1 *Article*

2 # Optical, dielectric and magnetic properties of

3 # La1-xNdxFeO3 powders and ceramics

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14

15 **Abstract:** Nanocrystalline La1-xNdxFeO3 powders with different concentrations of Nd^{3+} have been

16 synthesized by modified Pechini method. Their structure was studied by X-ray powder diffraction

17 (XRD). Further, La1-xNdxFeO3 nanoceramics were prepared by high pressure sintering technique.

18 The luminescence spectra of the powders were investigated as a function of concentration of active

19 dopant to check the possible energy transfers observed due to Nd^{3+} concentration changes. The

20 electrical and magnetic properties of the powders and ceramics were investigated to determine the

21 effect of Nd^{3+} doping on the dielectric permittivity and magnetization in the wide frequency range.

22 **Keywords:** perovskites, neodymium, luminescence, electric transport, magnetization
23

1. Introduction

25   The LaFeO3 (LFO) perovskite series have been extensively studied for their interesting physical

26 properties and potential applications in catalysis, solid oxide fuel cells, permeation membranes,

27 ultrasensitive magnetic read heads, gas sensors, interconnecting materials for the solar cells, and

28 magnetic memory elements [1, 2]. One of the most studied properties of rare-earth (RE) orthoferrites,

29 REFeO3, are their unique magnetic responses, such as spin reorientation, spin canting, ultra-fast spins

30 switching, magneto-optics, and magnetization reversal [3-6]. Spin reorientation is closely related to

31 excellent coupling between electric and magnetic degrees of order, and this coupling is very

32 important to search for the novel magneto-electric multiferrorics [7]. Another interesting properties

33 of such perovskites is due to their use as a proton-conductive material for efficient negative-electrode

34 for Ni-MH batteries [8]. Among the rare-earth perovskite orthoferrites LFO is a very well-known

35 canted antiferromagnetic insulator with an orthorhombically distorted perovskite structure (contain

36 only trivalent iron and exhibiting a high value of the Néel temperature (T_N ~ 740 K) [9]. Although a

37 number of papers, related to the structural and magnetic properties of LFO, has been reported [10,

38 11], only few present multiferroic behavior in LFO [12].

39   Substitution of lanthanum ions with other RE elements having smaller ionic radii leads to a

40 shrinkage of the unit cell accompanied with a modification of the oxygen octahedral rotation and

41 corresponding changes in the length and angles of Fe–O chemical bonds. Notable changes in the

42 structural parameters lead to a modification of magnetic, dielectric, transport, and optical properties

43 of the doped compounds. Doping with neodymium ions, which have small difference in the ionic

44 radii with lanthanum ions, allows controlling structural parameters and manipulating physical

45 properties of the LaFeO3–based compounds.

Application potential of $REFeO_3$ compounds depends strongly on their electric, magnetic, and optical properties. Therefore, it is important to study the influence of different parameters on the materials' characteristic. For example nanoparticles may show unusual magnetic properties due to the finite-size effects, surface anisotropy effects, interface effects or shape anisotropy effect [13], therefore it is interesting to study also ceramics composed of nanograins. Here, we discuss the properties of $LaFeO_3$ nanocrystals and nanoceramics varied with Nd^{3+} ions doping.

2. Materials and Methods

Nanocrystalline $La_{1-x}Nd_xFeO_3$ powders with different concentrations of Nd^{3+} ($x = 0 \div 0.1$) have been synthesized by modified Pechini method [14]. The material was prepared by dissolving the stoichiometric amount of La_2O_3 (Sigma-Aldrich, 99.9%) and Nd_2O_3 (Sigma Aldrich, 99.9%) in HNO_3 (POCH, 65% analytical grade) to obtain RE nitrates. To eliminate nitric acid, nitrates were dissolved in the deionized water and evaporated three times. The RE nitrates, $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich, 99.95%), citric acid (CA) (Sigma Aldrich, 99%), and ethylene glycol (Sigma Aldrich, 99.8%) were dissolved in deionized water. The stoichiometric molar ratio of metal ions to CA was 1:5. The mixtures were continuously stirred for 1 h and then transferred to a dryer. The temperature was kept at 80 °C. After one week, the sol formed brown resin that was transferred to the crucibles and fired at 850 °C in a furnace for 8 h. The powder products were grinded in the agate mortar and taken to the analysis and ceramic sintering process. The details of the ceramic sintering process based on the high pressure technique was reported elsewhere [15]. Briefly, $LaFeO_3$ and $La_{1-x}Nd_xFeO_3$ powders were formed in pellets under the pressure of 0.1 GPa at room temperature. The pellets were placed in a special shape container with a resistance heater and separated by boron nitride layers. The force exerted by the anvils produced quasi-isostatic pressure of 8 GPa and the ceramic was sintered at 500 °C.

Structural studies were performed by powder X-ray diffraction (XRD) using a PANalytical X'Pert diffractometer with Ni-filtered Cu Kα radiation, λ=0.15418 nm. Atomic force microscopy (AFM) methods were used to inspect grain structure of ceramics and their compositional homogeneity. AFM was done using commercial scanning probe microscope Ntegra Aura (NT-MDT Spectral Instruments, Russia) by Budget Sensors ElectriTap300-G tips with the curvature less 25 nm, resonance frequency about 300 kHz, and 20 N/m force constant. In order to clarify chemical homogeneity at the local scale we used Kelvin probe force microscopy (KPFM) allowing direct inspection of the work function distribution across the surface with high spatial resolution [16]. The possible secondary phases would result in an apparent variation of electronic structure and work function. KFPM was done using conventional two-pass approach with 2 V ac voltage applied to the tip and 50 nm lift distance.

Optical properties of the powders doped with Nd^{3+} ions were studied with Renishaw Microscope equipped with CCD camera (0.1 nm resolution), 2400 line/mm gratings and argon laser as an excitation source (λ_{exc}: 514 nm, 100 mW). Electric impedance was measured using Alpha analyser (Novocontrol GmbH) with active sample cell operating in a frequency range 10^{-2} - 10^6 Hz at room temperature with ac voltage amplitude of 0.1 V. The measured sample was supplied with gold electrodes. Isothermal magnetization measurements were performed in magnetic fields up to +/-14 T at 5 and 300 K using Physical Properties Measurement Systems from Cryogenic Ltd.

3. Results

3.1. Structure and morphology

$LaFeO_3$ is an orthorhombically distorted perovskite structure with space group Pbnm [17]. XRD patterns of all powders were consistent with the orthorhombic structure of $LaFeO_3$ in the standard from JCPDS 88-0641 (Fig. 1). The average crystallite sizes and cells parameters of all samples were calculated from X-ray line broadening of the peaks using Rietveld Refinement in X'Pert HighScore Plus software and are presented in Table 1. All samples have crystallites below 100 nm and

94   microstrains of about 0.02%. With increasing Nd content we observed shortening of the *b* and *c* axes
95   in the crystallites. This suggests that the distances between the ions located along [010] and [001]
96   directions decreases. It is interesting that after applying pressure during sintering the peaks are
97   broadened due to decrease of grain size and microstrains increased. The broad band observed about
98   18 degree for $La_{0.9}Nd_{0.1}FeO_3$ ceramic is related to the amorphous phase of the nanocrystal located on
99   the surface of the grains. This behavior was observed also for other ceramics prepared from
100   nanocrystals and it is related to the decomposition of the surface of nanocrystals and increase of the
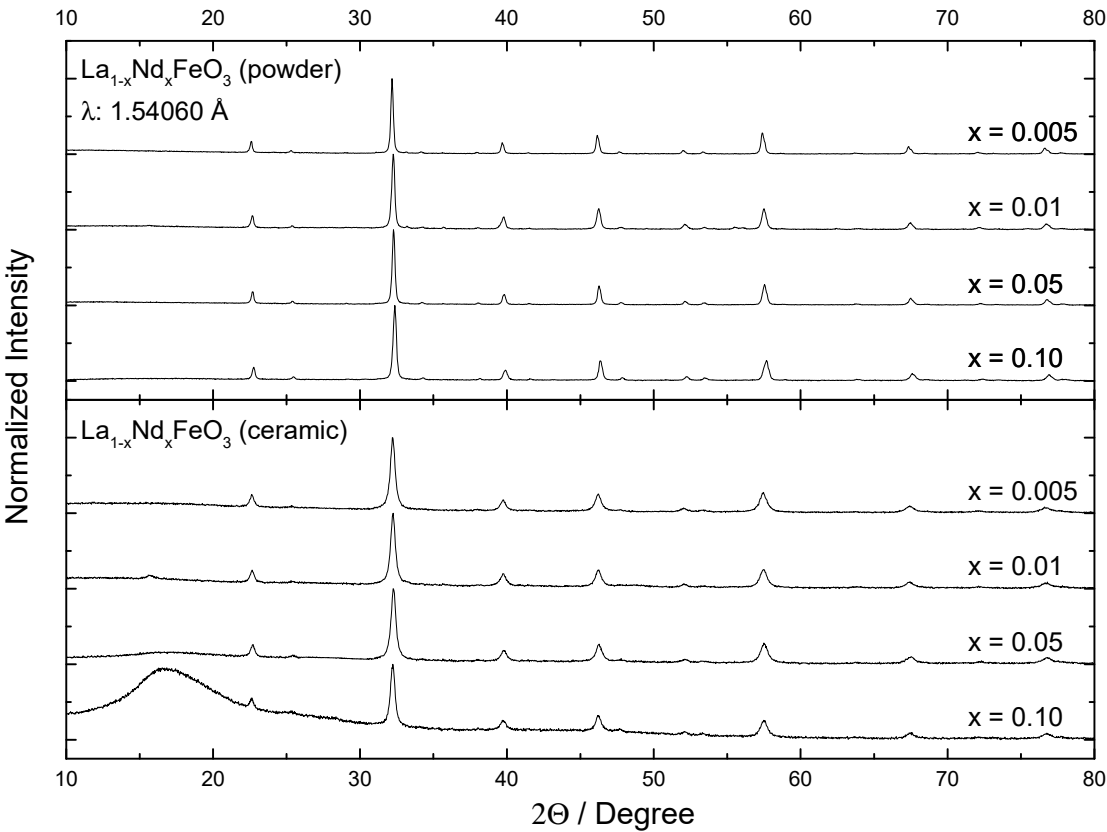101   strains on the grain boundaries [18].

102

103   **Figure 1.** XRD of the $La_{1-x}Nd_xFeO_3$ powders and ceramics doped with different concentration of
104   Nd^{3+}

105   **Table 1.** Cell parameters and crystallite sizes of the $La_{1-x}Nd_xFeO_3$ powders and ceramics.

$La_{1-x}Nd_xFeO_3$	Crystallite size / nm	*a*	*b*	*c*	Strains / %
powder					
x = 0.005	67	5.5633(2)	7.8510(3)	5.5529(9)	0.021
x = 0.01	52	5.5709(1)	7.8450(0)	5.5480(6)	0.021
x = 0.05	61	5.5657(6)	7.8448(7)	5.5447(0)	0.019
x = 0.10	50	5.5666(8)	7.8375(7)	5.5364(8)	0.022
ceramic					
x = 0.005	24	5.5656(9)	7.8833(4)	5.5339(7)	0.045
x = 0.01	25	5.5658(7)	7.8825(6)	5.5351(9)	0.042
x = 0.05	24	5.5625(3)	7.8780(2)	5.5333(5)	0.044
x = 0.10	30	5.5628(0)	7.8689(0)	5.5251(6)	0.044

106   Nano size of the grains in the ceramics are confirmed by AFM images (Fig. 2). The average grain size
107   in ceramics was about 20-30 nm and gradually increased with Nd^{3+} doping. Most of the compositions

108   had quite dense structure without significant amount of pores. KPFM analysis showed high quality
109   homogeneity of all compositions (see supplementary, Figure S1). The only variation of contact
110   potential difference was found at the grain boundaries, which can be attributed to typical artifacts of
111   KPFM measurements [16]. Measured contact potential difference values increased slightly with
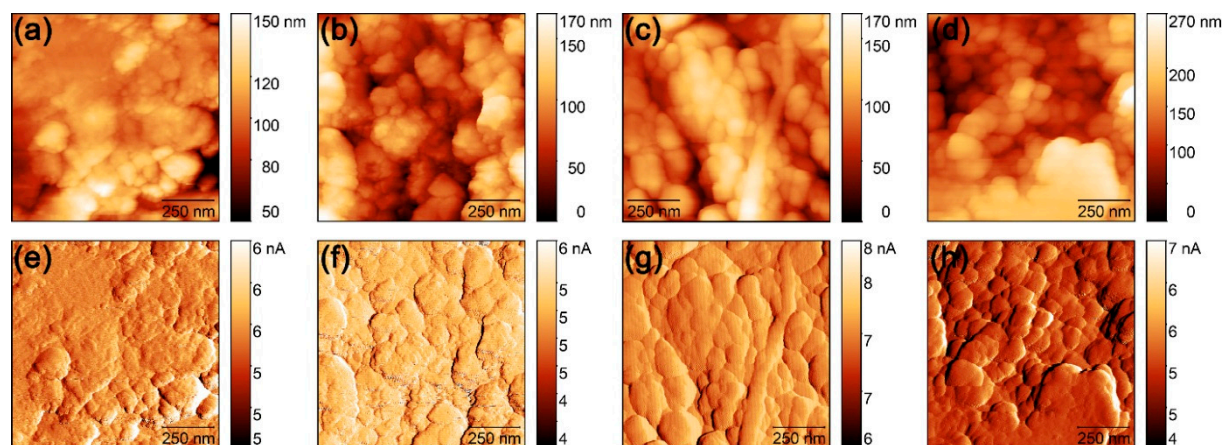112   doping due to apparent variation of the electronic structure of material with composition.

114   **Figure 2.** (a)-(d) Topography and (e)-(h) deflection signal (differential topography) of $La_{1-x}Nd_xFeO_3$
115   ceramics in dependence of Nd doping degree. (a), (e) 0.5%; (b), (f) 1%; (c), (g) 5%;
116   (d),(h) 10%.

117   *3.2. Optical properties*

118   The Nd^{3+} concentration dependence of photoluminescence of $La_{1-x}Nd_xFeO_3$ nanocrystals was
119   measured at room temperature (Fig. 3). The observed luminescence bands at 1057 and 1335 nm
120   were assigned to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{3/2} \rightarrow ^4I_{13/2}$ transitions of Nd^{3+}, respectively. Figure 3 shows
121   the effect of Nd^{3+} ions concentration on luminescence spectra and suggests that concentration
122   quenching effects took place when doped with 10 mol-% of Nd^{3+} ions. Low emission intensity and
123   unexpected shorter decay time of the $La_{0.995}Nd_{0.005}FeO_3$ nanocrystals is related low concentration
124   of the Nd ions and high absorption of the material (dark brown color). The concentration
125   quenching is related to the different distances between donors and acceptors and smaller
126   separation between pairs. For Nd^{3+} ion-ion energy transfer is generally described on the basis of
127   dipole-dipole interactions. The processes involved in cross-relaxation are $^4F_{3/2},^4I_{9/2} \rightarrow ^4I_{15/2},^4I_{15/2}$,
128   and/or $^4F_{3/2},^4I_{9/2} \rightarrow ^4I_{13/2},^4I_{15/2}$; and in energy migration is $^4F_{3/2},^4I_{9/2} \rightarrow ^4I_{9/2},^4F_{3/2}$. Additional process
129   that lead to the quenching of the luminescence is the thermalization effect that is strengthened
130   by the small size of the grains (due to inefficient removal of heat) and resulted in enhancement
131   of local temperature in individual grains. The concentration quenching have been confirmed by
132   measurement of kinetics of Nd^{3+} emission. The decay time of emission from $^4F_{3/2}$ level decreases
133   significantly when dopant concentration is higher than 1 mol%. For the ceramics,
134   photoluminescence measurements were impossible to be performed due to black color of the
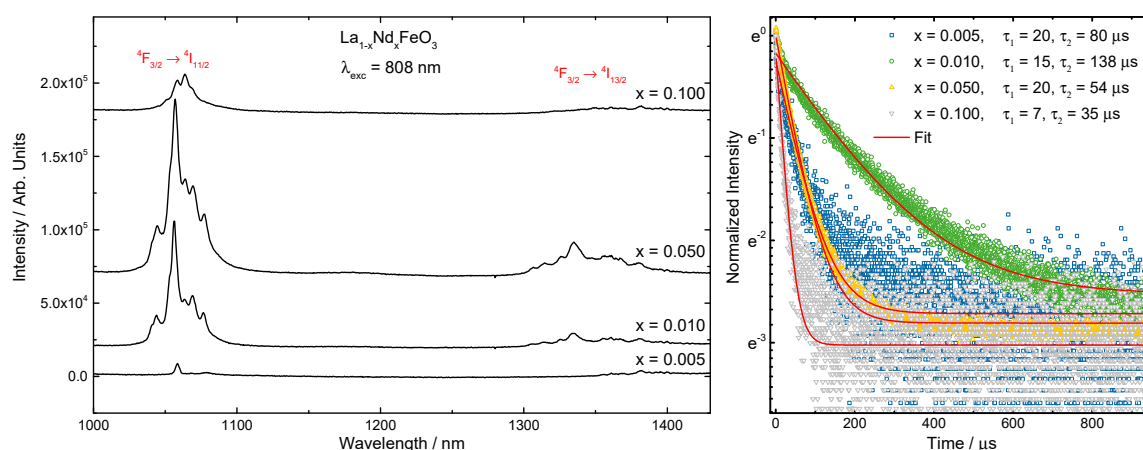135   ceramics after sintering and total absorption of the visible excitation light.

136

Figure 3. NIR luminescence of the $La_{1-x}Nd_xFeO_3$ powders under 808 LD excitation (left) and the decay time of $^4F_{3/2}$ level of Nd^{3+}, measured at 1057.5 nm (right).

3.3. Electric properties

The electrical properties were measured for ceramic samples. Frequency dependencies of the real part of permittivity as a function of Nd^{3+} doping level of the $La_{1-x}Nd_xFeO_3$ nanoceramics were measured and are shown in Fig. 4. Dotted line corresponds to undoped sample.
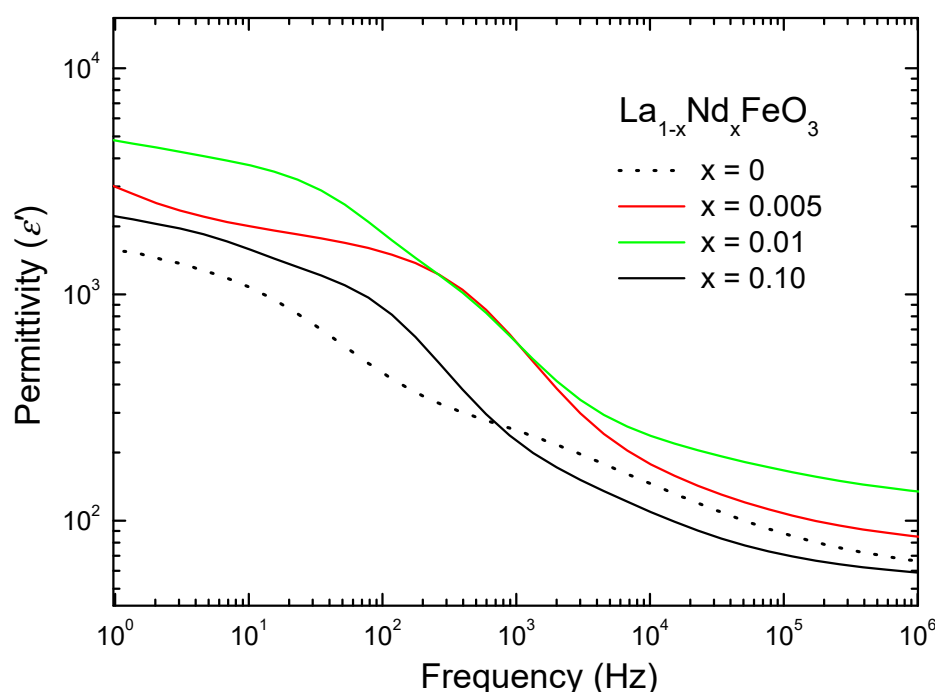

Figure 4. The real part of permittivity as a function of frequency for $La_{1-x}Nd_xFeO_3$ ceramics. Dotted line corresponds to the undoped sample.

All the samples revealed similar type of dependencies characterized by high values of the dielectric permittivity. Generally, the values of permittivity increase with doping, as it can be clearly seen for the samples doped from 0 to 1% of Nd. However, the values of sample doped by 10% of Nd are lower than those doped by 0.5% and 1%. Furthermore, permittivity of 10% doped sample is lower than for undoped sample at high frequencies. One of the reasons of such behavior can be an influence

152   of Nd incorporation on the charge transfer. Small amount of Nd can only increase permittivity by
153   introduction of localized charge carriers. However, at high concentration of Nd, the charge carriers
154   became partially delocalized thus contributing to the screening of applied electric field especially at
155   low frequencies.

156   The frequency dependence of conductivity allows to determine the direct influence of charge carriers
157   doping on the charge transport properties of the nanoceramics (Fig. 5).

158

159

160   **Figure 5.** Frequency dependence of the conductivity of $La_{1-x}Nd_xFeO_3$ ceramics. Dotted line
161   corresponds to the undoped sample. Inserted figure shows the dc conductivity as a function of
162   Nd content.

163   The character of dependencies is similar for all the samples suggesting ion conductivity contribution
164   since conductivity increases with frequency in the whole range. This type of conductivity can be
165   described by Eq. 1 [19, 20]:

166    $$\sigma'(\omega) = \sigma_0 + A\omega^n, \tag{1}$$

167   where ω is the angular frequency ($\omega = 2\pi f$, f is the frequency of the applied electric field), σ_0 is the dc
168   conductivity, A is a constant, and $0 < n < 1$. dc conductivity can be estimated from the plateaus at
169   low frequencies. As it can be seen, the values of dc conductivity increase with doping logarithmically
170   (see insert in Fig. 5). This is a result of doping by charge carriers. It is worth to note that doping by
171   10% of Nd^{3+} changes the values of conductivity by an order of magnitude.

172   The simple way to explore the relaxation processes is of the data representation in the Cole-Cole plot
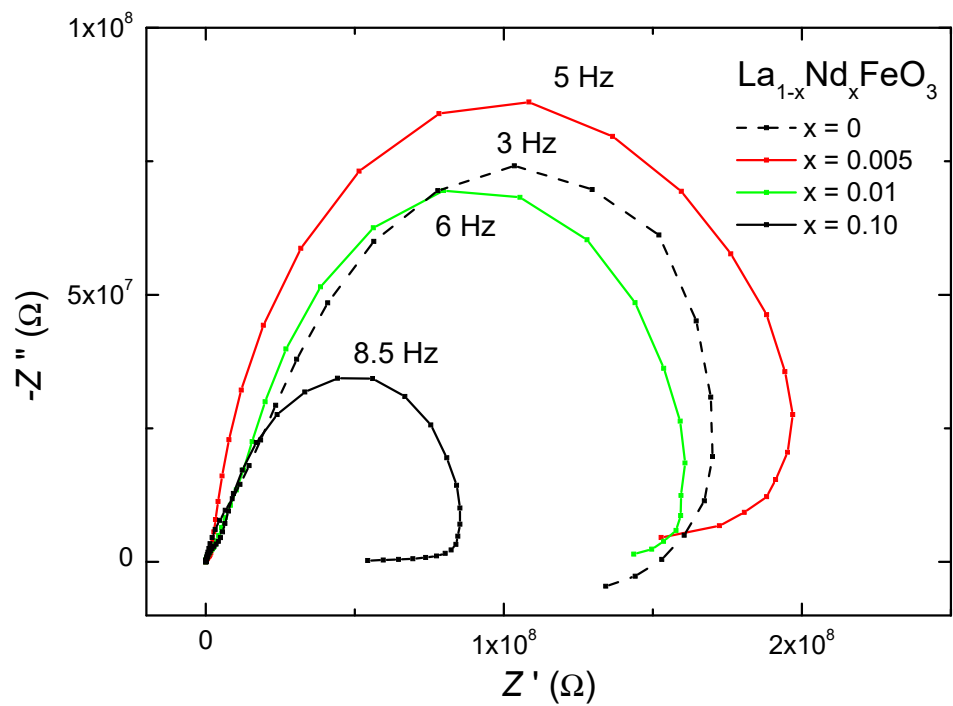173   (Fig. 6).

174
175 **Figure 6.** Cole-Cole plots for the $La_{1-x}Nd_xFeO_3$ ceramics. Dotted line corresponds to the undoped
176 sample.

177 It is clear that all the samples show relaxation depending on Nd content at low frequencies. The
178 relaxation frequency increases with amount of Nd. There are also relaxations at high frequencies,
179 but it is difficult to observe them in presented plots. In order to determine relaxation processes at
180 high frequencies, the dependencies of loss tangent were analyzed (Fig. 7).

Figure 7. Frequency dependencies of loss tangents of the $La_{1-x}Nd_xFeO_3$ ceramics. Dotted line corresponds to the undoped ceramic.

Depending on the doping level, relaxations appear in the wide frequency range. One can see that the frequency of the loss peak systematically decreases with doping. It should be noted that undoped sample revealed two relaxation peaks at 60 Hz and 20 kHz. Similar behavior was observed for 80 nm $LaFeO_3$ sample [21]. In this frequency range, the loss peaks could be explained by the dipole relaxations.

A summary of the influence of Nd doping on the relaxation processes and relaxation frequency as a function of Nd concentration is shown in Figure 8.
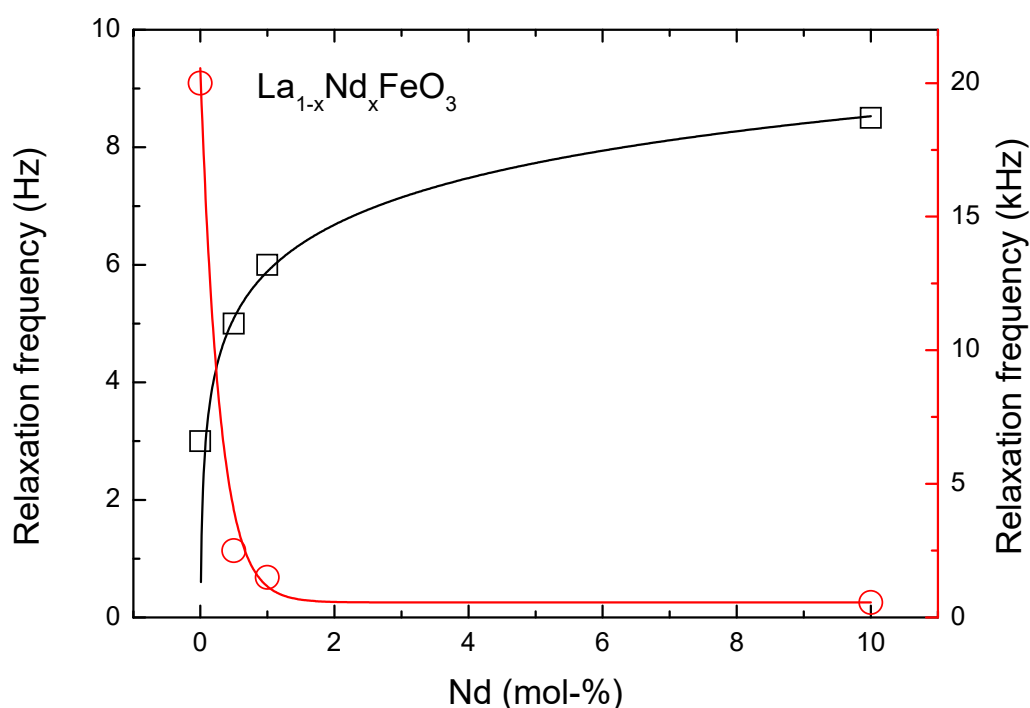
191

Figure 8. Relaxation frequency as a function of Nd mol. % content.

As it was mentioned above, doping with Nd shifts relaxation frequency to higher frequencies for low frequency relaxations. However, the increase of relaxation frequency is not linear in this case. Results of low frequency relaxations can be fitted by the relation (Eq. 2):

$$f_0 = 5.88 + 1.15 \ln(n), \tag{2}$$

where f_0 is the relaxation frequency; and n is the Nd mol-% concentration. As can be seen, weak doping has stronger effect than the high one.

High frequency relaxation processes have completely opposite character as compared to the low frequency ones. Increasing of Nd content decreases the relaxation frequency (see red line in Fig. 8). The values of relaxation frequencies can be fitted by asymptotic exponential dependency (Eq. 3):
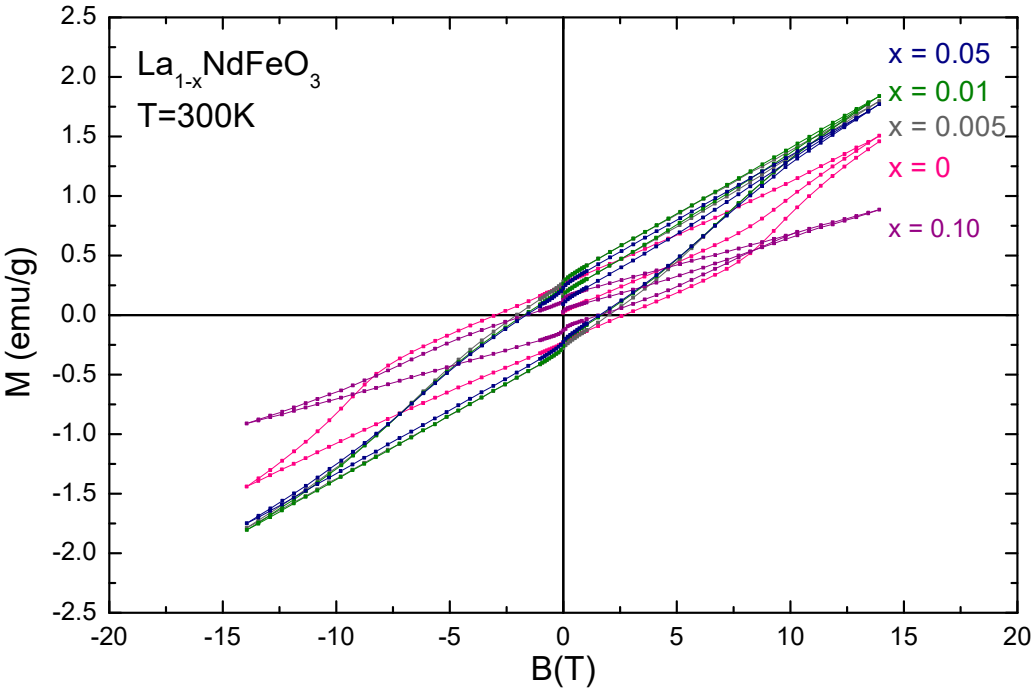
$$f_0 = 560 + 20\,000 \cdot 0.03^n, \tag{3}$$

Taking into account that low frequencies relaxation is mostly determined by the interfacial and space charge behavior, whereas high frequency relaxations are results of the dipole interactions, one can conclude: the Nd doping has an effect on both relaxations and electrical properties of the nanoceramics that can be adjusted by chemical composition via Eqs. 1 and 2.
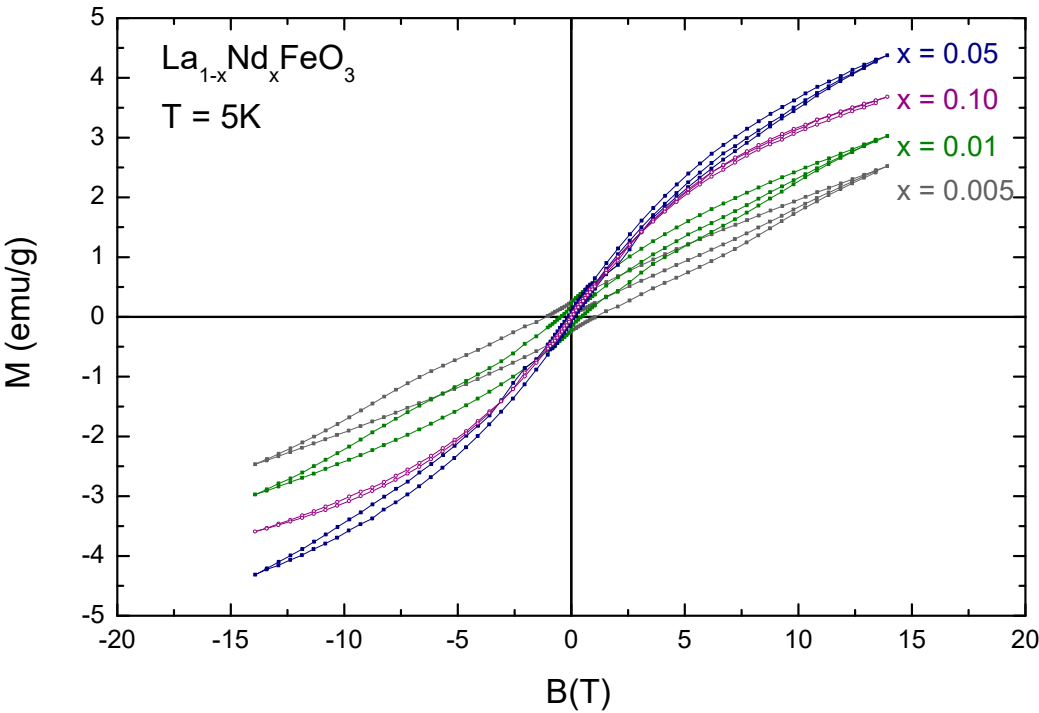
3.4. Magnetic properties

Magnetization measurements of the $La_{1-x}Nd_xFeO_3$ ceramics performed at 300 K and 5 K temperatures have testified an evolution of the magnetic properties as a function of dopant concentration and temperature (Fig. 9). The M(H) dependencies obtained at room temperature demonstrate a notable reduction in coercivity of the compounds with increasing dopant concentration. As small as 0.5% of neodymium concentration significantly modifies magnetic anisotropy of the compounds which leads to a drastic (40%) reduction in coercivity while a coercive field does not significantly change

214 with further increase of the dopant content in the measured concentration range (up to 10%).
215 Modification in the magnetic structure caused by the chemical substitution also leads to about 15%
216 increase in the in-field magnetization which is most probably associated with an alteration in the
217 chemical bond angle Fe-O-Fe. It should be noted than magnetic structure of the compounds remains
218 to be antiferromagnetic while small ferromagnetic contribution is related to uncompensated surface
219 spins originated from nanoscale crystallites as well as by weak ferromagnetism related to a canting
220 of the magnetic moment associated with Dzyaloshinsky-Moria interactions [22]. An increase in the
221 dopant content up to 10% causes a reduction of ferromagnetic component in the magnetic
222 interactions and compound $La_{0.9}Nd_{0.1}FeO_3$ is characterized by nearly collinear antiferromagnetic
223 structure.

224 Isothermal magnetization measurements performed at 5 K testify a strong reduction in the coercivity
225 of the compounds while magnetic moment becomes notably larger in strong magnetic fields. Strong
226 decrease in the coercive field of the compounds at low temperature is related to spin flip transition
227 occurred in $LaFeO_3$-based compounds at about 150 K. A decrease in coercivity of the compounds
228 takes place gradually upon dopant concentration increase thus pointing at progressive alteration of
229 the easy magnetization axis. An increase of magnetization occurred upon the dopant content is most
230 probably caused by positive exchange interactions formed between Fe and Nd ions. An increase in
231 the dopant content above 5% leads to a gradual strengthening of the antiferromagnetic component
232 caused by negative exchange interactions formed between Nd ions, while an in-field magnetization
233 observed for the compound with x=0.1 still remains much larger than that observed for the lightly-
234 doped compounds.

235

236

Figure 9. Field dependencies of magnetization recorded for $La_{1-x}Nd_xFeO_3$ ceramics at room temperature (top) and at temperature of 5 K (bottom).

The compounds having the same nominal chemical compositions as those mentioned above but in different form (powder and ceramic) are apparently characterized by different magnetic properties. The compounds in a form of ceramics pieces show gradual increase of room temperature in-field

242 magnetization with Nd content up to 10% while the ground compounds have nearly the same
243 magnetization which remains to be stable regardless of Nd concentration (except for the compound
244 with maximal content of the dopant ions). Gradual increase in the in-field magnetization points at
245 progressive modification of the magnetic properties of the compounds which is most probably
246 associated with an increased contribution from uncompensated spins formed near structural defects.
247 It should be noted that the magnetic structure of the compounds $0<x<0.1$ remains unaffected and it
248 is similar to that characteristics for the ground samples. The compounds with $x=0.1$ of both compared
249 series testify an alteration in their magnetic structure expressed as a drastic decrease in the
250 magnetization and coercive field which signifies a strengthening of antiferromagnetic interactions
251 induced by the chemical substitution. The difference of the magnetic properties observed for the
252 compounds in a form of ceramic pellets and ground ones is caused by their different crystalline
253 morphology and defectiveness of the compounds while the magnetic structure remains similar.

4. Conclusions

255 In this work we have fabricated and characterized a series of nanopowders and nanoceramics
256 of $La_{1-x}Nd_xFeO_3$ doped with different Nd^{3+} concentration. It was observed that with the increase of
257 doping the unit cell become smaller what have impact on the magnetic and dielectric properties of
258 the nanostructures. In the luminescence spectra we observed concentration quenching due to cross
259 relaxation, energy migration, and thermal depopulation of excited states. Luminescence may be
260 observed only for powder samples because in the ceramics due to change of the color after sintering
261 emission is absorbed by the material. An interesting observation was that magnetization of the $La_{1-x}Nd_xFeO_3$
262 is different for powders and for ceramics. This is caused by internal strains induced by
263 sintering process in nanoceramics. It was also observed that the change of the Nd concentration have
264 impact on the magnetization what is most probably caused by positive exchange interactions formed
265 between Fe and Nd ions. All samples revealed relatively high values of dielectric permittivity, which
266 can be improved by small amount of doping. There were observed ionic and dipole relaxations
267 appeared in different frequency ranges. Ionic relaxation frequency has logarithmic dependence on
268 Nd content, whereas dipole relaxation has an asymptotic exponential one. The most important
269 conclusion is the possibility to adjusting desired electric and magnetic properties of $La_{1-x}Nd_xFeO_3$
270 nanoceramics by changing the concentration of introduced Nd.

273 **Author Contributions:** powder synthesis, XRD analysis, luminescence studies, writing—original draft
274 preparation P.G.; electric properties measurements analysis, K.O.; ceramic preparation, R.T.; writing—review,
275 A.Ł; writing—review, supervision, W.S.; magnetic measurements and analysis, D.K.; AFM measurements, D.A.;
276 morphology analysis and discussion of results, A.K.;

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