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1 **Synthesis, Characterization, and Second Harmonic Generation of**
2 **Multiferroic Iron—Doped Lithium Niobate Powders**

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32
33 **Keywords:** Second Harmonic Generation, random media, lithium niobate, metal—doping,
34 ferroelectricity, ferromagnetism

35 **ABSTRACT**

36 Random granular media may exhibit characteristics more often related to ordered media. In
37 the present work, this feature is observed in the polarized Second Harmonic Generation
38 (SHG) response from reduced iron-doped lithium niobate (LN:Fe) powders, an effect that is
39 not expected due to multiple scattering. Besides, this subsisting order property of the powders
40 can be further controlled using magnetic induction to tailor the SHG response. The samples
41 were characterized employing X-Ray Diffraction (XRD) and confocal Raman Spectroscopy.
42 Their SHG response both in the absence and the presence of an external static magnetic field
43 was then studied as the fundamental beam focus was translated from air into the powder. The
44 SHG intensity polarization state was then studied as a function of the linear polarization of the
45 fundamental beam for different fundamental beam focus depths. These results demonstrate
46 that the SHG properties from LN:Fe powders can be modified through post-thermal treatment
47 in a reducing atmosphere in view of photonic applications.

48

49 **INTRODUCTION**

50 Lithium niobate (LN, chemical formula LiNbO_3) is a synthetic bi-metallic oxide that presents
51 high chemical stability and high melting point. It is insoluble in water and other organic
52 solvents. Intrinsically, LN adopts a crystalline ferroelectric phase for a wide range of
53 temperatures, from room temperature (RT) to approximately 1200°C . Large electro- and
54 acousto-optical coefficients are ascribed to this phase, lending to this material attractiveness
55 for applications in the fields of actuators, sensors, or transducers, notably for medical
56 ultrasound devices, thermal sensors, sonar systems or precise positioners among others.^[1,2]
57 Ferroelectric LN possesses a large nonlinear optical coefficients too. Efficient coherent
58 Second Harmonic Generation (SHG) can be obtained from this material within a broad range
59 of fundamental excitation wavelengths with the corresponding second-order susceptibility
60 tensor possessing three non-zero and independent tensor elements, namely d_{33} , d_{31} and
61 d_{22} .^[3] Coherent SHG is lost in the case of polycrystals, i.e. thin films or powders for example,
62 due to intrinsic material randomization which could be twofold: spatial randomization (single
63 nanocrystals in larger grains can have any possible orientation with respect to each other) plus
64 randomization of the refractive index (it can vary from nanocrystal to nanocrystal according
65 to the flexibility that characterizes the crystal structure of LN in adopting a continuous
66 chemical composition within the range of ratios Li:Nb from 50.0:50.0 to approximately
67 48.4:51.6, RT conditions).

68
69 Recent developments have put LN into the scene in the rapidly growing field of applications
70 in photonics,^[4] to the extent that the once coined term ‘the silicon of photonics’ (2009)
71 reverberates nowadays. LN is highlighted as the potential cornerstone in photonics, just as
72 silicon has been for electronics.^[5,6] But none of such applications could be possibly
73 envisioned for polycrystals as incoherent light is a serious hindrance regarding any thinkable
74 optical application. However, profit can still be obtained by studying the optical SHG
75 response from polycrystalline solid solutions of LN. The incoherent feature of the response
76 signal can be overcome by the combination of a proper experimental apparatus and the use of
77 ultrasensitive detection devices such as cooled photomultipliers and charge-coupled device
78 cameras. Any surface or interface can be assessed in this way by analysis of the SHG
79 response.^[7,8]

80
81 In this work, LN powders are being tested as they exhibit important ferromagnetic properties
82 at RT when suitably doped with Fe ions and post-thermally treated in a reducing

83 atmosphere.^[12] The connection between RT ferromagnetism in Fe—doped LN (hereafter
 84 referred to as LN:Fe) powders can be formally described based on the framework of Diluted
 85 Magnetic Oxides.^[13] Our group has recently reviewed the subject, and the earlier and current
 86 investigations regarding the manifestation of magnetic and ferromagnetic behavior in LN:Fe
 87 (single crystals and polycrystals) have been discussed in detail.^[14] In the present research, the
 88 consequences of the ferromagnetism properties of the LN:Fe powders are investigated and the
 89 order/disorder of the powders discussed using the SHG process and the deviation from the
 90 expected response from purely random powders.^[15, 16]

91

92

93 RESULTS AND DISCUSSION

94 A total of 21 samples were synthesized. They can be classified into three main groups after
 95 the application of post-thermal treatments: untreated, reduced and oxidized samples.
 96 According to this classification, the samples have been labeled as shown in Table 1.

97

98 **Table 1.** *Nomenclature of the synthesized samples.*

Fe—doping concentration → [wt. % Fe ₂ O ₃]	0 ^{a)}	0.8	1.5	2.2	3.3	4.5	6.0
Untreated	pLN	8LN:Fe	15LN:Fe	22LN:Fe	33LN:Fe	45LN:Fe	60LN:Fe
Reduced	pLN-re	8LN:Fe-re	15LN:Fe-re	22LN:Fe-re	33LN:Fe-re	45LN:Fe-re	60LN:Fe-re
Oxidized	pLN-ox	8LN:Fe-ox	15LN:Fe-ox	22LN:Fe-ox	33LN:Fe-ox	45LN:Fe-ox	60LN:Fe-ox

99 ^{a)} The pristine samples

100

101 Controlling the oxidization state of the samples is important because reduced LN:Fe powders
 102 have shown a saturation magnetization about two orders of magnitude higher than the
 103 corresponding oxidized samples.^[12] The coexistence of valence states Fe²⁺ and Fe³⁺ in LN:Fe
 104 nanocrystalline powders has been reported where a ratio of 0.15 holds for untreated
 105 samples.^[17] The value can be lowered by the application of a suitable oxidizing thermal
 106 treatment, or rather, a reducing atmosphere can be used to reach a stable thermodynamical
 107 state for which the fraction of the Fe²⁺ population is close to 1. Oxidized samples are regularly
 108 thought of as passivated samples in the sense that no oxygen vacancies (V_O) are expected in
 109 these samples. Thus, the redox state of the samples can be effectively controlled if the
 110 reducing treatments are applied first and oxidation takes place second. All the oxidized
 111 samples studied in the present contribution were first reduced. Reproducible and consistent

112 results are expected with this approach. On the other hand, because LN is tacitly
113 acknowledged to be a unique oxide without V_O 's,^[18] no significant differences are expected
114 between untreated LN:Fe and oxidized LN:Fe-ox powders, neither structurally nor regarding
115 their performances for nonlinear optics. In order to observe the impact of the state of the
116 LN:Fe powders, thorough characterization was performed.

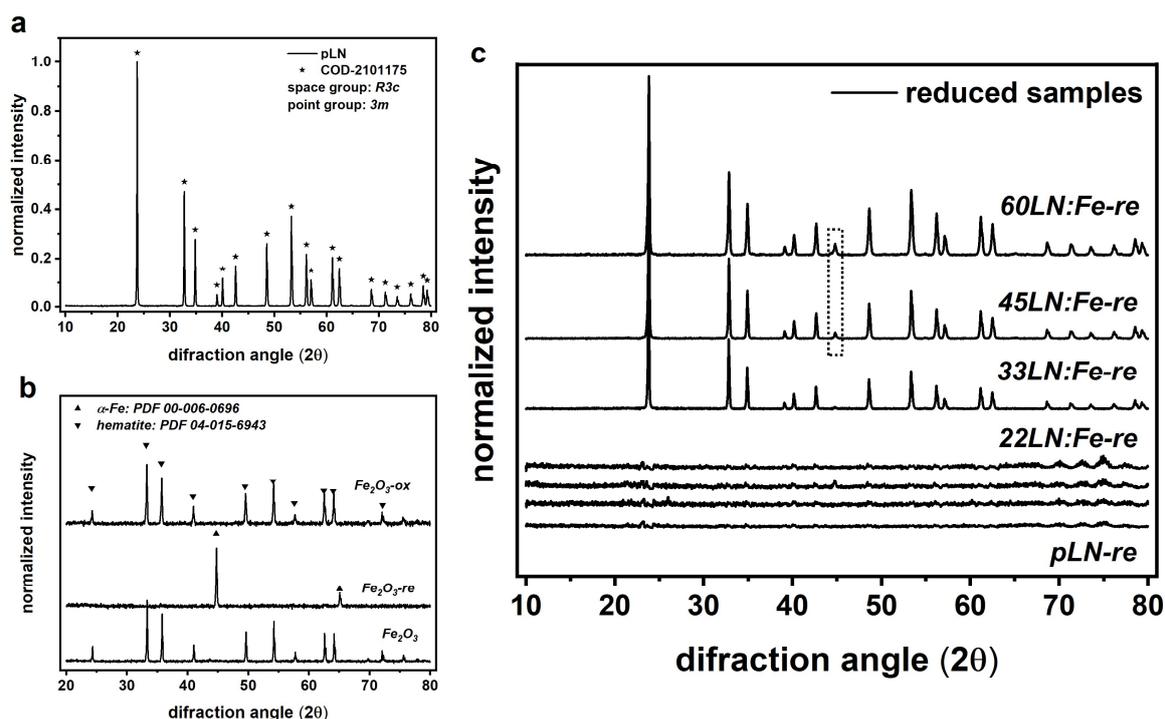
117

118 **2.1. Characterization**

119 2.1.1. X-Ray Diffraction

120 Figure 1 displays the recorded XRD patterns of (a) the untreated pristine LN powders (sample
121 pLN), (b) the raw iron oxide powder used for the Fe—doping and its evolution after being
122 reduced and oxidized and (c) the reduced LN:Fe samples. In Figure 1(a), the Bragg reflections
123 comprise only peaks of a trigonal crystal structure with a hexagonal basis (lattice constants a
124 $= b = 0.515$ nm and $c = 1.386$ nm) indicating the formation of the stable crystal structure
125 $LiNbO_3$ (COD 2101175). Original diffraction data come from the Crystallographic Open
126 Database.^[19] An averaged ratio $Li:Nb = 48.9:51.1$ is determined after structural refinement by
127 the Rietveld method and the use of Eq.(2) in Ref. 20 within the given absolute accuracy.^[20]
128 The pristine samples are thus off-stoichiometric with a chemical composition close to the
129 congruent point, namely $Li:Nb = 48.5:51.5$. The population of intrinsic point defects is
130 therefore rather high as targeted because the doping process becomes synergetic when
131 cationic vacancies are disposable. Figure 1(b) shows that Fe_2O_3 powder on the opposite when
132 undergoing phase-transitions into metallic iron (α -Fe, JCPDS PDF 00-006-0696) recovers its
133 structural characteristics (hematite- Fe_2O_3 , JCPDS PDF 04-015-6943) after being subjected to
134 the same thermal treatments as those used for the pLN and LN:Fe samples, i.e. reduction and
135 oxidation. Original diffraction data were taken from the Powder Diffraction File
136 (ICDD[®]).^[21]

137



138
 139 **Figure 1** : XRD characterization of the LN samples. (a) As obtained (without post-thermal
 140 treatment) pristine lithium niobate powders with near-congruent chemical composition
 141 denoted by a ratio $\text{Li:Nb} = 48.91:51.1$. (b) Iron oxide powders converted into powdered
 142 metallic iron and then recovered in their initial phase when first reduced and oxidized
 143 afterwards. (c) Reduced Fe—doped lithium niobate powders where the two samples of the
 144 highest doping concentration show the existence in small proportions of metallic iron as a
 145 secondary phase ($2\theta \approx 45^\circ$). For a doping concentration of 3.3 wt. % Fe_2O_3 , and below, solid
 146 solutions of lithium niobate were obtained as inferred from the straight lines resulting from a
 147 direct comparison between the corresponding patterns and that of the untreated pristine
 148 sample.

149
 150 In Figure 1(c), it is worth noticing that in the $\sim 50\text{--}65^\circ$ 2θ range, four peaks of intermediate
 151 intensity are located close to six ones of the LN phase which are of intermediate intensity too.
 152 These data show the unaltered recorded XRD patterns only for the three cases of higher
 153 doping concentrations. Identical curves of nearly constant intensity in the whole studied 2θ
 154 range are shown from sample 22LN:Fe-re down to sample pLN-re: these diffraction data are
 155 processed by simply calculating the quotient (normalized data in both inputs) between the
 156 corresponding sample and the pLN-re sample. The observed common baseline is interpreted

157 as the obtention of solid solutions of LN. Chemical solubility can be reached beyond a doping
 158 concentration of 3.3 wt. % Fe₂O₃. The XRD pattern of sample 33LN:Fe-re is also rather clean
 159 as well resembles that of the pure ferroelectric LiNbO₃ phase : neither the Bragg reflections of
 160 secondary phases related to iron can be tracked nor those of the precursors used for synthesis.
 161 On the other hand, an additional reflection of small intensity can be observed ca. $2\theta = 45^\circ$ for
 162 samples 45LN:Fe-re and 60LN:Fe-re. It pertains to the main diffraction peak of metallic iron
 163 (α -Fe, JCPDS PDF 00-006-0696) and its intensity is accordingly incremental to doping
 164 concentration. Interestingly, no distinctive features pointing towards having reached the limit
 165 of solubility at a doping concentration of 4.5 wt. % Fe₂O₃ can be observed in the XRD
 166 patterns of the untreated and oxidized sets of samples, (data not shown). This is possible due
 167 to an overlapping of diffraction peaks taking place in the 2θ range ~ 50 - 65° . Hence, possible
 168 misconceptions could arise regarding the structural characteristics of LN:Fe powders if they
 169 are not subjected to a reducing post-thermal treatment. However, as it is shown in Table 2,
 170 such a nefarious fact can be overcome with structural refinement : phase quantification
 171 analysis leads to correct conclusions irrespective of the oxidation state.

172

173 **Table 2** : Phase percentages in the synthesized samples, as obtained by simultaneous
 174 insertion of cards containing the Wyckoff positions of the involved crystal structures.

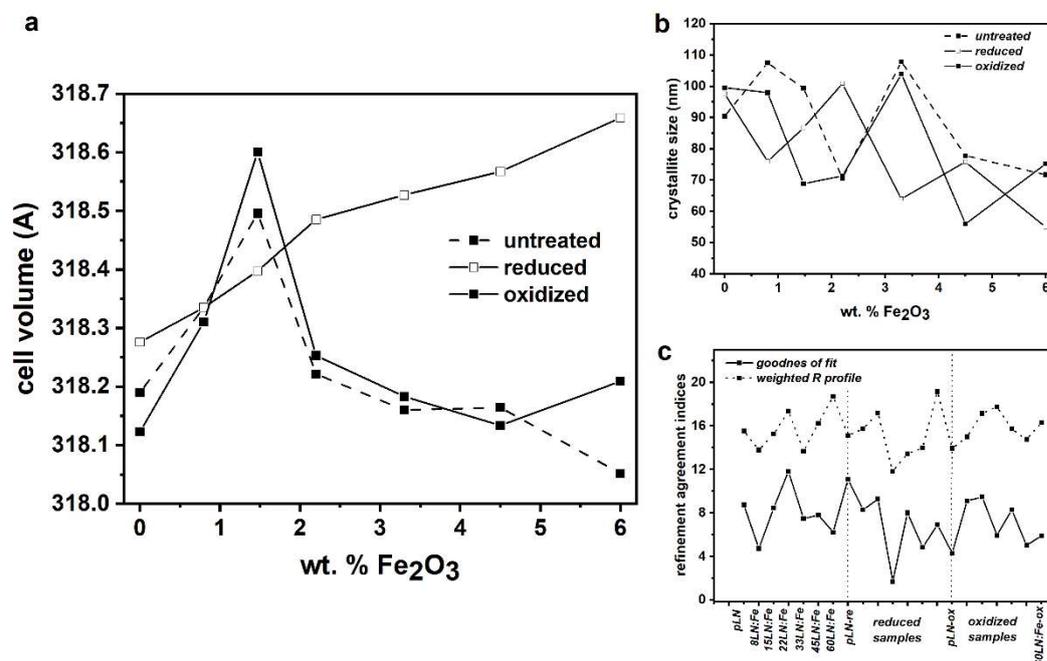
Sample \rightarrow ^{a)}	45Ln:Fe	45Ln:Fe-re	45Ln:Fe-ox	60Ln:Fe	60Ln:Fe-re	60Ln:Fe-ox
% LiNbO ₃	99.6	99.0	99.2	98.0	96.9	97.2
% α -Fe	0	1.0	0	0	3.1	0
% Hematite-Fe ₂ O ₃	0.4	0	0.8	2.0	0	2.8

175 ^{a)} The remaining samples are 100% LiNbO₃

176

177 From the data available in Table 2, it can be argued that a maximum of 1% (3%) of the
 178 secondary phase is present in the powders doped with a 4.5 (6.0) wt. % Fe₂O₃. Herein, it is
 179 worth mentioning that in view of the study of the Second Harmonic Generation (SHG)
 180 response, another classification of the synthesized materials holds in terms of the
 181 concentration of doped iron, as it can be the lowest, intermediate or the highest one. For
 182 practical purposes, the 1% of the second phase is considered marginal within the scope of this
 183 research and, thus, the samples 45LN:Fe have been denoted as the highest cases in the SHG
 184 analysis. Meanwhile, refinement of the crystal structures also sheds some light on the local
 185 environment to the unit cell, that is, a glance into the distribution of intrinsic and extrinsic
 186 point defect complexes.^[2] The evolution of the structure in terms of a parameter of synthesis

187 is conventionally assessed through the extraction of the resulting lattice constants for a given
 188 number of experimental points. Usually, small differences in plots having a lattice parameter
 189 as the ordered axis are more discernible or significant when the whole set of parameters is
 190 circumscribed into the unit cell volume defined with the formula $\sqrt{3}a^2c/2$ for a hexagonal
 191 setting.^[2,18] The unit cell volumes related to all the polycrystalline samples synthesized in this
 192 work are shown in Figure 2(a). Correspondingly, Figure 2(b) shows that the mean crystallite
 193 size is of the order of 60-100 nm whereas Figure 2(c) indicates that the executed routines
 194 converged giving satisfactory agreements between empirical and calculated patterns.
 195 Continuous relaxation of the crystal structure holds for the reduced samples as inferred from
 196 the observed monotonic increase of the unit cell volume with the doping concentration. A
 197 change of rate takes place at point 22LN:Fe-re. On the other hand, as expected, the untreated
 198 and oxidized crystal structures show identical local environments up to a critical point of
 199 45LN:Fe(-ox): relaxation of the structures takes place first, then followed by a contracting
 200 mechanism as the doping concentration increases (inflection points can be noted in 1.5 and
 201 2.2 wt. % Fe₂O₃ samples).
 202



203
 204 **Figure 2** : Crystal structure refinement with the Rietveld method. As a function of the doping
 205 concentration and of the applied post-thermal treatments : (a) Unit cell volumes in angstrom
 206 units. (b) Mean crystallite sizes calculated by implicit use of the Scherrer equation and weight

207 *averaging all the contributions to line broadening. (c) The estimated Rietveld error indices*
208 *are less than or close to 10 %.*

209
210 The most widely accepted defect scenario is the so-called lithium vacancy model.^[14] Within
211 this framework, neither oxygen vacancies (V_O) nor niobium vacancies (V_{Nb}) are assumed to
212 exist, and the formation of a single Nb antisite defect (Nb_{Li}) is compensated by the formation
213 of four Li vacancies (V_{Li}); its constitutional formula is $[Li_{1-5x}V_{4x}Nb_x]NbO_3$, $x=0.01$.^[22] Whilst
214 it is here acknowledged that debate still prevails on the most appropriate defect model that
215 solves electronic charge neutrality in off-stoichiometric LN—despite much research has been
216 done on the subject—, it must also be stated that all the available evidence, collected either
217 empirically or by ultimate computer simulations, points towards the univocal existence of
218 Nb_{Li} antisites.^[23] Such a point defect of intrinsic nature in LN denotes the occurrence of a
219 stacking fault that compensates the charge unbalance, which is compromised by the
220 inexorable tendency of this compound to crystallize forming solids with a Li deficiency (or
221 Nb surplus).^[2,14] Now in consideration of extrinsic defects in the fashion of elemental doping,
222 conceiving that the inserted cations occupy first V_{Li} 's while substituting Nb in Li sites
223 (replacement of Nb_{Li} 's) before it takes place a substitution mechanism for Li_{Li} and Nb_{Nb}
224 entities, is nothing else but logic.

225
226 Many factors influence the observed trends in site occupancy and doping mechanisms (dopant
227 concentration, ionic radii, valence states, etc.), but indeed, there seems to be concomitant
228 evidence that all kind of dopants (irrespective of their nature or functionality when doped in
229 LN) are predominantly localized in Li sites whenever small doping concentrations are used.
230 Regarding the occupancy/substitution mechanisms in doped LN, two statements can be made.
231 One is that the dopant ions tend to occupy Li sites first, either V_{Li} or Li_{Li} .^[14] Second, if the
232 content is being kept added, a critical instance is reached where the dopants begin to
233 substitute Nb in Nb sites just before the chemical solubility of the pristine LN crystal structure
234 is exhausted.^[14] Naturally, the latter depends on the initial intrinsic defect structure, that is, the
235 number of available V_{Li} 's and Nb_{Li} 's which is characterized by the macrostate chemical
236 composition with a given ratio $[Li]/[Nb] < 1$. Such a devised picture is constructed upon
237 several reports where Mg^{2+} and other optical damage-resistant ions (ODRI) have been used as
238 doping entities. Recently, Kovacs et al. have observed the same trends for ODRI in some
239 transition metals and in some lanthanide trivalent rare-earth ions too.^[24] Regarding the cases
240 of similar LN:Fe systems, there is evidence that iron tends to occupy Li sites rather than Nb

241 sites, irrespective of the oxidation state.^[25] Some pioneering works focused on controlling the
242 Fe^{2+} and Fe^{3+} populations employing annealing (of post-thermal treatments) are also worth
243 mentioning.^[26]

244
245 Although various counter examples can be found in the available literature,^[14] it is thus
246 possible to conceptualize that all kind of impurity ions adjust to the following order: 1)
247 simultaneous occupation of lithium vacancies and substitution of Nb antisites, and (once
248 depleted) 2) substitution for Li in Li sites followed by, 3) substitution for Nb in Nb sites, and
249 4) soon afterwards the limit of solubility is reached and segregation follows upon adding
250 further doping content. If such a depiction is adopted, then it is convenient to define the
251 critical instances of the starting points of stages 2) and 3) as the first concentration threshold
252 (FCT) and the second concentration threshold (SCT), respectively. The significance of the
253 term 'concentration threshold' herein stated has been proposed in earlier Refs. 18 and 24b
254 and it also must be noted that it differs slightly from the sense that is usually attributed to it
255 within the subfield of knowledge regarding LN doped (only) with ODRI.

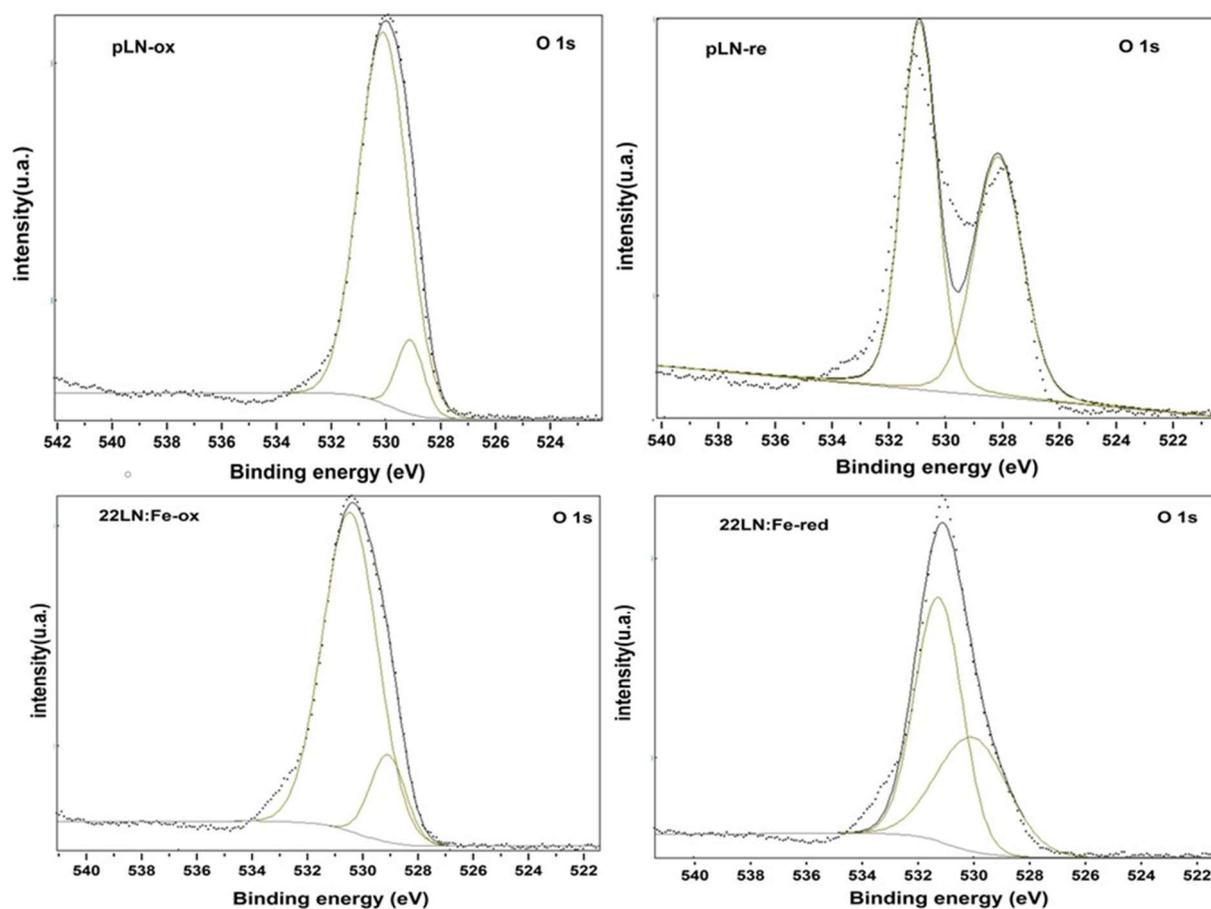
256
257 Hence, in consideration of the discussion given in the preceding paragraphs, the trends shown
258 in Figure 2(a) can be interpreted as follows. The FCT of the synthesized LN:Fe powders is
259 reached between the doping concentrations of 1.5 and 2.2 wt. % Fe_2O_3 . Post-thermal treatment
260 in a reducing atmosphere is only sensitive to the chemical/physical instance where all the Li
261 vacancies have been filled while all the Nb antisites are completely removed whereas the
262 untreated and oxidized curves discriminate between both occupancy/substitution mechanisms.
263 Under the assumption that most of the doped Fe ions share a common 3+ oxidation state for
264 the untreated and oxidized samples, the observed increasing-decreasing-constant behavior in
265 Figure 2(a) can be understood in simple terms of atomic size effects and their influence within
266 the crystal structure (see Table in the Supporting Information file for the effective ionic radii
267 for the species of interest with 6-fold coordination).^[27] Relaxation of the crystal structure
268 follows the filling of vacant Li sites (V_{Li}^-) with Fe^{3+} of comparable larger dimensions, about
269 64.5 pm, up to point 15LN:Fe(-ox). Then, it contracts due to cationic interchange with slightly
270 larger $\text{Nb}_{\text{Li}}^{4+}$ (size of about 69 pm), up to point 22LN:Fe(-ox) where a change of rate in the
271 ongoing contracting mechanism results from tuning the interchange to Li_{Li}^+ (size of about 74
272 pm). At some stage between points 33LN:Fe(-ox) and 45LN:Fe(-ox), the atomic size effects
273 should turn minimal because of the inferred cationic interchange with the regular Nb sites
274 ($\text{Nb}_{\text{Nb}}^{5+}$, size of about 64 pm), as it can be confirmed with the observed nearly constant

275 behavior. It is noticed that the quotient between the atomic radii for Nb^{5+} and Fe^{3+} is 0.99.
276 Likewise, if a multitudinous change in the oxidation state $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ is assumed after the
277 application of the reducing treatment, the same comparative analysis can lead to a satisfactory
278 explanation of the observed trend of the reduced samples (line with empty squares). However,
279 besides the fact that Fe^{3+} possess the largest ionic radius compared to the rest of the discussed
280 cationic species, perhaps it also should be considered that the thorough relaxation of the
281 structure is possibly assisted by volumetric electronic charge redistributions arising from the
282 multitudinous creation of oxygen vacancies at the surfaces.

283
284 LN powders of overall stoichiometric composition were used as the pristine samples and also
285 fit into the present discussion, see Ref. 12. On the other hand, the second concentration
286 threshold (SCT), cannot be resolved explicitly by refinement of the XRD results, Figure 2(a),
287 while it is expected to lie somewhere in between points 3.3 and 4.5 wt. % Fe_2O_3 . It will be
288 shown that analysis of the Raman spectra not only confirms the entailed arguments
289 concerning the FCT, but also sensitivity to the SCT can be reached. Lastly, Figure 2(a) can
290 also be considered as an excerpt of evidence neglecting the aesthetic idea that off-
291 stoichiometric LN can be turned stoichiometric through suitable doping, that is, by an
292 effective elimination of intrinsic defects by filling of the vacancy sites.^[14,28] That could only
293 be strictly correct if, for a given doping concentration, the unit cell volume would result to be
294 smaller than that of the pristine sample (off-stoichiometric in this work), since undoped (and
295 post-thermally untreated) LN shows a characteristic structural relaxation in going from the
296 stoichiometric chemical position to any off-stoichiometric point, see Figure 3 in Ref. 20, for
297 example.

298
299 2.1.2. X-Ray Photoelectron Spectroscopy
300 Further characterization of a small set of reduced and oxidized samples was done using X-
301 Ray Photoelectron Spectroscopy (XPS) to demonstrate that the doped Fe ions have reached a
302 population fraction close to 1 with oxidation states of 2+ and 3+, respectively. The selected
303 samples for analysis were pLN-ox, pLN-re, 22LN:Fe-ox and 22LN:Fe-re. Figure 3 and Table
304 3 display the obtained photoelectron spectra and the binding energy values, respectively. The
305 graphics show the O 1s core level spectrum which is typical for oxides. All the spectra
306 showed a shift in binding energy, and after curve fitting, the observed peaks were c.a. 529.1
307 eV, associated with the regular lattice of lithium niobate. In the pristine reduced sample, the
308 peaks around 530.1 eV and 528.1 eV are associated to distortion of the lattice, as discussed

309 previously in the results obtained by structure refinement. According to the process of
310 synthesis, the first stage was the application of a reduction treatment then followed by the
311 oxidation treatment. In the reduction treatment a loss of oxygen occurs, creating oxygen
312 vacancies and a reduction of Nb^{5+} to Nb^{4+} . In contrast, oxygen is absorbed during the
313 oxidation treatment. Such diffusion of oxygen causes the changes in binding energies
314 observed in the XPS spectra. On the other hand, regarding the iron doped sample with
315 reduction treatment, the 531.2 eV peak is assigned to the vacancy region.^[29] The highest
316 energy observed in the present study corresponds to sample 2LN:Fe-re, as it is shown in Table
317 3. Due to charge compensation, higher proportions of Fe^{2+} induce the formation of oxygen
318 vacancies.^[29,30]
319



320
321 **Figure 3 :** XPS spectra for O 1s in the LN samples with oxidation and reduction treatment.
322

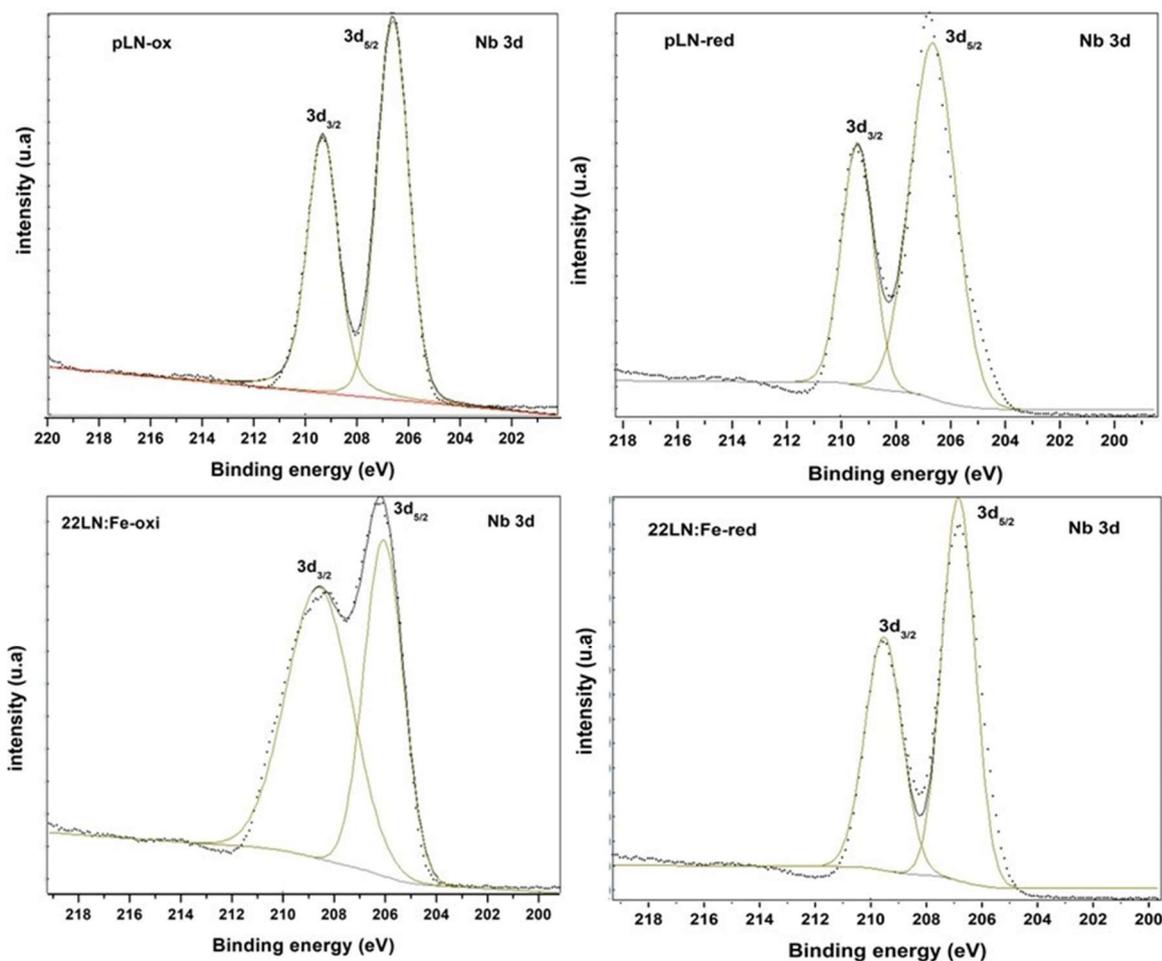
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327 **Table 3** : Binding energy values obtained from peak fitting of XPS spectra.

Sample	O 1s		Nb 3d		Fe 2p	
			3d _{5/2}	3d _{3/2}	2p _{3/2}	2p _{1/2}
pLN-ox	529.1 eV	530.1 eV	206.5	209.2	0	0
pLN-re	530.1 eV	528.1 eV	206.6	209.4	0	0
22LN:Fe-ox	530.3 eV	528.9	206.1	208.6	711.5	725.1
22LN:Fe-re	531.2 eV	530	206.8	209.5	711.3	724.2

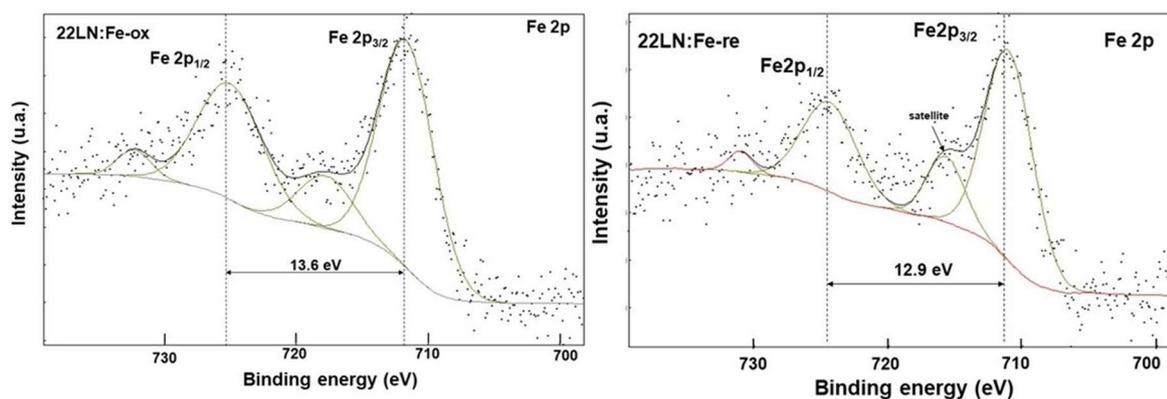
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329 In Figure 4, it is shown that the spin-orbit doublet corresponding to Nb 3d, contributions from
 330 3d_{3/2} and Nd 3d_{5/2}. In this case, the binding energies for most of the samples are around
 331 206.1eV and 206.8 eV, which correspond to stable niobium Nb⁺⁵. However, in the sample
 332 doped with an oxidation treatment, it can be noticed a reduction in the binding energy,
 333 particularly for the contribution 3d_{3/2} and it can be attributed for lithium substitution in regular
 334 sites. This causes a change in the density of charge for the Nb-Li bond, in correspondence
 335 with the discussion given from the XRD results, namely the observed reduction in the cell
 336 volume. On the other hand, the binding energies for contributions 3d_{5/2} and 3d_{3/2} increase in
 337 the case of sample 22LN:Fe-re, thus indicating the presence of oxygen vacancies produced
 338 during the reduction treatment and the presence of Fe²⁺ when lithium is replaced from its
 339 regular sites. The cell volume increases due to the larger ionic radii of Fe²⁺, changing the
 340 charge density differently from the Fe³⁺ case.^[31-33]



341
 342 **Figure 4 :** XPS spectra for Nb 3d in the LN samples with oxidation and reduction treatment.

343
 344 Lastly, Figure 5 shows the Fe 2p core level spectrum of samples 22LNFe-ox and 22LN: Fe-re.
 345 The two peaks correspond to Fe 2p_{3/2} and 2 p_{1/2}, and according to the obtained values, these
 346 samples have a mixture of both valences Fe⁺² and Fe⁺³. As it is shown in Table 3, the values
 347 of the peaks Fe 2p_{3/2} and Fe 2p_{1/2} are 711.5 eV and 725.1 eV for the oxidized sample, having a
 348 binding difference of 13.6 eV. These values are consistent with the trivalent oxidation state of
 349 iron. Likewise, for the reduced sample, the values of the peaks Fe 2p_{3/2} and Fe 2p_{1/2} are 711.3
 350 eV and 724.2 eV, with binding energy difference of 12.9 eV. The decreasing in the binding
 351 energy is ascribed to the Fe⁺³ → Fe⁺² reduction which comes from the increasing population
 352 of Fe⁺², as inferred from the 2p_{3/2} satellite observed in the spectrum at 715.7 eV. [34-36]



353

354 **Figure 5** : XPS spectra for Fe 2p in LN samples 22LN:Fe-ox and 22LN:Fe-ox.

355

356 2.1.3. Confocal Raman Spectroscopy

357 The structural evolution of all samples was also investigated using Raman Spectroscopy.

358 Representative data are shown in Figure 6. All spectra are plotted in the 100-1000 cm^{-1} 359 relative wavenumber domain. Raman spectra resembling that of (pure ferroelectric) LiNbO_3

360 were recorded under the same experimental conditions for all the pristine and LN:Fe samples.

361 Small deviations can be traced when the functional forms are compared to that corresponding

362 to the Raman spectra of the untreated pristine sample, see Figure 6(a). They can be ascribed to

363 slight registered differences regarding the centers and the linewidth of certain individual

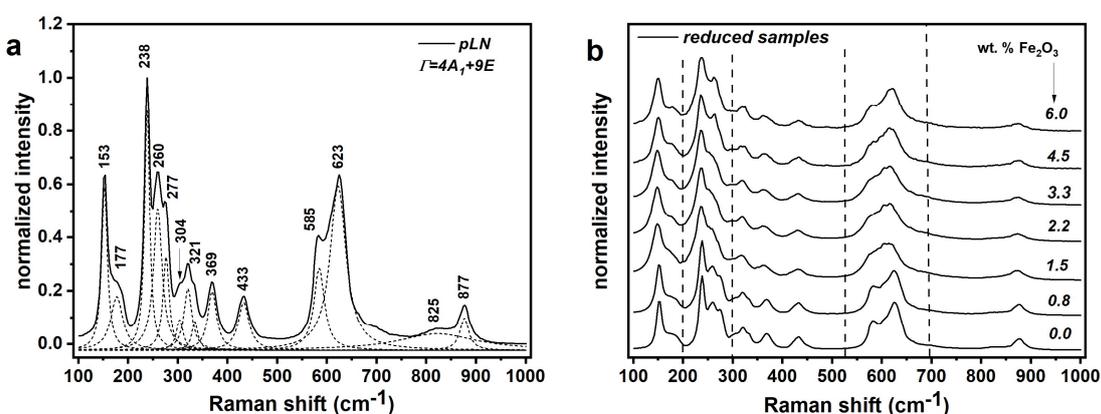
364 Raman bands or polar modes, from sample to sample. Such differences are likely to merge

365 with the controlled defect structure or lattice re-ordering induced through elemental doping,

366 i.e. the tuning of the phonon damping within the framework of damped harmonic oscillators.

367 They hold for all instances, but they are more notorious for the reduced samples, Figure 6(b).

368



369

370 **Figure 6** : Raman spectra in the Stokes-frequency domain containing the fundamental lattice

371 vibrations of lithium niobate (normalized to highest intensity). (a) Pristine powders, the

372 dotted curves show the individual polar modes contributing to the full spectra. (b) The doping

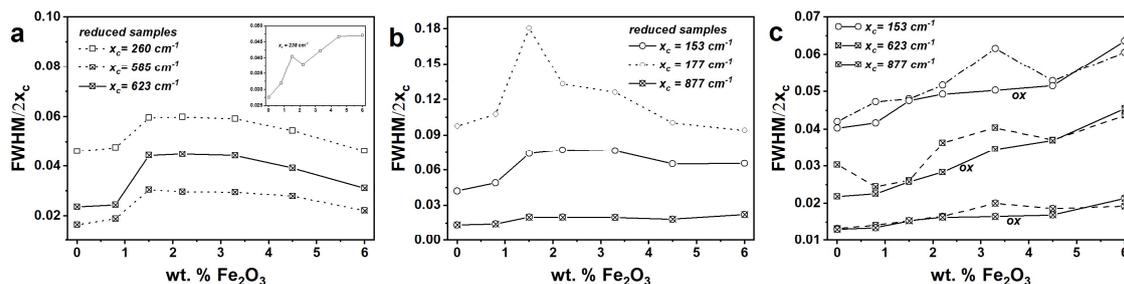
373 *effect on the different modes of lattice vibration is more evident for the reduced LN:Fe*
374 *powders, particularly near to $\Delta\tilde{\nu} = 250\text{ cm}^{-1}$ and $\Delta\tilde{\nu} = 600\text{ cm}^{-1}$.*

375
376 In the framework of group theory, lattice vibrations pertaining to the LN system (space group
377 R3c, point group 3m, RT) with vanishing k wave vector can be divided—in first
378 approximation—into 5A₁, 5A₂, and 10 (twofold degenerate) E phonon branches.^[37] Of these,
379 one A₁ and E are the acoustic branches, the five A₂ fundamentals are Raman and infrared
380 inactive, and the remaining 4 A₁ and 9 E optical branches are both Raman and infrared
381 active.^[38] Accordingly, with two molecules per unit cell, the irreducible representation of the
382 optical modes can be expressed as $\Gamma = 4 A_1 + 5 A_2 + 9 E$. Although the assignment of phonon
383 modes in LN has been a subject of debate for a long time, the above description has only been
384 adopted in few reports.^[37,38] Because the A₂ are nonpolar and inactive, therefore there are 13
385 directional dispersion branches of phonons.

386
387 LN has a strong ionic role in what respects its overall chemical binding characteristics.^[2]
388 Hence, nominally the incident macroscopic electric field splits each A₁ and E modes into
389 longitudinal optical (LO) and transverse optical (TO) components. Once the assignment of
390 phonon modes has been done, the existent types of interactions between the structural units of
391 LN can be deconvoluted into both components of each Raman active polar mode, as it has
392 been described, for example, by Caciuc et al. (2000) and Fontana et al. (2015).^[37] However,
393 this type of analysis is only consistent with single crystals which have definite principal axes
394 and, thus, knowledge of the state of linear polarization of the scattered light turns out to be of
395 great importance. While the so-called selection rules for Raman active phonons can be
396 determined univocally by standard methods of group theory, the relative intensities of given
397 Raman modes can be rationalized according to the polarization directions of the incoming and
398 scattered light.^[38] In contrast, the distinction between the LO and TO components is not
399 applicable for random media such as powders composed from myriads of single nanocrystals.
400 The polarization information is lost because of the arbitrary orientations of each given
401 crystallite, whereas the LO and TO can be assumed to overlap. For this reason, there is no
402 need in using polarized Raman Spectroscopy to resolve all the 13 fundamental lattice
403 vibrations of LN powders, see Figure 6(a) and the Experimental Section. Pezzotti (2013) has
404 given an overall description of the LN main features of cation displacements in terms of
405 relative wavenumber, summarized in a table presented in the Supporting Information file.

406 The small deviations shown in Figure 6(b) can be analyzed by rationalizing the characteristics
407 of a given Raman band into the dimensionless parameter $\text{FWHM}/2x_c$ where the numerator
408 stands for the Full Width at Half Maximum and the denominator for twice the spectral center
409 of the Raman band. Both entries are influenced by the substitution mechanism that follows
410 doping of the pristine LN structure with Fe ions and they are determined numerically after
411 performing a multi-peak fitting of the Raman spectra using a Lorentzian line shape. Because
412 the small deviations were also traced for the untreated and oxidized samples, although in
413 minor proportions, this type of analysis was done for all samples. It was done once for each
414 relative wavenumber domain of interest, namely the 200-300 cm^{-1} zone, the 550-700 cm^{-1}
415 zone, the 100-200 cm^{-1} zone, and close to 877 cm^{-1} . In each case, the experimental data was
416 abridged to specific limits sharing a common baseline (enlargement of the spectra around the
417 zone of interest) and the number of peaks on the fitting varied from one to three depending on
418 the case of analysis. The first two zones are those where the doping effect on the different
419 modes of lattice vibration resulted to be more evident, as it is highlighted in Figure 6(b) with
420 the dashed vertical lines. The remaining two zones were also studied so that the analysis could
421 effectively cover the whole domain of fundamental Stokes modes, dividing it into the
422 instances of low-, mid-, and high- Raman shift zones. They can also be considered as isolated
423 contributions to the full Raman spectra when compared to the first two zones.

424
425 The results derived from the described analysis are shown in Figure 7. Initially, only the most
426 intense Raman bands of each zone were targeted (solid curves in Figure 7(a) and Figure 7(b),
427 but their respective adjoining polar modes have been also accounted for (dashed curves), to
428 quantitatively assess any possible correlation between both contributions. Only the results for
429 the most intense Raman bands of each zone (153, 623, and 877 cm^{-1}) are shown in Figure 7(c),
430 where the untreated and oxidized samples have been represented with solid and dashed curves,
431 respectively. It is also worth mentioning here that the trends resulting from using only the
432 half-width ($\text{FWHM}/2$) are very similar to those shown in Figure 7, indicating that the latter
433 can be interpreted based on the same mechanisms involved in the broadening of spectral
434 bands, namely the increasing disorder in the lattice due to compositional inhomogeneity,
435 crystal imperfections, and insertion of impurities and dopant ions, among others.



436
 437 **Figure 7 :** Half-width divided by the center of individual Raman bands of interest. In function
 438 of the doping concentration and of the applied post-thermal treatments: (a) Reduced samples
 439 ca. $238\text{-}260\text{ cm}^{-1}$ and $585\text{-}623\text{ cm}^{-1}$, data for the 238 cm^{-1} band is shown in the inset figure.
 440 (b) Reduced samples ca. $153\text{-}177\text{ cm}^{-1}$ and 877 cm^{-1} . (c) Some results for the untreated and
 441 oxidized (solid curves) samples are given to show that no systematic behavior or
 442 characteristic trend can be ascribed to these cases.

443
 444 Interestingly, most curves shown in Figure 7(a) and Figure 7(b) show an identical behavior,
 445 excluding only the one obtained for the polar mode centered at $x_c = 238\text{ cm}^{-1}$ (inset figure),
 446 and perhaps more rigorously, the one for $x_c = 177\text{ cm}^{-1}$ too. Furthermore, in following the line
 447 of arguments given in the previous subsection, these results not only confirm the existence of
 448 the first concentration threshold (FCT) at the doping concentration of 1.5 wt. % Fe_2O_3 , as
 449 predicted to lie between this point and 2.2 wt. % Fe_2O_3 by XRD plus structure refinement.
 450 The second concentration threshold (SCT) can also be determined at 3.3 wt. % Fe_2O_3 , within
 451 the given absolute accuracy (doping concentration increments of $\Delta \approx 3.3\text{ wt. \% Fe}_2\text{O}_3$). Such
 452 inference agrees with the fundamental fact that the SCT should lie close to the limit of
 453 chemical solubility.^[14,18,24] Also, this information can only be extrapolated from the reduced
 454 samples, noticing that no clean trends or ‘well-behaved’ curves were obtained neither for the
 455 oxidized or the untreated samples, Figure 7(c). Thus, the application of post-thermal treatment
 456 in a reducing atmosphere is not only essential to avoid possible misfits in the interpretation of
 457 XRD patterns, see Figure 1c and derived discussion, but also to have more elements in hand
 458 for a deeper understanding of the dynamics behind the defect structure of LN:Fe.^[37] Reduced
 459 LN:Fe could also be of use for applications, specifically in the development of new generation
 460 materials for nonlinear optics.

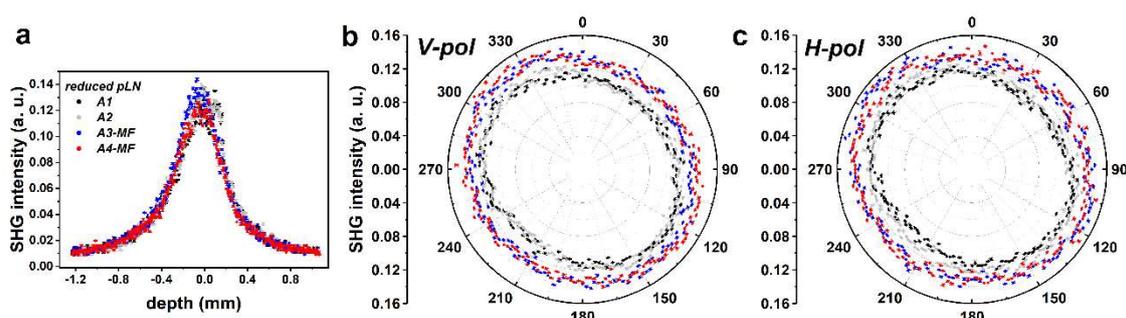
461 462 2.2. SHG response

463 The SHG response from the zero, lowest, intermediate and highest concentration of Fe doping
 464 samples under their powder form was then obtained. The complete set of analyzed data is put

465 at reach in the attached Supporting Information file along with a short video showing the
 466 strong sensitivity of sample 45LN:Fe-re to the applied magnetic field (MF). A not too strong
 467 applied MF may effectively alter the SHG response from LN:Fe powders. Figure 8 displays
 468 the obtained results for the reduced pristine samples. Depth-SHG-intensity profiles were
 469 recorded where the fundamental beam focus is translated from air into the powder. Then, two
 470 crossed-polarization plots of the SHG intensity recorded at $z = 0$, both in the absence (black,
 471 grey data points) and presence (blue, red data points) of the MF, see Figures 8(b)-(c). The $z =$
 472 0 depth is here defined as the maximum intensity of the SHG depth profile.

473
 474 The nonlinear polarization for a non-centrosymmetric material is of electric dipole origin.
 475 Higher order terms like the quadrupole electric and dipole magnetic nonlinear polarization
 476 contributions can be neglected if the crystal structure is assumed to remain non-
 477 centrosymmetric after metal doping and post-thermal treatment.^[40] To be noted though, the
 478 continuous relaxation of the crystal structure observed for the reduced samples, see Figure
 479 2(a) may to some extent leave open for further discussion the possibility of having an
 480 evolving system which becomes more symmetric as the doping concentration increases. Thus,
 481 the origin of SHG in the present LN:Fe powders is essentially of electric dipole character. It is
 482 thus expected that the material orientational randomness drives the SHG response and that the
 483 ferro-magnetic/electric properties provides a minor contribution.

484



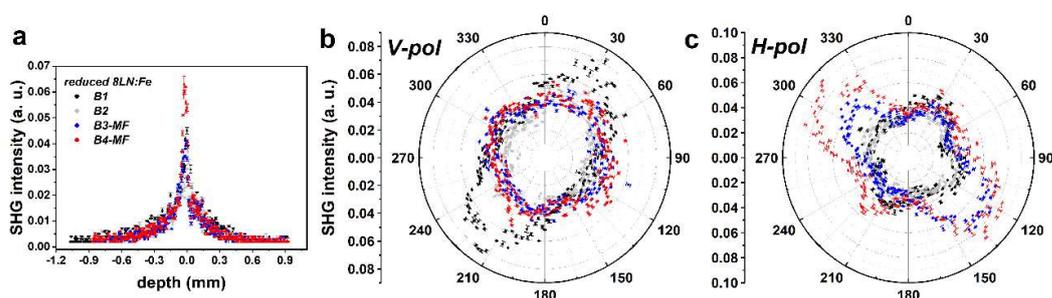
485
 486 **Figure 8 :** (a) SHG intensity depth profiles for sample pLN-re, b) Polar plot of the Vertically
 487 polarized SHG intensity as a function of the angle of polarization of the fundamental beam
 488 collected at depth $z = 0$ and (c) Polar plot of the Horizontally polarized SHG intensity as a
 489 function of the angle of polarization of the fundamental beam collected at depth $z = 0$. Blue
 490 and red points correspond to the data collected after application of the constant magnetic
 491 field whereas black and grey ones correspond to the data collected prior to the application of

492 *the constant magnetic field. The angular entries of the polar plots describe the input*
493 *polarization angle respect to the Vertical polarization configuration.*

494
495 The polar plots shown in Figure 8 exhibit a constant response at $z=0$ irrespective of the
496 incident linear polarization state of light, detection configuration and application of the MF.
497 Similar SHG intensity depth profiles and polarization plots were obtained for samples pLN
498 and pLN-ox. The observed polarization graphs exhibiting circular plots or constant SHG as a
499 function of the fundamental beam polarization result from the random nature of the granular
500 medium from the optical point of view. Scattering, including single and multiple events leads
501 to the complete loss of the polarization state of the emerging photons at the harmonic
502 frequency. It is however concluded that in this system, centrosymmetry due to the random
503 nature of the powder is not perfect and appears broken. Hence, a net non-zero SHG response
504 can still be observed. This imperfect cancelation of the many single powder grain dipolar
505 contribution cannot be reached because of the combination of imperfect random orientational
506 organization, differences in size and chemical composition from nano-grain to nano-grain.
507 The same arguments could be used to explain the observed differences in the SHG efficiency
508 for larger polycrystalline LN grains of about $2\ \mu\text{m}$ in size made of several aggregated
509 nanocrystals.^[39] It is also worth mentioning that the polar plots reported in Figure 8 do not
510 reproduce the results reported in Ref. 15 where more pronounced two-lobes polarization
511 patterns were observed for pristine LN powders of stoichiometric composition at equivalent
512 physical instances of $z = 0$. This feature may be ascribed to a different relative efficiency in
513 the collection of photons that undergo linear scattering events, the so-called multiply scattered
514 photons, as opposed to almost no linear scattering events, the so-called ballistic photons. In
515 the present case, the contribution from the multiply scattered photons dominates resulting in
516 close to undistorted circular polarization plots.^[15]

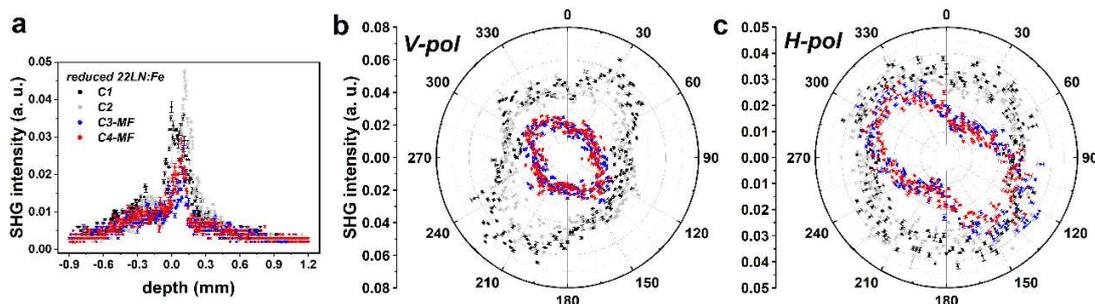
517
518 Sample 8LN:Fe-re exhibits to the contrary an important residual polarized SHG intensity with
519 a clear two-lobe patterns, see Figure 9. Therefore, the powder nano-grains illuminated during
520 the SHG intensity depth profiles and their corresponding polarization plots appear to preserve
521 some orientational order. This feature may occur due to the presence of intrinsic ferroelectric
522 domains. Interestingly, this initial orientational ordering characteristics appears to be modified
523 with the introduction of the magnetic field as seen through the changes in polarization, see
524 Figure 9(b)-(c). Also, interestingly, the application of the MF does change the polarization
525 plots, but does not change the SHG intensity depth profiles. The latter SHG intensity depth

526 profiles are also much narrower. Pristine LN powders are colorless or white regardless of
 527 post-thermal treatment whereas the untreated and oxidized LN:Fe samples are, respectively,
 528 pink and orange to the naked eye. Hence, absorption and multi-photon absorption processes
 529 also alter the relative weight between detected ballistic and multiply scattered photons. The
 530 mean free path of the latter in the sample is longer. Comparison between the SHG intensity
 531 depth profiles of samples 8LN:Fe-re in Figure 9(a) and sample pLN-re in Figure 8(a) shows
 532 that that this feature induces a collected intensity at $z = 0$ depth of the SHG intensity
 533 maximum is much weaker in the former case.
 534



535
 536 **Figure 9** : (a) SHG intensity depth profile for sample 8LN:Fe-re. b) Polar plot of the
 537 Vertically polarized SHG intensity as a function of the angle of polarization of the
 538 fundamental beam collected at depth $z = 0$. c) Polar plot of the Horizontally polarized SHG
 539 intensity as a function of the angle of polarization of the fundamental beam collected at depth
 540 $z = 0$. Blue and red points correspond to the data collected after application of the constant
 541 magnetic field whereas black and grey ones correspond to the data collected prior to the
 542 application of the constant magnetic field. The angular entries of the polar plots describe the
 543 input polarization angle respect to the Vertical polarization configuration.
 544

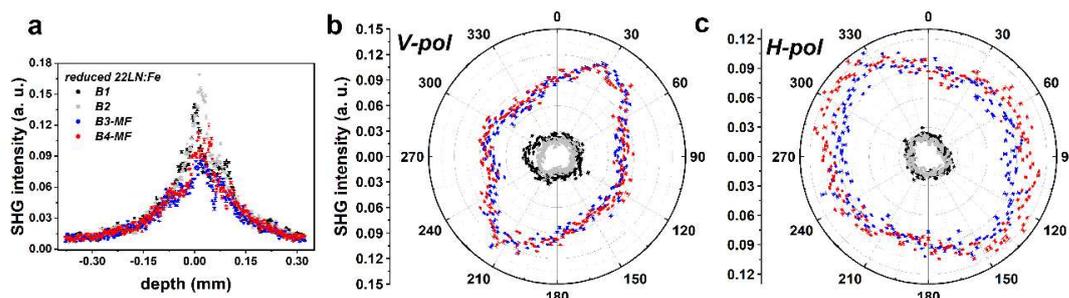
545 Figure 10 shows the obtained results for the sample of intermediate Fe doping concentration,
 546 that is, sample 22LN:Fe-re. Polarization distortions observed for already for sample 8LN:Fe-
 547 re persist although they present now a different behavior. Before application of the constant
 548 MF, the polarization plots show some initial ordering although not complete. In the presence
 549 of the applied MF, the polarization are modified and appears to tend to a more organized
 550 system with a more defined polarized SHG response.
 551



552
 553 **Figure 10** : (a) SHG intensity depth profile for sample 22LN:Fe-re. b) Polar plot of the
 554 Vertically polarized SHG intensity as a function of the angle of polarization of the
 555 fundamental beam collected at depth $z = 0$. c) Polar plot of the Horizontally polarized SHG
 556 intensity as a function of the angle of polarization of the fundamental beam collected at depth
 557 $z = 0$. Blue and red points correspond to the data collected after application of the constant
 558 magnetic field whereas black and grey ones correspond to the data collected prior to the
 559 application of the constant magnetic field. The angular entries of the polar plots describe the
 560 input polarization angle respect to the Vertical polarization configuration.

561
 562 Thus, it is observed that at this doping concentration rate, re-orientation affects the orientation
 563 distribution of the powder nano-grain. This feature can be suggested as a potential mechanism
 564 to optimize the SHG response from randomly oriented grains. Also, the SHG intensity depth
 565 profile appears rather unsymmetrical with a slow increase and a plateau in the SHG intensity
 566 as a function of depth. This feature further underlines the possible role of the MF. Figure 11
 567 reporting another run with this sample shows an important SHG signal enhancement and more
 568 dramatic changes in the polarization plots. Furthermore, run B in this series of experiments.
 569 This shows a strong alignment effect upon application of the external MF on the nano-grains
 570 powder. Therefore, the SHG response appears to be tailored by control of the numbers of
 571 intrinsic and extrinsic point defects within the hosting pristine structure and thereby setting
 572 the magnetization to an optimal value using doping concentration rates between 0.8 and 2.2
 573 wt. % Fe_2O_3 .

574

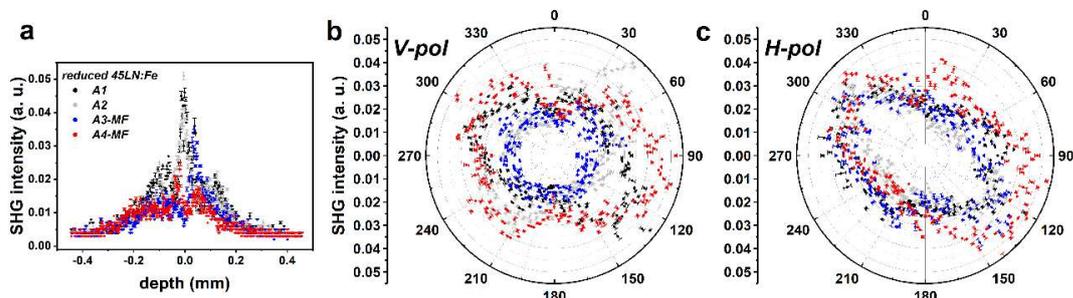


575
 576 **Figure 11 :** (a) SHG intensity depth profile for sample 22LN:Fe-re, second run. b) Polar plot
 577 of the Vertically polarized SHG intensity as a function of the angle of polarization of the
 578 fundamental beam collected at depth $z = 0$. c) Polar plot of the Horizontally polarized SHG
 579 intensity as a function of the angle of polarization of the fundamental beam collected at depth
 580 $z = 0$. Blue and red points correspond to the data collected after application of the constant
 581 magnetic field whereas black and grey ones correspond to the data collected prior to the
 582 application of the constant magnetic field. The angular entries of the polar plots describe the
 583 input polarization angle respect to the Vertical polarization configuration.

584
 585 Photo-induced change in the material seems to be another mechanism to be considered in the
 586 overall SHG response of the samples. This is more clearly seen for sample 45LN:Fe-re, see
 587 Figure 12. The recorded profiles are no longer invariant for repeated profiles. The SHG
 588 intensity almost entirely collapses into a baseline eventually. Polarization distortions are still
 589 discernible too, but they are neither well resolved nor reproduced from sample preparation to
 590 sample preparation. In this case, the incident fundamental beam is continuously transforming
 591 the material over time. Such photo-induced changes can be qualitatively explained in terms of
 592 the photo-refraction process. Photo-refraction is the process whereby an inhomogeneity in the
 593 refractive index is optically induced. It is characteristic of most insulators, and regularly, the
 594 irreversible change is generated by applying intense-laser light.^[14] LN is a photorefractive
 595 material by excellence. Accordingly, an irradiance as low as 20 W.cm^{-2} at a wavelength of
 596 532 nm is enough for its manifestation in a congruent crystal.^[41] Photo-refraction in LN can
 597 be either suppressed or enhanced by proper elemental doping. In the latter case, mainly
 598 transition metals are employed and some of the devised applications are holography storage,
 599 beam coupling, information processing, and computation. Iron has been considered for a long
 600 time the strongest photovoltaic-active impurity.^[14, 42-43] Thus, although the input power was
 601 kept fixed for all experiments performed in this investigation, the sample 45LN:Fe-re is more

602 susceptible to optical damage simply because it supports more iron in its structure, combined
 603 with the fact that the population of oxygen vacancies is at large values as well.

604



605
 606 **Figure 12 :** (a) SHG intensity depth profile for sample 45LN:Fe-re, second run. b) Polar plot
 607 of the Vertically polarized SHG intensity as a function of the angle of polarization of the
 608 fundamental beam collected at depth $z = 0$. c) Polar plot of the Horizontally polarized SHG
 609 intensity as a function of the angle of polarization of the fundamental beam collected at depth
 610 $z = 0$. Blue and red points correspond to the data collected after application of the constant
 611 magnetic field whereas black and grey ones correspond to the data collected prior to the
 612 application of the constant magnetic field. The angular entries of the polar plots describe the
 613 input polarization angle respect to the Vertical polarization configuration.

614

615 In contrast, samples 45LN:Fe and 45LN:Fe-ox do not show significant photo-induced
 616 changes. In 45LN:Fe-re, the innumerable coexistence of oxygen vacancies and Fe^{3+} ions
 617 promotes charge transport and trapping phenomena, main factors at play in photo-refraction.
 618 Lastly, in the polarization plots of the SHG response of the untreated and oxidized samples,
 619 weak distortions can be seldom traced. The same can be said for the doping concentration of
 620 2.2 wt. % Fe_2O_3 . Nevertheless, for practical purposes, samples 22LN:Fe, 22LN:Fe-ox,
 621 45LN:Fe and 45LN:Fe-ox can be assumed to be random or granular from the optical point of
 622 view, just as the pristine LN samples are. The application of a post-thermal treatment in a
 623 reducing atmosphere thus gives a deeper insight into some fundamental science problems in
 624 LN:Fe, but it also entails a modification of some of its intrinsic capabilities in the realm of
 625 nonlinear optics.

626

627 CONCLUSION

628 In this work, SHG intensity depth profiles and polarization analysis of iron doped LN
 629 powders are performed for several iron doping rates. The powders all exhibit similar SHG

630 intensity profiles driven by the competition between the Gaussian beam focus translation into
631 the powder from the air side providing SHG signal increase and multi-scattering with possibly
632 absorption leading to the loss of the SHG signal. The powders appear generally randomly
633 oriented, especially for the undoped and weakly doped ones with indication of a weak
634 remaining order possibly due to the ferroelectric property of LN. As the iron doping rate is
635 increased, changes in the polarization graphs upon application of the static magnetic field are
636 observed. Finally, at the highest doping rates, photo-refractive effects are observed. From the
637 measurements on all samples, the following conclusions can therefore be observed :

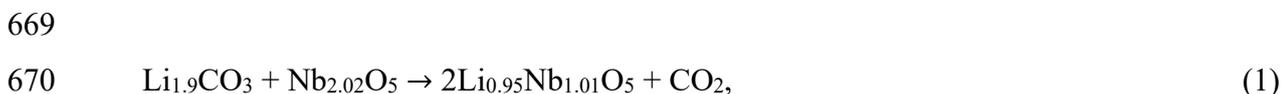
- 638 • For a given doping concentration (zero concentration included), the untreated and
639 oxidized samples present an SHG response of comparable intensity whereas the
640 intensities for their corresponding reduced samples are about one order of magnitude
641 weaker,
- 642 • SHG intensity depth profiles are slightly asymmetric correspondingly to a rise obeying
643 wave propagation of a TEM₀₀ Gaussian beam along the z-optical axis, at negative z
644 values, and a more rapid decay resulting from convolution between the same
645 propagation phenomena and exponential decay due to the strong optical extinction and
646 scattering, including multiple scattering, at positive z values,
- 647 • No material degradation was noticed from the invariance of the repeated four recorded
648 profiles within a given set of experiments,
- 649 • SHG intensity depth profiles were not modified upon the application of the MF, and
650 the definition of the $z = 0$ depth through the maximum of the SHG intensity is the
651 same, independently of the presence or absence of the MF.

652
653 Post-thermal treatment in a reducing atmosphere is essential for a deep understanding of the
654 static and dynamic characteristics of defect complexes in iron-doped lithium niobate (LN:Fe)
655 powders. It could also enable the development of a new generation characterization tool of
656 random or granular media based on nonlinear optics. Some specific aspects described in the
657 discussion of results should be addressed for formal explication, such as the origin of apparent
658 order in reduced LN:Fe powders before application of the magnetic field (probable due to the
659 intrinsic ferroelectricity in bulk LN) or its apparent lost after a first run of polarization
660 analysis (again, without application of the magnetic field), where loss of polarization
661 information due to multiple scattering of the SHG photons has been neglected here based on
662 arguments related to the inferred absorption properties of the studied materials.

663

664 **EXPERIMENTAL SECTION**

665 *Synthesis:* high purity lithium carbonate (Li_2CO_3) and niobium pentoxide (Nb_2O_5), from
666 Alpha Aesar, were used as starting reagents in 1:1 molar ratio. The respective masses of the
667 precursors were determined such that 3 g of congruent lithium niobate was produced, in
668 principle, from the following balanced chemical equation:



672 where the most widely accepted defect model to describe congruent solid solutions of LN has
673 been taken into consideration, the lithium vacancy model. The heterogenous mixture of the
674 precursors is then mechanically activated using a high-energy milling process carried out in a
675 SPEX SamplePrep 8000M Mixer/Mill (New Jersey, USA), using nylon vials with yttria-
676 stabilized zirconia (YSZ) balls; a powder-to-ball mass ratio of 0.1 was used for each sample
677 preparation. The milling was performed in 30 min cycles 30 min pauses, to avoid excessive
678 heat inside the milling chamber until 180 min of effective milling time was reached. The
679 resultant activated powders were then isothermally calcinated in an air atmosphere at 850 °C
680 for 180 min, using a tubular GSL1100X furnace (MTI Corporation, USA); no ramp was used,
681 and the samples were cooled down slowly to RT. High-quality, pure ferroelectric LN powders
682 with a near—congruent chemical composition are obtained at this stage of synthesis, as
683 confirmed by X-Ray Diffraction (XRD) and Raman Spectroscopy: the combination of
684 characterization techniques gives an averaged ratio $\text{Li:Nb} = 48.9:51.1$ (the congruent point is
685 described by the ratio $\text{Li:Nb} = 48.5:51.5$). The steps described so far are repeated several times
686 (characterizations included) to produce enough mass of pristine powder, which would be later
687 doped with Fe ions as it is described in the following paragraph.

688
689 In the doping stage of synthesis, heterogeneous mixtures of pristine LN and commercial
690 Fe_2O_3 (Alpha Aesar, Puratronic 99.998 %) were made with different rates: 0.8, 1.5, 2.2, 3.3,
691 4.5, and 6.0 wt. % Fe_2O_3 . Mixing, homogenization of particle size distribution, and lowering
692 of surface energy are simultaneously obtained after milling with the SPEX SamplePrep
693 8000M Mixer/Mill (New Jersey, USA) for an effective time of 60 min. Then, doping of Fe
694 ions was carried out through diffusion after calcination for 60 h at 850° (air atmosphere). The
695 resultant materials are labeled as it follows: 8LN:Fe, 15LN:Fe, 22LN:Fe, 33LN:Fe, 45LN:Fe
696 and 60LN:Fe. During the final stage of synthesis, reduction and oxidation treatments were

697 performed for 60 min at 850 °C in controlled atmospheres of ultra-high purity hydrogen and
698 oxygen, respectively.

699
700 *Characterization:* the XRD patterns of all the samples were recorded in the air at RT using a
701 Panalytical X-Pert system (Almelo, The Netherlands) with the Bragg-Brentano θ - θ geometry,
702 a radiation source of $\text{CuK}\alpha$ ($\lambda=1.54 \text{ \AA}$), a Ni 0.5% $\text{CuK}\beta$ filter in the secondary beam, and a 1-
703 dimensional position-sensitive silicon strip detector (Bruker, Linxeye, Karlsruhe, Germany).
704 The diffraction intensity, as a function of the 2θ angle, was measured between 10.00° and
705 80.00° , with a step of 0.016° every 30 s. Structural refinements by the Rietveld method were
706 performed using the computational package X'Pert HighScore Plus from PANalytical, version
707 2.2b (2.2.2), released in 2006.^[44] Diffraction data for phases LiNbO_3 (COD 2101175),
708 hematite- Fe_2O_3 (JCPDS PDF 04-015-6943), and α -Fe (JCPDS PDF 00-006-0696) were used
709 from the Crystallography Open Database and the Powder Diffraction File (ICDD[®]),
710 respectively.^[19,21] In the determination of the averaged crystallite sizes, a lanthanum
711 hexaboride (LaB_6) single crystal was used in this case as the standard sample, refined with the
712 diffraction data available in the ICSD-194636 card (FIZ Karlsruhe, Germany). The analysis
713 by X-Ray Photoelectron Spectroscopy (XPS) was performed in a spectrometer equipped with
714 $\text{AL } \text{K}\alpha$ (1486.7eV) monochromator, and a detector 1D DLD with analyzer Phoibos 150. The
715 electron energy analyzer is operated with a pass energy of 15 eV. The used step size is 0.1 eV
716 and the powders were deposited on Cu on Mo tape. The binding energy of the peak C 1s
717 284.8 eV was used as reference for calibration.

718
719 The structural evolution of all samples was also analyzed by Raman Spectroscopy.
720 Unpolarized Raman spectra were recorded in the air using a WITec confocal Raman
721 microscope (Alpha 300R, Germany) with a 532 nm source of excitation wavelength
722 (continuous wave diode laser) and $2\text{-}3 \text{ cm}^{-1}$ of spectral resolution. A CCD detector (cooled to
723 $-60 \text{ }^\circ\text{C}$) was used to collect Stokes Raman signals in a backscattering configuration under a
724 $0.4\text{NA}:20\text{x}$ objective lens (ZEISS, Germany). With this equipment, spectra were recorded
725 over the wavenumber range $100\text{-}3600 \text{ cm}^{-1}$ at RT, the light being incident on the normal
726 component of the sample with a power of 0.50 mW.

727
728 *Depth profiling and polarization-resolved SHG:* A picosecond laser (EKSPLA PL2231-50-
729 SH/TH Nd:YAG pulsed laser System, University Laboratory of Optics at Surfaces
730 (Laboratorio Universitario de Óptica de Superficies) into the Physics Institute of UNAM

731 (LOS-UNAM)) delivering 26 ps pulses at a repetition rate of 50 Hz was used as the source of
732 light for excitation. The fundamental wavelength was set to 1064 nm and no resonance
733 features were observed. The laser beam was then passed through a half-wave plate (HWP)
734 and polarizing cube to select the linear input polarization angle as well as for precise control
735 of the input power. For control and automation purposes, a reference arm is generated from
736 the reflected light at a transparent slide placed on the beam propagation with arbitrary
737 orientation, it is aimed toward a Thorlabs DET 10A fast photodiode coupled to a Tektronix
738 MSO 4034 Oscilloscope (USA). The transmitted light defines the experimental optical axis.
739 Depth-SHG-intensity profiles result from z-sectioning the SHG response of the samples along
740 the optical axis; a microscope-like experimental setup was constructed on a vertical plane for
741 this purpose. At the entrance, the light at the fundamental wavelength propagates downwards,
742 it first passes through a filter to reject any unwanted harmonic light ($\lambda_{\text{SHG}} \approx 532$ nm) and then
743 through an HWP mounted on a motorized rotation stage. A long-pass dichroic mirror follows
744 (650 nm Cut-On), positioned about 45 degrees with respect to the optical axis. The excitation
745 beam keeps propagating unaltered until it enters a 0.25NA:10x objective lens (Newport,
746 USA), and afterward, it impinges from the top into the powders being supported on a
747 microscope coverslip. The objective lens is mounted on a motorized linear-translation stage
748 with a minimum incremental step of 0.05 μm , which allows probing of the nonlinear optical
749 response at several experimental conditions, distinguishing between pre-focal ($z < 0$, beam
750 waist in air medium), focal ($z = 0$, beam waist at the air/powder interface) and post-focal
751 excitation conditions ($z > 0$, the physical instances for which a hypothetical undistorted
752 propagation would lead to focused beam penetrating the sample). On the other hand,
753 considering the stage just before the light beam enters the objective lens, all the experimental
754 procedures of this investigation were done at a fixed input power of (1.65 ± 0.01) mW. The
755 value represents the weighted average of several independent measurements carried on
756 routinely once or twice per day in a 2–3-week time interval.

757
758 The harmonic light from within the powders and from the air/powder interfaces propagates
759 randomly in all possible directions. Depending on the used objective lens and the scattering
760 properties of the samples, a given fraction of the harmonic light backscatters, or is retro-
761 reflected into the objective lens. It propagates upwards along the optical axis until reaching
762 the dichroic mirror, where its wavevector rotates close to 90 degrees. A long-pass filter is
763 placed on the propagation line to reject any fundamental light (if leaked from the dichroic
764 mirror). A set of three “blue” mirrors (with high reflectance at $\lambda_{\text{SHG}} \approx 532$ nm) is employed to

765 reset the propagation axis on a horizontal plane and direct it toward the detection stage. The
766 latter is composed of an analyzer (HWP plus polarizing cube) and a monochromator
767 (Princeton Instruments, Acton SP2300, USA) coupled to a photo-multiplier tube (PMT,
768 Hamamatsu H5784-04, Japan) working in the photon counting regime; the output signal is
769 decoded with the digital oscilloscope (Tektronix). A biconvex lens ($f=150$ mm) was used to
770 focus the harmonic light at the entrance of the monochromator which was held operating at a
771 fixed spectral position of 532 nm for all instances.

772
773 The cubic polarizer sets the detected light as linearly polarized and parallel to the horizontal
774 plane defining the cross section (or top surface) of the optical table. In what respects the
775 detection stage, the zeroth or original configuration is defined by putting the HWP fast-axis
776 perpendicular to the transmission axis of the polarizer, that is, parallel to the normal
777 component of the top surface of the optical table. It will be hereafter referred to as V-pol (V
778 stands for vertical). The horizontal H-pol configuration is also of interest –only in the
779 polarization analysis of the SHG response: it can be easily obtained by clockwise rotating the
780 HWP by $\theta_{HWP} = 45^\circ$ ($\theta_{pol. angle} = 90^\circ$). All the recorded intensity depth profiles were obtained
781 using the zeroth-zeroth experimental configuration, namely, the V-pol configuration at the
782 detection stage plus the setting of the first HWP (excitation stage, fundamental wave) at
783 position $\theta_{HWP} = \theta_{pol. angle} = 0^\circ$. The scanning resolution in the depth profiling was set to either
784 5 μm or 2 μm , depending on the optical absorption properties of the samples: wide profiles
785 (untreated and oxidized powders) or narrower profiles (reduced powders). Recall that strong
786 absorbance in the visible regime could be interpreted as a lower probability of the harmonic
787 photons being retro-reflected and re-inserting the objective lens, that is, a shortened detection
788 efficiency (narrower profiles).

789
790 A polarization analysis of the SHG response conveys an effective in-plane rotation of the
791 linear polarization state of the fundamental wave impinging on the samples. A full range
792 analysis (0-360°) can be effectuated by rotating the first HWP in a 0-180° range. It is done in
793 the present investigation regarding all the polarization-resolved SHG experiments, with a
794 resolution on the polarization angle of 2° (the incremental step used in every experiment was
795 of $\Delta\theta_{HWP} = 1^\circ$). Signal detection is done in the same fashion as for the case of the depth
796 profiles, but now using both configurations, V-pol first and H-pol afterwards. These
797 polarization-resolved measurements are done at the physical instance of maximum SHG

798 intensity, by the setting of the motorized linear-translation stage in such position (defined as z
799 $= 0$).

800
801 The procedure was performed three times for each studied sample so that three distinct points
802 are probed randomly from the same sample (runs A, B, and C). In each sample preparation
803 after the first one, the recently studied sample is recovered back into its container and
804 recombined with the rest of the synthesized powder. Before studying the SHG response of the
805 same powder for a second or third time, the powder was systematically chopped with a
806 coverslip to cancel out any possible orientation of grains induced by the applied MF in the
807 previous set of experiments. In this instance, only the pristine samples (pLN) and doped
808 samples 8LN:Fe, 22LN:Fe, and 45LN:Fe were studied; the three available states of oxidation
809 were considered (untreated, oxidized, and reduced samples), so that a total of 36 independent
810 sets of experiments were performed.

811

812 **Supporting Information**

813 Supporting Information is available from the Wiley Online Library or from the author.

814

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- 932
- 933

934

935 **Table of Contents Figure**

936 Second Harmonic Generation measurements convey the obtention of intensity depth profiles
 937 plus in-plane rotation of the linear polarization state of the light impinging on the samples.

938 Excitation takes place on a vertical plane. Input power does not represent a variable of study,
 939 whereas discussion of the results focuses into cases absence/presence of a constant magnetic
 940 field about 600 G.

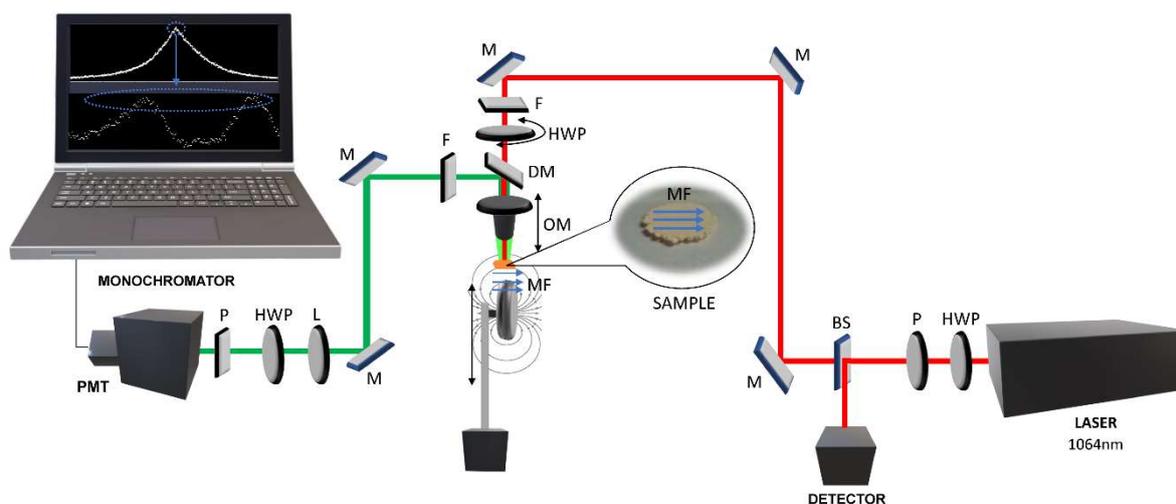
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942 Mónica J. García-Rodríguez, Oswaldo Sánchez-Dena,* Omar A. Velasco-Cortez, César L.
 943 Ordóñez-Romero, Milton O. Vázquez-Lepe, Rurik Farías, Pierre-François Brevet, and Jorge
 944 A. Reyes-Esqueda

945

946

947 Experimental setup for SHG depth profiling and polarized-resolved analysis.



948

949 Supporting Information

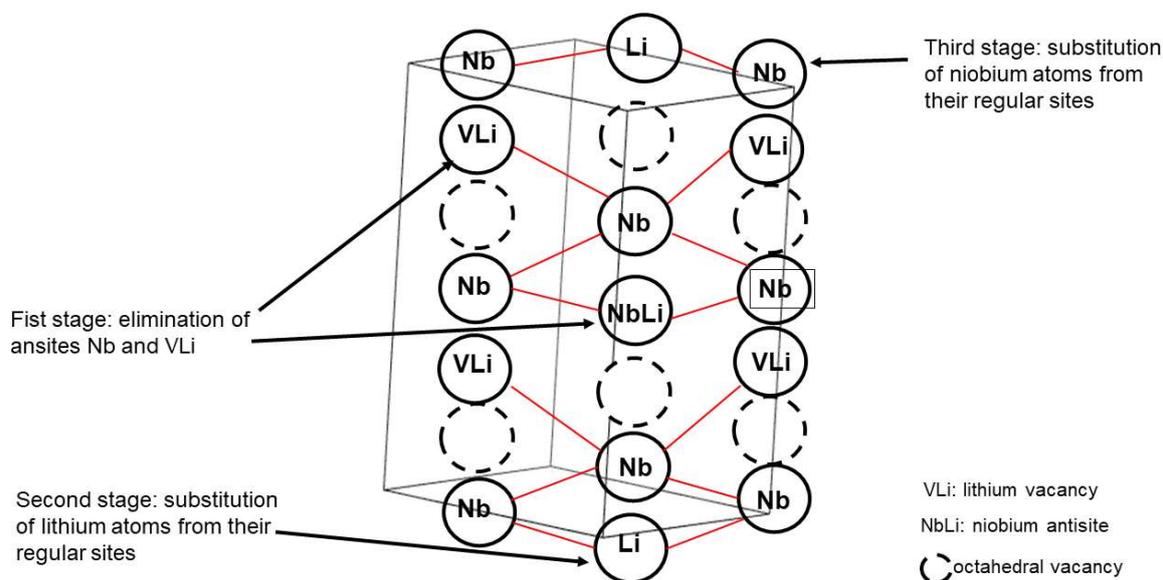
950 **Synthesis, Characterization, and Second Harmonic Generation of Multiferroic Iron—**
951 **Doped Lithium Niobate Powders**

952 *Mónica J. García-Rodríguez, Oswaldo Sánchez-Dena,* Omar A. Velasco-Cortez, César L.*
953 *Ordóñez-Romero, Milton O. Vázquez-Lepe, Rurik Farías, Christian Jonin, Pierre-François*
954 *Brevet, and Jorge A. Reyes-Esqueda*

955

956 **LiNbO₃ Crystal Structure**

957 A scheme of the congruent crystal structure of lithium niobate is presented to aid the reader in
958 following the derived discussions in the main document, specifically those corresponding to
959 the results on X-Ray Diffraction and Raman Spectroscopy.



960

961 **Figure S1.** Atomic arrangement for single crystal lithium niobate with congruent chemical
962 composition, showing the discussed dynamics regarding cationic substitution by means of
963 iron doping.

964

965 **Information in tables**

966 **Table S1.** 6-fold coordination ionic radii of iron, lithium, and niobium. Reproduced after
967 Shannon and Prewitt (1969).^[1]

Ion	Fe ²⁺	Fe ³⁺	Li ⁺	Nb ⁴⁺	Nb ⁵⁺
Effective radius [pm]	77.0	64.5	74.0	69.0	64.0

968

969 **Table S2.** Fundamental lattice vibrations of the LN system, as described by Pezzotti (2013) in
 970 terms of the relative wavenumber.^[2]

Raman shift [cm ⁻¹]	Type of vibration
153, 238	deformation of the Nb-O framework
250-400	Li displacements
277	Li-O stretching ⊕ O-Li-O bending
260, 321	O and Li (small) displacements
433	O-Nb-O bending
550-700	O displacement ⊕ Nb-O stretching
877	Nb-O stretching

971 a) Differences in the Raman shift entries to the original source might be addressed to an
 972 overlapping of the longitudinal and transverse components of the polar modes in
 973 random media. The given information has been herein adapted according to the
 974 resolution of individual bands shown in Figure 6a.

976 **SHG response (complete set of results)**

977 For all the figures given below:

978 **Note:** the blue and red points correspond to the data collected after application of the constant
 979 magnetic field, namely recording steps 8 to 15, as it is described in the main document. The
 980 angular entries of the polar plots describe the input polarization angle respect to the V-pol
 981 configuration.

982
 983 *Incises a, b, c:* first independent set of experiments for a single point randomly chosen on the
 984 sample, or simply run A.

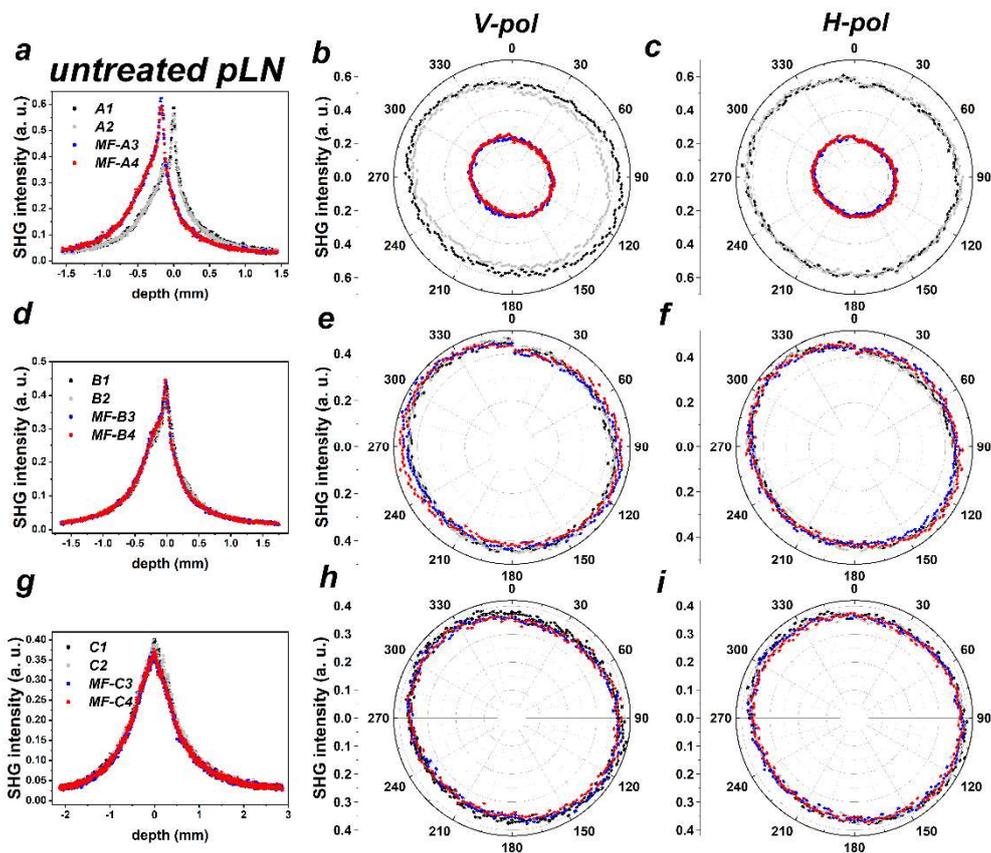
985 *Incises d, e, f:* run B.

986 *Incises g, h, i:* run C.

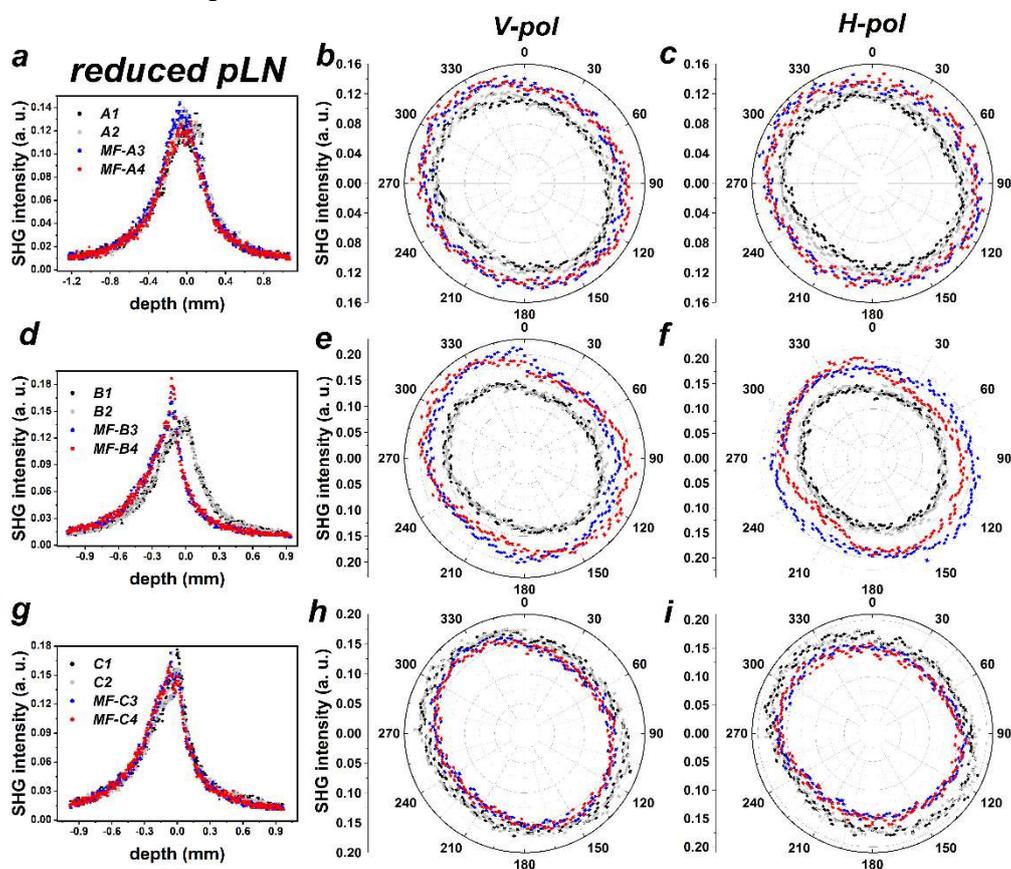
987 *Left sides:* intensity depth profiles (recording steps 1-black:2-grey:14-blue:15-red).

988 *Centers:* V-polar plots collected at maximum SHG intensity or $z=0$ (recording steps 4-
 989 black:6-grey:9-blue:11-red).

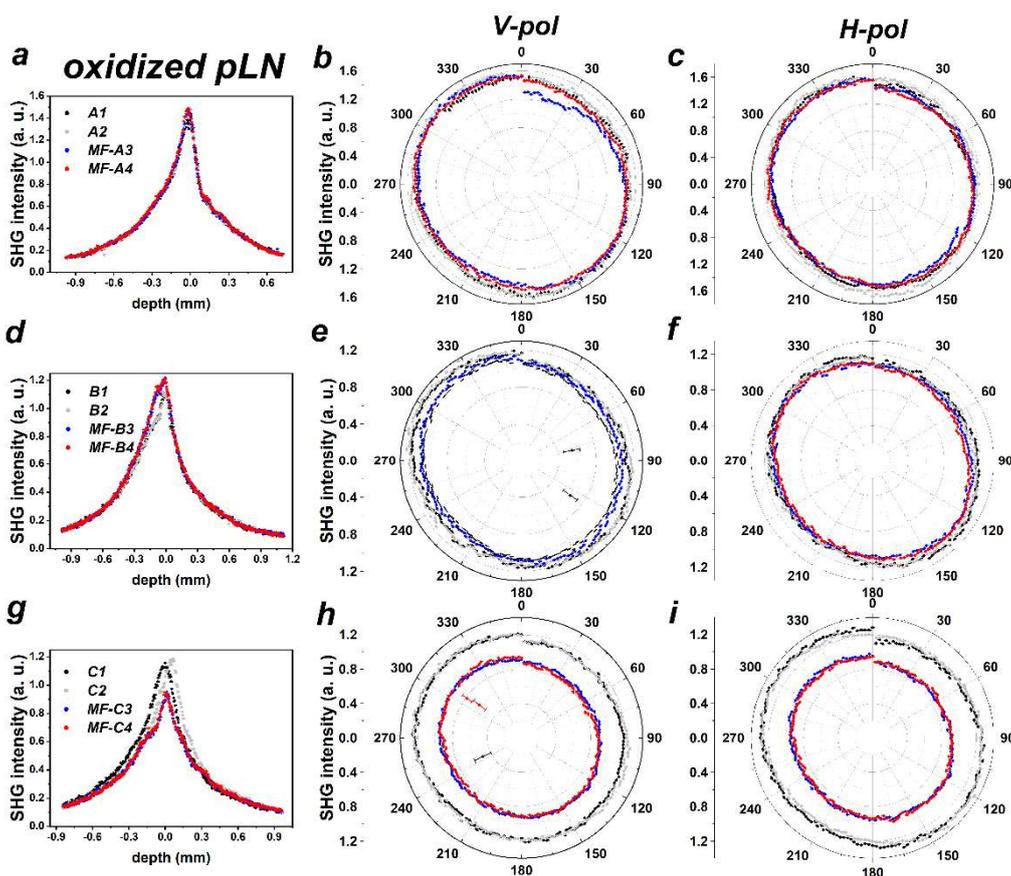
990 *Right sides:* H-polar plots collected at maximum SHG intensity or $z=0$ (recording steps 5-
 991 black:7-grey:10-blue:12-red).



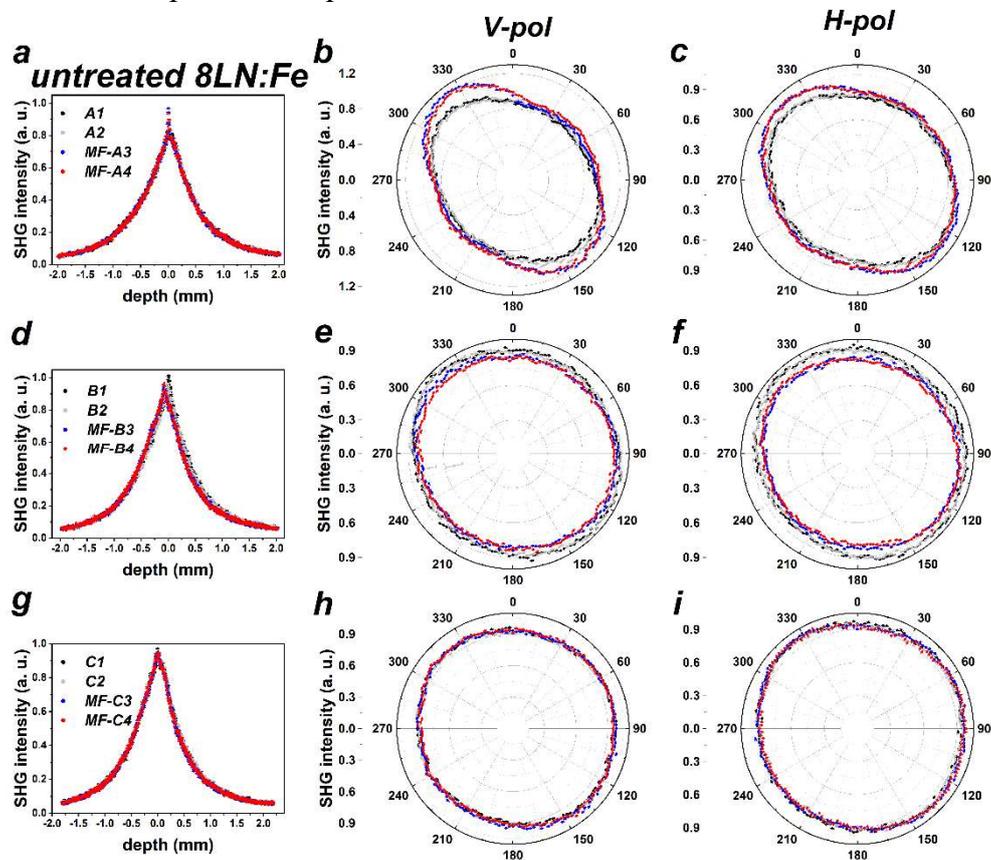
992
993 **Figure S2.** Pristine sample.



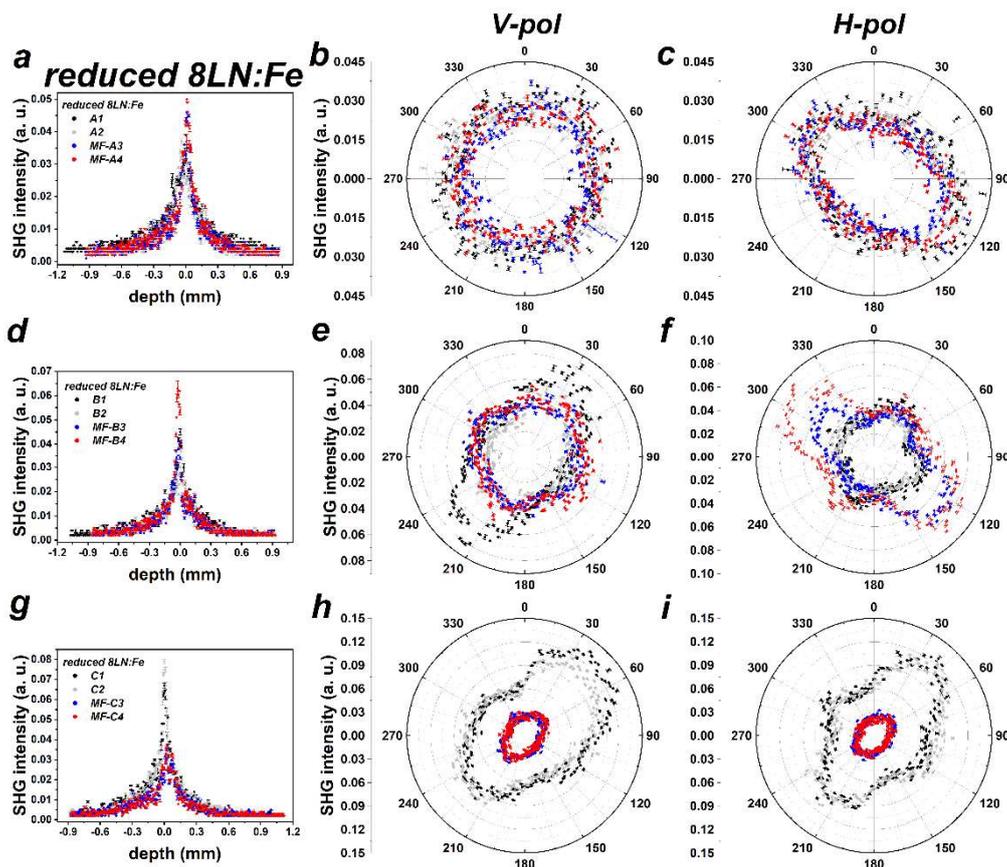
994
995 **Figure S3.** Reduced pristine sample.



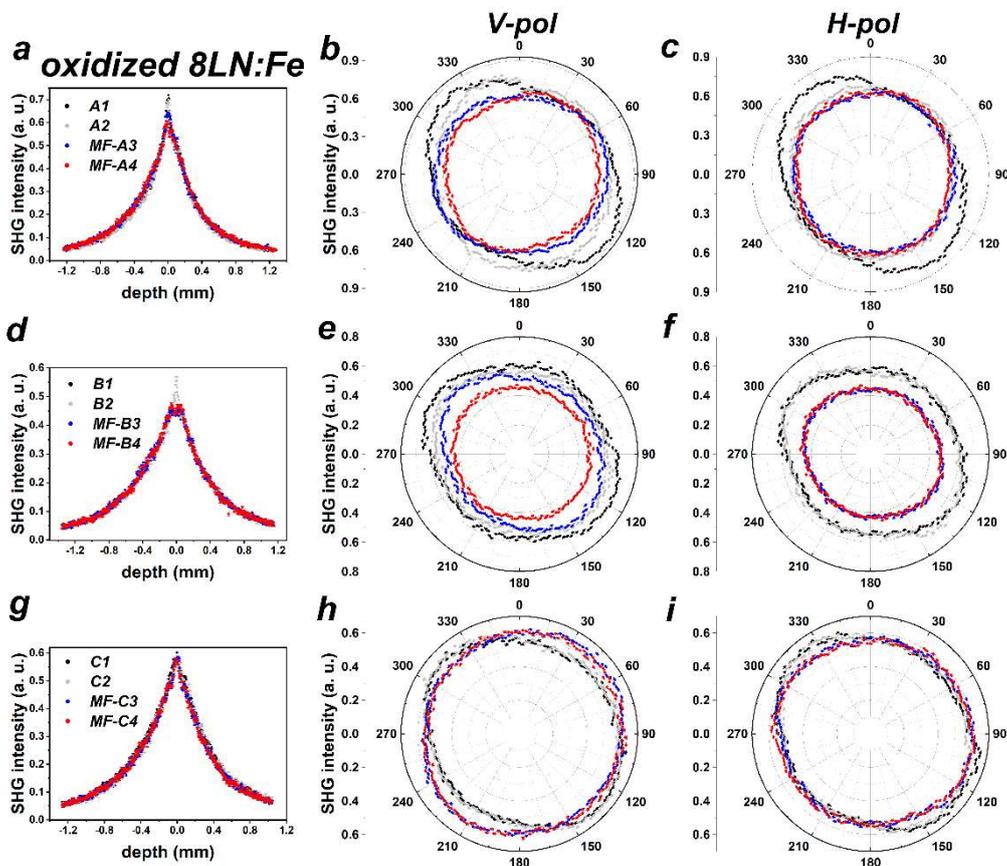
996
997 **Figure S4.** Oxidized pristine sample.



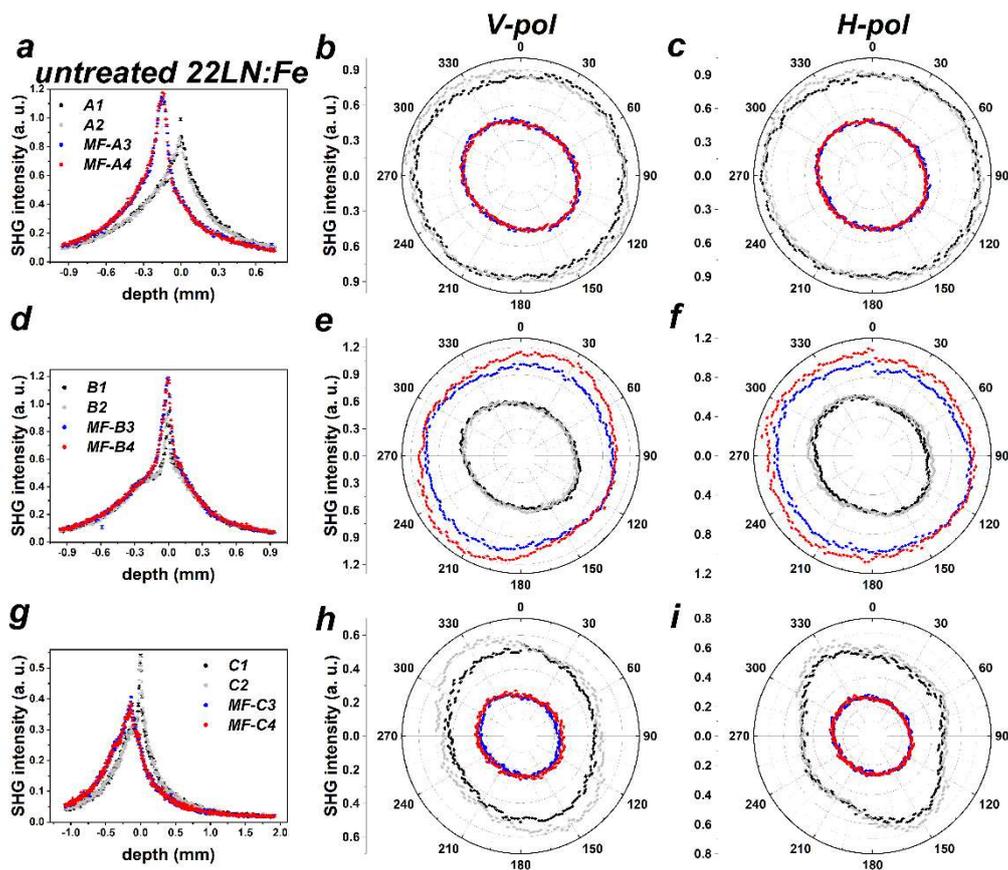
998
999 **Figure S5.** Iron doped LiNbO_3 powders with doping concentration of 0.8 wt. % Fe_2O_3 .



1000
1001 **Figure S6.** Reduced iron doped LiNbO_3 powders with doping concentration of 0.8 wt. % Fe_2O_3 .

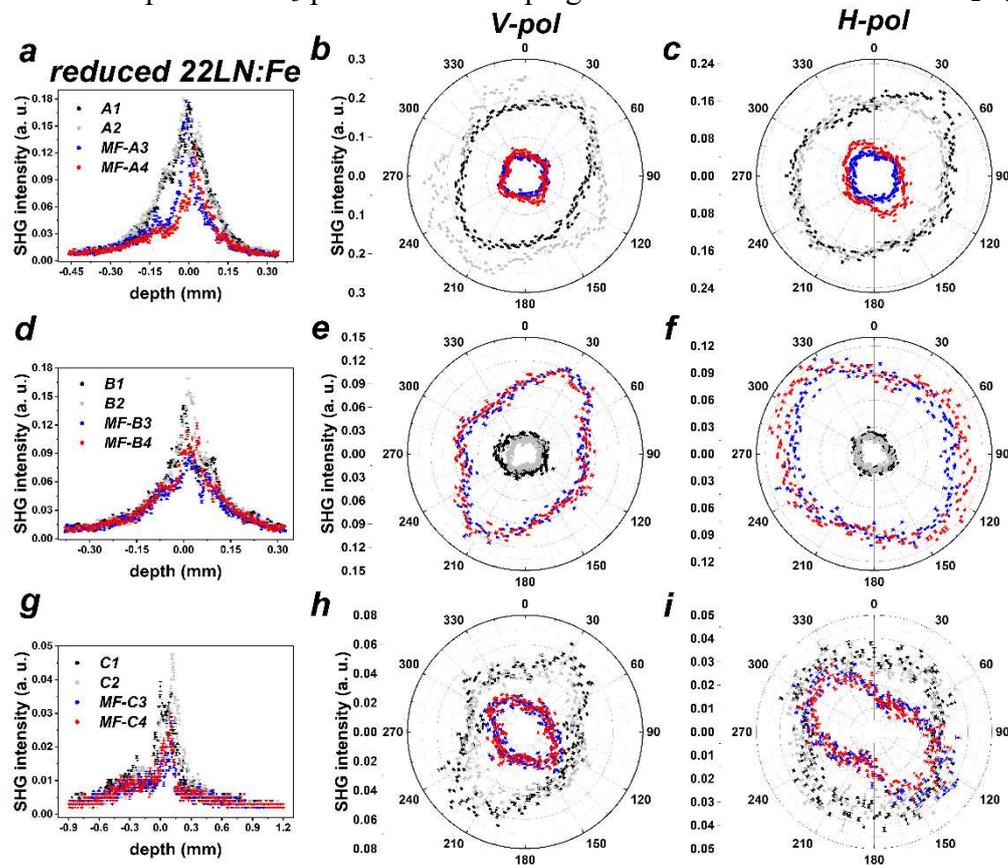


1002
1003 **Figure S7.** Oxidized iron doped LiNbO_3 powders with doping concentration of 0.8 wt. % Fe_2O_3 .



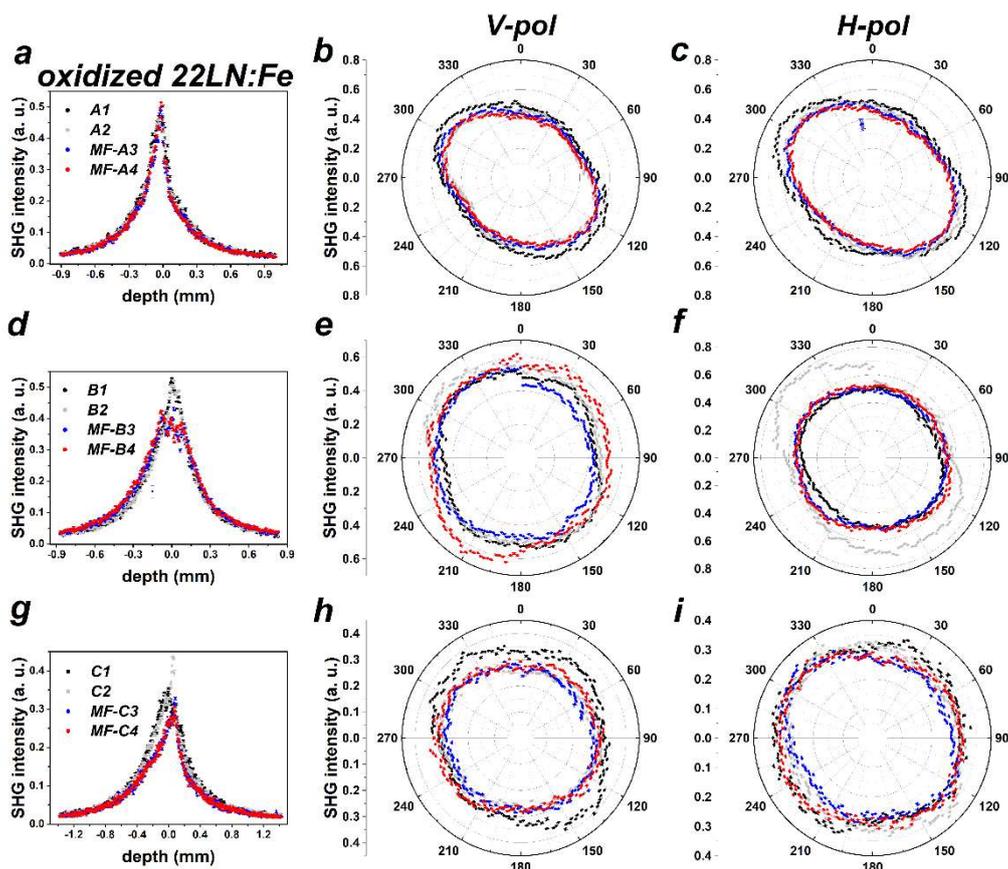
1004
1005

Figure S8. Iron doped LiNbO₃ powders with doping concentration of 2.2 wt. % Fe₂O₃.



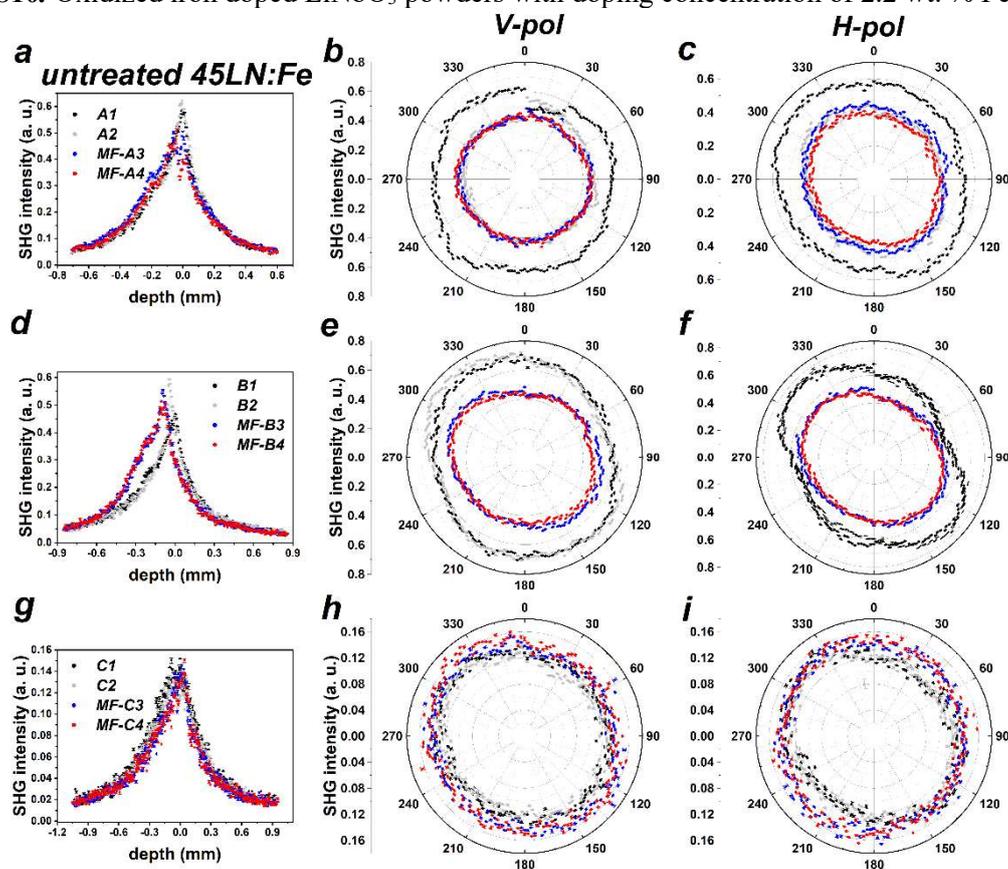
1006
1007

Figure S9. Reduced iron doped LiNbO₃ powders with doping concentration of 2.2 wt. % Fe₂O₃.



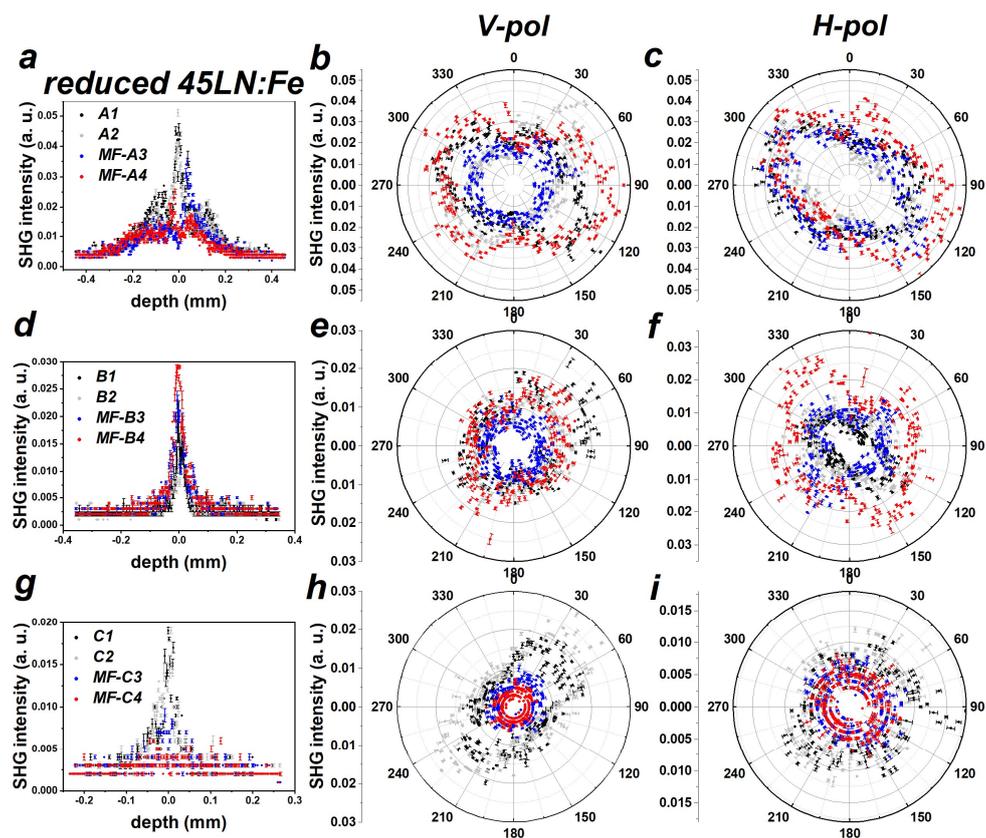
1008
1009

Figure S10. Oxidized iron doped LiNbO₃ powders with doping concentration of 2.2 wt. % Fe₂O₃.

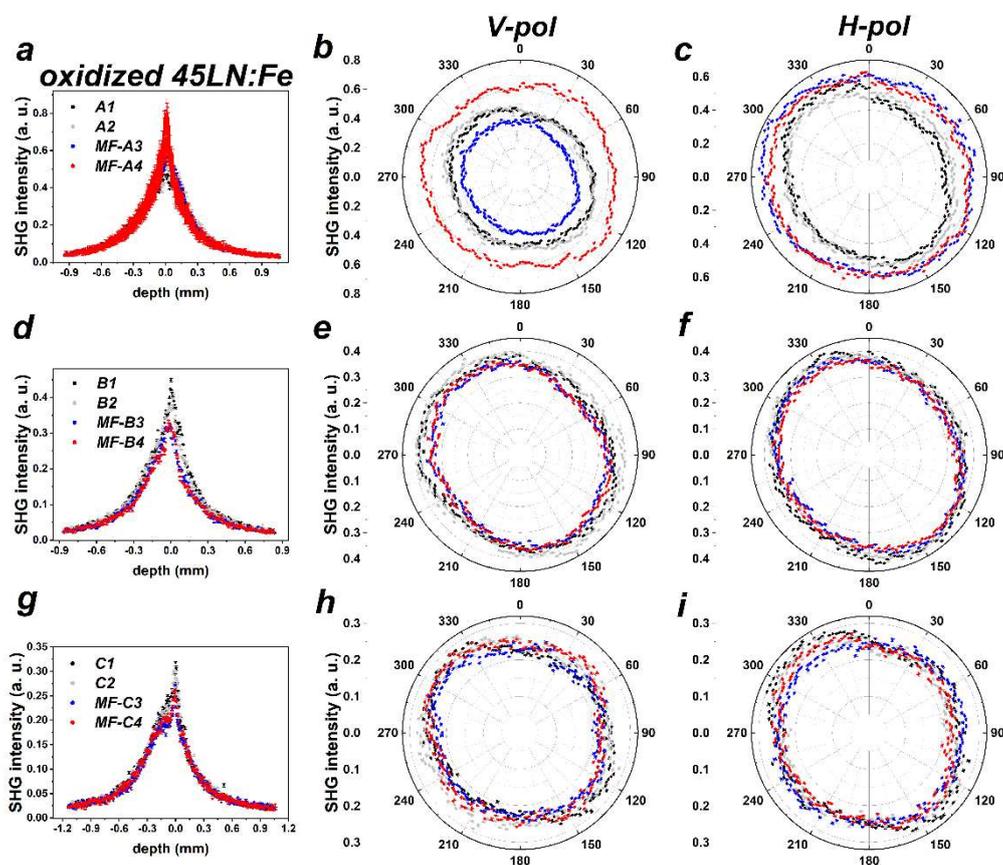


1010
1011

Figure S11. Iron doped LiNbO₃ powders with doping concentration of 4.5 wt. % Fe₂O₃.



1012
 1013 **Figure S12.** Reduced iron doped LiNbO₃ powders with doping concentration of 4.5 wt. %
 1014 Fe₂O₃.



1015

1016 **Figure S13.** Oxidized iron doped LiNbO₃ powders with doping concentration of 4.5 wt. %
1017 Fe₂O₃.

1018

1019 **References**

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