR spectra of mullites 0,012 at different temperatures.

For the Al_2O_3#200 sample the calculated g_{eff} –factor values for each line are as follows: g_{eff} =4.29 g_{eff} = 3.36, g_{eff} = 2.57, g_{eff} =1.97, g_{eff} =1.69. However, for the sample #325 we obtain the values: g_{eff} =4.28, g_{eff} =2.33, g_{eff} =2.23 g_{eff} =1.97. The estimated experimental uncertainty of the g-values is ±0.02. The analysis of the

line positions suggest that the lines with g_{eff}= 4.28 g_{eff} ≈2.00 may be attributed to Fe^{3+}(S=5/2) ions, because they present a typical spectrum for so called disordered systems (Griscom, 1980) present in a glassy hosts (Berger, Kliava, Yahiaoui, Bissey, Zinsou, Béziade, 1995). The line intensities decrease progressively showing the evolution of the relative line shapes and the intensities at g = 4.3 from isolated ions in local tetrahedral (and eventually octahedral) sites (Berger *et al*., 1995).

The line with g_{eff}=1.98 may be attributed to Cr^{3+} (S=3/2) ions in the slightly distorted octahedral sites (Simion *et al*.,1995; Karthein, Motschi, Schweiger, Ibric, Sulzberger, Stumm, 1991). For both mullites samples the calculated g_{eff} –factors for each line are: g_{eff} =4.29 and g_{eff} =2.06.

CONCLUSIONS

Identification of the paramagnetic complex and its surroundings based on the analysis of the EPR line shapes as well as the line positions in magnetic field was performed. The EPR lines with g_{eff} ≈2.0 and g_{eff} ≈4.3 in the spectra of the glass samples studied may be due the impurity Fe^{3+} ions substituted at octahedral sites.

Similarily, the EPR lines g_{eff} ≈2.0 may be due to the impurity Cr^{3+} ions substituted at slightly distorted octahedral sites.

The EPR spectra were analyzed to investigate the possible relationships between EPR spectra and the size of Al_2O_3 powder grain. For the sample Al_2O_3 #325, we observe two EPR signal near H ≈ 300 mT with g_{eff} = 2.23 and g_{eff} = 2.33. In spite of similar chemical composition as for the sample # 325 such line is not visible in sample # 200. However, the EPR lines near H = 130 mT, g_{eff} ≈ 4.3 and H = 330 mT, g_{eff} ≈ 2.0 for sample # 200 exhibit considerably larger intensity than that in sample # 325. This indicates considerably larger content of iron Fe^{3+} ions incorporated as impurities in this Al_2O_3 sample.

The EPR line near H = 300 mT (g_{eff} = 3.4) for sample # 200 may possibly be related to the change the iron valence from Fe^{3+} to Fe^{2+}. Further studies may lead to otential application of EPR technique as a fingerprinting method.

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