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Magnetic, optical, dielectric, and sintering properties of nano-crystalline

BaFe_{0.5}Nb_{0.5}O₃ synthesized by a polymerization method

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Magnetic, optical, dielectric, and sintering properties of nano-crystalline $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ synthesized by a polymerization method

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ABSTRACT

A one-pot polymerization method using citric acid and glucose for the synthesis of nano-crystalline $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ is described. Phase evolution and the development of the crystallite size during decomposition of the (Ba,Fe,Nb)-gel were examined up to 1100 °C. Calcination at 850 °C of the gel leads to a phase-pure nano-crystalline $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powder with a crystallite size of 28 nm. The shrinkage of compacted powders starts at 900 °C. Dense ceramic bodies (relative density $\geq 90\%$) can be obtained either after conventional sintering above 1250 °C for 1 h or after two-step sintering at 1200 °C. Depending on the sintering regime, the ceramics have average grain sizes between 0.3 and 52 μm . The optical band gap of the nano-sized powder is 2.75(4) eV and decreases to 2.59(2) eV after sintering. Magnetic measurements of ceramics reveal a Néel temperature of about 23 K. A weak spontaneous magnetization might be due to the presence of a secondary phase not detectable by XRD. Dielectric measurements show that the permittivity values increase with decreasing frequency and rising temperature. The highest permittivity values of 10.6×10^4 (RT, 1 kHz) were reached after sintering at 1350 °C for 1 h. Tan δ values of all samples show a maximum at 1–2 MHz at RT. The frequency dependence of the impedance can be well described using a single RC-circuit.

Introduction

Perovskite materials with high dielectric constants are of interest for applications in advanced technologies, e.g. memories and sensors [1–3]. $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ is interesting as an alternative for lead-containing dielectrics like PZT because it shows high


dielectric constants over a wide temperature and frequency range [4]. Patel et al. [5] showed that grain boundary effects are probably causal for the high permittivity values, and investigations by Wang et al. [6] suggest an oxygen defect-induced dielectric behaviour. Some authors describe $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ as a relaxor ferroelectric with monoclinic cell parameters [7–13]. In contrast, structural investigations by

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54 Tezuka et al. [14] and Galasso and Darby [15] reveal a
 55 centrosymmetric cubic space group, and XRD anal-
 56 yses by Bhagat and Prasad [16] point to a cen-
 57 trosymmetric monoclinic unit cell, indicating a non-
 58 ferroelectric nature of $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ [17–19]. In
 59 addition to its interesting and not fully understood
 60 dielectric properties, $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ is an antiferro-
 61 magnet with a Néel temperature of about 25 K [14]
 62 and can be used for the catalytic reduction of NO and
 63 the oxidation of CO [20]. Recently, Pan et al. [21] and
 64 Chung et al. [22] reported on the dry reforming of
 65 methane with CO_2 to form syngas in the presence of
 66 $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$. Usually, $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ is synthe-
 67 sized by the conventional mixed-oxide method,
 68 resulting into coarse-grained powders, which need
 69 high sintering temperatures [11, 12, 14, 17, 23–26].
 70 Additionally, only few wet-chemical synthesis routes
 71 have been reported, such as sol–gel and co-precipi-
 72 tate routes [5, 13, 27] as well as a microwave-assisted
 73 synthesis [28]. In addition, a nanoscaled $\text{BaFe}_{0.5}$ -
 74 $\text{Nb}_{0.5}\text{O}_3$ powder via biosynthesis was reported by Jha
 75 et al. [29]. Generally, soft-chemistry syntheses lead to
 76 fine-grained/nano-sized powders at low reaction
 77 temperatures. Using nano-sized powders, the sinter-
 78 ing behaviour can be improved, resulting in a
 79 reduction in sintering temperatures and soaking
 80 times to from ceramics with tuneable grain sizes.

81 For this purpose, we report on a one-pot Pechini-
 82 like polymerization method using citric acid and
 83 glucose to synthesize nano-crystalline $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$
 84 at low temperature with an improved sintering
 85 activity. Phase evolution and crystallite growth dur-
 86 ing the calcination process were monitored by XRD.
 87 The sintering behaviour of the nano-powder and the
 88 microstructure of resulting ceramic bodies were
 89 studied. Furthermore, magnetic and dielectric mea-
 90 surements were carried out, and the optical band
 91 gaps of the $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ samples were determined.

92 Experimental

93 Material preparation

94 NbCl_5 (0.007 mol, Alfa Aesar, 99%) and 10 g anhy-
 95 drous citric acid were dissolved in 60 ml 1,2-ethane-
 96 diol. Heating to about 100 °C led to a clear solution.
 97 Afterwards, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.007 mol, Merck,
 98 $\geq 99\%$) and barium acetate (0.014 mol, Sigma-
 99 Aldrich, $\geq 99\%$) were added. The resulting clear

100 solution had a volume of about 80 ml and was stirred
 101 at about 190 °C until the volume had decreased to
 102 70 ml. 25 g of glucose monohydrate was added under
 103 vigorous stirring, and the solution was continuously
 104 heated and stirred until it turned to a clear black-
 105 brown viscous gel. This (Ba,Fe,Nb)-gel was calcined
 106 for 2 h in static air at various temperatures (heat-
 107 ing/cooling rate 10 K min^{-1}), leading to $\text{BaFe}_{0.5}$ -
 108 $\text{Nb}_{0.5}\text{O}_3$ nano-powders.

109 To obtain ceramic bodies, a $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powder
 110 calcined at 850 °C for 2 h (rate 1 K min^{-1}) was mixed
 111 with 5 wt % of a saturated aqueous polyvinyl alcohol
 112 (PVA) solution as pressing aid and uniaxially pressed
 113 at about 40 MPa into pellets (green density
 114 2.7 g cm^{-3}). These pellets were placed on a ZrO_2 fibre
 115 mat and sintered to ceramic bodies. Two different
 116 sintering procedures were used, namely conventional
 117 sintering (heating with 5 K min^{-1} , soaking at this
 118 temperature for 1 h, cooling with 5 K min^{-1}) and two-
 119 step sintering (heating with 20 K min^{-1} to 1300 °C
 120 (T_1), then fast cooling with 20 K min^{-1} to 1200 °C (T_2),
 121 and soaking at T_2 for 10 h).

Characterization

122 X-ray powder diffraction patterns using Cu-K_α radi-
 123 ation were collected at room temperature on a *Bruker*
 124 *D8-Advance* diffractometer, equipped with a one-di-
 125 mensional silicon strip detector (LynxEye™). Cryst-
 126 tallite size and the strain parameter were determined
 127 from XRD line broadening (integral peak breadth)
 128 using the Scherrer and Wilson equation (software
 129 suite WinXPOW [30]). For Rietveld refinement, the
 130 FullProf software suite was applied [31]. Dilatometric
 131 measurements were carried out in flowing synthetic
 132 air (50 ml min^{-1}) in a *Setaram* TMA 92-16.18
 133 dilatometer. Simultaneous thermogravimetric (TG)
 134 and differential thermoanalytic (DTA) investigations
 135 in flowing synthetic air (20 ml min^{-1}) were performed
 136 using a *Netzsch* STA 449 system. The TG/DTA mea-
 137 surement of the decomposition of the (Ba,Fe,Nb)-gel
 138 was carried out on a sample preheated at 250 °C. The
 139 specific surface area (BET) was determined using
 140 nitrogen five-point gas physisorption (Nova 1000,
 141 Quantachrome Corporation). The equivalent BET
 142 particle diameters were calculated assuming a
 143 spherical or cubic particle shape. Scanning electron
 144 microscope images were recorded with a *Phenom*
 145 *ProX* SEM in the backscattered electron mode (BSE).
 146 TEM images were recorded with a *FEI* Titan 80-300
 147

operating with an electron energy of 300 kV. Temperature-dependent magnetic moments were measured in the temperature range 3–300 K under field-cooled (FC) and zero-field-cooled (ZFC) conditions using a *Quantum Design* PPMS 9. An Impedance Analyzer 4192A (Hewlett Packard) was used for permittivity measurements up to 10 MHz. Gold electrodes were sputtered onto the ceramic bodies in a *Cressington* Sputter Coater 108auto. Diffuse reflectance spectra were recorded at room temperature using a *Perkin Elmer* UV-Vis spectrometer Lambda 19 with BaSO₄ as white standard.

Results and discussion

Synthesis and powder characterization

Calcination of the viscous (Ba,Fe,Nb)-gel in static air at 250 °C for 0.5 h resulted in a black-brown amorphous powder. Simultaneous TG/DTA measurements up to 1000 °C with a heating rate of 10 K min⁻¹ in flowing air were carried out on this powder (Fig. 1). The sample shows a continuously weight loss of 6.7% up to 195 °C in combination with a very weak and broad endothermic signal, which is probably due to the release of absorbed molecules, such as H₂O. At higher temperatures, a two-step decomposition process, accompanied by exothermic signals, occurs. The first step results in a weight loss of 48.8% at 390 °C, and the second step leads to a loss of 81.1% up to 445 °C. The DTA shows a first weak exothermic signal with an onset temperature of 250 °C and a very strong second one with an onset temperature of 395 °C

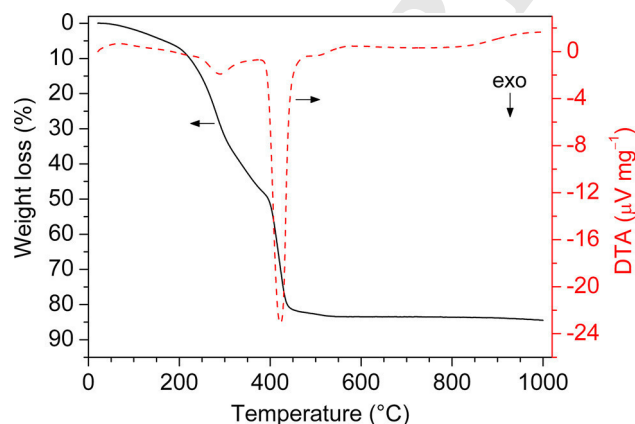


Figure 1 TG-DTA measurements of a preheated (Ba,Fe,Nb)-gel in flowing air (heating rate 10 K min⁻¹).

C. This strong exothermic reaction can be assigned to a combustion-like reaction in which the organic components (mainly glucose and citric acid) act as fuel and the nitrate ions as oxidizing agent. Between 445 and 530 °C, a last very small weight change can be observed, resulting in a total weight loss of 84.5%. The dark brown residue was identified as BaFe_{0.5}Nb_{0.5}O₃ by XRD measurement.

The phase evolution during the thermal decomposition of the (Ba,Fe,Nb)-gel is shown in Fig. 2. For these investigations, aliquots of the gel were heated in static air in a muffle furnace at different temperatures for 2 h (rate 10 K min⁻¹). Up to 500 °C, the calcination process results in amorphous compounds. After calcination at 600 °C, first reflections of BaFe_{0.5}Nb_{0.5}O₃ are visible (Fig. 2a). Calcination at 800 °C leads to well-pronounced BaFe_{0.5}Nb_{0.5}O₃ peaks, but very small traces of a secondary phase (not clearly assignable) are detectable (Fig. 2b). Heating at 900 °C (Fig. 2c) leads to a phase-pure brown powder. No peak splitting or asymmetric broadening was found in the XRD pattern, indicating the formation of cubic BaFe_{0.5}Nb_{0.5}O₃ (JCPDS 01-074-6520). The crystallite size increases from 27 nm after calcination at 850 °C to 83 nm at 1100 °C (rate 10 K min⁻¹), whereas the strain parameter decreases with temperature (Fig. 3). Decomposition with a lower heating rate of 1 K min⁻¹ leads to phase-pure BaFe_{0.5}Nb_{0.5}O₃ even at 850 °C after 2 h (Fig. 2d).

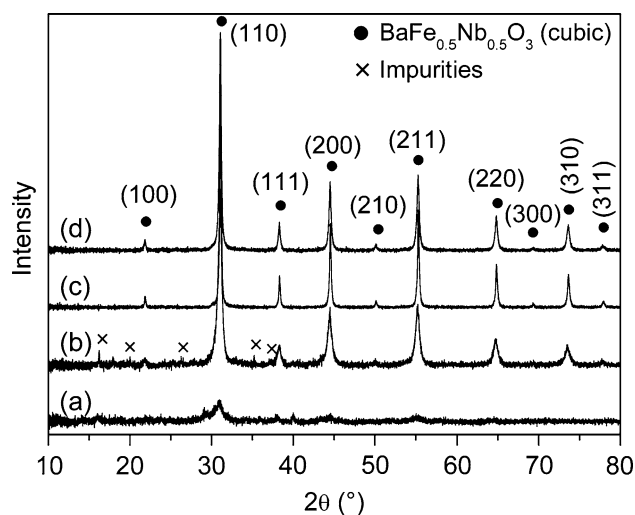


Figure 2 Room-temperature XRD patterns of the (Ba,Fe,Nb)-gel after calcination at various temperatures for 2 h: **a** 600 °C, **b** 800 °C, **c** 900 °C (heating rate 10 K min⁻¹), and **d** 850 °C (heating rate 1 K min⁻¹).

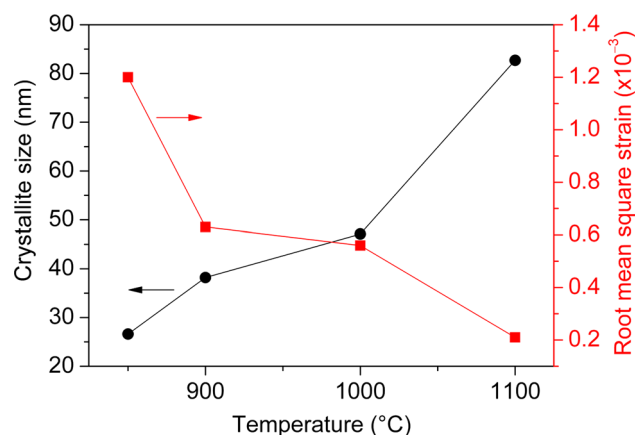


Figure 3 Dependence of volume-weighted average crystallite size and root-mean-square strain on the calcination temperature (heating rate 10 K min^{-1}).

207 The addition of glucose during the synthesis process
 208 results in a reduction in the crystallite size after
 209 thermal decomposition. For example, a crystallite size
 210 of 47 nm was obtained after decomposition at 1000 °C
 211 for 2 h, while the identical synthesis route without
 212 glucose led to a crystallite size of 63 nm. The decrease
 213 in crystallite size by adding glucose is probably due
 214 to the increased fuel (organic molecules)-to-oxidizer
 215 (nitrate ions) ratio, which leads to a reduction in the
 216 maximum combustion temperature [32, 33].

217 Sintering behaviour and microstructure 218 of ceramic bodies

219 To investigate the sintering behaviour and to obtain
 220 ceramic bodies, the (Ba,Fe,Nb)-gel was calcined at
 221 850 °C for 2 h with a heating rate of 1 K min^{-1} . This
 222 thermal treatment leads to a phase-pure nano-crystalline
 223 $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powder with a volume-weighted average
 224 crystallite size of 28 nm and a root-mean-square strain of 0.0013. The specific surface
 225 area was determined as $6.91 \text{ m}^2 \text{ g}^{-1}$ which corresponds to a calculated equivalent particle size of
 226 134 nm. The large difference between the crystallite size and the particle size from BET measurement can
 227 be explained assuming strong agglomeration and in turn surface areas unavailable for nitrogen adsorption.
 228 TEM images support this interpretation as they show agglomerates consisting of particles with diameters
 229 between about 20 and 45 nm (Fig. 4). The present synthesis method leads to a considerable reduction in the
 230 calcining temperature and time to form single-phase $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powders compared
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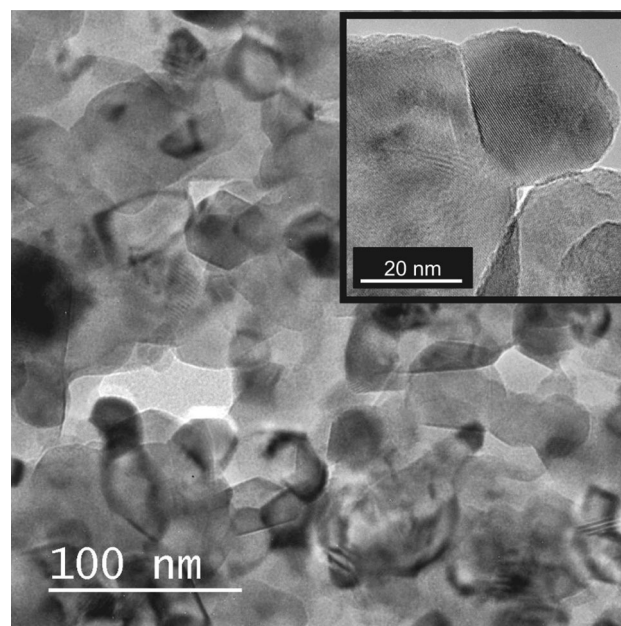


Figure 4 TEM image of $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powder calcined at 850 °C for 2 h (heating rate 1 K min^{-1}).

to the classical mixed-oxide method as well as to other sol-gel and co-precipitate routes [10, 13, 17, 22, 27].

A non-isothermal dilatometric measurement (up to 1500 °C) on a powder compact in flowing air shows that the shrinkage process starts at about 900 °C (Fig. 5). A first shrinkage process shows a broad maximum of the shrinkage rate of around $-0.5\% \text{ min}^{-1}$ between 990 and 1040 °C. This first step is completed at 1225 °C and results in a shrinkage of 23% (81% of the total shrinkage). Between 1225 and 1240 °C, a narrow plateau occurs. According to investigations by Hirata et al. [34], this plateau reflects grain growth processes within agglomerates without dwindling of pores. A similar behaviour was also observed for nano-sized MgFe_2O_4 [35]. A second shrinking process starts at about 1240 °C and shows a maximum shrinkage rate of $-0.23\% \text{ min}^{-1}$ at 1323 °C. Between 1385 and 1400 °C, a very weak expansion of the sample of 0.4% can be observed. The reason for this small expansion process is not yet clear although it was reproduced in several experiments. The whole shrinkage process is finished at 1450 °C.

The final bulk densities of ceramic bodies after conventional isothermal sintering for 1 h in static air (heating/cooling rate 5 K min^{-1}) is shown in Fig. 6. The absolute bulk densities of the sintered bodies were calculated from their weight and geometric

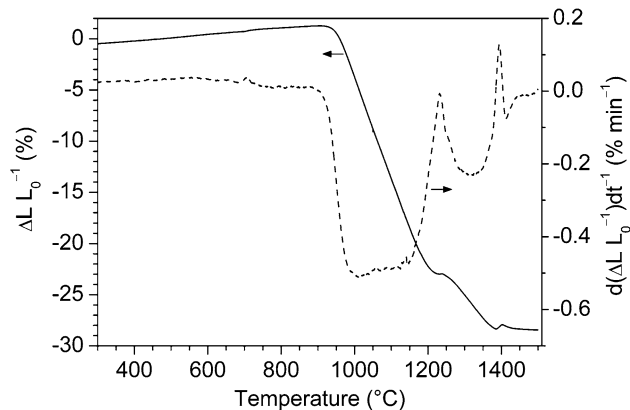


Figure 5 Non-isothermal dilatometric measurement up to 1500 °C (heating rate 5 K min⁻¹) of a compacted powder (calcined at 850 °C for 2 h).

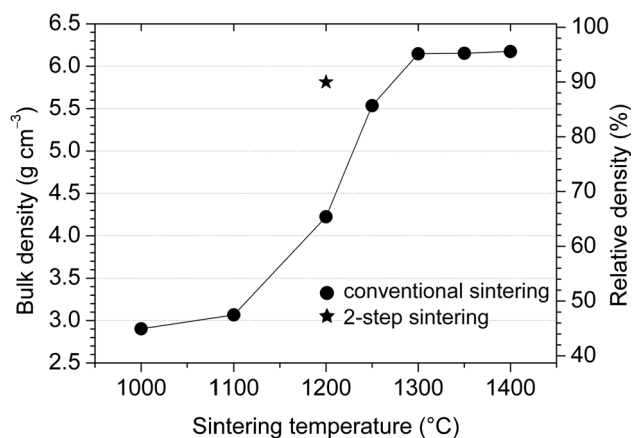


Figure 6 Final bulk densities versus sintering temperature of ceramic bodies after conventional sintering for 1 h and a two-step sintering procedure.

266 dimensions, and the relative bulk densities are related to the single crystal density of 6.46 g cm⁻³ [15].
 267 We obtained dense ceramics (relative density $\geq 90\%$)
 268 after 1-h sintering above 1250 °C. Sintering at 1300 °C
 269 results in a relative density of 95% which remains
 270 almost constant at higher temperatures. For comparison,
 271 dense ceramic bodies of BaFe_{0.5}Nb_{0.5}O₃ via a
 272 classical mixed-oxide route can be obtained after
 273 sintering at a minimum temperature of 1350 °C and
 274 soaking times more than 1 h [17, 27, 36].
 275

276 SEM images of selected ceramic bodies are depicted
 277 in Fig. 7. As can be seen, very compact microstructures
 278 were obtained and only few pores can be found in
 279 accordance with the high densities. The average grain
 280 size (\varnothing_{li}) was determined by the lineal intercept
 281 method [37]. One-hour sintering at

1200 °C results in very small grains between 0.18 and
 0.60 μm ($\varnothing_{li} = 0.33 \mu\text{m}$). Raising the temperature to
 1250 °C, the grain size ranges between 0.5 and 3.5 μm
 ($\varnothing_{li} = 1.9 \mu\text{m}$), while after sintering at 1350 °C the
 ceramic consists of grains between 7 and 34 μm
 ($\varnothing_{li} = 19.9 \mu\text{m}$). Additional values for further
 sintering temperatures are listed in Table 1.

To enhance the densification at lower temperatures,
 a two-step sintering regime was used. A compacted
 powder was first heated rapidly (20 K min⁻¹) to 1300 °C
 (T_1), then fast-cooled (20 K min⁻¹) to 1200 °C
 (T_2), and held at T_2 for 10 h (see inset in Fig. 6).
 The resulting ceramic body had a relative bulk density of
 90% and consisted of grains between 0.75 and 4.2 μm
 ($\varnothing_{li} = 2.3 \mu\text{m}$). The sintering temperatures are
 reduced by 200 °C compared to the two-step sintering
 process of a nano-powder from a co-precipitation
 method reported by Wang et al. [27].

XRD patterns of the powdered ceramic bodies
 sintered up to 1400 °C show only reflections of cubic
 BaFe_{0.5}Nb_{0.5}O₃, without any indications for impurities
 (Fig. S1, supported information). In contrast to the
 sol-gel synthesis described by Patel et al. [5], we
 did not observe the formation of secondary phases
 even at high sintering temperatures above 1250 °C.
 Additionally, our XRD patterns did not reveal any
 superlattice peaks, indicating a random distribution
 of iron and niobium ions in contrast to investigations
 by Tezuka et al. [14]. Therefore, the XRD pattern
 of the sample sintered at 1350 °C was refined on the
 basis of the cubic perovskite structure (SG Pm $\bar{3}$ m, no.
 221). The lattice parameter was calculated as
 $a = 406.11(1) \text{ pm}$ (see also Fig. S2, supported
 information), close to the value found by Galasso and
 Darby [15].

UV-Vis, magnetic, and dielectric measurements

The diffuse reflectance spectra of BaFe_{0.5}Nb_{0.5}O₆
 powder calcined at 850 °C for 2 h are shown in Fig. 8.
 The Kubelka–Munk theory was used for determining
 the optical band gap [38, 39]. The best fit to a straight
 line near the absorption edge was obtained assuming
 a direct allowed transition in accordance with literature
 [40]. Thus, the optical band gap (E_g) can be
 determined by plotting $(F(R) \cdot hv)^2$ versus hv (F
 (R) = Kubelka–Munk function) and extrapolating the
 slope to $F(R) \rightarrow 0$ (inset I in Fig. 8) [41]. The optical
 band gap of the pre-ceramic powder, calcined at 850 °C

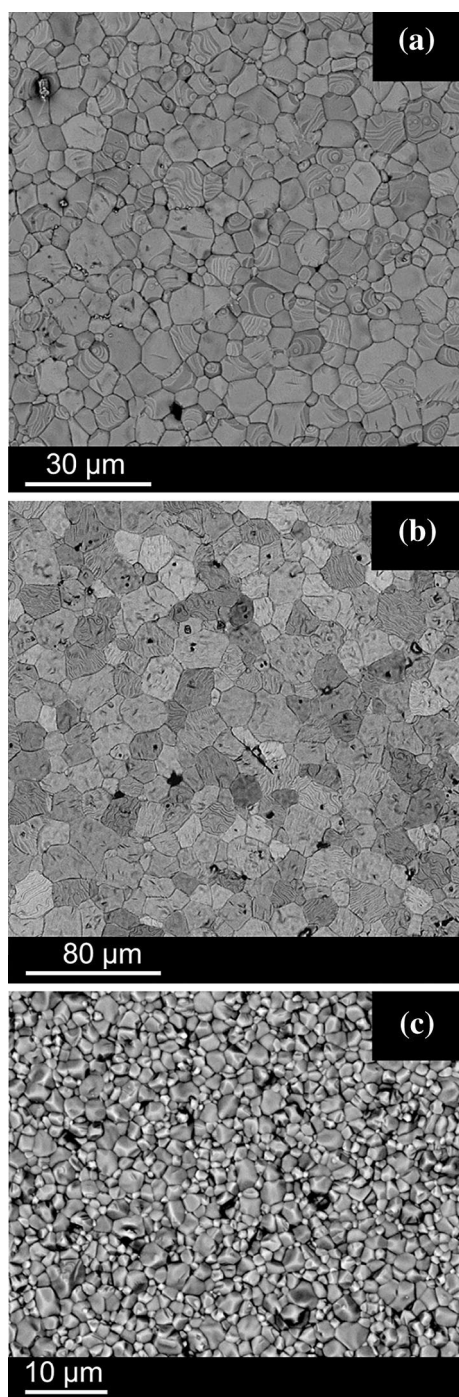


Figure 7 SEM-BSE surface images of selected ceramic bodies conventionally sintered at **a** 1300 °C/1 h, **b** 1350 °C/1 h, and **c** two-step sintering at $T_2 = 1200$ °C/10 h.

330 C for 2 h, was calculated as 2.75(4) eV. This value
 331 decreased after sintering (inset II in Fig. 8). After 1-h
 332 heating at 1000 °C, the ceramics revealed a band gap
 333 of 2.68(4) eV which is further reduced to 2.59(2) eV

after heating at 1200 °C but does not change significantly for higher sintering temperatures (e.g. 2.62 (2) eV after 1400 °C). The obtained optical band gap values are in the range reported by Patel et al. [40], whereas Kar et al. [42] surprisingly reported a much smaller band gap of only 1.3 eV.

BaFe_{0.5}Nb_{0.5}O₃ is an antiferromagnet with a Néel temperature (T_N) of about 25 K [14]. Figure 9 shows exemplarily the ZFC and FC curves of a ceramic body conventionally sintered at 1350 °C for 1 h. Below T_N , the ZFC curve reveals a reduced magnetic moment, whereas the FC curve only shows a kink at T_N . The Néel temperature depends slightly on the sintering temperature (inset I in Fig. 9). After sintering at 1000 °C, T_N is 19 K, rises to 23 K after sintering at 1300 °C and remains constant at higher sintering temperatures. Our values of $T_N \approx 23$ K are close to values reported in Refs. [14, 26]. Field dependent measurements at 300 K reveal a very weak spontaneous magnetization indicated by a hysteresis loop (inset II in Fig. 9). This weak spontaneous magnetization found in all ceramic bodies might be due to the presence of marginal traces of ferrimagnetic BaFe₁₂O₁₉, not detectable by XRD. By a linear extrapolation of the high-field region, we obtained saturation magnetizations of 0.13–0.21 emu g⁻¹ in different samples. Using the saturation magnetization of pure BaFe₁₂O₁₉ ($M_s = 57$ – 66 emu g⁻¹ [43, 44]), these values correspond to a weight proportion of 0.20–0.37% in our samples. Trace impurities of MFe₁₂O₁₆ have already been proposed as the origin of weak spontaneous magnetization at room temperatures in related systems like PbFe_{0.5}Nb_{0.5}O₃– and PbFe_{0.5}Ta_{0.5}O₃ ceramics [45–47]. On the other hand, even with very long counting times (10 s per data point) our XRD patterns of ceramic bodies showed no peaks corresponding to secondary phases. Still, such low contents as mentioned above might be below the detection limit even of modern diffractometers. Longer soaking times were found to lead to a reduction of the weak spontaneous magnetization corresponding to calculated BaFe₁₂O₁₉ contents of about 0.17 and 0.14 wt % after soaking times of 25 and 50 h at 1350 °C, respectively. As a result, the reported ferromagnetic behaviour and large magnetic moments for some BaFe_{0.5}Nb_{0.5}O₃ samples [23, 29] are due to such ferrimagnetic impurities.

Frequency-dependent dielectric measurements at room temperature (22 °C) between 0.1 kHz and 10 MHz of ceramics are shown in Fig. 10. Applying

Table 1 Grain sizes and dielectric values of selected ceramic bodies

Sintering regime	Average grain size ^a (grain size range)	ϵ_r^d	$\tan \delta^d$
Conventional sintering ^b			
1200 °C, 1 h	0.33 μm (0.18–0.6 μm)		
1250 °C, 1 h	1.9 μm (0.5–3.5 μm)	9540	0.26
1300 °C, 1 h	8.8 μm (1.5–14 μm)	59420	0.77
1350 °C, 1 h	19.9 μm (7–34 μm)	106480	0.88
1400 °C, 1 h	51.8 μm (15–84 μm)		
Two-step sintering ^c			
$T_1 = 1300$ °C, $T_2 = 1200$ °C, 10 h	2.3 μm (0.75–4.2 μm)	28580	0.72

^a Lineal intercept method

^b Temperature rate 5 K min⁻¹

^c Temperature rate 20 K min⁻¹

^d 22 °C, 1 kHz

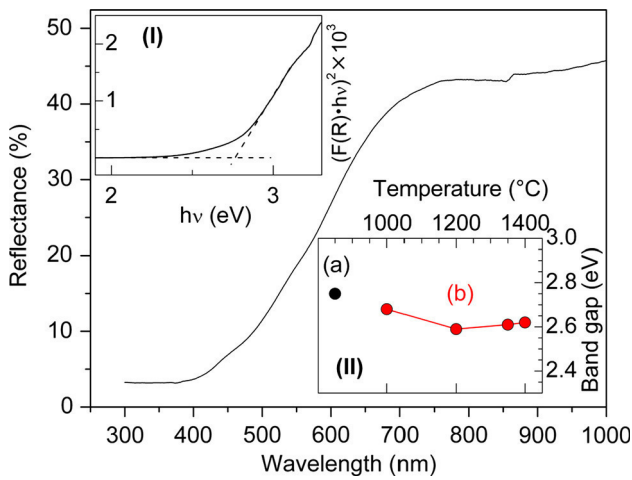


Figure 8 Diffuse reflectance spectra of the nano-powder calcined at 850 °C for 2 h. Inset (I) shows $(F(R) \cdot hv)^2$ versus $h\nu$. Inset (II) shows the band gap energy versus thermal treatment of **a** calcined powder at 850 °C and **b** sintered ceramics.

384 the model of a lossy capacitor, the ceramics show
 385 decreasing relative permittivities (ϵ_r) with increasing
 386 frequency. Up to a sintering temperature of 1350 °C,
 387 the relative permittivities increase with sintering
 388 temperature (Table 1). The values range between
 389 9.5×10^3 and 10.6×10^4 , and the $\tan \delta$ values vary
 390 from 0.26 to 0.88 at 1 kHz. At frequencies above
 391 100 kHz, the permittivity values of the conventionally
 392 sintered ceramics decrease drastically; however, the
 393 two-step sintered ceramic shows higher permittivity
 394 values. Above 10 kHz, the loss tangent increases and
 395 reaches a maximum at about 1 MHz for conventionally
 396 sintered ceramics and at 2 MHz for the two-step
 397 sintered one. The general trend of a strong
 398 decrease in the relative permittivity and a

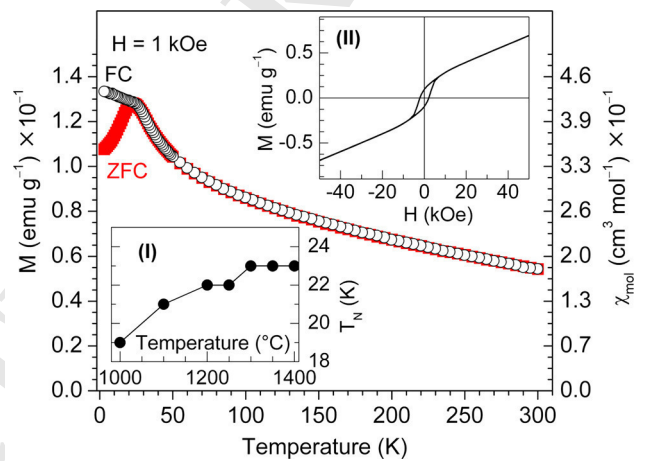


Figure 9 Temperature dependence (3–300 K) of the magnetization under zero-field-cooled (ZFC) and field-cooled (FC) conditions demonstrated for a ceramic sintered at 1350 °C for 1 h. Inset (I) shows the Néel temperature (T_N) versus sintering temperature (soaking time 1 h), and inset (II) shows the field-dependent magnetization at 300 K.

399 corresponding maximum of $\tan \delta$ is often found in
 400 BaFe_{0.5}Nb_{0.5}O₃ ceramics [17, 27, 42].

401 The temperature dependence of the relative per-
 402 mittivity and the dissipation factor at 1 kHz is shown
 403 in Fig. 11. All samples show rising permittivity and
 404 $\tan \delta$ values with temperature. Between 25 and 190 °
 405 C, the sample sintered at 1350 °C shows the highest
 406 permittivity values of 10.7×10^4 to 46.2×10^4 and \tan
 407 δ values in the range of 0.48 and 1.83. On the other
 408 hand, the ceramic sintered at 1300 °C shows the
 409 lowest dissipation factor at higher temperatures
 410 along with the lowest temperature dependency of \tan
 411 δ . Compared to samples prepared by the mixed-

Author Proof

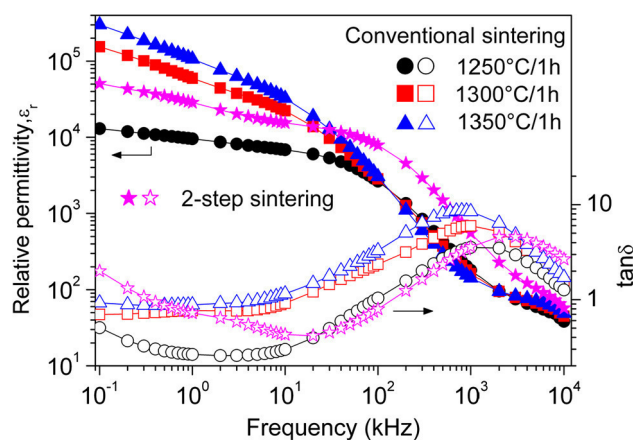


Figure 10 Dependence of the real part of the relative permittivity (closed symbols) and the dissipation factor (open symbols) on the frequency at 22 °C for ceramic bodies sintered at the indicated temperatures.

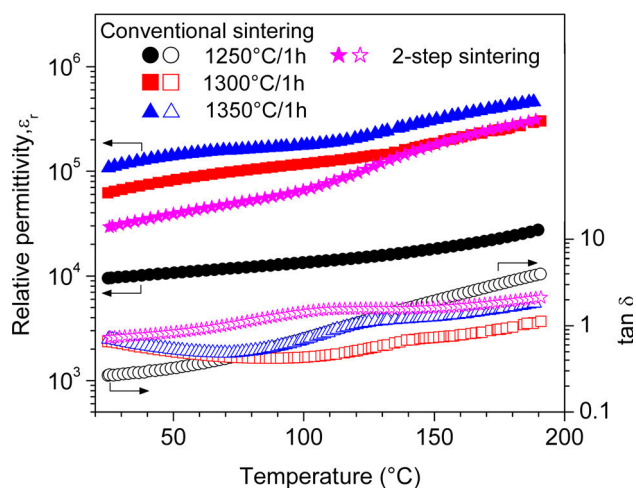


Figure 11 Temperature dependence of ϵ_r (closed symbols) and $\tan \delta$ (open symbols) at 1 kHz for ceramic bodies sintered at the indicated temperatures.

oxide method [9, 16, 24, 48] and a sol-gel route [5], the ceramics described herein show up to one order of magnitude higher permittivity values reaching 10.6×10^4 at 1 kHz and moderate $\tan \delta$ values (< 1) at room temperature.

The above discussion does not consider a possible dc-conductivity, which may be the origin of such high dielectric loss values. For a deeper understanding of the impedance data, the electrical properties therefore were modelled using a circuit of a resistance and capacitor connected in parallel (RC-element). The complex impedance (ρ^*) is described by:

$$\rho^* = \frac{\rho_{dc}}{1 + (i\omega\tau)^\beta} \quad (1)$$

where β is the constant phase shift (CPE) coefficient and $\tau = \rho_{dc}\epsilon\epsilon_0$. Details of this approach have been reported elsewhere [49]. As an example, Fig. 12 depicts the frequency dependence of the real (ρ') and imaginary (ρ'') parts of the specific impedance at room temperature for a ceramic body conventionally sintered at 1250 °C. The Cole-Cole plots reveal single semicircular arcs (Fig. S3, supported information) up to a temperature of 190 °C, proving that the impedance data of all ceramic samples can be well described by an equivalent circuit consisting of a single RC-element. From the fits, the calculated relative permittivities at room temperature of dense ceramics conventionally sintered at 1250, 1300, and 1350 °C are $2.09(2) \times 10^4$, $73(4) \times 10^4$, and $120(1) \times 10^4$, respectively. Simultaneously, the dc-resistivity (ρ_{dc}) decreases with rising sintering temperature from 4420(13) and 1330(19), to 277(5) k Ω cm. For the two-step sintered ceramic, values of $\epsilon = 4.83(4) \times 10^4$ and $\rho_{dc} = 219(5)$ k Ω cm were found. The activation energy (E_A) of the resistivity (ρ_{dc}) for the ceramic body sintered at 1250 °C was calculated as 0.39(3) eV using an Arrhenius plot (inset in Fig. 12). The activation energy is somewhat higher than that recently found for BaFe_{0.5}Nb_{0.5}O₃ samples prepared by a solution precipitation route [27]. Such a comparatively low activation energy ($E_A \ll E_g/2$) points

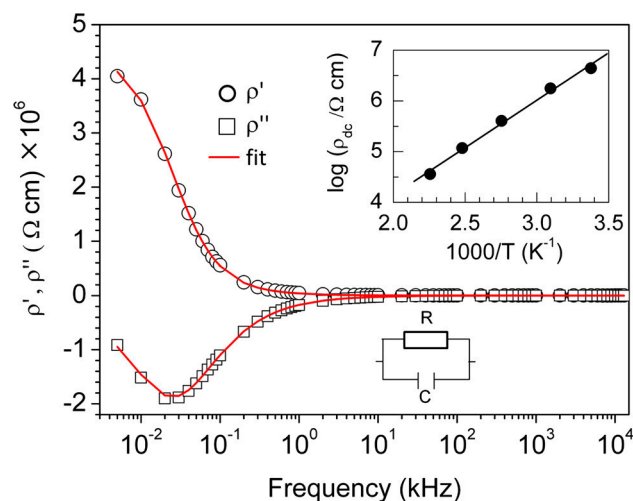


Figure 12 Dependence of the real and imaginary parts of the specific impedance (ρ' , ρ'') on the frequency at 22 °C for a ceramic body conventionally sintered at 1250 °C for 1 h. The inset shows the Arrhenius plot of $\log \rho_{dc}$ versus $1000/T$.

452 to defects possibly due to oxygen vacancies and in
453 turn partial reduction of Fe^{3+} and Nb^{5+} . Addition-
454 ally, the ceramics show a decrease in the dc-resistiv-
455 ity with rising measurement temperature, indicating
456 a semiconductor-like behaviour.

457 Conclusion

458 A nano-crystalline $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powder with an
459 enhanced sintering activity was synthesized by a
460 modified Pechini-like polymerization route using
461 glucose as additional component. The obtained (Ba,
462 Fe,Nb)-gel was calcined at 850 °C (rate 1 K min^{-1}) to
463 yield phase-pure $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ with a crystallite
464 size of 28 nm. Because of the nano-crystalline nature
465 of this powder, dense ceramic bodies with variable
466 grain sizes and different dielectric characteristics can
467 be obtained. Dense ceramic bodies (relative density
468 $\geq 90\%$) can be obtained after conventional sintering
469 above 1250 °C for 1 h or after a two-step sintering
470 procedure at 1200 °C. The optical band gap of the
471 nano-powder is 2.75(4) eV and slightly decreases
472 upon sintering to 2.59(2) eV. Magnetic measurements
473 show a Néel temperature of about 23 K for the dense
474 ceramic bodies. Dielectric measurements were car-
475 ried out depending on frequency and temperature.
476 The highest permittivity values at 1 kHz of 10.6×10^4
477 were reached after sintering at 1350 °C for 1 h. The
478 $\tan \delta$ values show a maximum at 1–2 MHz with
479 values between 4.6 and 8.6 at RT. The impedance
480 data can be fitted assuming an equivalent circuit with
481 one RC-element. The synthesis route described in this
482 article leads to phase-pure $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ powder at
483 lower calcining temperature and time compared to
484 other synthesis routes. The resulting nano-grained
485 powder compacts show a reduction in the sintering
486 temperature up to 200 °C, and the ceramic bodies
487 show much higher permittivity and moderate loss
488 tangent values compared to conventional syntheses.

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Compliance with ethical standards 496

Conflict of interest The authors declare that they 497
have no conflict of interest. 498
499

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1) contains supplementary material, which is avail- 502
able to authorized users. 503

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Supporting Information

J. Mater. Sci.

Magnetic, optical, dielectric, and sintering properties of nano-crystalline $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ synthesized by a polymerization method

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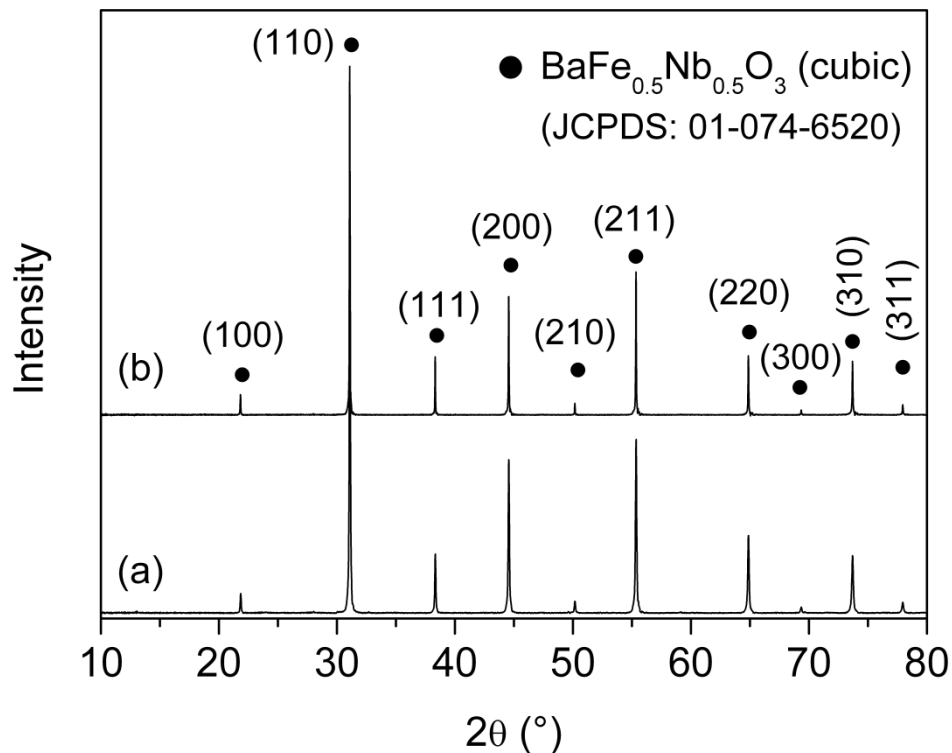


Fig. S1: XRD patterns of powdered ceramic bodies sintered (rate 5 K min^{-1}) at (a) 1000 °C , 1 h and (b) 1400 °C , 1 h.

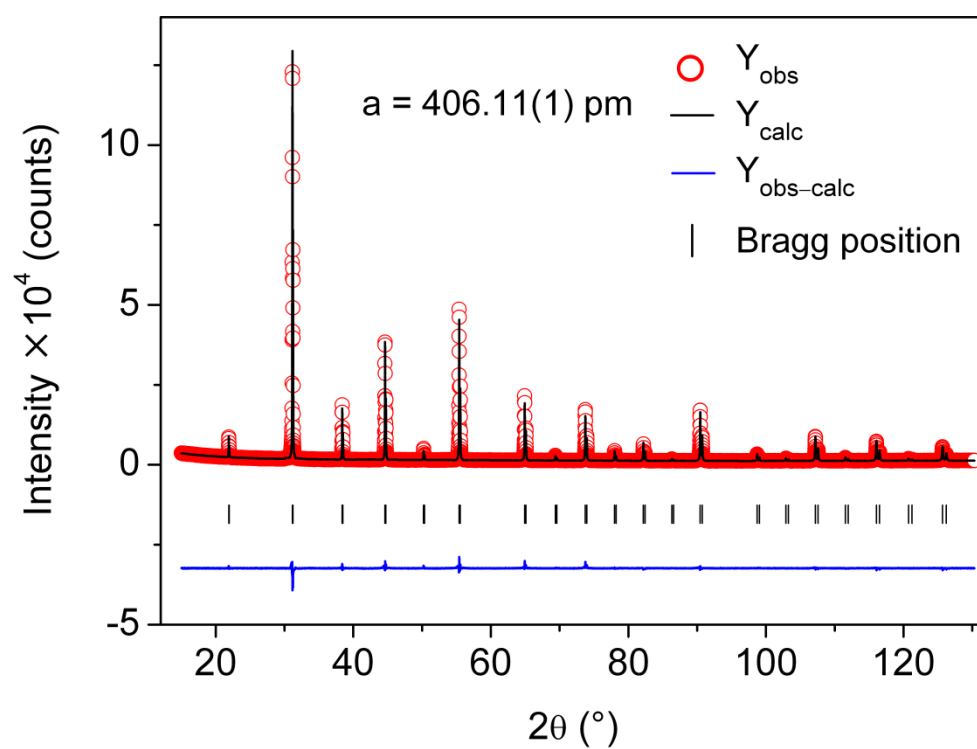


Fig. S2: Rietveld refinement (Cu- $K_{\alpha 1+\alpha 2}$ radiation) of a ceramic sample sintered at 1350 $^\circ\text{C}$ for 1 h. ($R_p = 3.19\%$, $R_{wp} = 4.46\%$, and $\chi^2 = 3.72$).

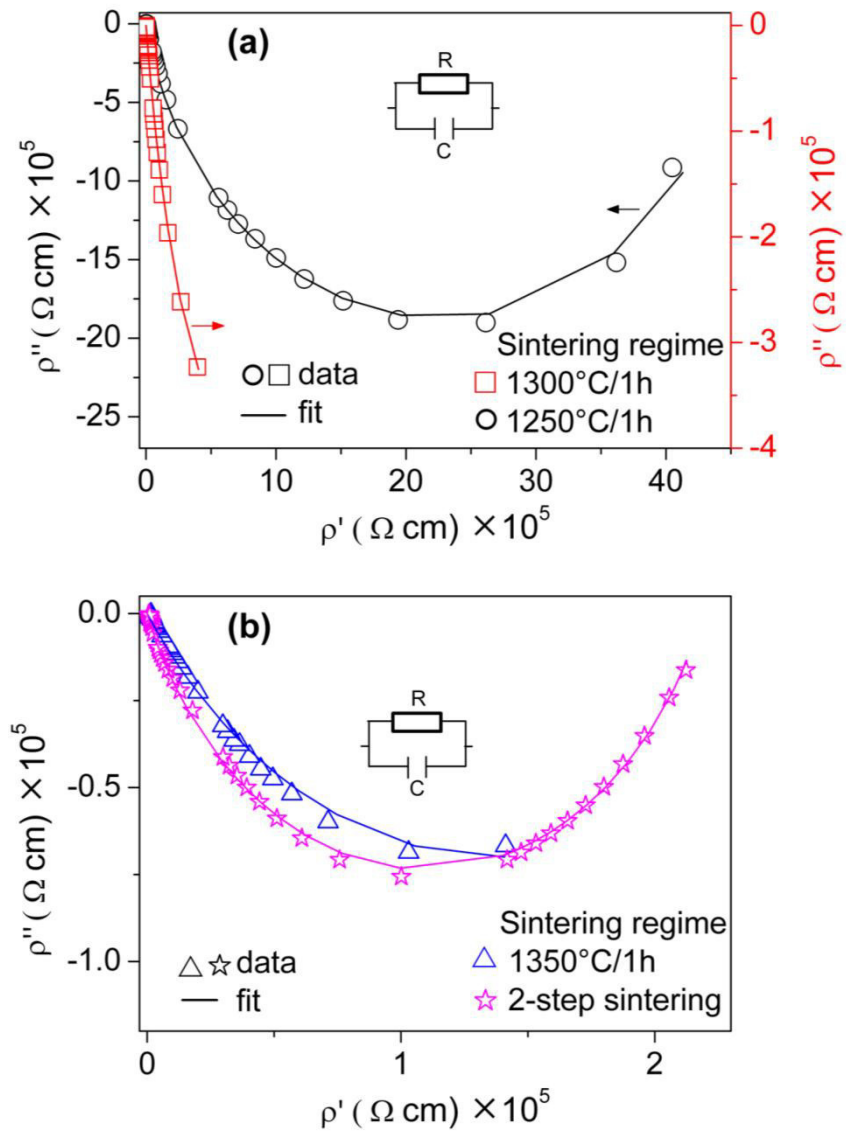


Fig. S3: Cole-Cole plots at room temperature of BaFe_{0.5}Nb_{0.5}O₃ ceramics sintered at the indicated regimes. The fit was carried out using the shown equivalent circuit.