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Application of the EPR method for the study of the impurities in the powders used in ceramic cores and forms in the aerospace industry

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Abstract

E In this work the electron paramagnetic resonance (EPR) spectra of Al2O3 powders were measured for different size of grains (0.074, 0.044 mm) as well as for the mullites (0.07 and 0.12 mm) and ZrO2 powders (0.149, 0.044 mm). We have used multifrequency EPR spectroscopy at X-band and Q-band, The measurements were performed at room temperature and in the temperature range from 140 K up to 380 K. The motivation for this study comes from the need to solve the problem of fractures of shape and ceramic cores. The purpose of this study is demonstrate the applicability of EPR methods for the assessment of impurities of Cr and Fe ions in the materials used as ceramic cores and forms in the aviation industry. The analysis of EPR spectra were obtained and the characteristic lines were selected to rating the level of impurities.

Keywords: *electron paramagnetic resonance (EPR), Al2O3, mullites, ZrO2 powders*

1. Introduction

The ceramic nano-powders are widely used in different industry branches. The polymer nanocomposites stiffened by ceramic nano-filling they are characterized by very high hardness and resistance for abrasion with comparison in composites in micrometric scale[1,2].

The problem of cracking of composite materials has been studied in detail in various works, for example in [3] describes how to produce Al_2O_3-Fe composites by casting of ceramic masses of successive, developed for the improvement of fracture toughness. In [4] ceramics based on alumina and mullite takes into account chemical reactions have been studied and highlights the problem of cracking.

In work [5] authors presents the results of numerical calculations of temperature distribution and thermal stresses induced in the various layers and zones of samples (ceramic coating-interlayer- creep-resisting alloy) annealing in the temperature range from 200 to 1200 °C, annealing isothermally and cooled in air, which is results allowed us to deepen the analysis of the destruction of ceramic coatings during cyclic changes of temperature.

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. This work is a part of a PhD project.

The motivation for this study comes from the need to solve the problem of fractures of shape. In work [6] using shape criterion, the classifications of inclusions in regular composites ZrO_2-Al_2O_3 on convex and about variable the curvature both positive, as and negative were made. The probable mechanisms responsible for appearing of inclusions with classified shape among others, connected with shape of particles of initial Al_2O_3 powder, were showed. For the evaluations of influence of inclusions shape on evolution of crack the thermal stresses called out the maladjustment of thermal expansion coefficient of the zirconium warp and corundum inclusions the method of rank elements (MES) was used.

Mulgrain and mullite-based materials are prepared by calcinations of mixtures of white clays, kaolinites, and quartz sands containing different mineral components such as oxides of titanium, manganese, and iron. They apart from giving color to mullite, can exert an influence on its strength [7] owing to the ability of transition metals to enter the crystal lattice of mullite [8]. The mechanism of metal incorporation and the effect of incorporated metal on the strength properties of mullite were studied in some detail in [9, 10].

2. Experimental details

For the experiment, the samples of corundum Al_2O_3, mullite and ZrO_2 with different size and incorporating a second phase were used.

The electron paramagnetic resonance (EPR) spectra of of Al_2O_3 powders were measured for different size of grains (0.074, 0.044 mm) as well as for the mullites (0.07 and 0.12 mm) and ZrO_2 powders (0.149, 0.044 mm). The detailed data for samples are given in Table 1.

The EPR spectra were investigated in a wide range of temperatures from 120 K to 380 K using an EPR X-band and Q-band spectrometer (Bruker multifrequency and multiresonance FT-EPR ELEXSYS E580). Measurements at low temperatures were carried out using a helium cryostat with the Helium Temperature Control System ER4112HV.

Table 1. The specification of samples.

Sample	Al_2O_3	Al_2O_3	ZrO_2	Mullite	Mullite
Size grains	0.074 mm	0.044 mm	0.044 mm	0.07 mm	0,12 mm
Qualitative analysis of phase composition by X-ray diffraction methods	α Al_2O_3 – corundum 93,9±0,1 [%] $NaAl_{11}O_{17}$ – β-Al_2O_3 6,1±0,1 [%]	α Al_2O_3 – corundum 95,5±0,1 [%] $NaAl_{11}O_{17}$ – β-Al_2O_3 4,5±0,1 [%]	~100%	Al2O3 - 76.86[%] SiO2 - 22.8 [%]	Al2O3 - 75.04[%] SiO2 - 24.5[%]

3. Results and discussion

Selected EPR spectra are shown in Fig. 1 to 4.

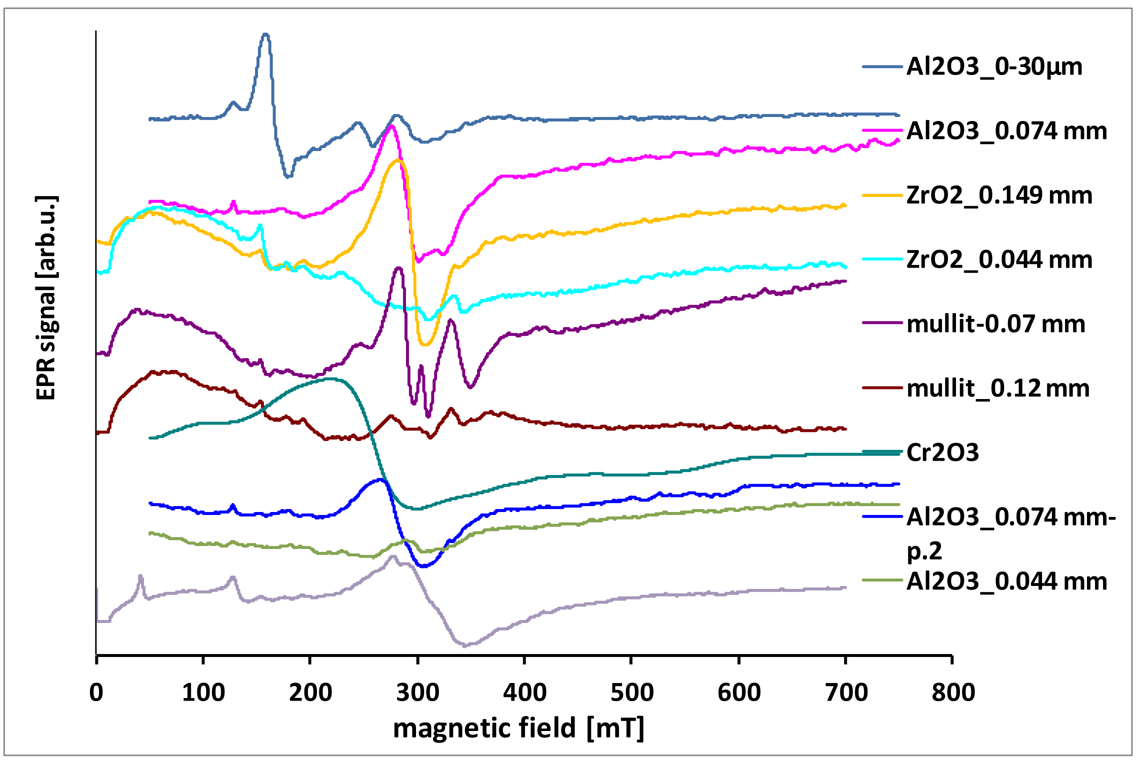


Fig. 1. EPR spectra in X-band for selected samples from the investigated materials.

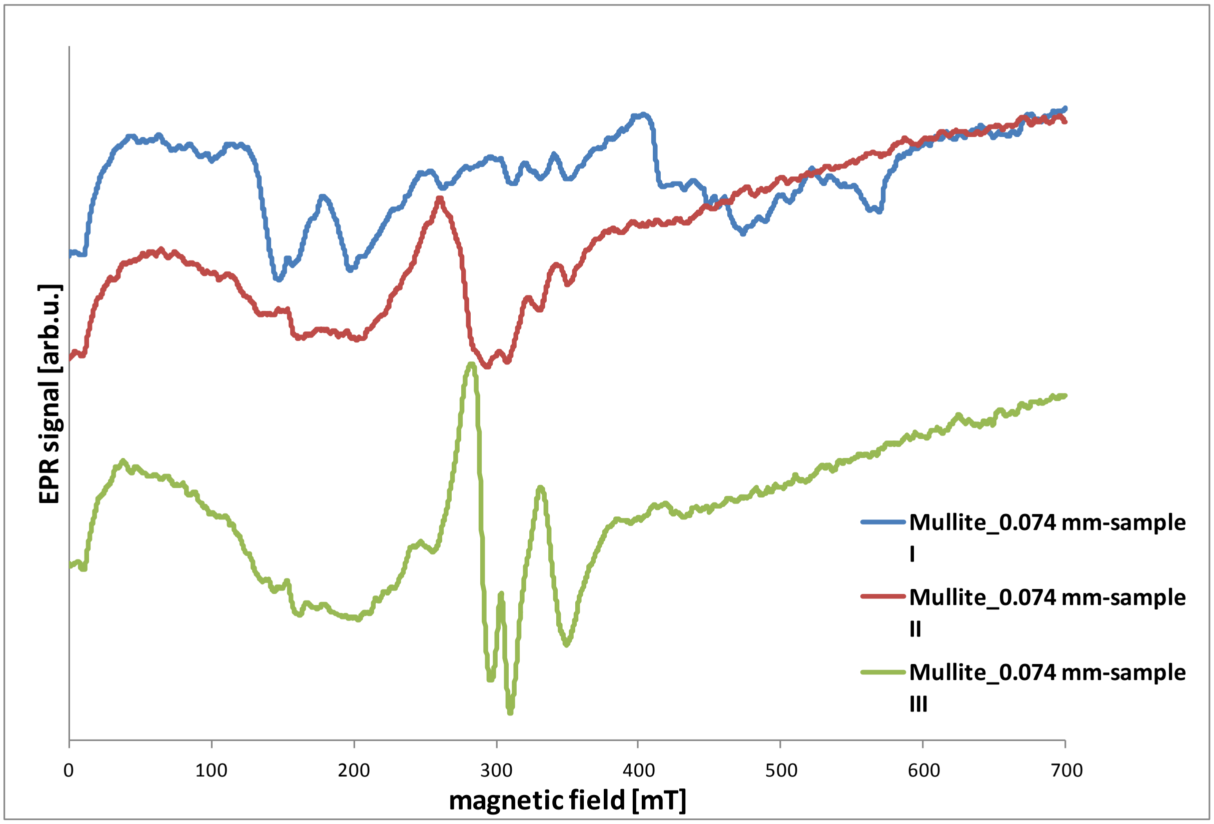


Fig. 2 . EPR spectra in X-band for mullite samples from different part of materials commercially available.

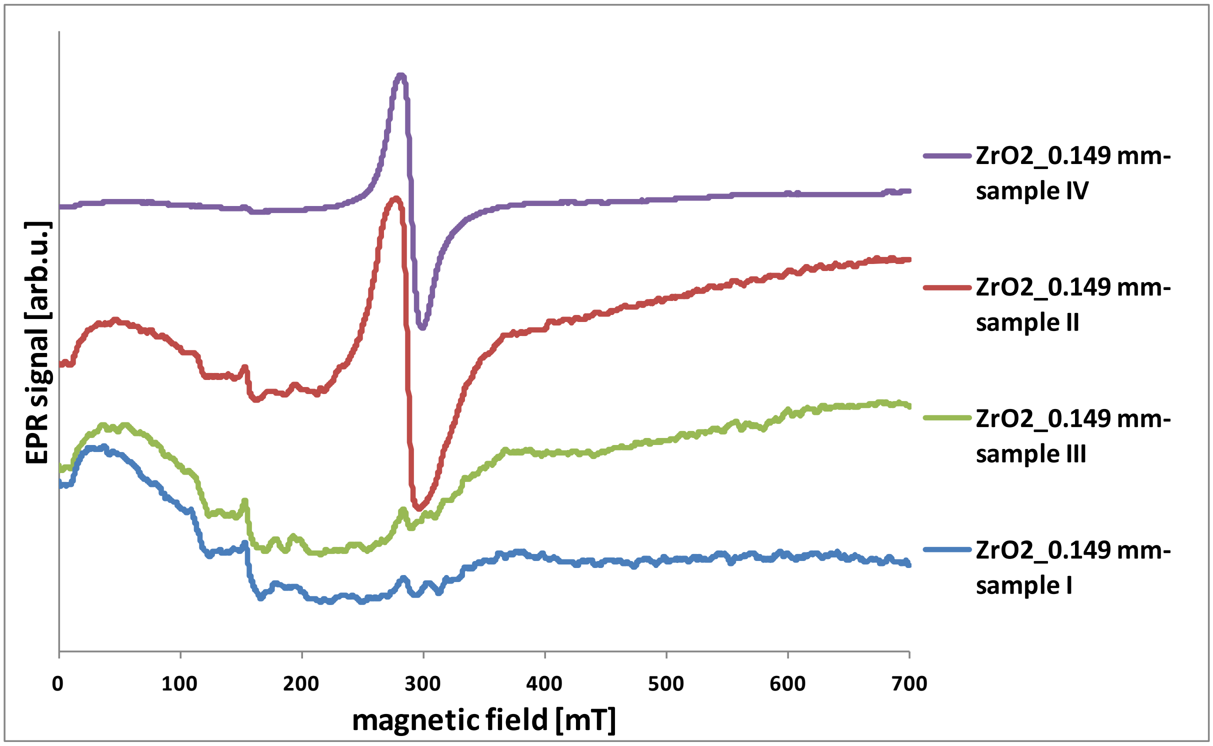


Fig. 3. EPR spectra in X-band for ZrO_2 samples from different part of materials commercially available.

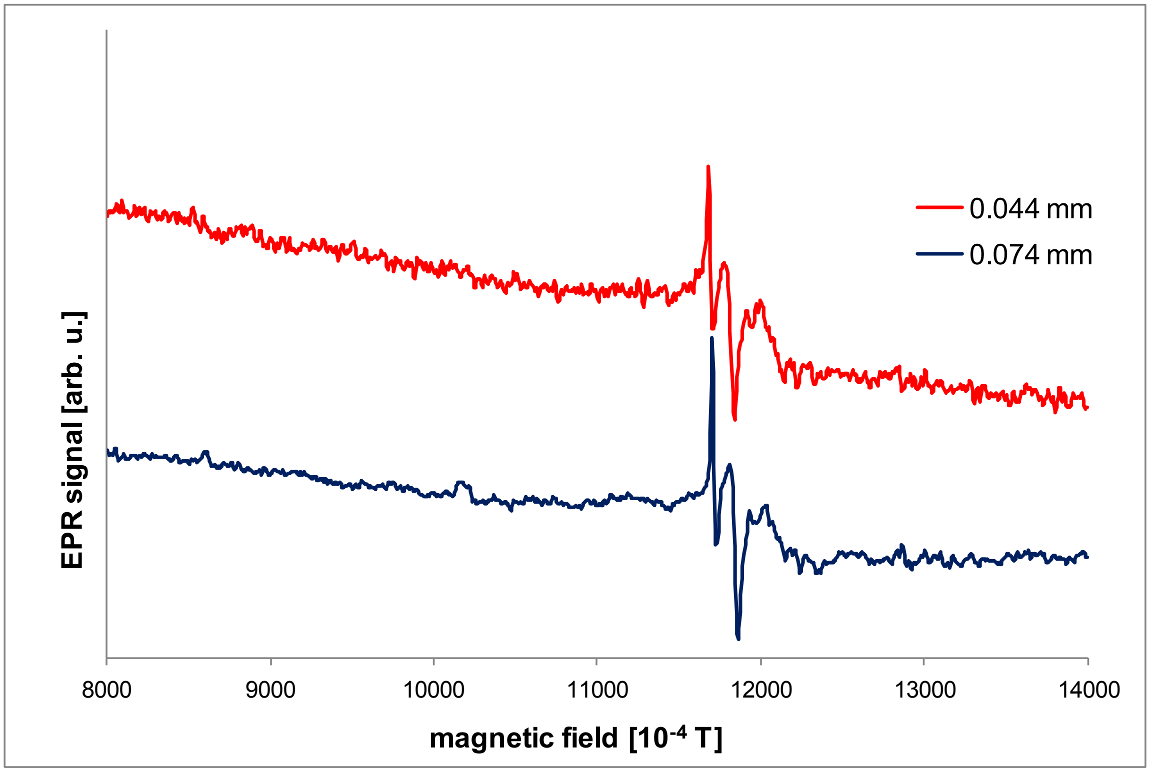


Fig. 4 . EPR spectra in Q-band for Al_2O_3 samples

For samples Al_2O_3 the spectral analysis were performed in our early work [11]. As the results of analysis the Fe^{3+} and Cr^{3+} ions were detected in all sample of corundum.

For the Al_2O_3 sample the calculated g_{eff} –factor values for each line are as follows: g_{eff} =5,6 g_{eff} =4.29 g_{eff} = 3.36, g_{eff} = 2.57, g_{eff} = 2.26, g_{eff} =2,00, g_{eff} =1.97, g_{eff} =1.69. However, for the mullites samples the calculated g_{eff} –factors for each line are: g_{eff} =5,6, geff =4.29 and geff =2.06, g_{eff} =1.97. The estimated experimental uncertainty of the g-values is ±0.02.

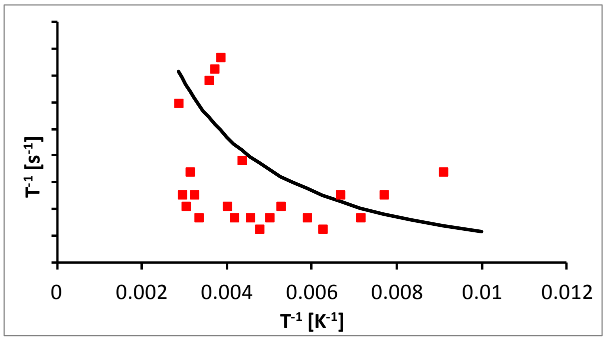
For the ZrO_2 sample the calculated g_{eff} –factor values for each line are as follows: g_{eff}=6.84; g_{eff} =4,23; g_{eff} =2.54, g_{eff} =2.24, g_{eff} =2.37; g_{eff} =1.88.

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 [12] present in a glassy hosts [13]. 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 [13]. The line with g_{eff}=1.98 may be attributed to Cr^{3+} (S=3/2) ions in the slightly distorted octahedral sites [14].

In the studied materials differences in ion content of Cr^{3+} and Fe^{3+} were observed and heterogeneity have been linked as a possible source of cracking if the core components have not been good mixed. [15]

For Al_2O_3 powders from different parts of the some size of grain, different EPR spectra was obtained. As a result of the analysis, the identification of existing complexes of paramagnetic ions were performed, where nanoparticles Cr_2O_3 in addition to chromium and iron were detected. Cr_2O_3 phase occurs only in part II of Al_2O_3 powder with a particle size 0.074 mm, and a small amount in mullite powder.[15]

The temperature dependence of the EPR line of the peak-to-peak (Bpp) linewidths were also measured for Fe^{3+} ions in mullite. From these measurement, the values of the broadening (ΔB) of the EPR line width, can be determined. The analysis of the temperature dependence for the EPR line width in mullite powders was performed with the Orbach process (Fig. 5).



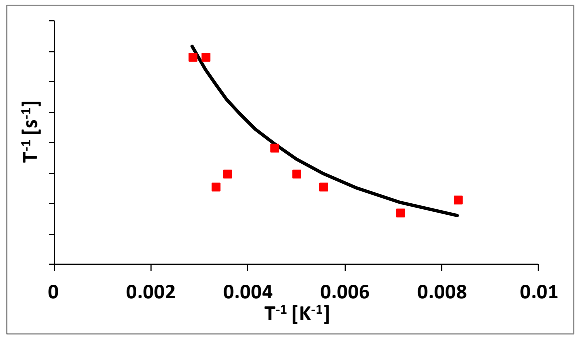


Fig.5. Temperature dependence of the spin-lattice relaxation time T1, of the mullites (0.07 mm-left and 0.12 mm-right figure). The solid curve is an exponential fit to the obtained data by the equation 2. Obtained value is A[s^{-1}]=2,7E+11 and δ [cm^{-1}]=105.

The estimation of the spin-lattice relaxation time T_1 can be made using the conventional method of line broadening, using the expression:

$$T_1^{-1} = 2.8 \times 10^{10} \pi g \Delta B \quad (1)$$

In the temperature range 140 – 380 K the relaxation time T_1 is governed by the Orbach process:

$$T_1^{-1} = A\left(exp^{\left(\frac{\delta}{k_B T}\right)} - 1\right)^{-1} \quad (2)$$

where δ represents the energy splitting between the ground paramagnetic centers state and the first excited state, whereas A is a constant characteristic of the Orbach process (in s^{-1}).

4. Conclusion

Oxides of 3d-transition elements of composition Me_2O_3 form mullite-based solid solutions via mechanism of isomorphous- isovalent replacement of aluminum atoms by a transition metal at octahedral positions of the crystal lattice of mullite. The concentration of a transition metal in the solid solution is determined by structural and crystal chemical properties of the corresponding oxide.

Identification of the paramagnetic centers present in the examined materials having position and shape of the EPR lines have been performed.

The EPR spectra for these samples have differ quite considerably in shape, the intensity of individual components of the line, the width and the resolution and the signal-to-noise ratio, even though they are made using the same spectrometer EPR in the same conditions. These results correlate with the content of impurities in the powders from different manufacturers. Analyzing changes in line widths with Orbach model for materials which are composed of different dopants can be detected of character line width changes even if the overlapping EPR lines.

The analysis of the temperature dependence for the EPR line width in mullites (0.07mm and 0.12 mm) was performed with of Orbach process. Parameters obtained from the model of Orbach is presented in this work.

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