In-situ formation of barium ferrite in iron-doped "tetragonal tungsten bronze": Elaboration of room temperature multiferroic composites

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ABSTRACT

Recent studies of ceramics of formula $Ba_2LnFeNb_4O_{15}$ (Ln = rare earth) with the "tetragonal tungsten bronze" (TTB) structure have correlated their room temperature multiferroics properties to the occurrence of barium ferrite parasitic phases. This work presents the elaboration of $Ba_2LaFeNb_4O_{15}$ and $Ba_2EuFeNb_4O_{15}$ composite samples with an excess of hematite in the TTB nominal composition. The influence of crystal-chemistry on the phase content and properties of $Ba_2LnFeNb_4O_{15}$ TTB composites is discussed. A particular focus on the mechanisms related to the in-situ formation of barium ferrite is given. We show that we can control the spurious ferrite phase in TTB multiferroic composites and thus modulate their magnetic response.

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1. Introduction

Multiferroics are materials which exhibit two or more switchable states simultaneously such as polarization, magnetization or strain. The majority of magnetic oxides crystallize with a centrosymmetric space group, which excludes any ferroelectric properties. Also, most of ferroelectric materials do not contain paramagnetic ions. That is why single phase multiferroics that exhibit both ferroelectricity and magnetic order are rare, and usually display only weak magnetoelectric coupling, taking place at low temperature [1–3]. Recently, new approaches were proposed for the design and the application of new generation storage devices, sensors, actuators, using multiferroics materials [4–6]. However, the main drawback is that the operating temperatures of the proposed systems are still far below room temperature. More suitable materials are thus needed, and we report in this paper our progress in the elaboration of "TTB" composite multiferroics.

Tetragonal tungsten bronze (TTB) niobates (the projection of the structure in a plane perpendicular to the z-axis is given on Fig. 1) form an important family of dielectric materials, which exhibit piezoelectric, pyroelectric, ferroelectric and non-linear optical properties. The TTB framework consists of corner-sharing distorted $[NbO_6]$ octahedra that define open channels in which are located 9-,12- and 15- coordinated cationic sites. These triangular, square and pentagonal-shaped channels can host several kinds of cations with related variations in physical properties, like non-linear optics, existence of a polar state (…). With the introduction of rare earth in square channels and Fe^{3+} in the octahedral

framework both spontaneous polarization and magnetization were expected at room temperature as proposed by Roth [7] and Krainik [8].

We recently have shown that a barium ferrite parasitic phase was responsible for RT magnetic hysteresis [9]. A relationship between the chemical stability of $Ba_2LnFeNb_4O_{15}$ compounds (Ln = La, Pr, Nd, Sm, Eu, Gd), the distortions of the TTB framework (induced by the rare earth) and the presence of byproducts was found. Practically, the anionic network does undergo increasing distortions to accommodate small rare earths. Even if these distortions are proofs of the flexibility of the structure, they are not sufficient enough to allow accommodation of the entire amount of small rare earth that the $Ba_2LnFeNb_4O_{15}$ chemical formulation suggests. Then the excess of rare earth forms a $LnNbO_4$ fergusonite phase, and to preserve electrical neutrality of the TTB matrix, a corresponding amount of iron is not accommodated and forms barium ferrite. It was observed that the dielectric properties (polar state) of BLnFN samples were not significantly altered by the small of that barium ferrite phase.

To go further in our investigation we intend to demonstrate that the magnetic properties of "TTB" composites" can be controlled by adequate chemical processing. Such processing allows inducing the in-situ formation of barium ferrite. In the following, the Ln and Fe substituted TTB structures will be called BLFN (lanthanum) or BEFN (europium), the weight percentage of excess iron oxide being reported as +X (BEFN+5 for example).

2. Experiments

Reagent grade of $BaCO_3$, Fe_2O_3, Nb_2O_5 and Ln_2O_3 of 99.9% minimum purity were used to prepare, by conventional solid state route, BLnFN+X (Ln = La, Eu; X = 1%, 2%, 5%) samples. Iron oxide

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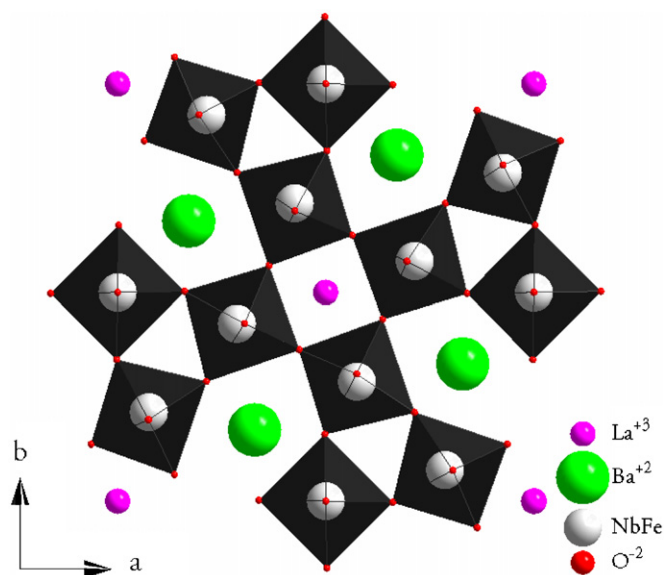 E-mail address: josse@icmcb-bordeaux.cnrs.fr (M. Josse).

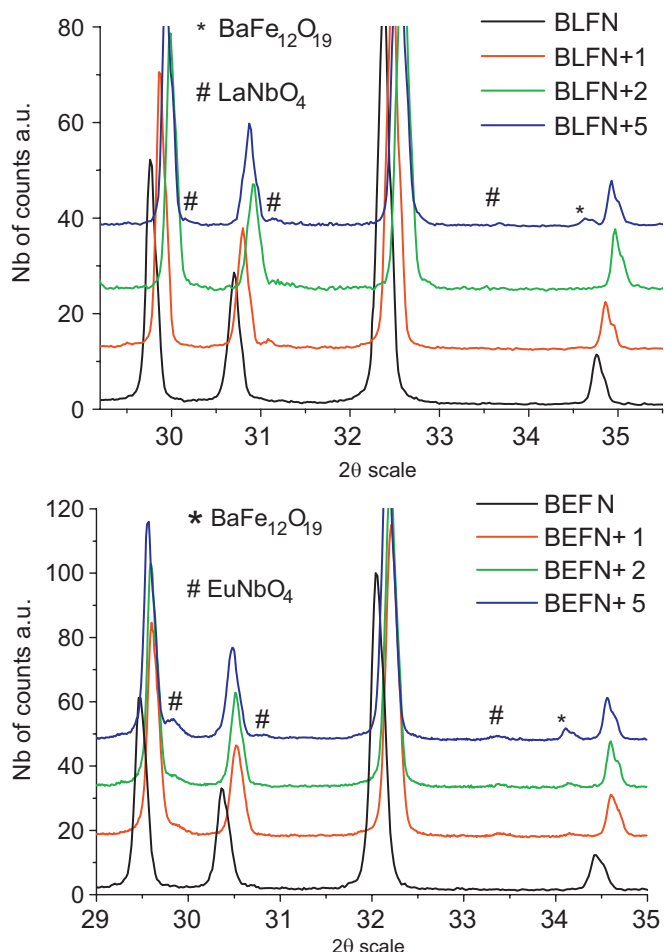**Fig. 1.** Crystal structure of $Ba_2LnFeNb_4O_{15}$ viewed along the *c*-axis.

Fig. 2. XRD patterns for BLFN and BEFN composites.

(referred to as hematite in the following) excess was added to the stoichiometric mixture of reacting products. These mixtures were ball-milled in absolute ethanol in a planetary grinder. The dried

slurries were calcined in a tubular furnace, and the green pellets were sintered at 1340 °C in an oxygen-rich atmosphere. The resulting ceramics exhibited densities ranging from 91% to 95% of the nominal density of the products.

X-ray diffraction data were recorded on a PANalytical X'Pert diffractometer (CuK_α, $\lambda = 1.5418$ Å) with $25° < 2\theta < 40°$ and a 400 s step of 0.01° for all the composites pellets.

X-ray microprobe analyses were performed on a Cameca SX100 apparatus (operating voltage: 20 kV).

Dielectric measurements were performed on a Wayne–Kerr 6425 component analyser under dry helium, using gold electrodes, at frequencies ranging from 10^2 to 2.10^5 Hz.

Magnetic hysteresis loops were obtained on a SQUID magnetometer (MPMS, Quantum Design Inc.).

3. Results

3.1. X-ray diffraction patterns

The diffraction patterns (Fig. 2) of all composites pellets show that the "pseudo-tetragonal" orthorhombic cell (Pba2 S.G. no. 32) previously observed [9] is maintained. For lanthanum composites, the Bragg diffraction peaks related to the fergusonite $LaNbO_4$ are identified, despite their relative low intensities. A very small broadened contribution is also detected around 34.5° 2θ for BLFN+5 which is attributed to the barium ferrite phase. For europium composites, the relative intensities of Bragg peaks of both parasitic phases increase with the excess of hematite.

3.2. XR microprobe analyses

XR microprobe analyses show that the BLFN sample is perfectly single-phased. For all composites samples, several local analyses show an homogenous cationic composition for the tetragonal bronze. In all the samples except BLFN, small iron-rich areas are detected on the Fe-mapping. These iron-rich areas also have a specific signature (higher O content) on the O-mapping. Local analyses indicate that they contain a small amount of barium, in agreement with the formula $BaFe_{12}O_{19}$ associated with barium ferrite. The iron and oxygen maps get on well together, concerning barium ferrite detection, for all the samples except BLFN (no ferrite) and BEFN+5. In this latter sample, in addition to barium ferrite, an iron-rich phase which does not contain barium is observed. This iron-rich phase, contrary to barium ferrite, have no specific signature on the O-mapping. It is likely that this additional iron-rich phase is Fe_2O_3, for which the O/Fe ratio (1.5) is slightly lower than for $BaFe_{12}O_{19}$ (1.58), accounting for the different contrast in the O-mapping (Fig. 3).

3.3. Magnetic measurements

Magnetic hysteresis loops at room temperature (Fig. 4) have been measured for all TTB composites. Note that no hysteresis loop was observed for BLFN sample. The lanthanum composites magnetizations at 20,000 Oe evolve between 200 and 2900 emu/mol, while for the europium composite magnetizations range from 900 to 3400 emu/mol. With regards to the amount of hematite, magnetizations are systematically higher in europium samples, compared to lanthanum ones. For all samples, the values of remnant magnetization are increasing with respect to the hematite excess. However, the magnetization of the BEFN+5 sample appears weaker than it could have been expected when comparing to the BEFN+2 sample. The value of coercive field for lanthanum composites is the same for all samples, i.e. 1000 Oe.
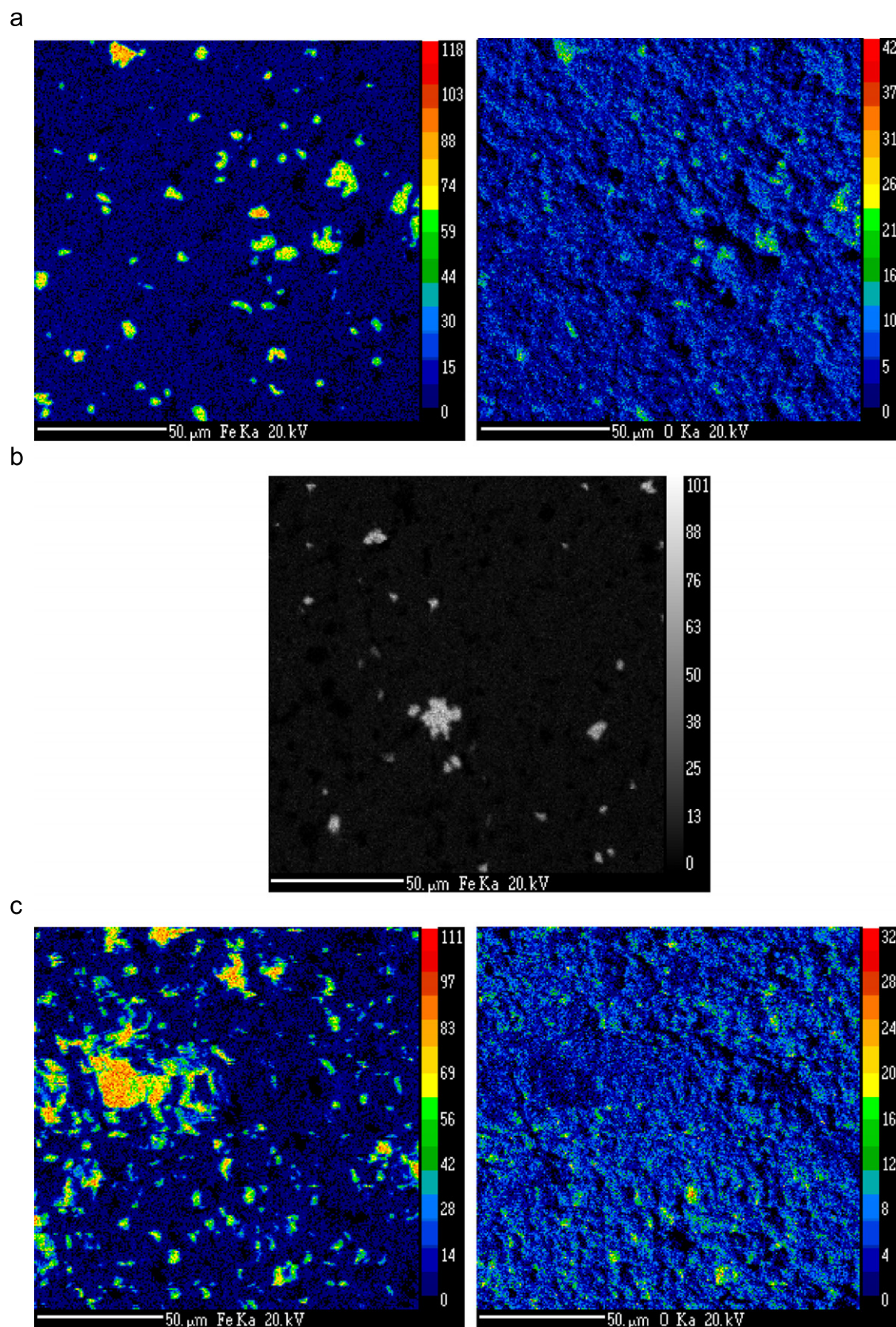
Fig. 3. XR-microprobe analysis, value of iron and oxygen concentration in BLFN+5 (a), BEFN+1 (b) and BEFN+5 (c).

Nevertheless the values of coercive field are decreasing with respect to the hematite excess in the europium series. Since the TTB matrix is able to fully accommodate La^{3+} ions, while the accommodation of Eu^{3+} ions is incomplete, the evolution of the coercive field in BELFN composites may be related to Eu doping of the barium ferrite.

3.4. Dielectric measurements

BLFN exhibit no dielectric transition down to 80 K and BEFN is a ferroelectric with a Curie temperature of 440 K. For BLFN+1 sample, the dielectric properties are unchanged and the dielectric losses remain very low until 420 K. The value of the real part of the dielectric constant is decreasing with the increase of the temperature. For BLFN+2 and BLFN+5, the dielectric losses are very high from 240 K: a conductivity regime is established and deteriorates the evaluation of the real part of the dielectric constant. In the BLFN+5 sample, a relaxation is observed around 150 K, which is not explained yet. For the three europium composites, the ferroelectric transition is maintained and also

occurs at 440 K. The dielectric losses increase after the ferroelectric transition in the three composites, similarly to what is observed in BEFN sample.

4. Discussion

The XRD, X-ray microprobe and dielectric studies show that the TTB matrix is not significantly affected by the introduction of a hematite excess during the elaboration process. The crystal structure, the chemical composition, the dielectric properties of the TTB matrix, which constitutes the ferroelectric part of these "TTB" composites, are almost unchanged.

Yet the observation of barium ferrite (X-ray microprobe, XRD) in the BLFN composites indicates that the excess of introduced hematite accommodates some barium, this account for the in-situ formation of the barium ferrite, the magnetic part of the "TTB" composites. This suggests also that the addition of hematite forces the TTB matrix to release some barium from pentagonal tunnels to allow the formation of the ferrite phase.

The magnetic hysteresis loops observed for lanthanum composites, and particularly the identical coercive fields in all the samples, suggests that barium ferrite composition is not varying in these samples. This is not the case for their europium counterparts, in which the coercive field evolves with respect to the excess of hematite, indicating that the chemical composition of the barium ferrite is also varying. This could be correlated to the fact that the accommodation of europium is limited in the TTB matrix. Thus some europium is available for accommodation in the barium ferrite, inducing these coercive field variations.

But the other interesting feature in the europium composite series is the iron oxide phase observed in BEFN+5 sample. Since the magnetization of this sample appear weaker than expected, it supports the hypothesis that this iron oxide phase is Fe_2O_3, as hematite is antiferromagnetic at room temperature. From a chemical point of view, the BLFN+5 and BEFN+5 samples are different, since in BLFN+5 only barium ferrite is detected. This could be related to the fact that the formation of barium ferrite requires the release of barium from the TTB matrix. This means that the observation of Fe_2O_3 in BEFN5+ sample shows that the TTB matrix has a limited ability to empty its channels, i.e. to release barium while some europium vacancies are already present.

Table 1 resumes the physical properties of the "TTB" composites investigated in this work. It is worth noticing that while the dielectric properties remain mostly stable (or even evolve in a positive way for BLFN+5) with the hematite excess, the magnetization can be controlled by this excess. Moreover the coercive field may be modified, depending on the rare earth introduced in the TTB framework.
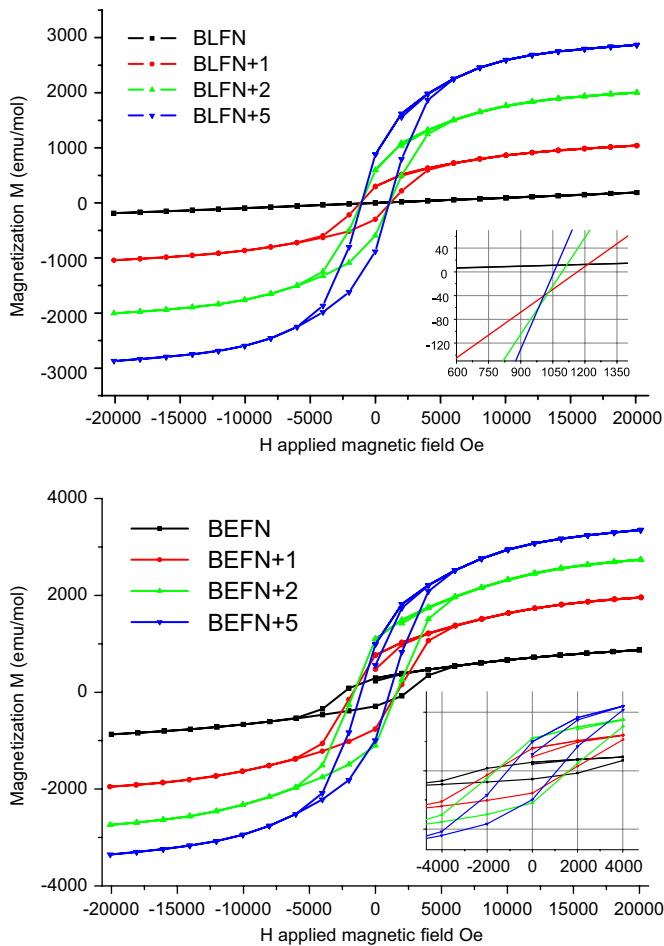

Fig. 4. Room temperature magnetic hysteresis loops in lanthanum and europium composites.

Table 1
Physical properties of BLnFN+X composites.

Composition	Name of the sample	Dielectric anomaly	Dielectric losses, 300 K, 1 kHz	Magnetization (300 K, 2 T emu mol^{-1})	Coercive field (Oe)
$Ba_2LaFeNb_4O_{15}$	BLFN	N/A	0.005	200	0
$Ba_2LaFeNb_4O_{15}$+1% Fe_2O_3	BLFN+1	N/A	0.01	1000	1000
$Ba_2LaFeNb_4O_{15}$+2% Fe_2O_3	BLFN+2	N/A	0.03	2000	1000
$Ba_2LaFeNb_4O_{15}$+5% Fe_2O_3	BLFN+5	Relaxation 160 K	0.21	2900	1000
$Ba_2EuFeNb_4O_{15}$	BEFN	Ferroelectric 440 K	0.06	900	1100
$Ba_2EuFeNb_4O_{15}$+1% Fe_2O_3	BEFN+1	Ferroelectric 440 K	0.14	2000	1600
$Ba_2EuFeNb_4O_{15}$+2% Fe_2O_3	BEFN+2	Ferroelectric 440 K	0.07	2900	1600
$Ba_2EuFeNb_4O_{15}$+5% Fe_2O_3	BEFN+5	Ferroelectric 440 K	0.27	3400	2400

5. Conclusion

The crystal-chemical behaviour of $Ba_2LnFeNb_4O_{15}$ TTBs has been used to develop room temperature multiferroic composites. By adding various excess of hematite, the in-situ formation of barium ferrite was induced. The room temperature magnetic properties of the multiferroic "TTB" composites can be tuned by varying the excess of hematite introduced during the preparation. Although these composites are elaborated by a conventional solid state process, knowledge of the crystal-chemical behaviour of the TTB matrix allows understanding and controlling this multiferroic system. Such room temperature multiferroic composites, based on TTB phases, may be interesting candidates for the design of devices operating at room temperature.

Acknowledgements

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