EPR studies of the mechanochemically Er$^{3+}$-activated fluorite nanoparticles

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Abstract. In the present work we show with EPR spectroscopy that the simultaneous grinding of the crystalline CaF$_2$ and ErF$_3$ salts leads to the mechanochemical doping of the single Er$^{3+}$ ions in the CaF$_2$ host. Dependence of the EPR spectra intensity on the grain size indicates clearly that the Er$^{3+}$ centers are created at the surface of the particles. Dominant part of the observed paramagnetic centers represent the Er$^{3+}$ ions substituting the regular quasicubic Ca$^{2+}$ lattice site ($g = 6.7$) perturbed by the vicinity of the surface. Fine particles of CaF$_2$ reveal also the nearly-isotropic EPR signal at $g \approx 1.97$ that originates from the surface defects and can be used for characterization of the obtained samples with respect of the average grain size. Grinding of the of the CaF$_2$ and ErF$_3$ mixture in the ratio of 100:1 during 12 hours gives the surface density of the Er$^{3+}$ ions of $\sim 0.1$ nm$^{-2}$, or $\sim 10^4$ Er$^{3+}$ ions per the 190-nm size particle.

1. Introduction

Nowadays the nanostructured high-surface area metal fluorides are of increasing importance for different applications like heterogeneous catalysis, thin films, nanoceramics, bioceramics or glasses. Furthermore, investigations of the ionic crystals doped with the rare-earth (RE) ions are actual both for investigations of the mechanisms of the impurity ion and host lattice interaction and for development of the theoretical concepts and practical applications (solid-state lasers, superionic conductors, scintillators etc.) [1].

Electron paramagnetic resonance (EPR) is one of the most informative methods for investigating the crystals doped with RE ions since the EPR spectra allow determining of the structural properties of the impurity in the lattice, characterization of powder samples with respect to its average particle size, investigating the phenomena occurring on the particle size reduction. Papers [2, 3] notice that till year 2006 only few papers existed on the application of the magnetic resonance spectroscopy methods to studies of the mechanically activated solids and, especially, solid fluorides. This fact motivated our study the fluorides by EPR.

One of the important applications of the RE ions is magnetic resonance imaging (MRI). Contrast agents (CAs) often comprising the gadolinium ions are widely used to improve the sensitivity and diagnostic confidence in MRI [4]. Despite the progress in the design and synthesis of these agents, many are still limited by low relaxivity, low specificity and potential toxicity. In particular, aqueous Gd$^{3+}$ ions are toxic and therefore need to be sequestered using a variety of linear and macrocyclic helates. However, chelation can reduce the contrast enhancement because it decreases the number of coordination sites available for water proton exchange. Paper [5] provides a new approach to solve the...
above-mentioned problems which is based on confining of the magnevist, gadofullerenes and gadonanotubes inside the nanoporous structure of the silicon particles.

Mechanochemical synthesis can also serve as the perspective method for confining of the RE ions inside the crystal structure. Moreover, mechanochemical synthesis has an important advantage compared with the traditional method of the impurity-doped crystal synthesis (method of the directed crystallization), namely the low temperature, which lifts many limitations associated with different melting points of the components, their vapor pressures, thermal decomposition, and other factors. As a host lattice the CaF$_2$ compound was chosen since it is one of the main initial components in the mixture for the mechanochemical synthesis of the nanostructured fluoroapatite [6]. The aim of our work was to investigate the mechanoactivated centers of the RE elements in the fine powders of the crystals with fluorite structure. We have studied the fluorite nanoparticles activated by the Er$^{3+}$ ions. Er$^{3+}$ ions were chosen due to the fact that its resonance EPR line occurs at the g-factor value different from g ~ 2 which gave an opportunity to study explicitly the mechanochemically activated Er$^{3+}$ centers. In our opinion, results the paper may be generalized to the Gd$^{3+}$ ions incorporated to the fluorite nanoparticles in a similar way.

2. Sample preparation

Fluorite fine particles mechanochemically activated with RE ions have been obtained by means of grinding of the mixtures of CaF$_2$ and RE fluoride high purity crystalline salts. In this paper we studied the samples prepared from the initial mixture of 99 wt.% of CaF$_2$ and 1 wt.% of ErF$_3$. The series of the fine powders with various average grain sizes <d> was produced by grinding of the initial mixture for 12 hours in an agate mortar followed by the successive sedimentation in extra-pure isopropyl alcohol. The studied series consisted of the fine powders obtained after the 48, 17, 6 and 2 hours sedimentation.

Obtained samples were characterized with a scanning electron microscope (SEM). Commercial Philips XL 30 microscope was used for this purpose. The images of the 48 h and 2 h sedimentation samples are shown in Figure 1. The corresponding grain size distributions are presented by the histograms shown in Figure 2. In order to find out the average grain size <d>, grain size distributions were fit to the log-normal distribution function

$$f(x) = A \exp \left( - \frac{\left[ \ln x - \ln \langle d \rangle \right]^2}{2w^2} \right).$$

Results of the analysis are summarized in Table 1.

![Figure 1](image-url) Scanning electron microscopy images of the samples obtained by the 48 hours (a) and 2 hours (b) sedimentation.
Figure 2. Grain size distributions of the samples obtained by the 48 hours (a) and 2 hours (b) sedimentation.

Table 1. Mean particle sizes for the studied sample series

| Sedimentation (h) | Size (µm)       |
|------------------|-----------------|
| 48               | 0.19 ± 0.01     |
| 17               | 0.29 ± 0.02     |
| 6                | 1.58 ± 0.09     |
| 2                | 1.61 ± 0.12     |
| residue          | 2.04 ± 0.13     |

3. Results and discussion

EPR spectra of the obtained samples were measured with a commercial Bruker ESP 300 X-band (~9.5 GHz) spectrometer equipped with the standard TEM₀₁₂ mode rectangular cavity. Temperature of the samples was controlled with the Oxford Instruments ESR9 helium flow cryogenic system.

Effect of grinding on the EPR spectra of CaF₂, ErF₃ and of (0.99·CaF₂ + 0.01·ErF₃) mixture ground in the agate mortar for 45 minutes is shown in Figure 3. The spectra were measured at T = 15 K. Compared with the spectra of the ground for the same time CaF₂ and ErF₃ salts, the spectrum of the ground mixture clearly contains a new component observed at g ~ 6.71 (1010 Oe). In the other words, we see that the ground (0.99·CaF₂ + 0.01·ErF₃) mixture is not the same as the mixture of the ground CaF₂ and ErF₃. The origin of the g ~ 6.71 component becomes evident if one studies the papers on the EPR spectroscopy of the CaF₂:Er³⁺ crystals [7-11]. This component fits well the properties of the cubic symmetry Er³⁺ ion center.

Another component that is found both in the ground CaF₂ and (0.99·CaF₂ + 0.01·ErF₃) mixture occurs at g ~ 1.97. And, finally, no any pronounced spectral features are found in the EPR spectrum of the ground concentrated ErF₃.

Thus, the mechanochemical activation of the CaF₂ particles with Er³⁺ ions clearly takes place on grinding of the CaF₂ and ErF₃ mixture.

In order to achieve better understanding of the mechanoactivation process we have studied the series of the fine powder samples described in a previous section, that differ essentially in the grain size only. The spectra of the samples measured in the identical conditions with the intensity normalized to the sample mass are shown in Figure 4.
Figure 3. EPR spectra of CaF$_2$ (black), ErF$_3$ (blue) and (0.99·CaF$_2$ + 0.01·ErF$_3$) mixture ground for 45 minutes; $T = 15$ K.

Figure 4. EPR spectra of the various size samples of the ground for 12 hours (0.99·CaF$_2$ + 0.01·ErF$_3$) mixture; $T = 15$ K.

Figure 5 depicts the dependencies of the peak-to-peak line intensities for the components found at $g = 6.71$ and $g = 1.97$ on the mean particle size $<d>$. The fits shown in Figure 5 indicate clearly that the intensities of both components dominating in the spectra are proportional to $<d>^{-1}$. As for any shape of the particle its volume and surface are related by $S/D \propto <d>^{-1}$, the described observation shows that both the $g = 6.71$ and $g = 1.97$ features originate from the particle surface. Thus, mechanoactivation of the CaF$_2$ fine particles with Er$^{3+}$ ions occurs at the particle surface which looks natural. Relation of the $g = 6.71$ spectral feature to Er$^{3+}$ ions is of no doubt: in the spectra of the two smallest grain samples the hyperfine structure is observed for the $^{167}$Er isotope ($I = 7/2$, natural abundance 22.9%).
Figure 5. Grain size dependencies of the EPR lines observed at $g = 6.71$ (circles), $g = 1.97$ (squares) and the linear fits of the dependencies.

The component at $g = 1.97$ is also interesting and important. It originates from the particle surface but is not related to erbium ions. This component was observed in the spectrum of the ground CaF$_2$ in Figure 3. Therefore it is most probably the intrinsic signal from the defects that form at the CaF$_2$ surface. Then, the intensity of the $g = 1.97$ spectral component can serve as a measure of the mean particle size in the CaF$_2$ fine powders prepared by means of grinding.

There are two signals caused by contamination of the CaF$_2$ salt. The first, which is revealed as the six-line hyperfine pattern at $g \sim 2$, obviously originate from the Mn$^{2+}$ ions. The second, which is an asymmetric line at $g \sim 4.3$, clearly scales with the mass of CaF$_2$; its origin is not clear.

In the range of the $g$-factor values typical for Er$^{3+}$ centers in CaF$_2$ additional spectral features are resolved that are especially pronounced for the samples of 1.61 mm and 2.04 mm. Thus, one can clearly see the signals that can be characterized with the $g$-factor values of 9.78, 4.22, 3.42 and 3.76. None of these values characterize the known Er$^{3+}$ centers found in the CaF$_2$:Er$^{3+}$ crystals. However, if these, quite well defined centers are localized at the particle surface, the $g$-factor values may differ from those in the bulk due to the lattice constant relaxation nearby the surface. Note the shift of the $g$-factor for the surface quasicubic Er$^{3+}$ centers ($g = 6.71$) with respect to its value in the crystal ($g = 6.78$).

Finally, we compare the spectra of the mechanoactivated Er$^{3+}$ centers at the surface of the CaF$_2$ particles and the doped ones in the CaF$_2$ single crystal (Figure 6). Obviously, the two spectra essentially reproduce each other, except of the linewidth. This indicates that in the process of mechanoactivation the “cubic” structure doped Er$^{3+}$-centers are predominantly formed. Linewidth increase can naturally be assigned to the disorder that takes place in the particle volume close to its surface. It is worth mentioning that the substantial value of the Er$^{3+}$-ion spectrum linewidth in the crystal is related to the comparable terms that occur due to the dipole interaction and non-resolved superhyperfine structure from the neighboring fluorine ions.

The absolute microwave absorption value registered for the Er$^{3+}$-mechanoactivated CaF$_2$ particles and CaF$_2$:Er$^{3+}$ single crystal that was grown from the initial charge that contained 0.8 wt.% of ErF$_3$ allowed us to estimate the surface density of the mechano-doped Er$^{3+}$ centers. We have found that if one prepares the sample by 12 hours grinding from the mixture of (0.99-CaF$_2$ + 0.01-ErF$_3$), there will be about 0.1 Er$^{3+}$-ion per nm$^2$, or $\sim 10^5$ Er$^{3+}$-ions per the particle 190 nm in size.
Figure 6. EPR spectra of the CaF$_2$ nanoparticles ($<d> = 190$ nm) with mechanoactivated Er$^{3+}$ centers and CaF$_2$:Er$^{3+}$ single crystal with 0.8 wt.% of ErF$_3$ in initial charge; $T = 10$ K. Resonance frequencies of the two spectra and the peak intensities were adjusted one to the other.

4. Conclusions
Results presented in the paper can be summarized as follows:

- On grinding of the CaF$_2$ and ErF$_3$ mixtures mechanochemical activation of the CaF$_2$ fine particles with Er$^{3+}$ single ion centers occurs.
- In all the so far studied samples of the CaF$_2$ nanoparticles mechanoactivated with Er$^{3+}$ ions the two most intense EPR lines are observed at $g = 6.71$ and $g = 1.97$, with the intensities that scale with the amount of surface ($\propto <d>^{-1}$). This undoubtedly indicates that both lines originate from the surface defects. The line with $g = 1.97$ is caused by the intrinsic CaF$_2$ surface defects and thus can be used to estimate the mean grain size of the sample.
- Majority of the mechanochemically doped Er$^{3+}$ centers is represented by the nominally high-symmetry cubic centers of Er$^{3+}$ ions perturbed by the disorder nearby the surface.

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