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Electron paramagnetic resonance and X-ray diffraction study of PbF$_2$ fine powders mechanochemically doped with Er^{3+} ions

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Investigation of the mechanochemical doping of PbF$_2$ powders with Er^{3+} ions with electron paramagnetic resonance and X-ray diffraction is presented. In the analysis of the results a possibility of the structural transformation between the cubic β-PbF$_2$ and orthorhombic α-PbF$_2$ phases in the course of synthesis was taken into account. It is shown that regardless of the initial state of PbF$_2$ it reveals high efficiency of the mechanochemical doping with Er^{3+} ions. Obtained particles are found in (α/β)-PbF$_2$ structurally inhomogeneous state with the majority of the Er^{3+} ions located in the equilibrium α-PbF$_2$ fraction. Preferrable location of the Er^{3+} ions in the α-PbF$_2$ phase is related to the fact that the formation of the cation vacancies necessary for a mechanically activated diffusion of erbium ions into the particles and nucleation of the α-PbF$_2$ phase proceed in parallel and is mediated by dislocations created in the course of synthesis. Annealing of the sample leads to a conversion of its entire volume into the metastable β-PbF$_2$ phase with all the Er^{3+} centers possessing the cubic symmetry.

1. Introduction

Nowadays, β-PbF$_2$ single-crystalline optical fibers doped with rare-earth (RE) ions compete with the traditional ones produced from doped glasses [1]. Optical properties of the crystalline β-PbF$_2$ fibers are more attractive than those of the glass fibers. However, the technology of the crystalline fiber production is significantly more complex and expensive. An alternative approach is based on the synthesis of the RE-doped β-PbF$_2$ glass-ceramics, as it is much simpler while the optical properties are comparable [2, 3].

Mechanical activation or, briefly, "mechanoactivation" can serve as an alternative and effective means for incorporation of the RE ions into the crystal structure as well as one of the steps of the doped ceramics synthesis. Mechanoactivation in general is a complex, multistage process of changing the state of a solid under a delivery of the mechanical energy [4]. Moreover, mechanochemical synthesis has an important advantage with respect to the traditional method of the doped crystal growth by means of directional crystallization, namely, the low (room) temperature, which allows to overcome the restrictions associated with different melting points of the components, vapor pressure, thermal decomposition, and other factors [5]. Therefore, it is important to study processes that occur in the course of the mechanochemical doping of PbF$_2$ with Er^{3+} ions.

Our previous studies [6–8] of the mechanochemical doping of MF$_2$ (M = Ca, Sr, Ba) fine powders with Er^{3+} ions performed with electron paramagnetic resonance (EPR) spectroscopy

have shown that the cubic symmetry Er^{3+} ion impurity centers are formed. Investigations of the EPR spectra intensity dependences on the particle size have shown that doping proceeds differently for various MF$_2$ hosts. In the case of CaF$_2$, impurity centers are located in a thin surface layer of the particles. In SrF$_2$, the impurity is distributed over the particle volume. In BaF$_2$, there is a layer of a finite thickness for which the probability of the mechanochemical doping is small, and RE impurities are located in the cores of the large enough particles. These observations were explained assuming that the result of the mechanosynthesis of the fluorite-structure particles doped with Er^{3+} ions is governed by two processes: mechanically-activated diffusion of RE ions into the particles, and segregation of the impurity ions to the grain boundaries. In this case, characteristic depth values for various MF$_2$ differ considerably from each other. Also, it has been shown that MF$_2$ powders mechanochemically doped with Er^{3+} ions are in a long-lived metastable state characterized by a high concentration of vacancies and dominating cubic symmetry Er^{3+} ion centers [9]. Annealing of the samples brings the powders to the ground state with most of the vacancies healed, and trigonal symmetry Er^{3+} centers are formed in SrF$_2$ and BaF$_2$ due to the local charge compensation by the interstitial fluorine ion.

In [6–9], we studied MF$_2$ fluorites that exist only in the cubic phase. It was interesting to study the mechanochemical doping with RE ions of a crystalline host with higher complexity. It is known that under normal conditions PbF$_2$ can exist in the two structural phases [10]: thermodynamically equilibrium orthorhombic α-PbF$_2$ (space group Pnma) and metastable cubic β-PbF$_2$ phase. The latter has the fluorite structure with the space group Fm3m.

It follows from the above that the studies of the mechanosynthesis of the PbF$_2$ powders doped with rare-earth ions are promising and relevant, due to both the possibility of a simplified doped ceramics synthesis as well as an assessment of the approach applicability to different MF$_2$ hosts.

2. Sample Preparation and Experiment Techniques

PbF$_2$ powders mechanochemically doped with Er^{3+} ions were obtained by grinding of the (97 wt.% PbF$_2$ + 3 wt.% ErF$_3$) mixtures of high purity crystalline salts in an agate mortar in extra-pure isopropyl alcohol. The choice of isopropyl alcohol as a buffer medium is due to its low chemical activity in the series of alcohols. Grinding of the powders in the isopropanol allowed to avoid their prolonged contact with air and, accordingly, excluded the interactions with oxygen and water vapor, which could significantly complicate the interpretation of the results. To control better the concentration of the RE impurity, before grinding of the mixture the mortar was cleaned with a corundum-based abrasive followed by a two-time self-lining with the PbF$_2$ compound.

Since PbF$_2$ can exist at room temperature in two modifications (α, β)-PbF$_2$ [10], it was necessary to control a sample phase composition, both in the initial mixture and in the prepared fine powders. From the X-ray diffraction (XRD) analysis, the major part of the PbF$_2$ powder initially was in the orthorhombic α-PbF$_2$ phase. Transformation of the orthorhombic to the cubic phase (β-PbF$_2$) can be achieved by the annealing at a temperature of 650°C. Subsequent cooling down to the room temperature at atmospheric pressure does not lead to a reverse transition. In this study, the annealing of the α-PbF$_2$ powder for 12 hours has led to the transformation of more than 90% of its volume to the β-PbF$_2$ cubic phase. β-PbF$_2$ is in fact a metastable state, and, according to [10], under a mechanical stress α-PbF$_2$ nucleates in the β-PbF$_2$ at the structural defects like slip lines and bands. As far as the ErF$_3$ is concerned, according to the powder-XRD analysis its whole volume was in the orthorhombic phase (space group Pnma [11]).

Series of the fine powder samples with different mean particle size $\langle d \rangle$ were prepared from the (97 wt.% PbF_2 + 3 wt.% ErF_3) mixture with the predominant β-PbF_2 phase by grinding for 12 h in an agate mortar. Separation of the fractions with different particle sizes was performed by means of the successive sedimentation in isopropanol. Prior to sedimentation the powders were dispersed in a small amount of the solvent with ultrasound. Studied series that differed only in the grain size consisted of fine powders obtained after 48, 17, 6 and 2 hour sedimentation.

Samples were characterized with the Philips XL30 scanning electron microscopy (SEM). In order to determine the mean particle sizes $\langle d \rangle$, the distributions of grain sizes were fit to the log-normal distribution function [8]. The results of this analysis are presented in Table 1.

EPR spectra of the samples were measured with the continuous wave X-band ($\sim 9.5\,GHz$) Bruker ESP300 spectrometer. Experiments were performed at a temperature of $15\,K$. The temperature was controlled using an Oxford Instruments ESR-9 liquid helium flow cryostat.

Powder X-ray diffraction patterns were obtained with the Bruker D8 Advance diffractometer using the Cu-K_α radiation ($\lambda = 1.5418 Å$) in the Bragg-Brentano geometry.

3. Results and Discussion

In Fig. 1 EPR spectra are shown of the two PbF_2:Er^{3+} samples obtained by means of mechanosynthesis from lead fluoride with the dominating α-PbF_2 (volume fraction 94%) and β-PbF_2 (90%) phases (see Table 1). Both spectra in Fig. 1 contain a component at the g-factor of 6.78, characteristic for the cubic symmetry Er^{3+} impurity ion centers [2]. This is additionally approved by the observation for a sample produced from the β-PbF_2 of the hyperfine structure due to the ^{167}Er-isotope (nuclear spin $I = 7/2$, natural abundance 22.9%). However, for the sample synthesized from the β-PbF_2 the intensity of the line at $g \sim 6.78$ is almost an order of magnitude higher than for the sample produced from the α-PbF_2. In the EPR spectra of both samples, a new spectral component at $g \sim 12.7$ appears which has an asymmetric shape characteristic for the powder spectra of anisotropic centers. The intensity of the new component, which was not observed in the MF_2 before is similar for the samples produced from the α- and β-PbF_2.

Since high-purity chemical components were used for the preparation of the samples, and no signals were observed in the EPR spectrum of the mixture before grinding neither at $g = 6.78$ nor at $g = 12.7$, it may indicate that both signals originate from the impurity Er^{3+} centers. One may expect that in the course of grinding phase transformation between the α- and β-PbF_2 phases occurred with the transition from the metastable β- into the equilibrium α-phase more probable. Obviously, impurity Er^{3+} ion in the orthorhombic α-PbF_2 phase cannot have symmetry higher than the symmetry of the nearest surrounding, and therefore, should possess anisotropic g-tensor.

Table 1. Mean particle size and phase composition for a series of PbF_2 fine powder samples mechanochemically doped with Er^{3+} ions.

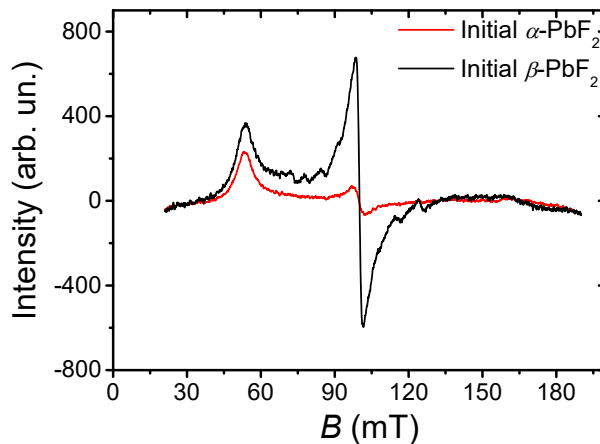| Fraction	Size (μm)	β-PbF_2(%)	α-PbF_2(%)
Initial PbF_2	~ 100	6 ± 2	94 ± 2
Annealed PbF_2	~ 100	90 ± 2	10 ± 2
48 h sedimentation	0.15 ± 0.01	15 ± 2	85 ± 2
17 h sedimentation	0.23 ± 0.02	20 ± 2	80 ± 2
6 h sedimentation	0.66 ± 0.09	31 ± 2	69 ± 2
2 h sedimentation	1.49 ± 0.12	36 ± 2	64 ± 2

Figure 1. EPR spectra of PbF$_2$ fine powders mechanochemically doped with Er^{3+} ions and produced by 3-hour long mechanosynthesis from (97 wt.% PbF$_2$ + 3 wt.% ErF$_3$) mixtures with dominating α-PbF$_2$ (red line) and β-PbF$_2$ (black line) phases; $\nu = 9.4864$ GHz, $T = 15$ K.
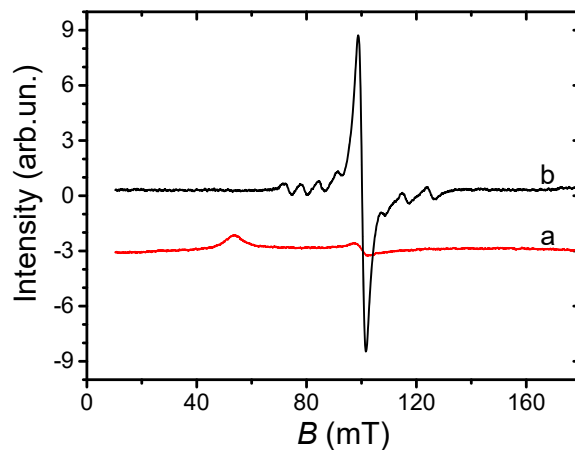

Figure 2. EPR spectra of PbF$_2$ fine powder mechanochemically doped with Er^{3+} ions (initial α-PbF$_2$) before (a) and after (b) the annealing for 12 hours at 650°C; $\nu = 9.4892$ GHz, $T = 15$ K.

To check whether the above assumptions are true, the PbF$_2$:Er^{3+} sample produced from the α-PbF$_2$ was annealed for 12 hours at 650°C. This annealing is a typical procedure used to transform PbF$_2$ from the α- to the β-phase. The results of the annealing are shown in Fig. 2. Clearly, EPR spectrum of the sample has changed drastically: while the asymmetric component at $g \sim 12.7$ has vanished, the spectrum of the cubic Er^{3+} center has increased in intensity more than 20 times, and hyperfine structure due to ^{167}Er-isotope has become obvious.

Thus, impurity Er^{3+} centers that resided in the orthorhombic phase due to the annealing and structural transition have acquired the cubic symmetry. Consequently, the intensity of the Er^{3+} cubic center spectrum increased at the expense of the anisotropic component. The intensity increase of the cubic Er^{3+}-center spectrum may seem too large. However, as the measured signal is in fact a derivative of the absorption spectrum, its amplitude for the powder samples in the case of a substantial g-factor anisotropy is significant mainly at the edges of the absorption pattern characteristic for powders. As an appropriate measure for the amount of paramagnetic centers is the integral intensity of the absorption spectrum, there is no inconsistency in our observations.

The shape of the observed anisotropic Er^{3+}-center powder spectrum allows us to conclude that, first, the largest of its g-tensor components corresponding to the low-field edge of the

absorption spectrum, is ~ 12.7. This value is quite ordinary for anisotropic Er^{3+} impurity centers; similar values of the g-factor were found for Er^{3+} ions in, e.g., CaO, Y_2O_3, $YCl_3 \cdot 6H_2O$, LaF_3 [12], SrY_2O_4 [13]. Second, low-symmetry Er^{3+} centers dominate in the sample produced from the orthorhombic α-PbF_2: less than 5% of the impurity Er^{3+} centers possess the cubic symmetry.

To learn more about the structural transformations in PbF_2 powders that occur in the course of the mechanosynthesis we studied it with X-ray diffraction. Sample series was prepared from β-PbF_2 by means of successive sedimentation from the (97 wt.% PbF_2 + 3 wt.% ErF_3) mixture ground for 12 hours. In Fig. 3 powder-XRD patterns of the series are presented. Clearly, two principal components dominate, from α- and β-PbF_2. Phase compositions obtained from the data analysis, are indicated in Figs. 3 and 4 and in Table 1.

In the initial mixture, about 90% of the PbF_2-powder volume was in the cubic β-phase. After grinding, the volume fraction of the cubic phase has decreased significantly. Thus, grinding
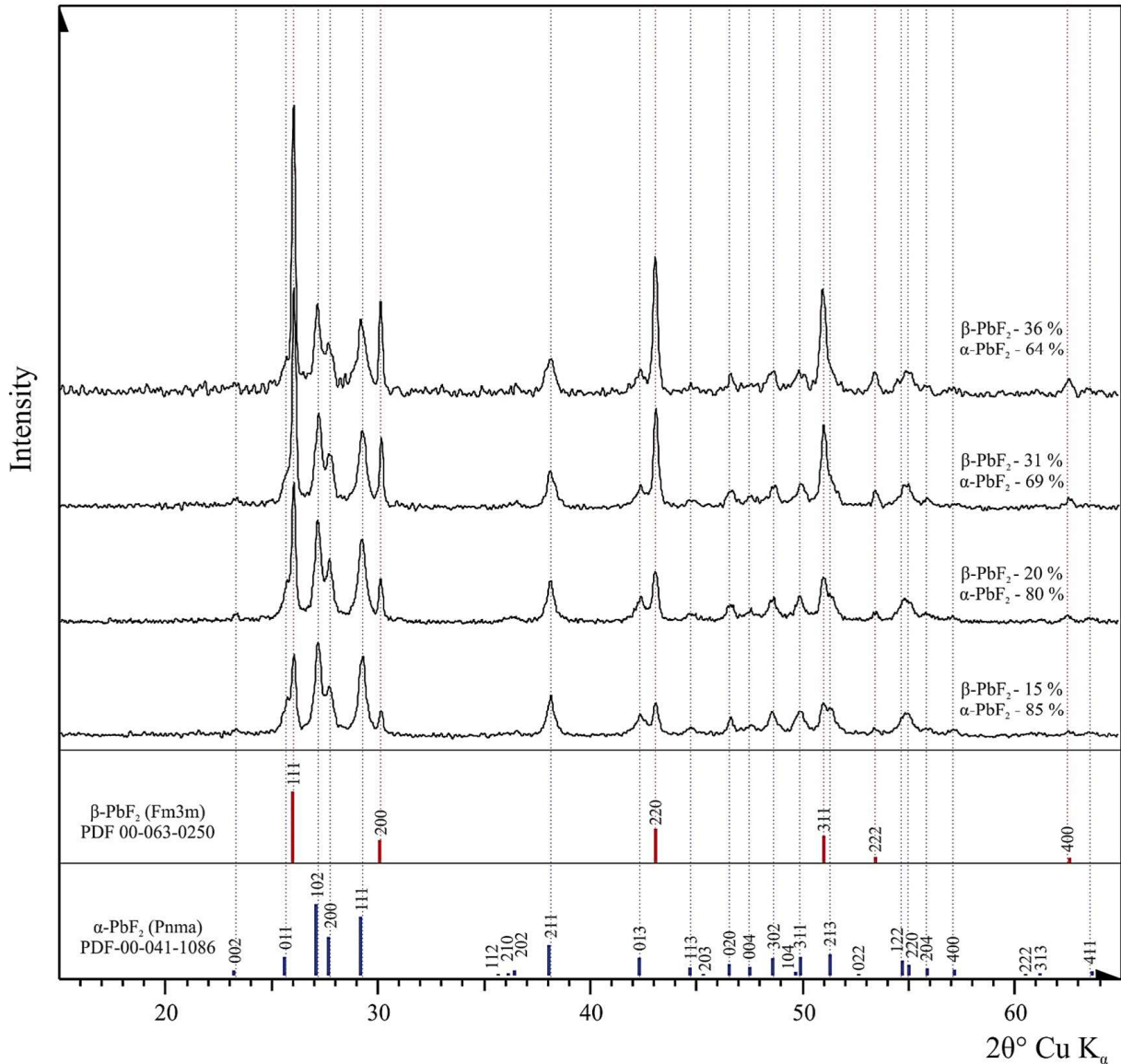

Figure 3. X-ray diffraction patterns of PbF_2:Er^{3+} powder samples produced by mechanosynthesis from (97 wt.% PbF_2 + 3 wt.% ErF_3) mixture with dominating β-PbF_2 phase. Mean particle size (from top to bottom): 1.49 μm, 0.66 μm, 0.23 μm and 0.15 μm.
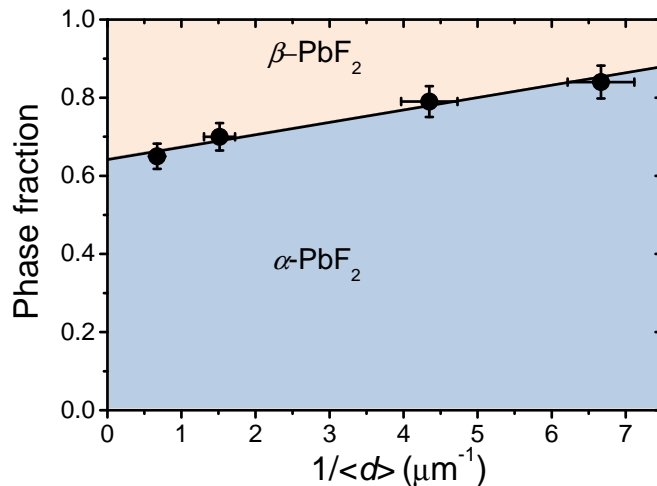
Figure 4. Dependence of the α- and β-phase content in the PbF$_2$ fine powders mechanochemically doped with Er^{3+} ions on grain size and its linear fit.

of PbF$_2$ in a mortar indeed leads to the transition of a part of the volume from the metastable cubic to the equilibrium orthorhombic phase. In our case, grinding for 12 hours has led to the transformation of most of the PbF$_2$ volume into a rhombic α-phase. Moreover, the content of the latter systematically increases with a decrease of the grain size reaching 85% for the finest fraction (Fig. 4).

Formation of the α-phase during the mechanochemical doping of β-PbF$_2$, in our opinion, proceeds in the following way. According to [10], on stress application the α-PbF$_2$ phase nucleates in the β-PbF$_2$ matrix at structural defects - slip lines and bands - created when deformation exceeds the elastic limit. Then the volume fraction of the α-PbF$_2$ increases under stress application/variation due to the growth of the α-phase droplets in the β-phase host. Therefore, an amount of the orthorhombic α-PbF$_2$ phase in the samples increases with the duration of the mechanosynthesis. Then one can expect that in the smaller particles the volume of the initially dominating cubic phase will be less that in the larger ones. This indeed is observed in our data. After 12-hour grinding in all the fractions of the sample most of the volume (64–85%) is in the α-PbF$_2$ phase.

In this situation, it is not surprising to observe in the EPR spectra of the β-PbF$_2$-based ground mixture the signal of the low-symmetry Er^{3+} ion centers. This signal originates from the impurity Er^{3+} ions in the α-PbF$_2$ phase. High intensity of the cubic Er^{3+}-center component in the EPR spectrum of the sample produced from the initial β-PbF$_2$ phase in Fig. 1, in our opinion, is due to the shorter duration of grinding (3 hours) compared with the series described above.

Knowledge of the anisotropic spectrum origin and the analysis of the spectra shown in Figs. 1 and 2 bring us to the following conclusions. First, we note that while the intensities of the anisotropic peaks at $g \sim 12.7$ for the samples obtained from α- and β-PbF$_2$ are practically identical (Fig. 1), the intensity of the cubic Er^{3+}-center spectrum for the sample obtained from the β-PbF$_2$ is approximately an order of magnitude greater. Therefore, it becomes clear that mechanically activated doping of the cubic β-PbF$_2$ phase is notably more efficient than of the rhombic α-PbF$_2$. Second, comparing the intensities of the Er^{3+} cubic center in the sample obtained from the α-PbF$_2$ before and after the annealing (Fig. 2), and the intensities of the anisotropic spectrum in the samples produced from the α- and β-phases (Fig. 1), one can conclude that in the sample prepared from β-PbF$_2$ the number of Er^{3+} anisotropic centers is greater than that of the cubic ones.
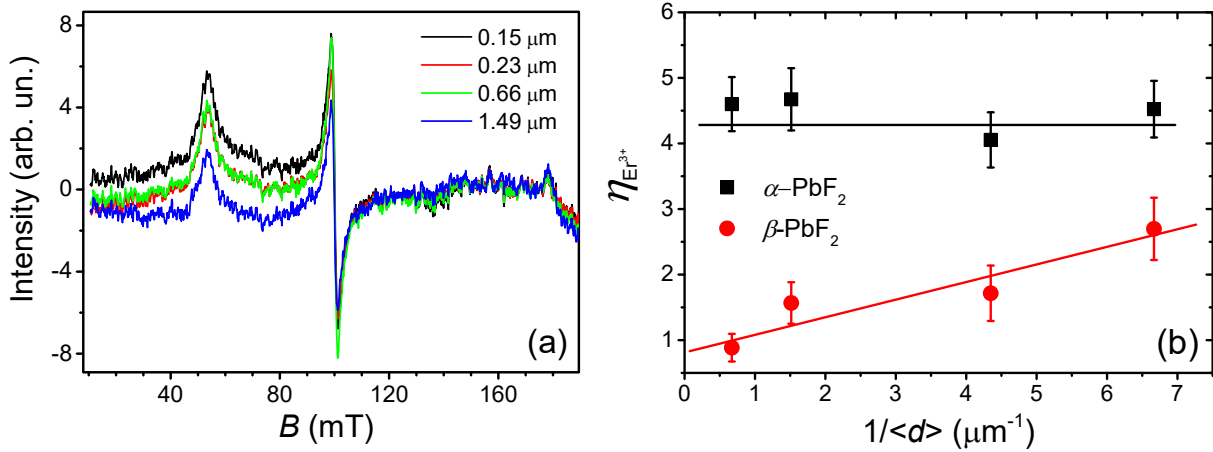
Figure 5. EPR spectra of the mechanosynthesized $PbF_2:Er^{3+}$ fine powder samples with different grain sizes (a); spectra intensities are normalized to the sample mass, $\nu = 9.484$ GHz, $T = 15$ K. Dependences on the particle size of the Er^{3+} impurity concentration in the α- and β-phases of PbF_2 and their linear fits (b).

Fig. 5(a) shows the EPR spectra of the $PbF_2:Er^{3+}$ grain size series. At first sight, there is no significant difference in the intensities of the principal spectral components. However, since both α- and β-phases are present in the samples, correct interpretation of the results demands the intensity of each component to be normalized to the volume fraction of the respective phase. The results are shown in Fig. 5(b). Here, the peak-to-peak intensity of the cubic Er^{3+} center spectrum served as a measure of its concentration, and the peak amplitude at $g \sim 12.7$ was used for Er^{3+} ions in the α-PbF_2 phase. The latter is correct within an assumption that the shape of the absorption spectrum of the Er^{3+} ions in the α-PbF_2 does not change from sample to sample.

The used approach obviously provides with an information on the relative changes in concentrations of two types of the Er^{3+} centers but not on the absolute amount of centers. It can be seen from Fig. 5(b) that the concentration of Er^{3+} ions in α-PbF_2 does not depend on the particle size. It means that the rhombic phase is evenly doped with Er^{3+} ions. Concentration of the Er^{3+} ions in the β-phase of PbF_2 increases with the decrease of the particle size. On plastic deformation of β-PbF_2 the α-phase is found both in the near-surface layer and in the volume of β-PbF_2 particles [10]. Rhombic α-PbF_2 nucleates at structural defects like slip lines and bands. Formation of these defects is associated with the creation of dislocations. Motion and annihilation of dislocations in turn generates cationic vacancies that serve as a necessary step in mechanoactivated diffusion of RE-ions into cubic fluorites CaF_2 and SrF_2. Thus, the source of the defects at which α-phase nucleates in β-PbF_2 and of those promoting RE-ions into fluorites is the same. Therefore, it is not a big surprise that on grinding of $(\beta$-$PbF_2 + ErF_3)$ mixture impurity Er^{3+}-ions are located mainly in the rapidly growing α-phase. Concentration of the Er^{3+} ions in α-PbF_2 does not change with the particle size of the powder, since, probably, the growth of α-PbF_2 occurs homogeneously throughout the sample.

Increase in the impurity Er^{3+} ion concentration in the cubic phase of PbF_2 with the decrease of the particle size can be explained in the following simple way. Since the volume fraction of the cubic phase is reduced in the particles of a smaller size, it is likely that the droplets of the residual cubic phase in these particles are smaller than in the larger ones. Then, assuming that a diffusion depth of the Er^{3+} ions from the saturated rhombic phase to the cubic one is small compared to the size of the cubic phase inclusions, it would be an expected situation that the concentration of the erbium ions in the cubic phase of large particles is smaller than in the small ones. Then, mechanochemical doping of the β-PbF_2 phase results in formation of a structurally
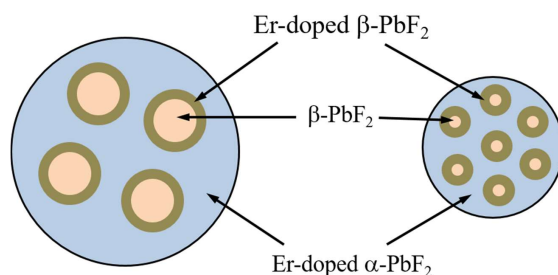
Figure 6. Schematic models of the inhomogeneous structure of larger (left) and smaller (right) PbF$_2$ fine particles mechanochemically doped with Er^{3+} ions.

phase-separated, inhomogeneously doped with Er^{3+} impurity powders schematically shown in Fig. 6 for larger and smaller particles.

4. Summary

Thus, a complementary study of mechanochemical doping of PbF$_2$ powders with Er^{3+} ions with electron paramagnetic resonance and X-ray diffraction has been performed. It has been shown that whatever is the initial crystal structure of PbF$_2$ (α/β-phase) the doping proceeds efficiently. Grains of PbF$_2$:Er^{3+} fine powders obtained by mechanosynthesis are in the structurally-mixed state with most of the volume in the orthorhombic α-phase. Mechanoactivated diffusion and transformation to the α-PbF$_2$ proceed in parallel and is mediated by dislocations created in the course of the synthesis. Full volume of the powders can be brought to the cubic β-PbF$_2$ phase by the appropriate annealing.

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