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Crystallographic, Structural, and Electrical Properties of W^{6+} Substituted with Mo^{6+} in Crystalline Phases such as TTB Structure

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Abstract: Owing to their low dielectric loss and high permittivity values, dielectric ceramics have garnered a lot of interest from the scientific and industrial sectors. These properties allow for their downsizing and use in a variety of electronic circuits. This present work focuses on the impact of the substitution of W^{6+} with Mo^{6+} on the structural and dielectric features of the crystalline phases in a similar TTB structure within the Ba$_{0.54}$Na$_{0.46}$Nb$_{1.29}$W$_{(0.37-x)}$Mo$_x$O$_5$ system, with $0 \leq x \leq 0.33$ mol%. These crystalline phases were elaborated using the conventional solid-state reaction method and analyzed with XRD, Raman, and dielectric techniques. The Rietveld refinement method showed that all these phases are characterized by tetragonal structure and the P4bm space group. The Raman spectra corresponded well to a TTB-like structure, and all the bands were assigned. The dielectric measurements of the prepared ceramic samples facilitated the determination of their phase transition temperature (T_c) and the dielectric responses. This investigation focused on determining dielectric permittivity (ε') and its correlation with increases in MoO$_3$ content in the ceramic structure.

Keywords: TTB ceramics; structure; X-ray diffraction; Rietveld method; Raman spectroscopy; dielectric permittivity

1. Introduction

Materials of the tetragonal tungsten bronze (TTB) structure type are well-known for their ferroelectric properties [1–5]. Many researchers have investigated these materials for several industrial applications, such as optoelectronics, energy conversions, and chemical sectors [6–10]. This high attention depends on the materials' structural properties. The TTB structure has numerous crystallographic interstices, which enable a broad range of cation replacements. The general chemical formula for the TTB structure is (A1)$_2$(A2)$_4$C$_4$Nb$_{10}$O$_{30}$, where A1, A2, and C stand for various oxygen sites. The A1 site is surrounded by twelve oxygen ions, while the A2 site is enclosed by eight oxygen ions. The C site is coordinated by six oxygen ions. The cations that can be accommodated by the TTB structure depend on the size of the sites and the charge balance of the structure. Common examples of cations that can be accommodated by the TTB structure include Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Ag$^+$, Tl$^+$, Cu^{2+}, and Pb^{2+} [11–13]. Currently, the advancement of solid solutions has resulted
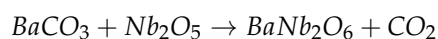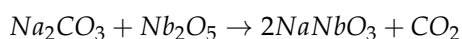
in a multitude of varied distributions of metal cations across different crystallographic locations. This has the potential to enhance physical characteristics, such as dielectric and ferroelectric abilities [14,15]. Several approaches have been developed for enhancing either the structures or properties of ceramics. The usual method to control the electrical characteristics of TTB oxides is nonisovalent replacement based on transition-metal substitution in niobium octahedral sites. This focuses on the property tuning required to produce new phases, including microwave dielectrics [16,17], ionic conductors [18], and ferroelectrics [19–21]. This will eventually lead to the identification of a highly desired, room-temperature multiferroic material. As a result of the variable oxidation state [22], many TTB ferroelectric and ferroelectric-related materials [23–26] exhibit relaxer ferroelectric and dielectric phenomena [27–30]. TTB structures are classically derived from well-known perovskite-type structures and characterized by high electrical performance [31,32]. Compounds similar to tetragonal tungsten bronze oxides, along with perovskites, comprise one of the most significant groups of ferroelectrics. Many works have reported the existence of phases containing different transition metals related to the tetragonal tungsten bronze structure [33]. There have been initiatives to use Ta, Mo, or Nb in place of W [33]. For instance, Ikeda et al. [34] investigated the results of replacing Nb ions with W ions in the niobates of the TTB structure. Similarly, a detailed investigation of "Ferroelectric and Related Substances on $Ba_3Na_3MoNb_9O_{30}$" has also been reported [35]. According to Marinder [36], an X-ray diffraction analysis of the $NaNbO_3$-Nb_2O_5-WO_3 system illustrated that a few phases are associated with the TTB structure. High-resolution electron microscopy analysis of the aforementioned system revealed many structural types that are linked to the TTB structure [37]. Further, the $NaNbO_3$-WO_3 system's mixed oxides are a subject of attention among the numerous current TTB structures. When a low-temperature method is used, the composition with a 1:1 ratio of the end members of this system appears effective for producing $NaNbWO_6$, exhibiting a phase that resembles the TTB structure. However, this shows that a complex X-ray pattern has been considered as a combination of different phases [38–41]. Alternatively, the ceramic method was claimed to be able to prepare a single phase of $NaNbWO_6$ that is similar to TTB [42], but an electron diffraction examination showed that this composition comprises two closely related tetragonal and monoclinic phases [43].

The primary focus of the present exploration is to examine the influence of Mo^{6+} content on the structural and dielectric characteristics of tetragonal tungsten bronze (TTB) within the $NaNbO_3$-WO_3-$BaNb_2O_6$ system. For this purpose, the incorporation effect of molybdenum into tungsten sites on the structural and electrical properties of $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ ($0 \leq x \leq 0.33$) ceramics is investigated.

2. Experimental Section

2.1. Ceramic Sample Synthesis

The conventional solid-state technique was applied to synthesize the crystalline phases of the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ system (x = 0.04, 0.08, and 0.33), as described in the experimental protocol for our previous work [44]. This experimental protocol for preparation of the crystalline phases within the $NaNbO_3$-$BaNb_2O_6$-WO_3/MoO_3 system involves two steps. The first one is focused on preparation of the crystalline phases $NaNbO_3$ and $BaNb_2O_6$ from the raw materials $BaCO_3$, Na_2CO_3, and Nb_2O_5 (purchased from Merck (Merck, 99.95%)) according to the following reactions:

$$Na_2CO_3 + Nb_2O_5 \rightarrow 2NaNbO_3 + CO_2$$

$$BaCO_3 + Nb_2O_5 \rightarrow BaNb_2O_6 + CO_2$$

These raw materials were mixed and ground in agate mortar around one hour later, according to their stoichiometry coefficient, and then subjected to thermal treatment at 1100 °C for 24 h. The second stage involved mixing and grinding for two hours: the obtained oxides, $NaNbO_3$ and $BaNb_2O_6$, were processed in stoichiometric proportions

with the oxides WO_3 and/or MoO_3 (bought from Merck, 99.95%) for about an hour. The mixture was then put into an alumina crucible and heated to 1200 °C for 12 h, then reapplied while ethanol was used for about one hour so that it could be calcined. In an alumina crucible, calcination was carried out for 24 h upon reaching a temperature of 1300 °C for the final heating. The grinding and calcination processes were carried out two more times. XRD analysis was utilized to investigate the formation of the compound.

2.2. Characterization Techniques

The prepared ceramics were examined at ambient temperatures using a Bruker D8 Advance diffractometer utilizing CuKα (α = 1.540598 Å). The X-ray diffractograms were recorded from 10° to 100°, with a step size of 0.01°. GSAS-II software [45] was utilized to apply the Rietveld refinement to validate and quantify the crystalline phases found in the composite ceramics, followed by sinterization. The phases that were present in the composites under study were identified using the Crystallography Open Database (COD) [46]. The ceramics were subjected to Raman analysis at room temperature, utilizing a spectrometer with a HORIBA-Jobin laser light that was directed onto each sample through a microscope lens. To conduct dielectric analysis, the disk-shaped samples were initially smoothed down, and to ensure optimal electrical contact, silver paste was applied on both sides of each specimen. The capacitance (Cp) and loss factor (tanδ) were analyzed over a frequency range of 20 Hz to 1 MHz. An impedance analyzer was used to apply a 0.5 V source to the electrode pellets. Measurements were conducted between 25 °C and 550 °C using a Linkam TS 93 hot stage that offered a temperature stability of ±0.1 K. To create the capacitor-shaped pieces, platinum electrodes were positioned on two of the ceramic's round faces. The real part (ε') and loss (tanδ) of the dielectric permittivity, as well as the ac conductivity (σ_{ac}), were determined using Equations (1)–(3) [32,47]:

$$\varepsilon\prime = \frac{C_P t}{\varepsilon_0 A} \tag{1}$$

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon'' \tag{2}$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon\prime} \tag{3}$$

In these equations, t, A, ω, ε_0, and ε'' (equal to ε' multiplied by the tangent of δ) represent the layer of the disk-shaped piece, the cross-sectional area of the electrode, the angular frequency, the permittivity of free space, and the imaginary component of the complex dielectric constant, respectively.

3. Results and Discussion

3.1. X-ray Diffractograms

Figure 1a displays the XRD diffractograms of all the examined samples. The XRD pattern of the sample (x = 0) significantly changed as the concentration of Mo^{6+} increased, as shown in Figure 1b. All examined sample ceramics had very significant diffraction peaks, which suggested that these compounds were well-crystallized. Additionally, all XRD patterns of the prepared ceramics exhibited a tetragonal-type structure. However, it seems that except for (x = 0), the patterns contained a secondary phase: scheelite-type $BaMoO_4$ (barium molybdate). The peak of the index (004) was the characteristic secondary phase located at 2θ position 26.42, which was identified according to JPDS NO: 029-0193. This peak appeared from the ceramic composite where x = 0.04, and it was characterized by low intensity (see Figure 1b). Figure 1c–e display the X-ray diffractograms of the samples obtained from the Rietveld refinement process. The constituent features of the composites where x = 0.04, x = 0.08, and x = 0.33 were guaranteed by the Rietveld refinement; however, the composite where x = 0.33 was guaranteed to have the properties of both the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{0.04}Mo_{0.33}O_5$ and purity ($BaMoO_4$) constituents. Each plot displays the parameters derived with the Rietveld refinement. For all compositions, the

goodness of fit (GOF), or χ^2, parameters were below three, which points to the improved XRD patterns' high dependability (see Table 1). Furthermore, Rietveld refinement confirmed the tetragonal structure of a similar TTB phase with the P4bm space group and a minor $BaMoO_4$ impurity peak (marked with ♦) (see Figure 1b). As opposed to this, the ferroelectric phase and the P4bm space group created a similar TTB structure. G. Yanalak et al have already provided in-depth descriptions of the $BaMoO_4$ phase [48]. A structure of this type is consistently favored, as it promotes better interaction between the ferroelectric and $BaMoO_4$ phases, consequently leading to a robust microwave dielectric effect in composites [49]. Improvement in the volume of the composites was readily observed as the lattice parameters, a, b, and c, were somewhat raised with rising MoO_3 content in the ferroelectric phase. The substitution of W^{6+} (0.74 Å) with Mo^{6+} (0.73 Å) [50] led to the formation of the $BaMoO_4$ phase (tetragonal with the I41/a space group). In comparison of the x = 0.00 composite to other composites, the cell parameters and volume increased as the peak intensity of the $BaMoO_4$ composite increased from x = 0.00 to x = 0.33. This variation may be associated with the increase in the content of the $BaMoO_4$ phase in the composites. To ensure the secondary phase would be dependent on the $BaMoO_4$ phase type, the dielectric properties of the current pieces were studied to see how their dielectric permittivity would change with increased $BaMoO_4$ composite (see the dielectric measurements section).
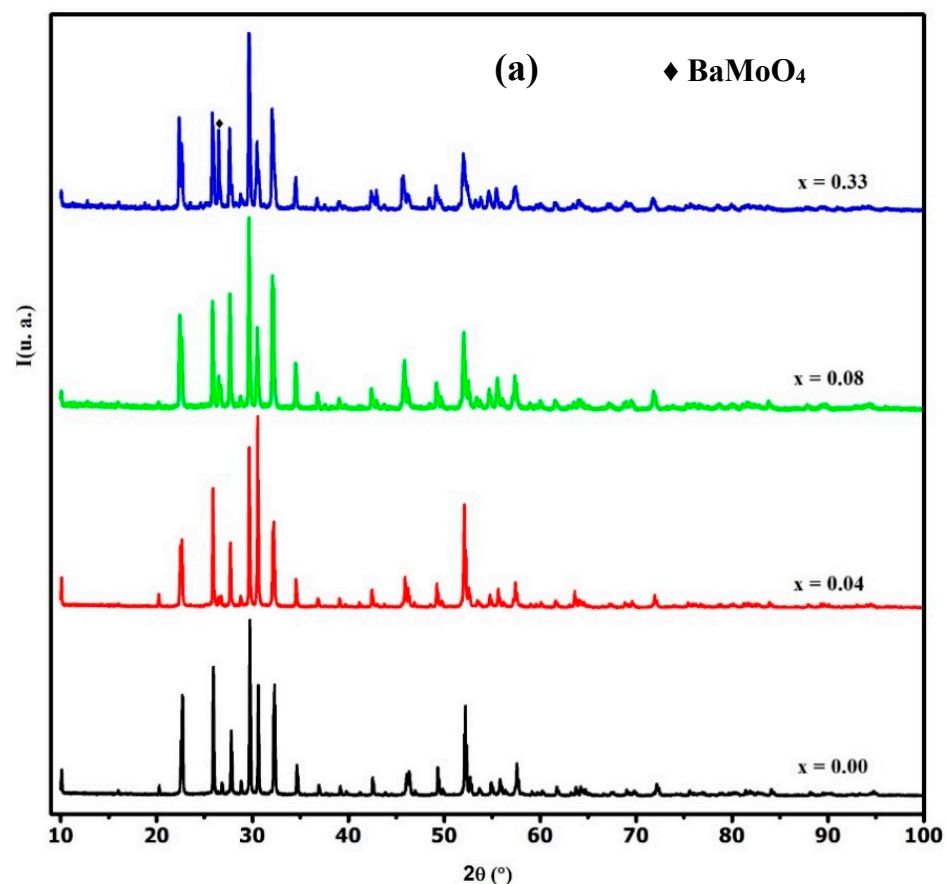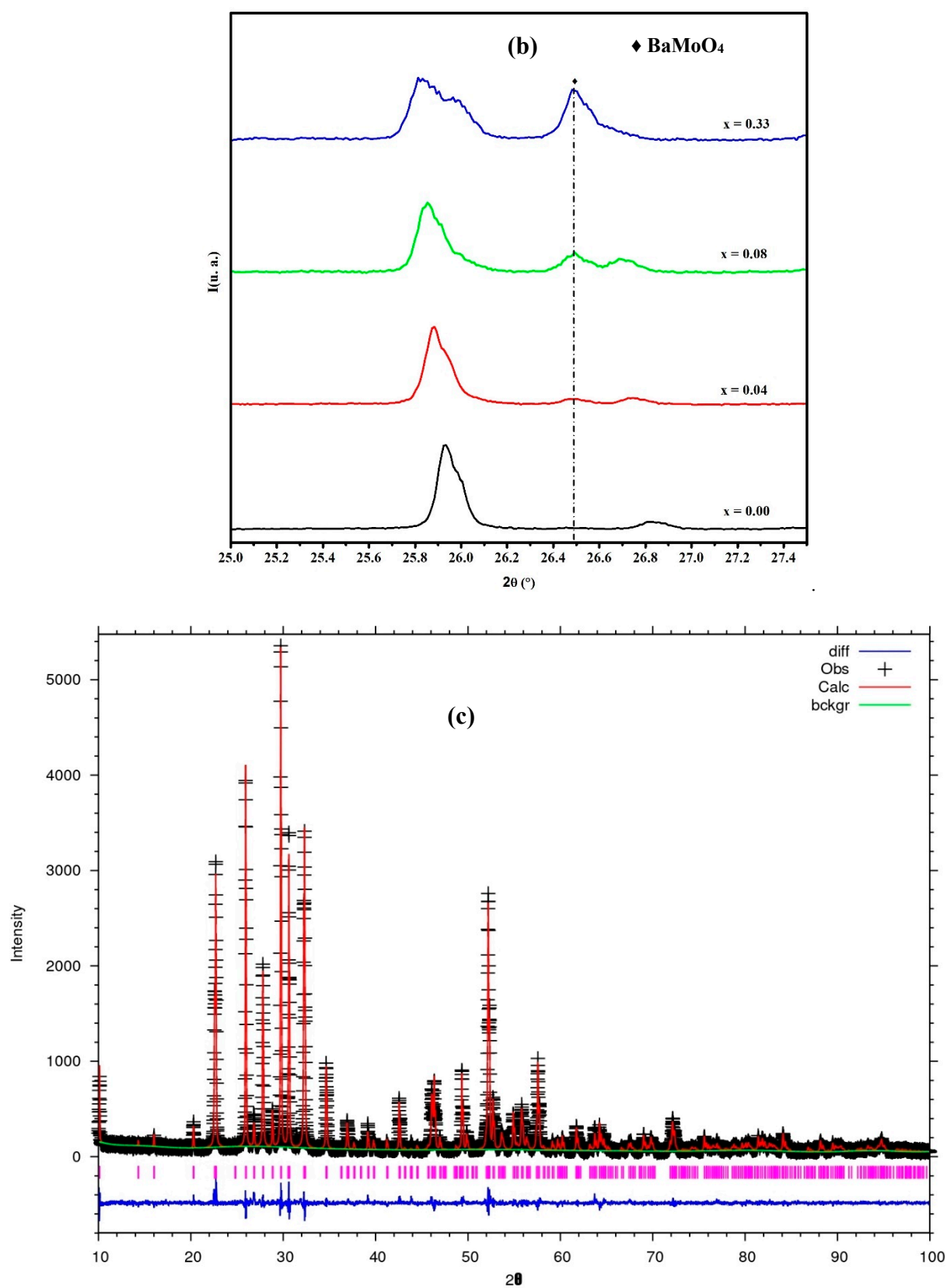

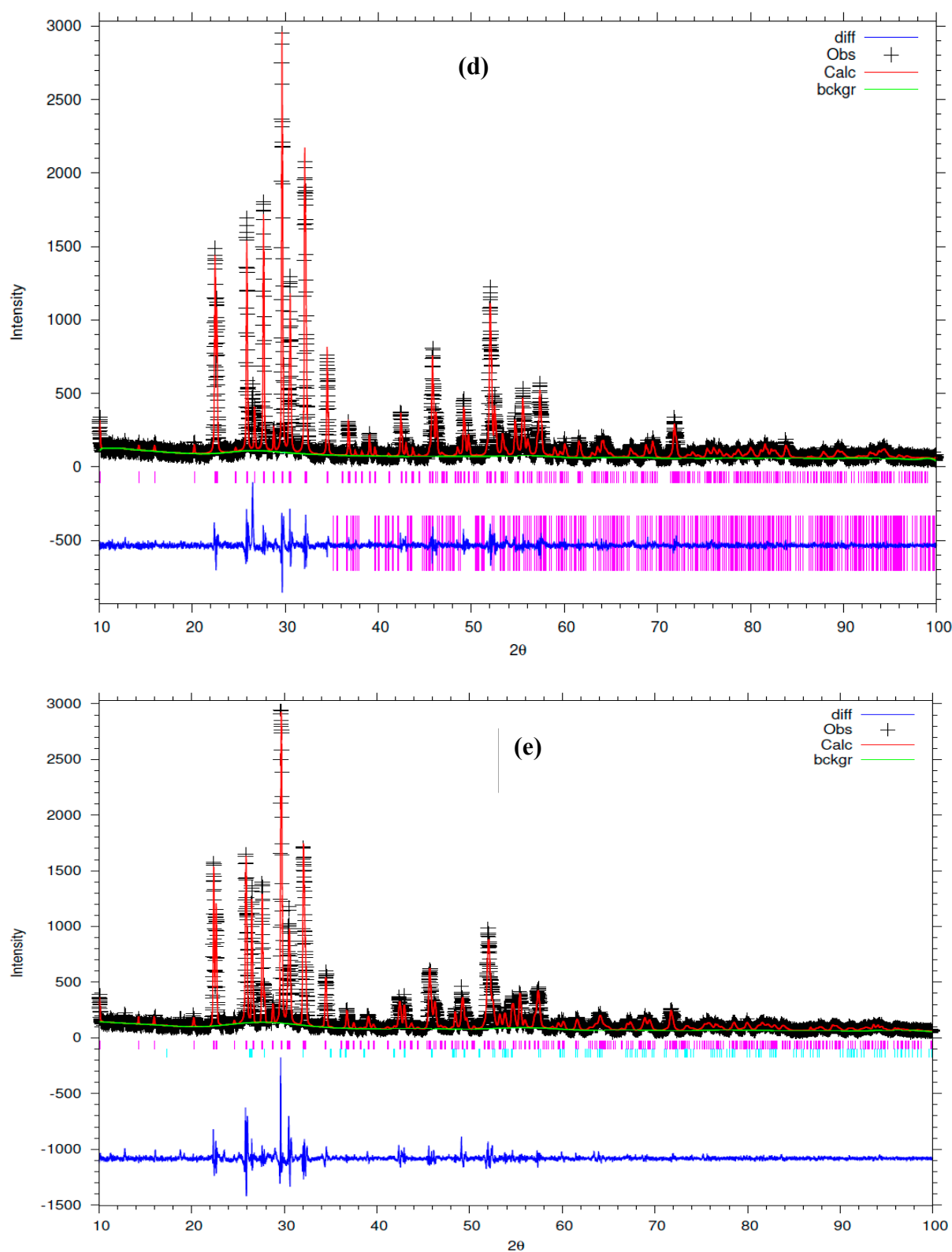**Figure 1.** *Cont.*

Figure 1. *Cont*.

Figure 1. Combined X-ray diffraction patterns (**a**,**b**) and Rietveld refinement of $Ba_{0.54}Na_{0.46}$ $Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ ceramics (x = 0.04 (**c**), x = 0.08 (**d**), and x = 0.33 (**e**)).

Table 1. The data from the Rietveld refinement for the crystalline phases of the $Ba_{0.54}Na_{0.46}$ $Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ system (x = 0.04, 0.08, and 0.33).

Composition	x = 0.04	x = 0.08	x = 0.33
Symmetry	Tetragonal	Tetragonal	Phase 1: Tetragonal; Phase 2: Tetragonal
Space Group	P4bm	P4bm	Phase 1: P4bm Phase 2: I 41/a
Z	6	6	Phase 1: 6 Phase 2: 4
Lattice Parameters (Å)	a = b = 12.40430 (10); c = 3.95059 (6)	a = b = 12.41525 (12); c = 3.95844 (7)	Phase 1: a = b = 12.41681 (17); c = 3.97203 (8) Phase 2: a = b = 5.59091 (22); c = 12.8173 (7)
Volume ($Å^3$)	607.865 (15)	610.146 (15)	Phase 1: 612.396 (21) Phase 2: 400.65 (4)
Calculated Density (g/cm^3)	5.729	5.698	Phase 1: 5.272 Phase 2: 4.928
Chemical Formula Weight (g/mol)	349.52	348.96	Phase 1: 324.02 Phase 2: 297.27
R_p	7.79	9.51	10.11
R_{wp}	10.48	12.69	13.26
χ^2	1.837	2.249	2.744
GOF	1.36	1.50	1.66

The Rietveld refinement of the XRD patterns corresponding to the prepared ceramics of $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ (x = 0.04, 0.08, and 0.33) was fitted with a tetragonal (P4bm) model developed from the model of the previous crystalline phase [44]. Starting where x = 0.04, the Ba^{2+} and Na^+ cations occupied two sites in this developed model. Here, Na_1^+ was placed in the Wyckoff position of Ba_1^{2+} at the 2a (0, 0, z) sites, and Na_2^+ was placed in Ba_2^{2+} at the 4c (x, y, z) sites, respectively. However, the Nb^{5+}, W^{6+}, and Mo^{6+} occupied two different sites in the Wyckoff position. That is, the Nb_1^{5+}, W_1^{6+}, and Mo_1^{6+} were placed in the 2b (0, 0.5, 0.5) sites, whereas the Nb_2^{5+}, along with the W_2^{6+}, occupied the 8d (x, y, z) sites. Further, the O^{2-} oxygen dianions occupied the 8d (x, y, z), 4c (x, y, z), and 2b (0, 0.5, z) Wyckoff sites. While comparing the x = 0.04 composition with the x = 0.08 composition, we found a difference in that where x = 0.08, which manifested as Nb_1^{6+} with Mo_1^{6+} occupying the 2b (0, 0.5, 0.5) sites and Nb_2^{6+} with Mo_2^{6+} occupying the 8d (x, y, z) sites (see Table 2). However, in the composition (x = 0.33) model, Nb_1^{5+} and Mo_1^{6+} occupied the 2b (0, 0.5, 0.5) sites, and Nb_2^{5+} and Mo_2^{6+} with W_2^{6+} occupied the 8d (x, y, z) sites (see Table 2). Furthermore, the atomic positions of the secondary phase, $BaMoO_4$ (a = b = 5.5909 Å and c = 12.8173 Å), were determined. In this structure (x = 0.33), the Ba^{2+} and Mo^{6+} cations occupied, respectively, the 4b (0, y, z) and the 4a (0, y, z) sites, and the oxygen dianions occupied the 16f (x, y, z) Wyckoff sites. In Table 3, we list the interatomic distances. The crystallographic parameters of the refined compositions (x = 0.04, 0.08, and 0.33) revealed that oxygen atoms surrounded sodium and barium atoms, creating deformed and irregular surroundings. The average distance between the sodium (1) and barium (1) atoms and the oxygen atoms was approximately 2.71 Å (x = 0.00)–2.88 Å (x = 0.33) [44]. Figure 2 illustrates the [1 1 1] projection of the crystal structure where x = 0.33. The Na^+ and Ba^{2+} cations were found to occupy sites with coordination numbers of 15 and 12, respectively. The octahedral sites were occupied by two cations of Nb^{5+}, W^{6+}, and/or Mo^{6+}. In addition, the crystal structure exhibited a P4bm space group, allowing for small, off-center displacements of Nb, W, and Mo within the $(Nb/W/Mo)O_6$ octahedra. The Ba (1)/Na (1) atoms were encompassed by 12 O- atoms, with the faces of the Nb1/W1/Mo1@O6 octahedra being shared. The polyhedron distances ranged from 1.93 Å (x = 0.00) to 1.98 Å (x = 0.33), with an estimated value of less than d(Ba(1)/Na(1)@O) = 2.71 Å (x = 0.00)–2.88 Å (x = 0.33). It is worth noting that an average of
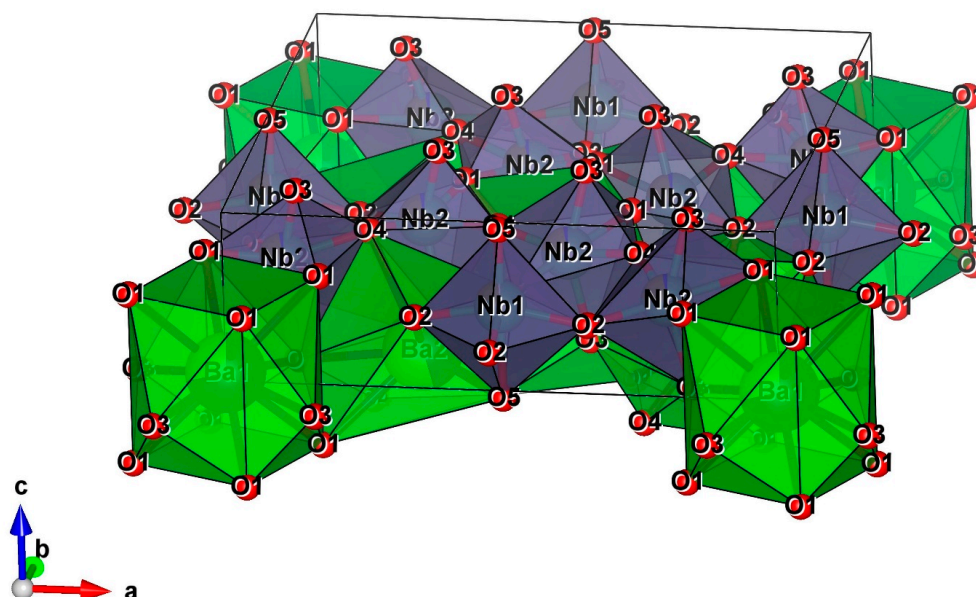
15 oxygen atoms enclosed the barium (2) and sodium (2) atoms, with the distance varying from 3.02 Å (0.00) to 2.74 Å (x = 33). Nonetheless, there was a slight distinction in the atomic positions of the Ba (2) and Na (2) atoms, as shown in Table 2 [44]. The Nb(1), Mo(1), or W(1) atoms were surrounded by six oxygen atoms, forming octahedrons that were linked together at their tips. The average distance between the atoms ranged from 2.04 Å (x = 0.00) to 2.05 Å (x = 0.00).

Table 2. Atomic positions of the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ system (x = 0.04, 0.08, and 0.33).

Composition	Atom	Wyckoff	x	y	z	Occupation	U_{iso}
X = 0.04	Ba1	2a	0	0	0.05	0.716	0.800 (12)
	Na1	2a	0	0	0.05	0.284	0.800 (12)
	Ba2	4c	0.17310 (15)	0.67310 (15)	0.01270 (15)	0.454	0.0524 (9)
	Na2	4c	0.17310 (15)	0.67310 (15)	0.01270 (15)	0.546	0.0524 (9)
	Nb1	2b	0	0.5	0.5	0.82	0.0301 (9)
	W1	2b	0	0.5	0.5	0.039	0.09
	Mo1	2b	0	0.5	0.5	0.125	0.03077
	Nb2	8d	0.07581 (8)	0.20922 (8)	0.50822 (8)	0.761	0.2105 (19)
	W2	8d	0.07581 (8)	0.20922 (8)	0.50822 (8)	0.239	0.00555
	O1	8d	0.1337 (9)	0.0825 (8)	0.446 (10)	1	0.1174 (30)
	O2	8d	0.3543 (8)	0.0126 (10)	0.402 (9)	1	0.1174 (30)
	O3	8d	0.0473 (10)	0.1997 (8)	0.065 (7)	1	0.1174 (30)
	O4	4c	0.294	0.794	0.575	1	0.1174 (30)
	O5	2b	0	0.5	−0.02	1	0.65 (6)
X = 0.08	Ba1	2a	0	0	0.05	0.716	0.800 (11)
	Na1	2a	0	0	0.05	0.284	0.800 (11)
	Ba2	4c	0.17347 (13)	0.67347 (13)	0.01308 (13)	0.454	0.0204 (7)
	Na2	4c	0.17347 (13)	0.67347 (13)	0.01308 (13)	0.546	0.0069 (7)
	Nb1	2b	0	0.5	0.5	0.75	0.0332 (8)
	Mo1	2b	0	0.5	0.5	0.25	0.0329 (8)
	Nb2	8d	0.07595 (9)	0.20935 (9)	0.50835 (9)	0.761	0.01819 (34)
	W2	8d	0.07595 (9)	0.20935 (9)	0.50835 (9)	0.239	0.79798 (34)
	O1	8d	0.1567 (9)	0.0724 (10)	0.535 (12)	1	0.1116 (16)
	O2	8d	0.3447 (6)	0.0140 (6)	0.519 (12)	1	0.0092 (16)
	O3	8d	0.0560 (7)	0.2038 (6)	0.032 (7)	1	0.0287 (16)
	O4	4c	0.2844 (7)	0.7844 (7)	0.581 (5)	1	0.0190 (16)
	O5	2b	0	0.5	−0.02	1	0.0532 (16)
X = 0.33	Ba1	2a	0	0	0.05	0.716	0.800 (13)
	Na1	2a	0	0	0.05	0.284	0.800 (13)
	Ba2	4c	0.17500 (19)	0.67500 (19)	0.01460 (19)	0.454	0.0239 (10)
	Na2	4c	0.17500 (19)	0.67500 (19)	0.01460 (19)	0.546	0.0239 (10)
	Nb1	2b	0	0.5	0.5	0.82	0.0328 (12)
	Mo1	2b	0	0.5	0.5	0.164	0.0328 (12)
	Nb2	8d	0.07176 (13)	0.21142 (14)	0.4854 (16)	0.761	0.0324 (4)
	Mo2	8d	0.07176 (13)	0.21142 (14)	0.4854 (16)	0.20775	0.0324 (4)
	W2	8d	0.07176 (13)	0.21142 (14)	0.4854 (16)	0.03125	0.0324 (4)
	O1	8d	0.1609 (8)	0.0615 (8)	0.568 (4)	1	0.0294 (21)
	O2	8d	0.3426 (8)	0.0055 (8)	0.411 (5)	1	0.0294 (21)
	O3	8d	0.1022 (8)	0.1772 (8)	−0.069 (5)	1	0.0294 (21)
	O4	4c	0.2860 (8)	0.7860 (8)	0.582 (5)	1	0.0078 (21)
	O5	2b	0	0.5	−0.045 (12)	1	0.0078 (21)
$BaMoO_4$	Ba	4b	0	0.25	0.625	1	−0.0085 (11)
	Mo	4a	0	0.25	0.125	1	0.0402 (27)
	O	16f	0.175 (8)	0.203 (12)	0.0231 (26)	1	0.08796

Table 3. Different interatomic distances (Å) of the crystalline phases of $Ba_{0.54}Na_{0.46}Nb_{1.29}$ $W_{(0.37-x)}Mo_xO_5$ (x = 0.04, 0.08, and 0.33).

Composition	0.04	0.08	0.33
Principal Interatomic Distances (Å) Ba1/Na1–O			
Ba1/Na1–O1	3.080 × 4	2.8773 × 4	2.8705 × 4
Ba1/Na1–O1	2.501 × 4	2.9578 × 4	2.9678 × 4
Ba1/Na1–O3	2.546 × 4	2.650 × 4	2.5836 × 4
(Ba1/Na1–O)	2.709	2.8283	2.88073
Principal Interatomic Distances (Å) Ba2/Na2–O			
Ba2/Na2–O1	3.465 × 2	-	-
Ba2/Na2–O1	3.153 × 2	-	-
Ba2/Na2–O2	3.145 × 2	2.826 × 2	2.6375 × 2
Ba2/Na2–O2	2.539 × 2	-	-
Ba2/Na2–O4	2.7364 × 2	2.593 × 2	2.5984 × 2
Ba2/Na2–O4	3.0713 × 2		2.9797
(Ba2/Na2–O)	3.0182	2.7095	2.7385
Principal Interatomic Distances (Å) Nb1/W1/Mo1–O			
Nb1/W1/Mo1–O2	1.855 × 4	1.9374 × 4	1.9873 × 4
Nb1/W1/Mo1–O5	2.05431	1.9001	1.8073
Nb1/W1/Mo1–O5	1.89629	2.0584	2.1648
(Nb1/W1/Mo1–O)	1.93519	1.9353	1.9864
Principal Interatomic Distances (Å) Nb2/W2/Mo2–O			
Nb2/W2/Mo2–O1	1.745	1.9572	2.1904
Nb2/W2/Mo2–O1	2.190	1.9766	-
Nb2/W2/Mo2–O2	2.340	-	1.9133
Nb2/W2/Mo2–O3	1.791	1.9030	1.8591
Nb2/W2/Mo2–O3	2.230	2.0887	2.2743
Nb2/W2/Mo2–O4	1.9451	-	2.0308
Nb2/W2/Mo2–O	2.0402	1.9813	2.0535

Figure 2. Crystal structure where x = 0.33, projected in 3D space ([1 1 1]).

3.2. Characterization with Raman Spectroscopy

The crystallographic study of the crystalline phases of $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ (x = 0.04, 0.08, and 0.33) showed that the structures of these ceramics are formed from different bonds, such as Ba/Na-O, Nb/W/Mo-O, and Ba/Na-Nb/W/Mo. The vibration modes of these principal bonds were able to be identified with Raman spectroscopy. As shown in Figure 3, the Raman spectra were recorded between 1200 and 100 cm^{-1} of these prepared ceramics, characterized by different bands. The identification of these bonds with their bands has been made (see the Table 4) in reference to our previous work focused on crystalline phases (x = 0.0) [44].

Figure 3. Raman spectra of the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ (x = 0, 0.04, 0.08, 0.33) ceramics.

Table 4. The Raman bands in the range of 1200–100 cm^{-1} were identified for the $Ba_{0.54}Na_{0.46}$ $Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ ceramics.

Band Position (cm^{-1})	Assignment
485→115	Octahedra (Mo/W/NbO$_6$) or cation translation vibrations (Ba^{2+}, Na$^+$)
650→485	Mo/W/Nb–O stretching vibrations caused by deformation
840→650	Mo/W/Nb-O bonds

Stretching vibrations of Mo/W/Nb-O bonds were the primary Raman bands within the 840–650 cm^{-1} region, while the deformation modes of Mo/W/Nb-O bonds were found in the bands between 650 cm^{-1} and 485 cm^{-1}. The bands in the range of 485–115 cm^{-1} may have been linked with W/Mo/Nb-O bonds in the octahedra (W/Mo/NbO$_6$) or vibrations of cation translation (Ba^{2+}, Na$^+$). Additionally, according to Shudong Xu et al. [50], the band at 250 cm^{-1} is attributed to O-Nb-O bending vibrations. The bands located between 280 and 650 cm^{-1} are related to NbO$_6$-octahedron bending and stretching vibrations. This is similar to the modes observed in LiNbO$_3$ at 248 cm^{-1} and 628 cm^{-1} and in $Pb_{2(1-x)}K_{1+x}Gd_xNb_5O_{15}$ at 260–280 cm^{-1} and 630–650 cm^{-1} [51]. In addition, there is a possibility that the highest-frequency mode, in the range of 850–938 cm^{-1}, could be associated with the stretching vibration of (Nb/W/Mo)O$_6$ octahedra, similarly to perovskites [52]. The Raman spectrum of $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{0.37}O_5$ displayed a broad and strong peak at approximately 650 cm^{-1}, as well as another intense peak around 280 cm^{-1}. These peaks are attributed to Nb-O vibrations in the NbO$_6$ octahedra (Figure 3) [44]. Furthermore, from the composition where x = 0.04 with the substitution of W^{6+} (0.74) with Mo^{6+} (0.73), the intensity of the Raman peaks at the 280 cm^{-1} and 650 cm^{-1} positions increased with increasing MoO$_3$

content. These two Raman peaks are associated with the $Nb/W/MoO_6$ octahedra, and the increasing of their peak intensities can be explained via an increased number of MoO_6 octahedra. Furthermore, increasing the MoO_6 content in the framework had no effect on the Raman peak positions because the W^{6+} and Mo^{6+} ions were the same size and occupied the same sites (Wyckoff 2 and 8). On the other side, few Raman peaks of low intensities were observed from the composition where x = 0.04, and their intensities began to increase as MoO_3 content increased; these Raman peaks may be characteristic of the formation of the scheelite-type $BaMoO_4$ composite. Thus, the Raman analysis validated the Rietveld refinement of the X-ray data obtained using the proposed refinement models and verified the presence of a secondary phase (BaMoO4).

3.3. Dielectric Analysis

3.3.1. Evolution of Dielectric Permittivity (ε^*) with Temperature

Figure 4a–d depict the thermal evolution of the dielectric permittivity (ε') during heating of different solid-solution compositions (x = 0.00, 0.04, 0.08, and 0.33) at different frequencies.

The ferroelectric character of the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ solid solution at room temperature was confirmed for all compositions. Thus, we were able to highlight the characteristic anomaly of a phase transition, ferroelectric–paraelectric, at the transition temperature, Tc. The position of the peak was independent of the frequency; hence, the behavior of the ferroelectric studied was of a classical character. As a result, we observed a decrease in the ceramic's dielectric permittivity of an increase in the rate of substitution (x) (see Figure 1e). It should also be noted that at high frequencies, the anomaly completely vanished and the ceramic lost its properties; this behavior was brought on by a reduction in contribution of polarization mechanisms. As is well known, conductivity contributes to loss of storage energy, as seen with the drop in the maximum of ε' at the level of the transition. Ionic conduction or space charges are related to this evolution. Consequently, degradation of dielectric characteristics can be used to explain this phenomenon (related to the increase in conductivity, which presents a disadvantage for ferroelectrics) [53]. The ferroelectric characteristics of the ceramics under study, such as those where x = 0.00, x = 0.04, x = 0.08, and x = 0.33, are grouped in Table 5. It should be observed that the effect of the substitution showed up as a reduction in the real permittivity's maximum $\varepsilon_r'_{max}$ value, which would typically fall as "x" rose (see Table 5). Depending on the substitution, this drop can be explained by a loss of stored energy in the ceramic samples [53] or can be demonstrated with the formation of phase-type $BaMoO_4$, characterized by low dielectric permittivity, as F.A.C. Nobrega et al. [49] confirmed.

Table 5. The ferroelectric properties of the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ solid solution where $0 \leq x \leq 0.33$.

Composition	T_c	$\varepsilon_r'_{max}$ 1 KHz	$\varepsilon_r'_{max}$ 10 KHz	$\varepsilon_r'_{max}$ 100 KHz	$\varepsilon_r'_{max}$ 1000 KHz
0.00	250.84	1770.90	668.33	408.37	328.97
0.04	276.57	844.84	342.88	242.48	222.40
0.08	288.36	399.49	235.21	191.40	174.97
0.33	285.48	369.48	189.51	161.58	155.37

3.3.2. Evolution of Dielectric Losses (tanδ) with Temperature

The dielectric losses, $\tan(\delta) = \frac{\varepsilon_r''}{\varepsilon_r'}$, in the ferroelectric phase were reasonably low for all of the compositions examined, as shown in Figure 5a–d. We saw that the losses significantly rose during the paraelectric phase. At low frequencies and high temperatures, this rise was larger. This demonstrates that conductivity plays a vital role at high temperatures [54].
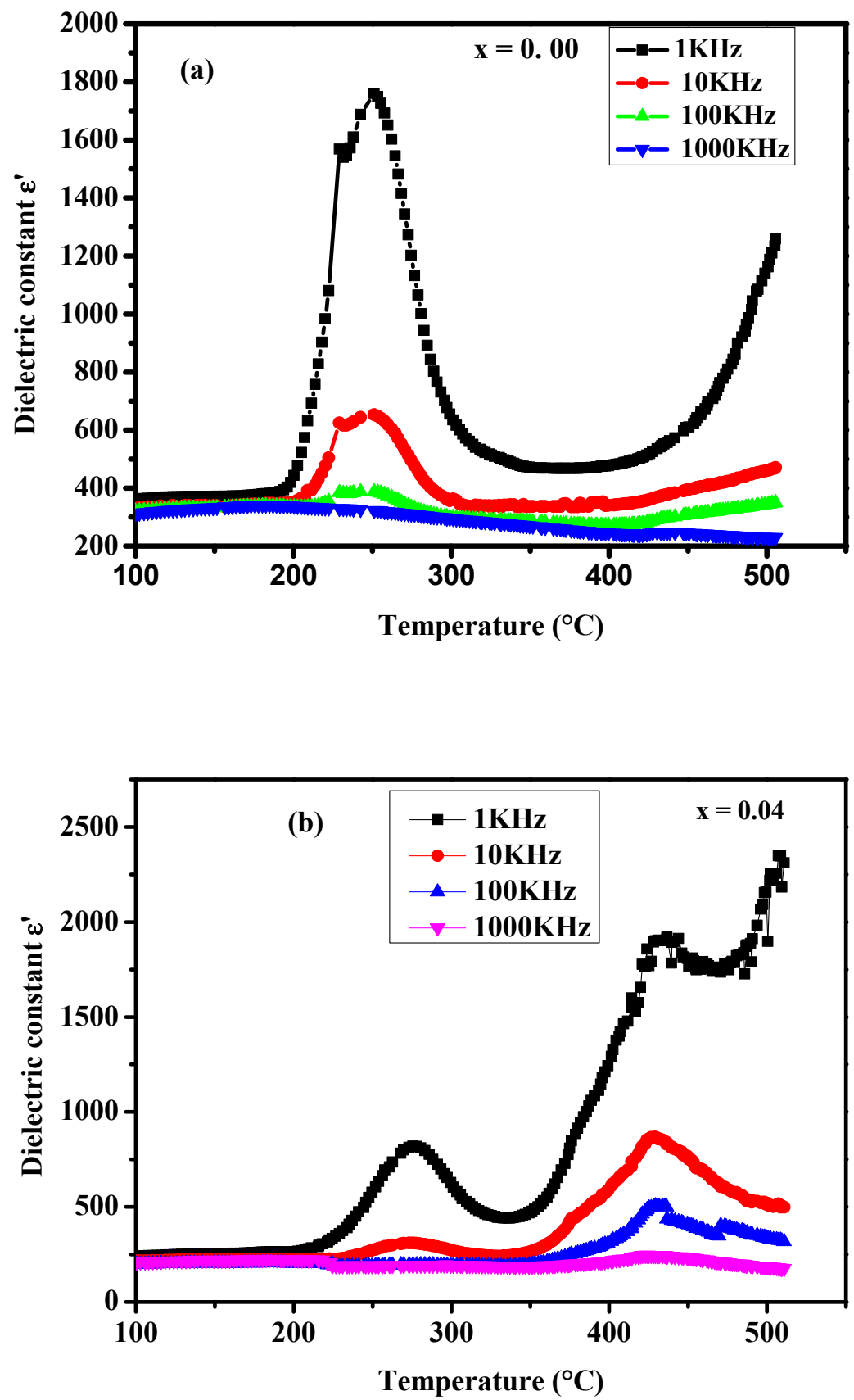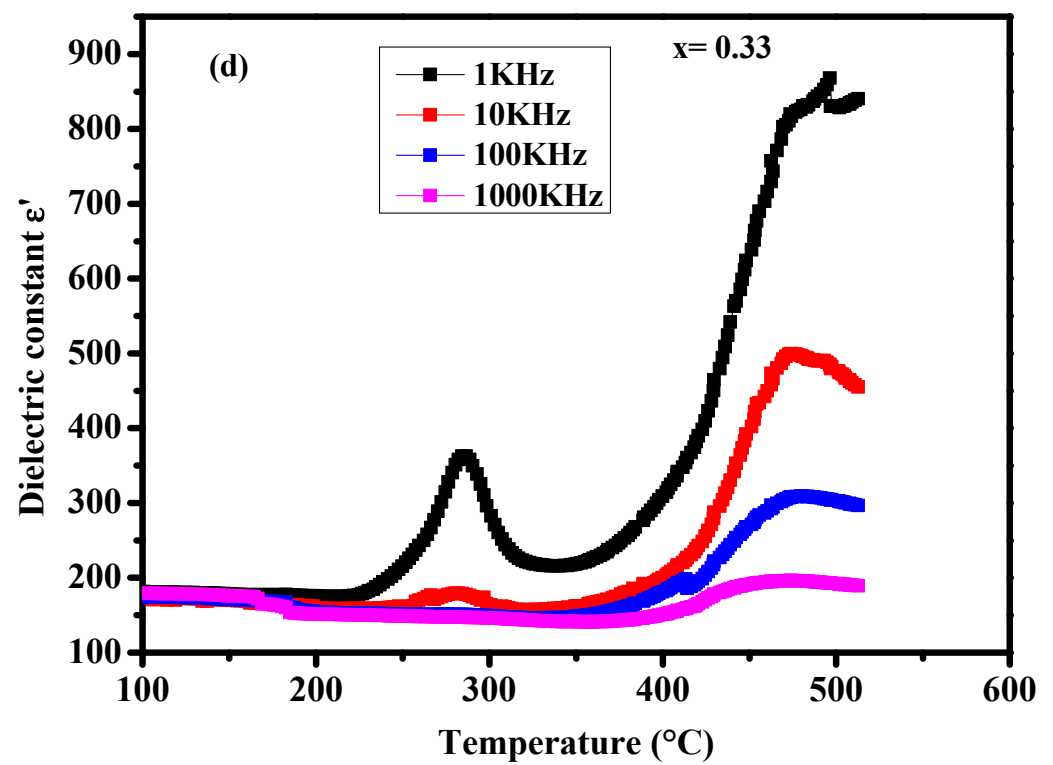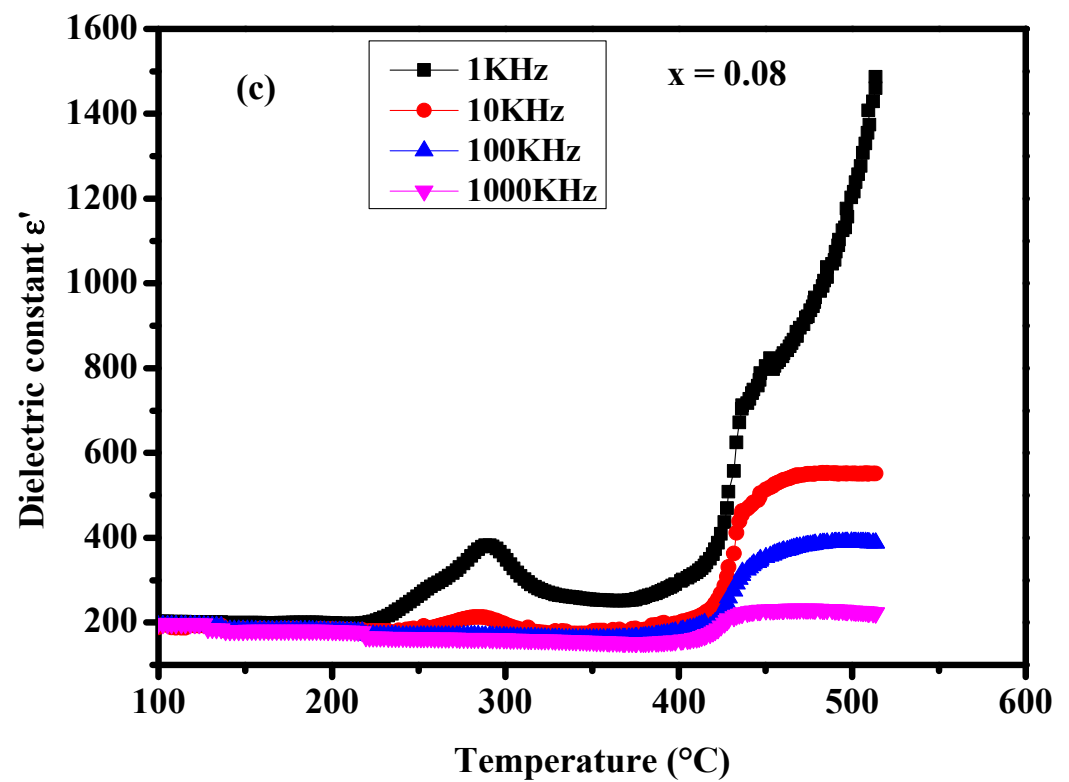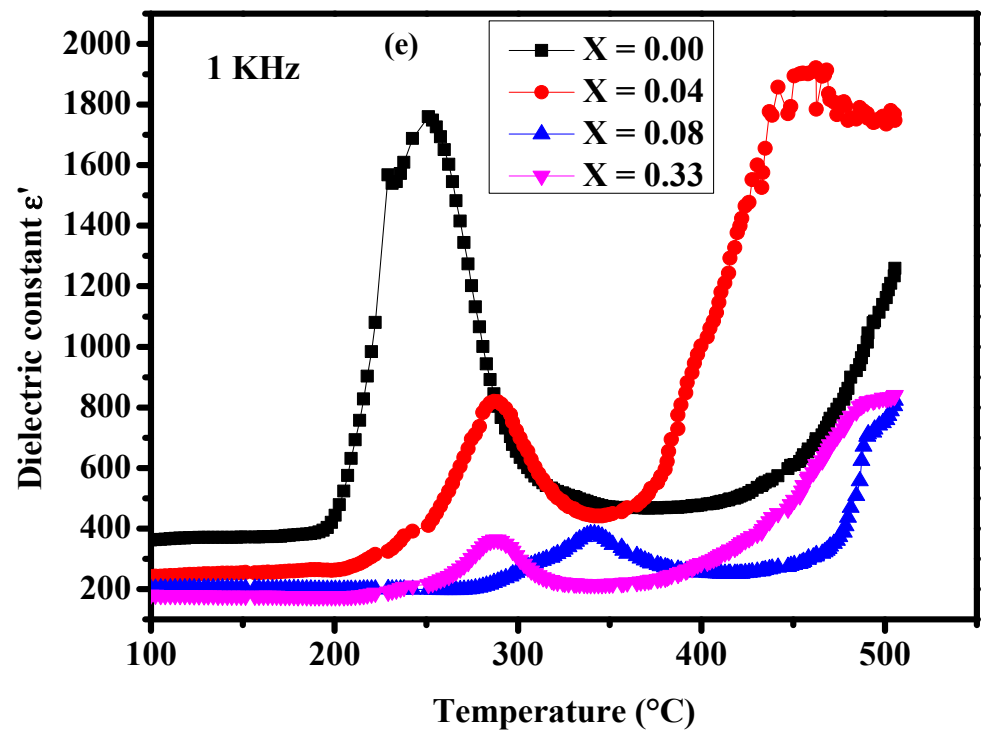
Figure 4. *Cont.*

Figure 4. *Cont*.

Figure 4. (**a**–**e**) Thermal evolution of ε_r' at different frequencies and at different compositions for x = 0.00, 0.04, 0.08 and 0.33.
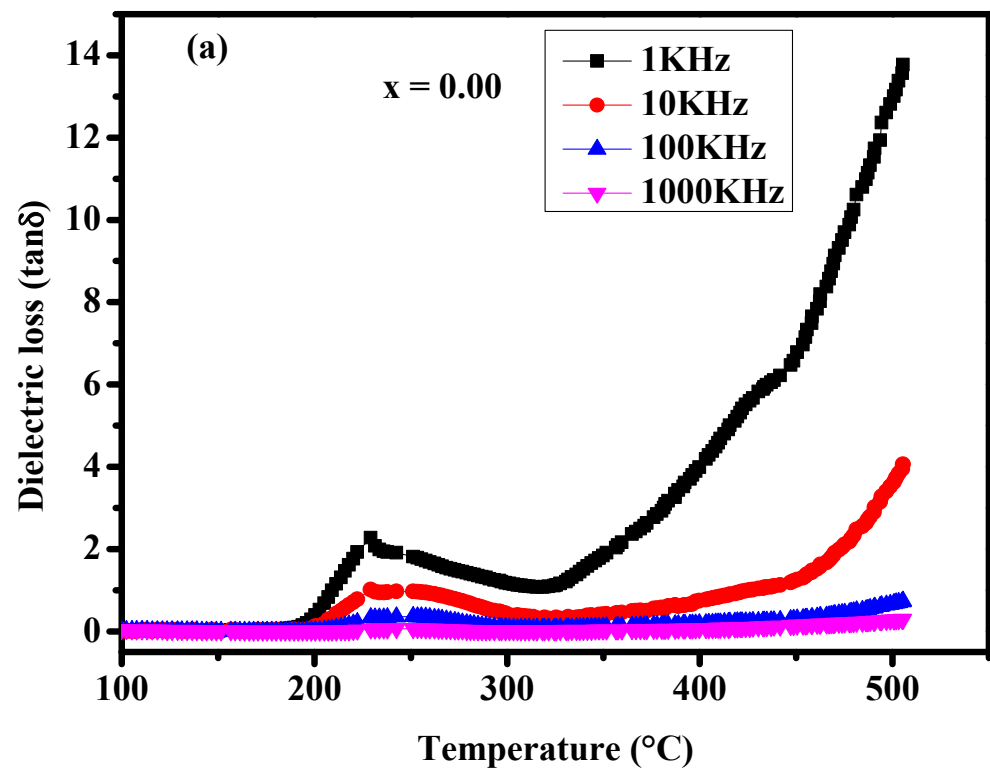

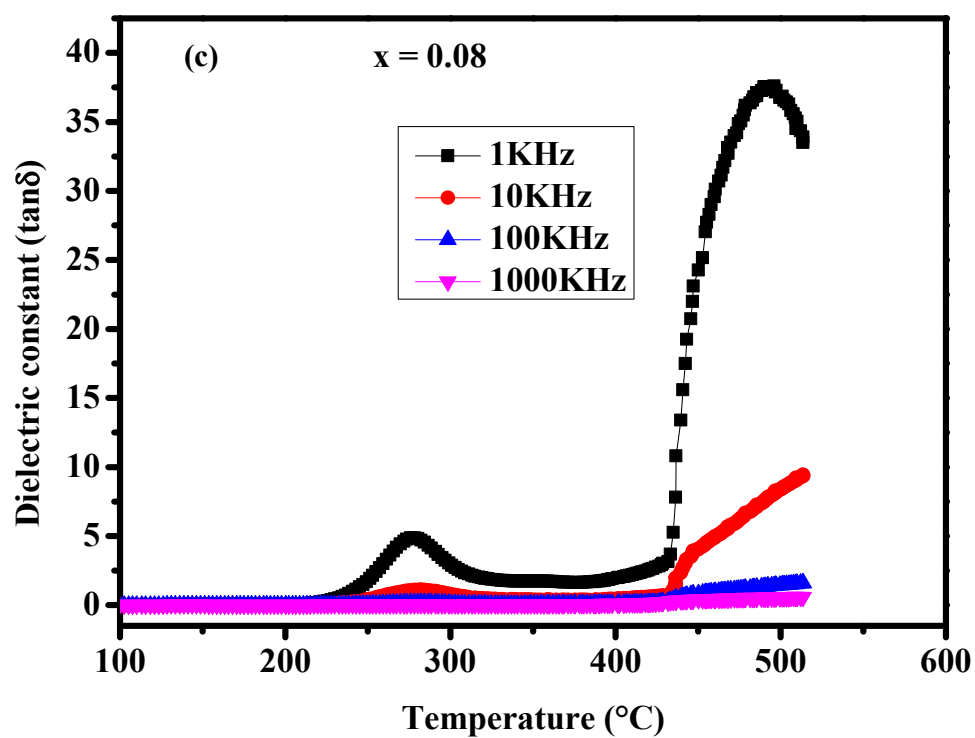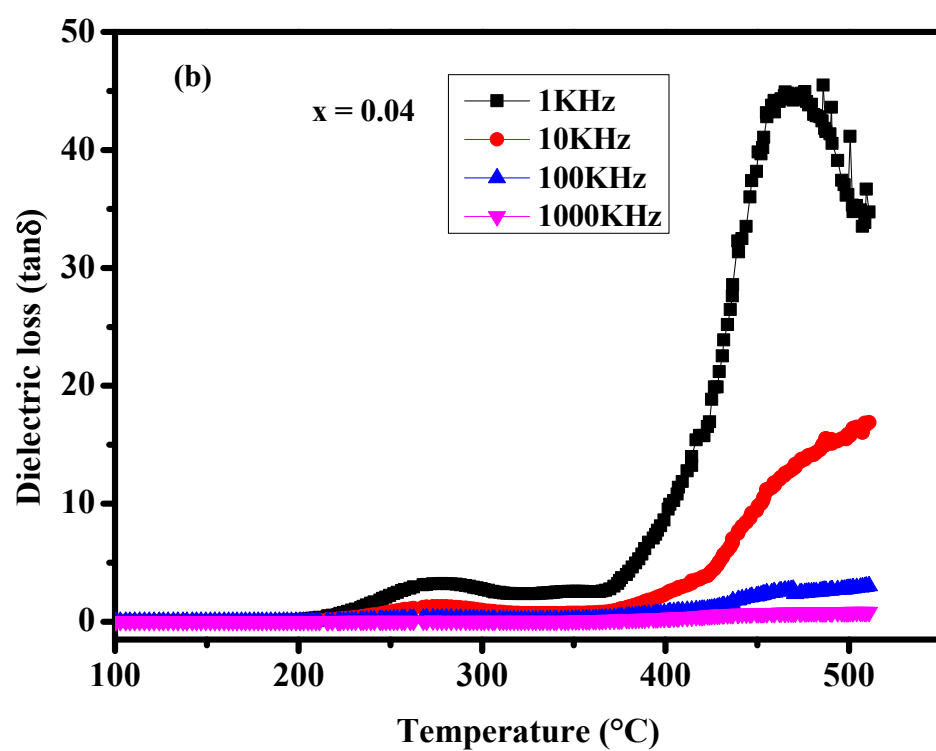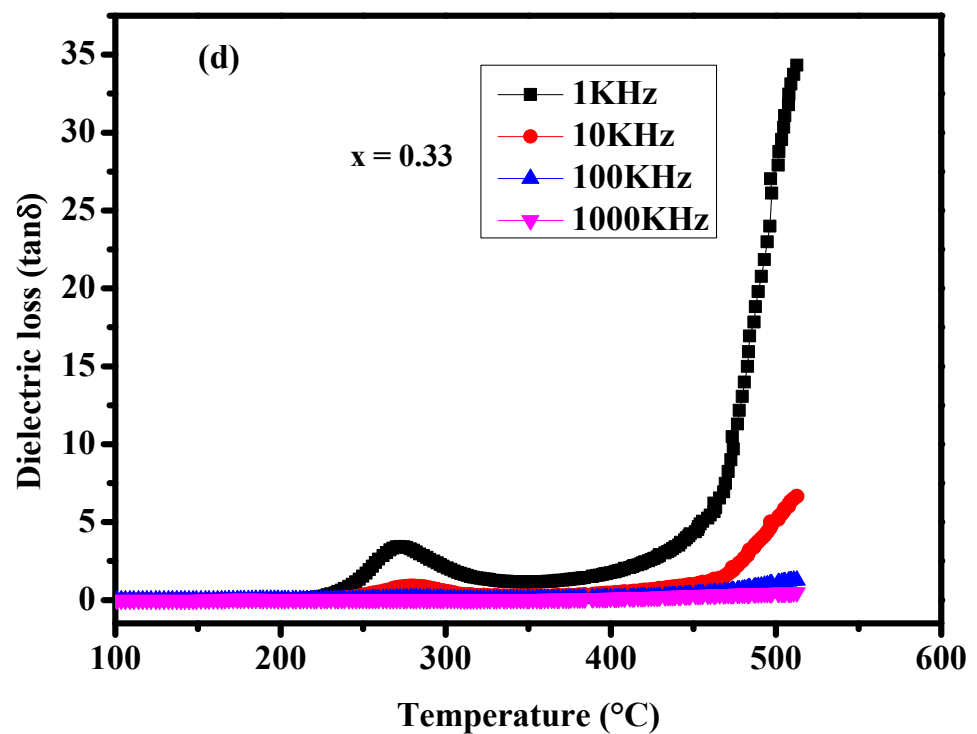**Figure 5.** *Cont.*

Figure 5. *Cont.*

Figure 5. (**a–d**) Evolution in dielectric loss with respect to temperature is plotted for the prepared ceramics.

3.3.3. Phase Transition Order

This study focused on analyzing changes in inverse dielectric permittivity with temperature to understand the characteristics of phase transitions. Figure 6a–d depict the variation of the opposite dielectric permittivity versus temperature during heating at a frequency of 1 kHz. The shape of the curve for all of the compositions followed the Curie–Weiss law well in the paraelectric phase defined by Equation (4) [55]:

$$\varepsilon' = \frac{C}{T - T_0} \tag{4}$$

The experimental data fitted were used to calculate the Curie constants and the Curie–Weiss temperatures for various compounds (see Figure 6a–d). The comparison of the calculated temperatures, T_0, and those deduced from the curves of variation of the real part and the value of the Curie–Weiss constant allowed us to determine the transition order and type.

The Curie–Weiss law was clearly observed in the ceramic samples, and the paraelectric phase exhibited a linear dependence that described the law. Table 6 lists the results in groups. The transition was of the first order, since T_c and T_0 were not coincident. The Curie constant, C, was of the order of 10^3 K in the case of an order–disorder-type transition; however, displacive transitions take values 100 times higher, as demonstrated in the literature [56]. Because the Curie constant values for the different ceramics ranged from 10^4 to 10^5 K, the transition was displacive in nature.
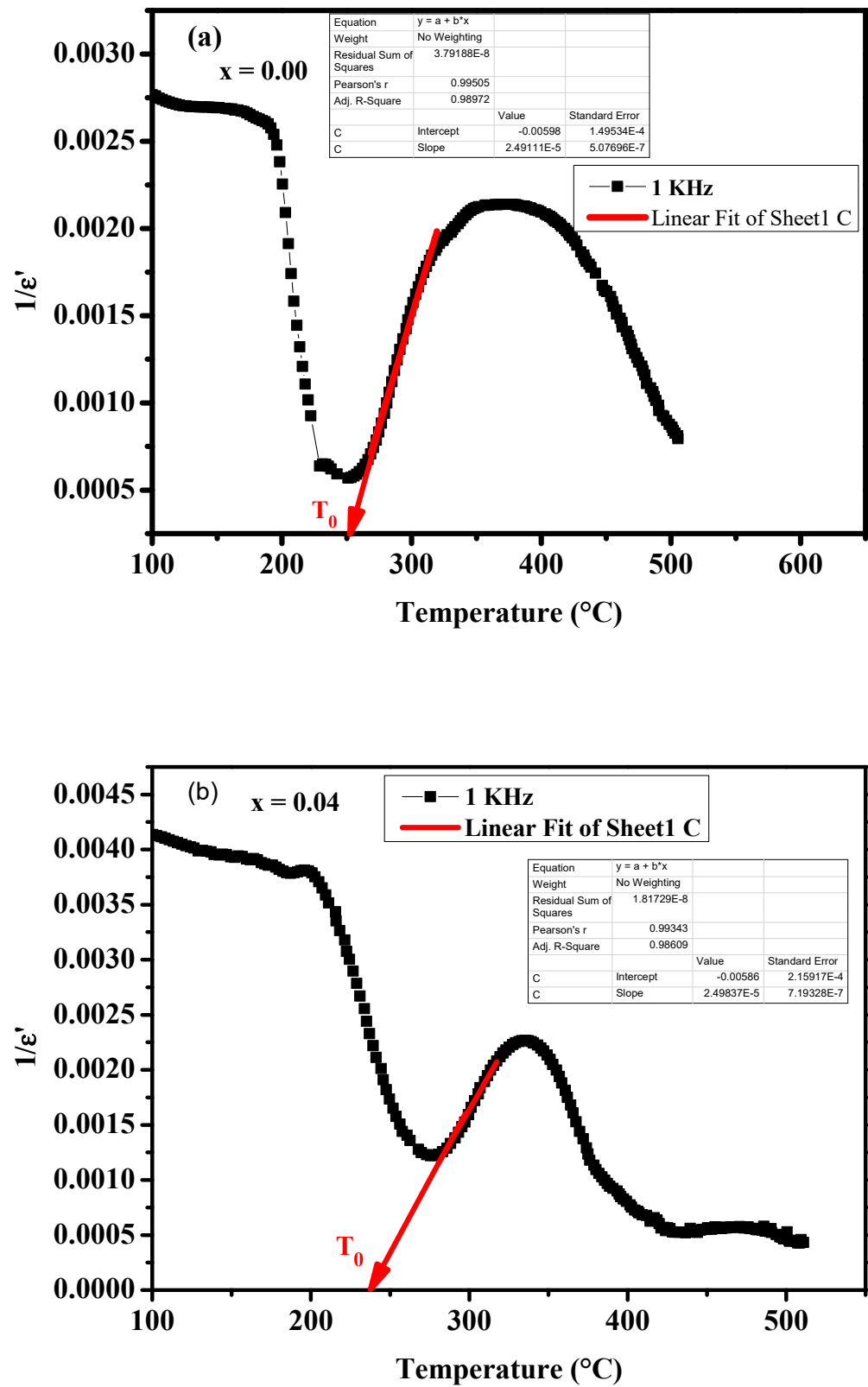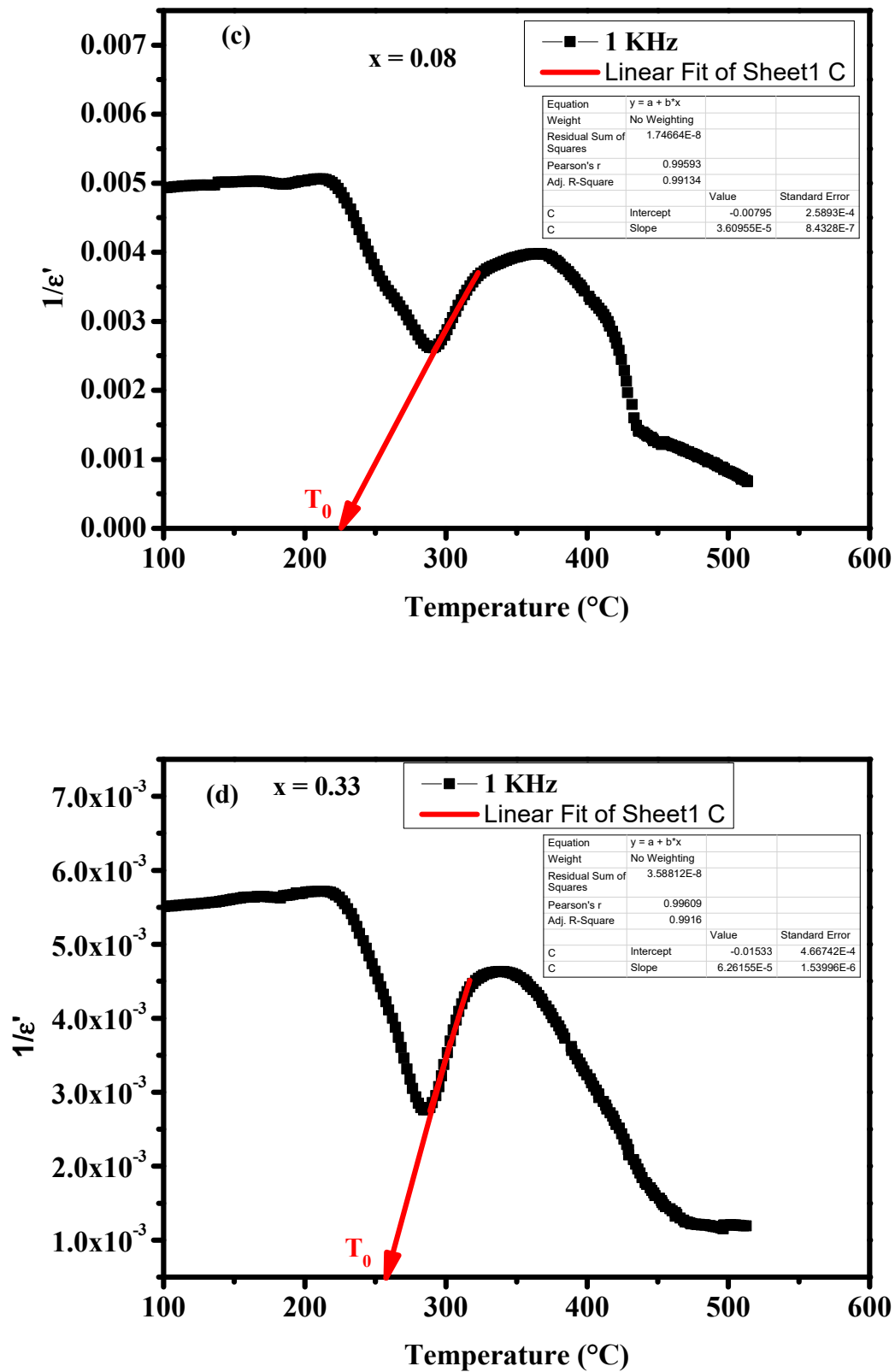
Figure 6. *Cont.*

Figure 6. (**a**−**d**) Thermal evolution of $\frac{1}{\varepsilon_r\prime}$ at a 1 KHz frequency for the ceramics.

Table 6. Curie–Weiss parameters for the investigated solid solution.

Composition	T_c	T_0	C
x = 0.00	250.84	253.18	40.16×10^3
x = 0.04	276.57	237.68	40.00×10^3
x = 0.08	288.36	225.70	27.70×10^3
x = 0.33	285.48	257.57	15.92×10^3

Additionally, from Table 6, it is noted that the temperature, Tc, passed through a high where x = 0.08 (T_c = 288.36) and then decreased where x = 0.33 (T_c = 285.48), highlighting the impact of the replacement on the ferroelectric characteristics. J. Ravez [56] stated that although the size of alkaline earth cations and the size of alkaline cations do not appear to be directly related to the Curie temperature (T_c), an increase in distortion occurs. The single lone pair of electrons in $5s^2$, which caused an increase in the distortion of the octahedra, and the strongly polarized nonspherical cations in Ba^{2+} were both responsible for the composition's high Tc value (x = 0.08) [57]. As a result, the structural distortion and the contribution of the W^{6+} cations to spontaneous polarization were increased; thus, the substitution of Mo^{6+} in W^{6+} increased the T_c range for the ceramics of the compositions where x ≤ 0.08 [58]. Further, the Mo–O bond's deterioration also supported this increasing trend. However, a slight decrease in the Curie temperature was observed in the compositions where x > 0.08; this behavior is explained by the fact that the pace at which the Mo^{6+} cations occupied the octahedral sites surpassed that of the W^{6+} cations. Additionally, ferroelectricity is more likely to arise when a metal cation is smaller. Other experimental research on TTB-structured ferroelectric materials, with $Ba_{2(1-x)}Pb_{2.05x}Na_{1-0.1x}Nb_5O_{15}$ and $Pb_{2(1-x)}Gd_xK_{1+x}Nb_5O_{15}$, has been conducted [59–62]. In it, this process was explained by changes in the polarization axis, which can also occur in the solution investigated in this work, as well as reorientation of dipoles [55].

3.3.4. Study of the Conductivity in the Solid Solution

Furthermore, there was a significant increase in the loss coefficients for high temperatures, phase paraelectrics, and low frequencies, indicating the presence of conductivity in the ceramics [63]. These anomalies in the dielectric loss curves near the transition temperature were also noted during the study of the thermal variation of the real part of the dielectric permittivity. Consequently, we can see that the loss decreased as the frequency increased, as shown in Figure 7a–d.

Ionic conduction, which is caused by movement of charge carriers, can account for this increase in conductivity at high temperatures and low frequencies [64]. The charge carriers' inability to adhere to excitation of the electric field at high frequencies accounts for conductivity's diminishing tendency at these frequencies [65].
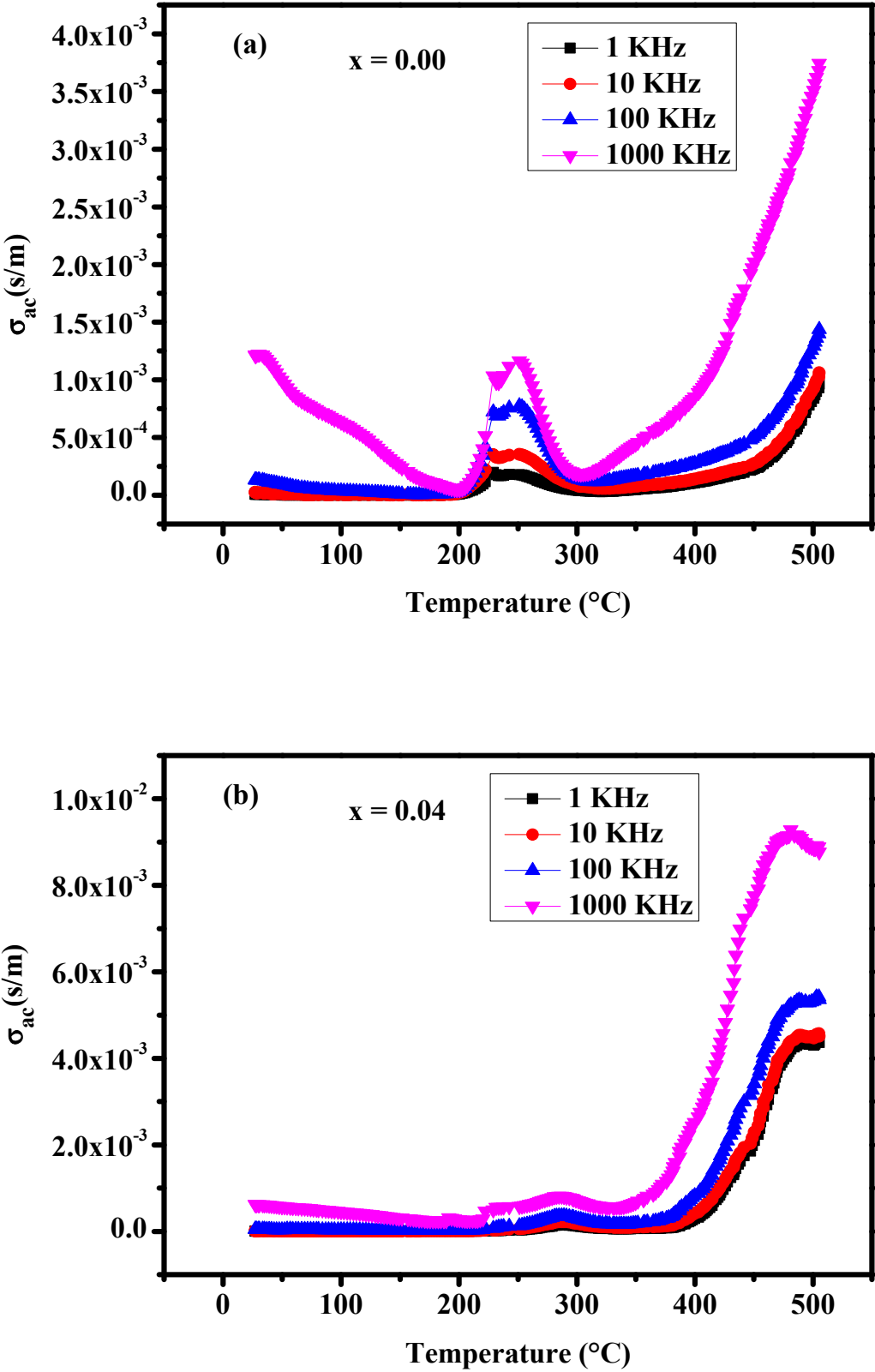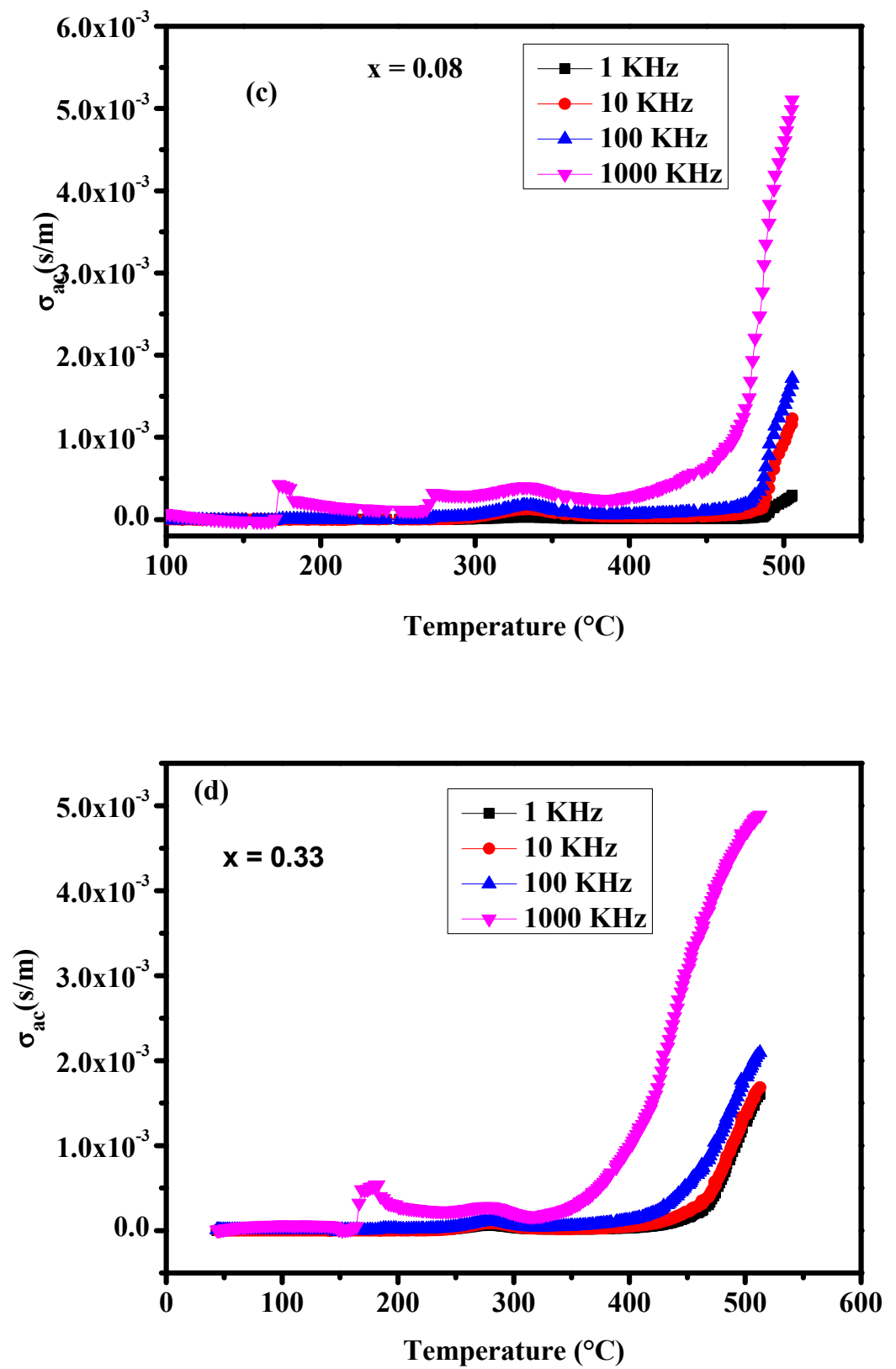
Figure 7. *Cont.*

Figure 7. (**a**–**d**) Thermal development of electrical conductivity at different frequencies for the ceramics.

4. Conclusions

The crystalline phases of the $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ system were synthesized through a solid-state route. The Rietveld method was used to simulate the XRD data of various $Ba_{0.54}Na_{0.46}Nb_{1.29}W_{(0.37-x)}Mo_xO_5$ samples, confirming that these samples crystallize in a tetragonal structure with the P4bm space group, in addition to the presence of a small amount of the $BaMoO_4$ phase type (tetragonal with the I41/a space group). Raman investigation results confirmed that substitution of W^{6+} (0.74 Å) with Mo^{6+} (0.73 Å) prompts the formation of the secondary phase, $BaMoO_4$. The dielectric measurements of these ceramics across a wide range of temperatures (from 25 °C to 550 °C) and frequencies (from 20 Hz to 1 MHz) led to the observation of a transition from the ferroelectric phase to the first-order paraelectric phase. This investigation demonstrated a decrease in ε'_{max} due to the substitution of W^{6+} with Mo^{6+} at a certain frequency. This dielectric study also allowed us to analyze under study the evolution of the system according to the substitution. The Curie–Weiss law's parameters brought to light the examined system's behavior, which shifted from a displacive-type transition to an order–disorder-type transition. The charge carriers' inability to adhere to the excitation of the electric field at high frequencies accounted for the conductivity's diminishing tendency at these frequencies.

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