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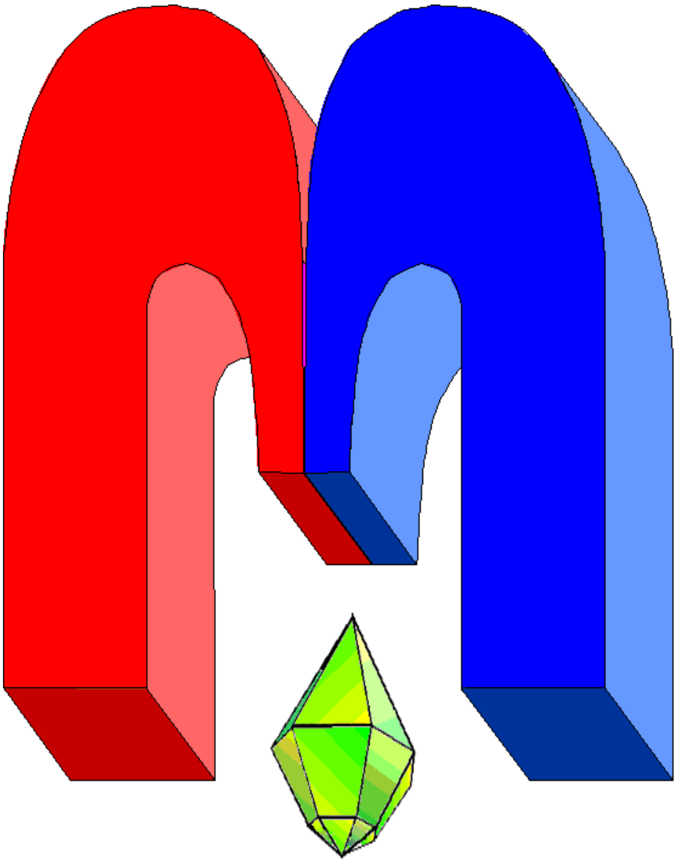

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[*] In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

EPR study of the CaF_2 powder mechanochemical doping with rare-earth ions

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In the present work we show with electron paramagnetic resonance (EPR) spectroscopy that in the process of the mechanochemical doping of the CaF_2 fine particles with Er^{3+} and Yb^{3+} ions the cubic symmetry rare-earth (RE) ion centers are formed with the concentration proportional to the particles surface in the sample. Amount of the mechano-doped RE-ion centers is proportional to η^{α}, where η is the weight fraction of the RE fluoride in the initial mixture and $\alpha \sim 0.8$. Cubic symmetry centers dominate in the EPR spectrum up to $\eta = 0.1$. A hypothesis of the cubic RE-ion center formation is proposed according to which its origin is associated with the presence of the ideal cleavage planes in the CaF_2 crystals: during the mechano-doping a considerable fraction of the rare-earth ions is trapped between the cleavage planes of the agglomerating particles, thereby getting into the crystal field of the cubic symmetry.

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keywords: fluorite, rare-earth ions, mechanochemical doping, electron paramagnetic resonance

1. Introduction

Although nanostructured high-surface area metal fluorides are of increasing importance for different applications like heterogeneous catalysis, thin films, nanoceramics, bioceramics or glasses, only few papers exist on mechanical doping and mechanochemical reactions of solid fluorides. This is due to the peculiar properties of solid fluorides such as the high ionic bonding character, their comparably low hardness accompanied by some elasticity and the high moisture sensitivity [1].

Electron paramagnetic resonance (EPR) spectroscopy is one of the most informative methods for investigation of the paramagnetic centers which appear, in particular, at the particle surface on grinding of the crystalline samples. The advantage of the EPR as compared with diffraction and other methods consists not only in higher sensitivity but also in the ability by means of the spectra analysis to determine the nature and concentration of the impurity atoms, their location in the crystal structure, the origin of the charge compensators and their position with respect to the detected impurities.

From a lot of the experiments performed by the different authors it is well known that rare-earth (RE) ions can substitute the calcium ions in the single crystals of the calcium fluoride CaF_2 (fluorite). The point symmetry in the positions substituted by the RE ions can be cubic, tetragonal or trigonal [2]. Formation of the axial-symmetry centers is caused by a necessity of compensation their excess positive charge (RE^{3+}) with respect to the substituted Ca^{2+} ions.

After Bleaney suggested [3] that the RE elements ions with odd number of electrons in the cubic environment can be used as active medium for masers if their ground state is Γ_8 quadruplet, a lot of both theoretical and experimental works appeared in which the properties of these ions in the cubic symmetry crystals are investigated [4]. Traditional methods of sample preparation were crystallization from the melt, solid-phase synthesis, and hot pressing. However, a number of multicomponent fluoride materials cannot be obtained by these methods because of the high volatility, thermal dissociation, pyrohydrolysis, and other unfavorable characteristics of some initial components, which are difficult to combine with refractory, nonvolatile, and thermally stable initial components. In the mechanochemical synthesis, such limitations either are absent or influence the result only to a minor degree [5].

The natural consequence of a necessity in charge compensation upon heterovalent substitution is a dependence of the fractions of different types of centers on an impurity concentration. Thus, in the EPR study of Er^{3+} paramagnetic centers in doped BaF_2 and SrF_2 single crystals [6] it was shown that with an increase of a total Er^{3+} ion concentration (from 0.001 to 0.1 at.%) the fraction of the cubic centers decreased. Moreover, these fractions are the complex functions of the initial dopant concentration and the conditions of a sample synthesis.

In the present work we report on studies of the fluorite (CaF_2) particles doped mechanochemically with Er^{3+} and Yb^{3+} ions. The dependency of the EPR spectra intensity and shape on ErF_3 concentration in the initial mixture are studied. It is shown that up to 10 wt.% of the dopant concentration the cubic symmetry RE-ion centers are formed. A hypothesys is proposed that a specific self-organization in the ensembles of the mechanochemically-doped fluorite nanoparticles is responsible for a predominant formation of these cubic RE-ion centers. Thereby the base for a development of an effective and economically sound method of synthesis of powders with predefined properties is created.

2. Sample preparation and experiment techniques

Fluorite powders mechanochemically doped with rare-earth ions have been obtained by mean of grinding of the mixtures of CaF_2 and RE fluoride (ErF_3 or YbF_3) high purity (99.8%) crystalline salts in an agate mortar in extra-pure isopropyl alcohol. Both ErF_3 and YbF_3 starting compounds were in the orthorhombic (*Pnma* space group [7]) phase revealed in the x-ray powder diffraction pattern. Initially, a mixture of CaF_2 and ErF_3 with 1 wt.% of the last was ground for 12 hours and a series of different size samples was obtained by a successive sedimentation of the particles in isopropanol for 48, 17, 6 and 2 hours. The powders were characterized in size with scanning electron microscopy (SEM) and the mean sizes for each sample were found by the fits of the size histograms to the log-normal distribution [8].

In order to exclude incorrectness in the RE impurity concentration, before the beginning of sample preparation the mortar was polished with a corundum-based abrasive which was followed by the two times grinding of the CaF_2 pure salt in it. Concentration series of the samples were prepared with a sequential increase of a RE-salt content in the mixture. The ErF_3 concentration dependences in CaF_2 were studied for two sample series. The first series is different from the second one only in a preliminary grinding of CaF_2 salt for 20 minutes. Both series of 6 samples consisted of CaF_2 + 0.1, 0.3, 1.0, 3.0, 10, 30 wt.% ErF_3 fine powders, respectively. The CaF_2 powder doped with Yb^{3+} ions was prepared from the initial mixture of 97 wt.% CaF_2 and 3.0 wt.% YbF_3.

Additionally, four samples were studied that were prepared by grinding of the CeO_2 + 0.3, 1, 3.0, 10 wt.% Er_2O_3 mixture, respectively. CeO_2 has the same crystal structure as CaF_2.

We have consciously avoided any heat treatment of the obtained samples as this can modify the situation due to the activation of the rare earth ion diffusion within the particle.

EPR spectra of the obtained samples were measured with a commercial Bruker ESP 300 X-band (~ 9.5 GHz) spectrometer equipped with the standard TEM_{012} mode rectangular cavity. Temperature of the samples was controlled with the Oxford Instruments ESR9 helium flow cryogenic system.

3. Results and discussion

The fact of the fluorite particles mechanochemical doping with Er^{3+} ions is clearly illustrated by Figure 1, where the EPR spectra of ($0.99{\cdot}\mathrm{CaF}_2{+}0.01{\cdot}\mathrm{ErF}_3$) mixture before and after grinding are presented. Before grinding the EPR spectrum is a superposition of the EPR spectra of CaF_2 and ErF_3 components. Undoubtedly, after grinding of the mixture as a result of a mechanoactivation in the range of the magnetic fields of ~ 1000 Oe the spectrum typical for cubic centers of Er^{3+} ions in the crystalline CaF_2 appears. This is evidenced also by the coincidence of the effective g-factor value of $g = 6.785$ [2] and a lineshape not revealing any specific for anisotropic centers signs of a "powder" structure. There is also a weak signal present in both EPR spectra in Fig. 1 at the field value of ~ 1600 Oe. This signal originates from a small admixture of Fe^{+} ions ($S = 1$) in CaF_2 salt and in the further will be subtracted from the spectra.

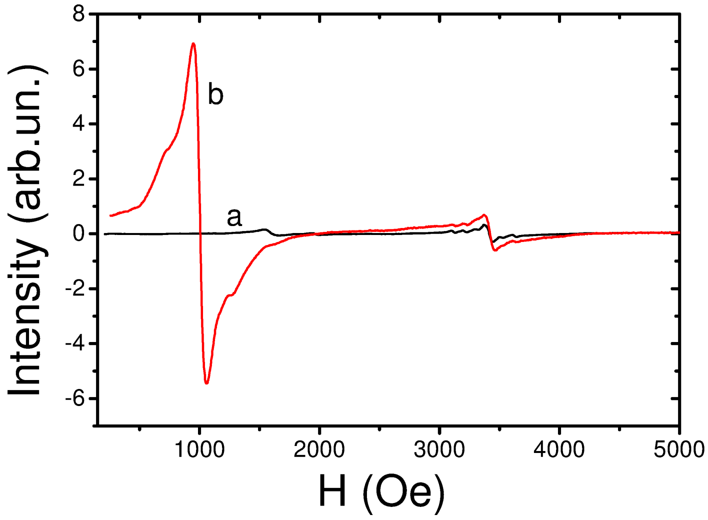

Figure 1. EPR spectra of ($0.99{\cdot}\mathrm{CaF}_2 + 0.01{\cdot}\mathrm{ErF}_3$) mixture before (a) and after grinding (b); $T = 15\,\mathrm{K}$.

This spectrum intensity dependence of the mechano-doped Er^{3+} centers on the size of the particles has been addressed in our previous paper [8]. Ground for 12 hours mixture of ($0.99{\cdot}\mathrm{CaF}_2 + 0.01{\cdot}\mathrm{ErF}_3$) was divided into the fractions of different grain sizes by means of successive sedimentation. The spectra of the samples measured in the identical conditions with the intensity normalized to the sample mass are shown in Figure 2. Linear fits shown in the inset of Figure 2 indicate clearly that the intensities of the components at $g = 6.785$ and $g = 1.97$ dominating in the spectra are both proportional to $\langle d\rangle^{-1}$, where $\langle d\rangle$ is the average grain size in the sample. The volume and surface of particle are related by $S/V \propto \langle d\rangle^{-1}$. The volume of the particles that are large enough is strictly proportional to the mass. Therefore on normalization of the spectra intensity to the sample mass the particle surface area in the sample is proportional to $\langle d\rangle^{-1}$. Thus, the described observation indicates unambiguously that the centers responsible for the signals at $g = 6.785$ and $g = 1.97$ are localized at the CaF_2 particle surface. The signal at $g = 1.97$ corresponds to the intrinsic surface defects of CaF_2 [8]. Signal at $g = 6.785$ are clearly related to the single Er^{3+} ions in an essentially cubic crystal field.

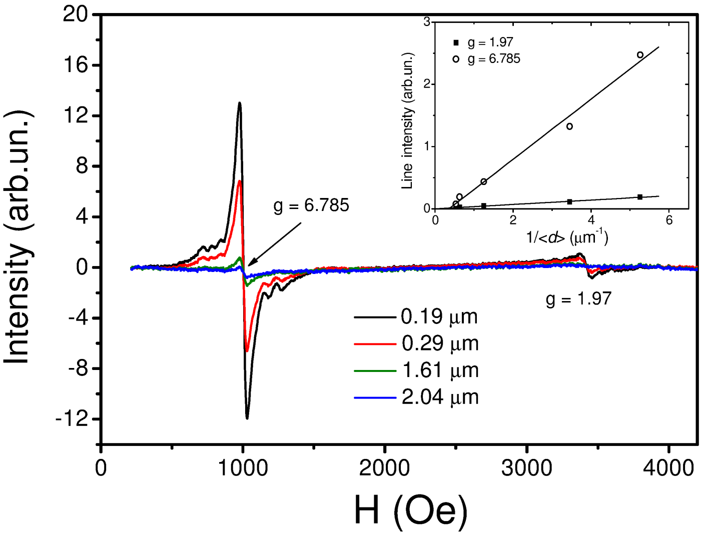

Figure 2. EPR spectra of (0.99·CaF$_2$ + 0.01·ErF$_3$) sample series with various grain sizes normalized to the sample mass; $T = 15$ K. Insert: EPR line intensity dependences at $g = 6.785$ and $g = 1.97$ on grain size and their linear fits.

Summarizing the observations, we are reaching two controversial conclusions: i) localization of the mechano-doped Er^{3+} centers at the fluorite particle surface and ii) cubic symmetry of these centers. It is obvious that the centers localized at the crystal-vacuum interface cannot possess the high symmetry. Solution of this contradiction as well as the establishment of further regularities describing a mechanodoping process of CaF$_2$ particles with RE ions from the EPR spectroscopy data have become a subject of the present work.

One of the regularities that we were interested in was the dependence of the mechanically-doped centers concentration as well as their qualitative composition on mass fraction η of REF$_3$ salt in the $[(1-\eta)\cdot\text{CaF}_2+\eta\cdot\text{REF}_3]$ initial mixture. This dependence was studied on doping of the CaF$_2$ particles with Er^{3+} ions. The concentration dependence of the EPR spectra normalized to the sample mass for one concentration series of the two prepared is shown in Figure 3. EPR spectra of the second series were very close to the spectra presented in Figure 3 both in structure and in intensity.

All the EPR spectra contain a component observed at $g \sim 6.785$. As it was already described previously, this component reproduces the properties of the cubic symmetry Er^{3+} ion impurity center in crystalline CaF$_2$. At concentrations less than 1 wt.% of ErF$_3$ in the initial mixture the spectrum of the Er^{3+} ions increased in intensity staying unchanged in a shape. In the samples with concentration less than 3 wt.% of ErF$_3$ the spectrum of ^{167}Er isotope ($I = 7/2$, natural abundance 22.9%) with a typical eight-component hyperfine structure is clearly revealed.

The tendency of the Er^{3+} cubic center formation dominates up to the 10 wt.% ErF$_3$ concentration. In crystalline CaF$_2$:RE^{3+} already at a RE-ion concentration as low as 0.1 wt.% various axial-symmetry centers appear and dominate (Table 1) [9, 10]. We have not found the EPR signals at the g-factor values indicated in Table 1, but the typical spectrum of Er^{3+} cubic centers only.

With an increase of the ErF$_3$ concentration in the initial mixture the dual effect occurs in

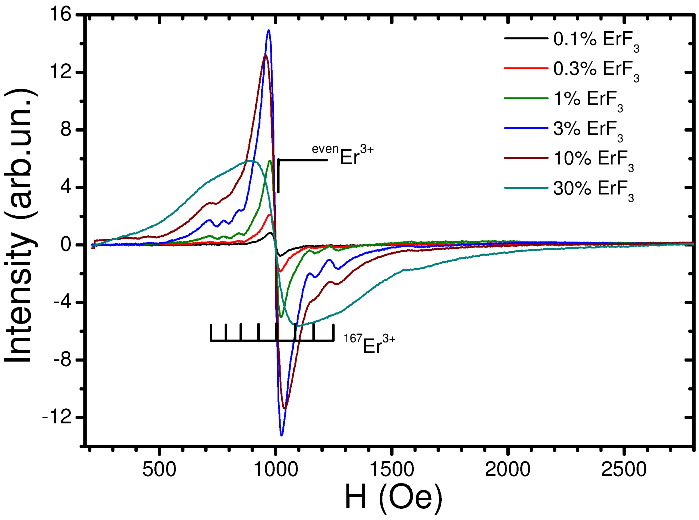

Figure 3. EPR spectra of the samples with different $\mathrm{ErF_3}$ concentrations ground for 1 hour; $T = 15\,\mathrm{K}$. Spectra intensities are normalized to the sample masses.

the EPR spectrum of the samples. First, the width of spectral components corresponding to the $\mathrm{Er^{3+}}$ cubic centers gradually grows. Second, a clear redistribution of spectrum intensity from narrow well-defined signals of cubic centers to the wide wings is observed. Note that the wide structureless line is present in the EPR spectra of the samples even at low $\mathrm{ErF_3}$ concentrations in the ground mixture. This is evident from comparison of EPR spectra of the powder and $\mathrm{CaF_2{:}Er^{3+}}$ single crystal with 1 at.% $\mathrm{Er^{3+}}$ concentration presented in Figure 4.

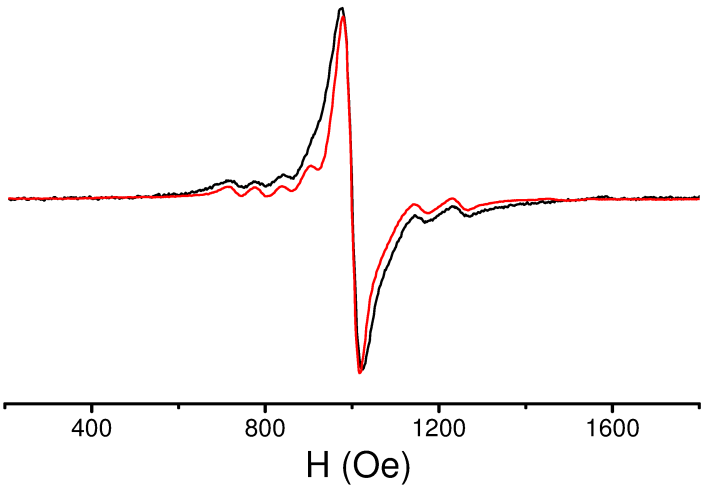

Figure 4. EPR spectra of the mechanochemically doped $\mathrm{CaF_2{:}Er^{3+}}$ fine powder (1 wt.% of $\mathrm{ErF_3}$ in the initial mixture) and $\mathrm{CaF_2{:}Er^{3+}}$ single crystal with 0.8 wt.% of $\mathrm{ErF_3}$ in initial charge; $T = 15\,\mathrm{K}$. Peak intensities of the two spectra are adjusted one to another.

The width of the components of the EPR spectrum of the $\mathrm{Er^{3+}}$ impurity ions in $\mathrm{CaF_2}$ single crystal even at low temperatures is large enough, about 40 Oe. It can be associated with several factors as, e.g., unresolved superhyperfine structure from the interaction with the nuclear spins of the nearest fluorine ions ($I = 1/2$, 100% natural abundance), dipole interactions with

Table 1. g-factor values of the impurity Er^{3+} centers in monocrystalline CaF_2 [9, 10].

Site	Cubic	Tetragonal(I)	Tetragonal(II)	Trigonal(I)	Trigonal(II)
$g_\parallel$	6.785 ± 0.002	7.78 ± 0.02	1.746 ± 0.002	3.30 ± 0.01	2.206 ± 0.007
$g_\perp$		6.254 ± 0.005	9.16 ± 0.01	8.54 ± 0.02	8.843 ± 0.010

the surrounding Er^{3+} ions as well as the distribution of the g-factor values due to the random strains in the crystal. The last term should become even more pronounced for the Er^{3+} ions located at the surface of the CaF_2 particles. Most likely, this is the reason why the dependence of the width of the spectral components on the concentration of mechano-doped Er^{3+} centers was found rather weak. For the same reason the effects associated with the dimensional restriction to the 2D inherent to the surface centers are poorly identified. The nature of wide structureless line of the EPR spectrum will be discussed below.

In Figure 5 the concentration dependencies of the $g \sim 6.785$ spectrum integral intensity are presented. Dependencies can be fit well by the power law $I_{int} = A\eta^{\alpha}$. The power values obtained for the two studied series are 0.79 ± 0.04 and 0.87 ± 0.04. In order to understand the nature of such character of the dependencies, the two limiting cases can be considered, which can be realized in the course of the mechanochemical doping:

1. the first case corresponds to the "soft" with respect to the CaF_2 "dopant" - ErF_3. It means that in this limit the compound used for mechanoactivation is completely transformed into the RE^{3+} paramagnetic single centers. Obviously, integral intensity of the EPR spectrum will be proportional to the concentration η, and $\alpha = 1$, correspondingly;

2. the second limit corresponds to the "hard" with respect to CaF_2 activator. In this case very thin surface layer of ErF_3 particles will transform into the Er^{3+} single ion centers. The intensity of the spectrum will be proportional to the area of the dopant particles: $I_{int} \propto S_{surf} \propto V^{2/3} \propto m^{2/3} \propto \eta^{2/3}$, i. e., $\alpha = 2/3$.

Both cases are the limit ones and in practice probably are not realized. Then one can expect the observation of some intermediate cases which was indeed found in the experiment.

In order to confirm systematic character of our rather unusual observations on the mechano-doped CaF_2:Er^{3+} powder, we have also performed an experiment on the mechano-synthesis of CaF_2 powder doped with Yb^{3+}. The sample was prepared from the (97 wt.% CaF_2 + 3 wt.% YbF_3) initial mixture. EPR spectrum of the sample is shown in Figure 6. Noteworthy that like the case of mechano-doping with Er^{3+} ions, the spectrum can be presented by superposition of signals of Yb^{3+} cubic centers well-known from the spectra of monocrystalline samples and a wide structureless line. In the spectrum of the cubic centers a hyperfine structure for ^{171}Yb isotope ($I = 1/2$, natural abundance 14.31%) and ^{173}Yb isotope ($I = 5/2$, natural abundance 16.13%) is revealed rather well.

Our further efforts were aimed at the establishment of the origin of the RE-ion cubic centers formed in the mechanochemically doped powders of CaF_2. We have prepared and studied by the EPR spectroscopy the ceric oxide CeO_2 powders also mechano-doped with Er^{3+} ions. CeO_2 has the fluorite crystal structure. In the EPR spectra of the four prepared samples of CeO_2 with Er_2O_3 portion of 0.3, 1.0, 3.0, 10 wt.% in the initial mixture any well-defined signals had not been observed, only a wide structureless line was found near $g \sim 6.78$ (Figure 7).

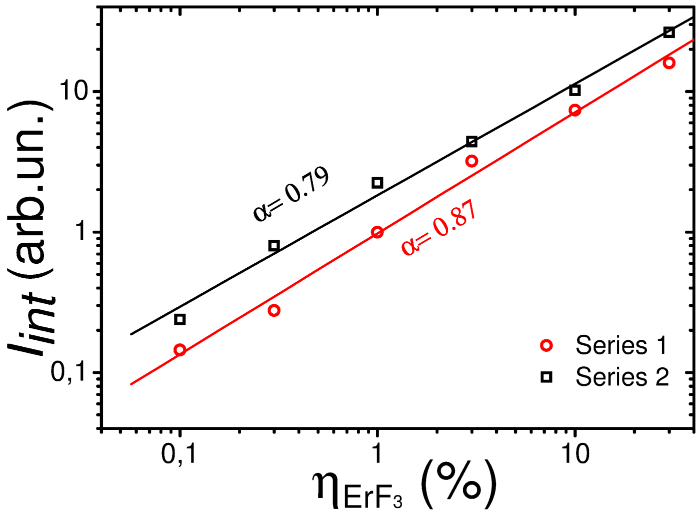

Figure 5. ErF$_3$ concentrations dependencies of the EPR lines observed at $g = 6.785$ for the samples in the first series (circle), second series (square) and the power law fits (lines) of the dependencies.

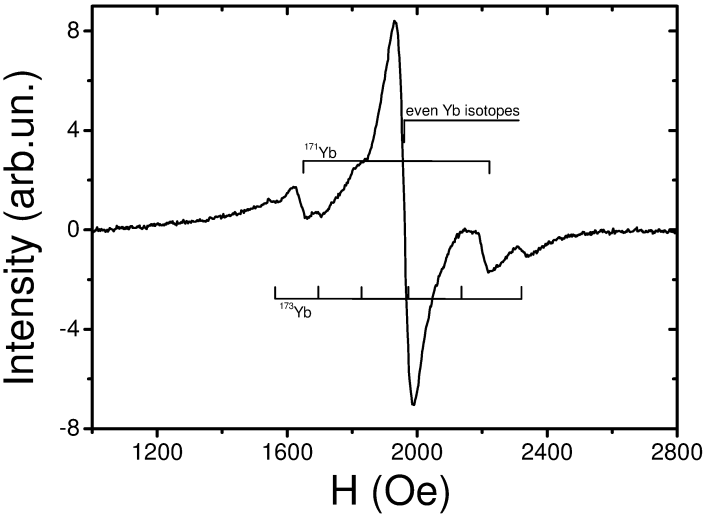

Figure 6. EPR spectrum of the (97 wt.% CaF$_2$ + 3 wt.% YbF$_3$) mixture ground for 1 hour; $T = 15\,$K.

Basing on the differences observed in the spectra of the CaF$_2$:Er^{3+} and CeO$_2$:Er^{3+} powders the following hypothesis can be proposed for a formation of the "surface" cubic centers of the RE-ions in CaF$_2$ (Figure 8). Key point here is that CaF$_2$ cleaves ideally along the (111) crystal planes which is not the case for CeO$_2$ [11–14]. Respectively, the differences between CeO$_2$ and CaF$_2$ samples can be attributed to the CaF$_2$ particles aggregation with the cleaved planes "sticking" to each other. Rare-earth ion, if trapped in between these planes, would possess the symmetry close to cubic, and an amount of these centers would be proportional to the particle surface.

Basing on our hypothesis a large difference in the shapes of the EPR spectra of the mechano-doped samples with 10 and 30 wt.% of ErF$_3$ in the initial mixture can be explained as follows (Figure 3). Up to the concentration of 10 wt.% of ErF$_3$ the most of the Er^{3+} ions for some reason are trapped between the cleavage planes and reveal itself as the cubic centers. At higher

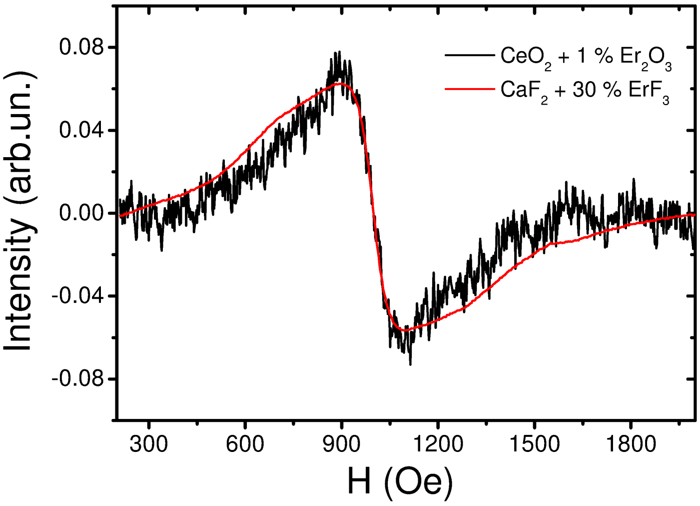

Figure 7. EPR spectra of the CaF_2 (with 30% ErF_3) and CeO_2 (with 1% Er_2O_3) nanoparticles mechano-doped with Er^{3+} centers; $T = 15\,K$. Resonance fields of the two spectra and the peak intensities were adjusted one to the other.

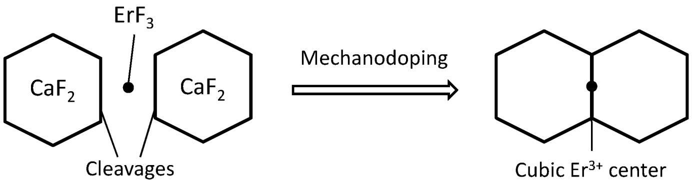

Figure 8. Formation of the "surface" cubic centers of RE ion in CaF_2

concentrations of ErF_3 the Er^{3+} centers localized at the exposed surface of the particles start to dominate. The spectrum of these centers, as expected, has a large inhomogeneous width, and is very similar to the EPR spectrum of CeO_2:Er^{3+} powder (Figure 7).

4. Conclusions

Results presented in the paper can be summarized as follows:

- In the course of a mechanochemical doping of the CaF_2 particles with Er^{3+} and Yb^{3+} ions the cubic symmetry centers are formed with the concentration proportional to the particle surface in the sample
- EPR spectra of the rare-earth ions in the obtained samples are represented by a superposition of the well-defined signal of the cubic centers and the wide structureless absorption band caused by the Er^{3+} centers at the surface of the particles
- Origin of the observed centers is associated with the presence of the ideal cleavage planes in the CaF_2 crystal. During the mechano-doping as a result of a specific self-organization a considerable fraction of the rare-earth ions is trapped between the cleavage planes of the agglomerating particles, thus reproducing the crystal field of the cubic symmetry.

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