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Ordering in Lead Iron Tungstate Relaxor Ceramics*

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Abstract

The ordering behavior of sodium doped lead iron tungstate ceramics, $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$, was investigated together with their dielectric properties. The 1:1 type ordering of iron and tungsten cations, on the B sites, was evidenced by $\{h+\frac{1}{2}, k+\frac{1}{2}, l+\frac{1}{2}\}$ superlattice reflections in both X-ray and transmission electron microscopy diffraction. The ordering degree increases with Na content when $Na \leq 8$ at% and decreases when $Na > 8$ at%. Besides the perovskite PFW phase, a second phase, $PbWO_4$, was observed in Na doped PFW ceramics and its amount increases with increasing Na content. The dielectric permittivity decreases with the increase in the Na content, while the diffuseness increases. It is suggested that the substitution of Na^+ for Pb^{2+} leads to a decrease in the charge imbalance between ordered and disordered regions, enhancing the ordering of PFW ceramics. The competition between the enhancement of ordering and the formation of the $PbWO_4$ phase is suggested to be responsible for the decrease of ordering, when $Na > 8$ at%. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

$Pb(B'_{1-x}B''_x)O_3$ ferroelectric relaxor materials have been successfully used as dielectrics for the manufacture of low temperature firing multilayer capacitors.[1]

A typical relaxor material exhibits a high dielectric permittivity value, a diffuse phase transition, a strong relaxation of the permittivity with frequency, with a shift of the dielectric maxima (permittivity and loss factor) to higher temperatures as the frequency increases and an absence of macroscopic polarization at temperatures far below the temperature of the permittivity maximum.

The most recent theories[2,3] attribute the relaxor behavior to a nanopolar cluster structure that evolves to a frozen state (ferroelectric state) below a characteristic temperature. According to this idea the origin of the macroscopic dielectric diffuseness is related to local polarization fluctuations, instead of being due to a multitude of classic ferroelectric-paraelectric transitions of different Känzig regions, as Smolenskii[4] first suggested. The correlation between the diffuse phase transition and the structural disorder on the B site cations of the perovskite lattice was established in $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST).[5–7] Suitable heat treatments allowed the Sc^{3+} and Ta^{5+} ions to get ordered and a normal ferroelectric behavior was observed, whereas the disordered one exhibits typical relaxor properties.[6]

It seems that there is a direct correspondence between the polar regions and the chemically inhomogeneous regions in the relaxor materials, which however has not been well defined.

$Pb(Fe_{2/3}W_{1/3})O_3$ (PFW), a member of the relaxor ferroelectric family, has a disordered perovskite structure, where the Fe^{3+} and W^{6+} ions are randomly distributed on the octahedral positions. It was observed[8] that the ordering degree of PFW is hardly modified by annealing treatments, but evident modifications of the macroscopic dielectric response were found out for defective PFW samples[9] and attributed to different degrees of order of the structure.

In the present work, the ordering degree of the PFW structure was modified by doping with sodium. The mechanism responsible for the enhancement of the ordering is proposed and discussed.

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2 Experimental

The compositions studied are represented by the general formula $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ in which $x = 0{\cdot}03$, 0·05, 0·08, 0·10 and 0·12.

Reagent grade lead, iron and tungsten oxides and sodium nitrate were used to prepare the samples indicated in Table 1.

According to the columbite precursor method, previously described,[10] Fe_2O_3 and WO_3 powders were first batched in appropriate proportions to prepare the columbite. After ball-milling/mixing in an ethanol medium for 4 h and subsequent drying, the mixture was prereacted at 1000°C for 2 h. The products were then mixed with the desirable amounts of PbO and $NaNO_3$ in ethanol for 4 h. The calcination of the dried powders was conducted at 800°C for 2 h. The calcined powders were remilled during 10 to 15 h until the particle size of the powders was less than 5 μm.

Pellets with 10 mm of diameter and around 2 mm of thickness were uniaxially pressed at 100 MPa, followed by isostatic pressing at 300 MPa.

The green samples were sintered between 870 and 900 °C according to the composition, for 2 h, as indicated in Table 1.

Phase identification and structural analysis of sintered samples, ground into powder, was carried out by X-ray diffraction (XRD) analysis. The microstructure of the samples was observed in polished sections, using Scanning Electron Microscopy (SEM). Thin foil specimens were prepared by mechanical polishing followed by ion-beam thinning, for transmission electron microscopy (TEM) analysis. For the dielectric measurements, sintered samples were polished and gold electrodes were sputtered on both sides. Dielectric permittivity was measured, at 10 KHz, as a function of temperature, using a Solartron 1260 impedance/Gain-Phase Analyzer and a Displex APD-Cryogenics cryostat.

The diffuseness coefficient, δ, which characterizes the breadth of the diffuse ferroelectric/paraelectric transition, was calculated by the Gaussian distribution relation:[11]

$$\varepsilon_{r\max}/\varepsilon_r = \exp[(T - T_0)^2/2\delta^2]$$

where $\varepsilon_{r\max}$ is the dielectric permittivity maximum, ε_r the dielectric permittivity at T and T_0 the temperature at which $\varepsilon_{r\max}$ occurs (transition temperature).

3 Results

The sintering characteristics of the $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ compositions are shown in Table 1. All the samples show high density and low weight loss, which are nearly unchanged with increasing the Na content.

The microstructure of the 8 at% Na doped PFW sample is shown in Fig. 1, together with the microstructure of undoped sample[10] [designated as (P)FW]. In both cases, dense microstructures and homogeneous grain sizes can be observed. All the doped samples showed similar microstructures. Doping with Na has not introduced variations in the microstructure.

Figure 2 shows the XRD patterns of the Na doped PFW compositions. As can be seen, besides the PFW cubic perovskite phase, a second phase, identified as $PbWO_4$, was observed and its amount increases with the increase of the sodium content.

The XRD patterns (Fig. 2) also show a series of superlattice reflections, the intensity of which varies with the sodium content. For Na$\leq$8 at%, the superlattice reflection intensity increases, decreasing for Na > 8 at%. These superlattice reflections were identified to be $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{3}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{3}{2},\frac{3}{2},\frac{1}{2})$, $(\frac{3}{2},\frac{3}{2},\frac{3}{2})$ and $(\frac{5}{2},\frac{3}{2},\frac{1}{3})$, being indexed as $h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2}$.

The variation of the lattice constants of the Na doped PFW samples with Na content, determined from their correspondent XRD patterns, is shown in Fig. 3. A nearly linear decrease of the lattice constant with increasing Na content is observed. This probably results from Na^+ ions having a smaller ionic radius (1·02 Å[12,13]) than Pb^{2+} ions (1·49 Å[12,13]) and also indicates that the Na ions are incorporated into the lattice of PFW, as expected.

Figure 4 shows a <110> zone-axis TEM diffraction pattern of the PFW-8Na sample, where the superlattice reflections are evident (superlattice F spots are indicated), confirming the XRD analysis results.

Table 1. Sintering characteristics of the studied compositions

Designation	*Compositions*	*Sintering temperature time*	*Weight loss (%)*	*Density ($g{\cdot}cm^{-3}$)*
(P)FW-3Na	$Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3, x = 3$ at%	870°C/2 h	0·31	8·9
(P)FW-5Na	$Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3, x = 5$ at%	870°C/2 h	0·29	8·9
(P)FW-8Na	$Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3, x = 8$ at%	890°C/2 h	0·32	8·8
(P)FW-10Na	$Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3, x = 10$ at%	890°C/2 h	0·30	8·9
(P)FW-12Na	$Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3, x = 12$ at%	900°C/2 h	0·31	8·8

(a) (b)

Fig. 1. SEM microstructures of (a) (P)FW-8Na and (b) (P)FW ceramics.

The super structure, evidenced by the above results, points out for an ordering process of the PFW structure, chemically induced by sodium doping.

The dielectric properties of the Na doped samples, including the permittivity maximum value, the transition temperature and the diffuseness coefficient, are presented in Table 2. The dielectric permittivity, as a function of temperature, at 10 KHz, is shown in Fig. 5. The dielectric properties of undoped sample[10] are also represented in Table 2 and Fig. 5. The dielectric permittivity decreases with increasing the Na content, while the diffuseness increases and the transition temperature is almost unchanged.

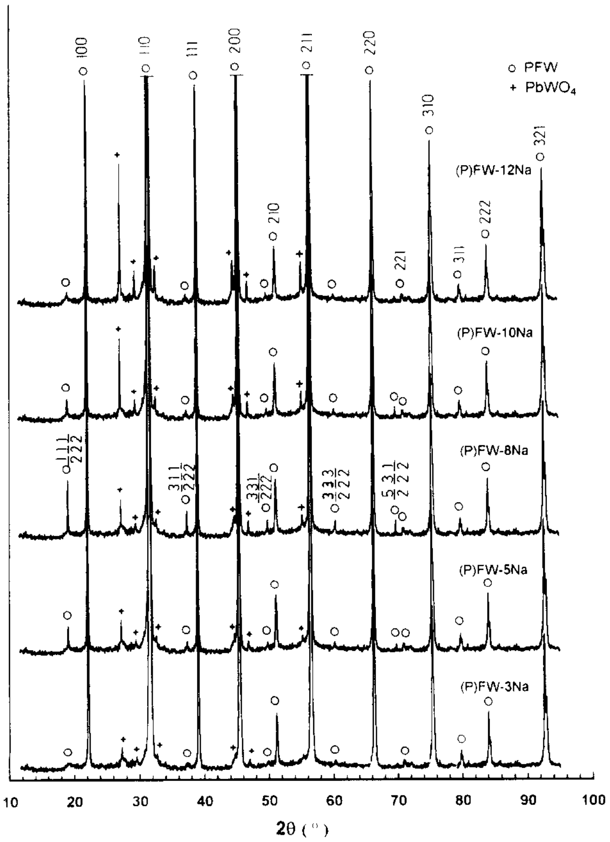

Fig. 2. XRD patterns of compositions of the $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ system. Superlattice reflections are: $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{3}{2},\frac{1}{2},\frac{1}{2})$, $(\frac{3}{2},\frac{3}{2},\frac{1}{2})$, $(\frac{3}{2},\frac{3}{2},\frac{3}{2})$ and $(\frac{5}{2},\frac{3}{2},\frac{1}{2})$.

4 Discussion

Like in other relaxor materials,[5] the observed superlattice reflections can be associated with the ordering of the B cations, Fe^{3+} and W^{6+}, of the PFW perovskite structure.

In systems where the ratio of B site components is 2:1, two types of ordering can occur: 1:1 or 2:1. Consistent with this, two possibilities of ordering should be considered for PFW: $B'-Fe^{3+}$ and W^{6+}, $B''-Fe^{3+}$ ($Fe^{3+}:W^{6+}=2:1$, 2:1 type) and $B'-Fe^{3+}$, $B''-W^{6+}$ ($Fe^{3+}:W^{6+}=1:1$, 1:1 type).

In the first type of order (2:1) where the B′ sites are randomly occupied by iron and tungsten ions

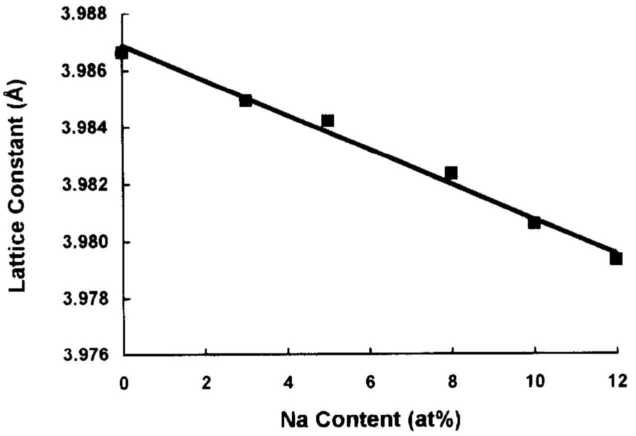

Fig. 3. Dependence of the lattice constant of $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ compositions on Na content.

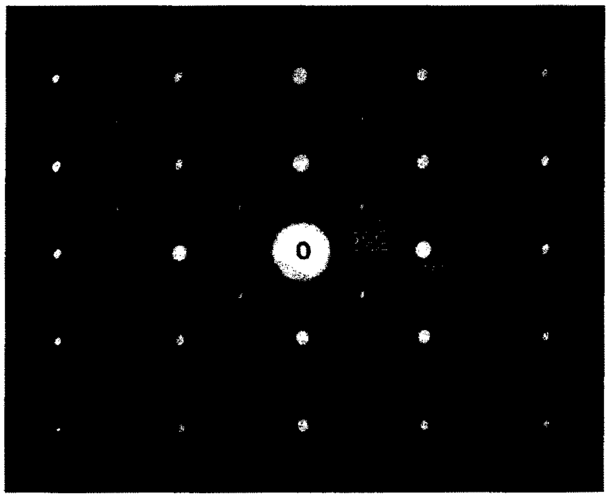

Fig. 4. < 110 > zone-axis diffraction pattern of (P)FW-8Na ceramics. The superlattice F spots are indicated.

Table 2. Dielectric characteristics of $Pb_{1-x}Na_x(Fe_{(2-x)/3}W_{(1+x)/3})O_3$ ceramics, at 10 KHz

Designation	$\varepsilon_{r\,max}$	$T_0(K)$	$\delta(K)$
(P)FW	12180	184	53
(P)FW-3Na	8330	180	60
(P)FW-5Na	6640	180	62
(P)FW-8Na	5460	178	65
(P)FW-10Na	4700	182	68
(P)FW-12Na	2760	176	70

and the B″ sites are only occupied by iron ions, the average composition of the ordered regions is identical to that of the PFW bulk and no charge imbalance occurs between ordered and disordered regions. So, the ordered region can be expected to easily grow, for example, by annealing treatment. However, this was not observed for PFW. No long range ordering could be detected for undoped PFW ceramics before and after annealing.[8,9]

In the second type of order (1:1), the ordered regions, where the B′ sites are exclusively occupied by iron ions and B″ sites exclusively occupied by tungsten ions (Fe^{3+}:W^{6+} = 1:1), are tungsten rich relatively to the bulk composition (Fe^{3+}: W^{6+} = 2:1), resulting in excess positive charges in the ordered regions with respect to the disordered matrix. This charge imbalance will inhibit the growth of ordered regions. This was thought to be the reason for the observed behavior of PFW ceramics.[8,9]

For the sodium doped PFW ceramics, the substitution of the divalent lead ions by the monovalent sodium ions caused a charge difference that was compensated by adjusting the composition according to the formula $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$, or in other words, by decreasing the Fe^{3+}/W^{6+} ratio of the PFW. For increasing Na content, the Fe^{3+}/W^{6+} ratio of PFW gets closer to 1:1, decreasing the charge imbalance between ordered and disordered regions and consequently the ordering degree of the PFW structure could easily increase. This was indeed observed when Na≤8 at%, as can be seen in Fig. 2. However, when Na > 8 at%, the ordering decreases and the superlattice reflections are almost undetectable for the (P)FW-12Na composition.

As was pointed out before (Fig. 2), a second phase, $PbWO_4$, is present in Na doped PFW ceramics and its amount increases with the increase of sodium content.

According to the $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ formula, the increasing amounts of tungsten needed when the sodium increased, will probably favor the formation of the $PbWO_4$ phase, as observed. Simultaneously the formation of $PbWO_4$ phase will lead to an increase of the Fe^{3+}/W^{6+} ratio in the PFW and then to a decrease of the ordering. So, it seems that there is a competition between the enhancement of ordering and the formation of the $PbWO_4$ phase in Na doped PFW ceramics. When Na≤8 at%, the ordering is favored, while the formation of $PbWO_4$ is favored when Na > 8 at%.

It was shown in PST,[5-7] where the ratio of B cations is 1:1, that the dielectric diffuseness decreases as the degree of B site ordering increases. However, in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) doped with La,[14] where the ratio of B cations is 1:2, the diffuseness increases as the degree of B site ordering increases. Results from XRD (Fig. 2) show that the ordering degree of PFW increases when Na≤8 at%. However, as can be seen in Fig. 5 and Table 2, the dielectric diffuseness increases gradually with the Na content; a similar behavior to La doped PMN.[14] The reasons for this are at the moment still not very clear, but they could be related, in our case, to the presence of increasing amounts of the non ferroelectric $PbWO_4$ phase, which will lower the dielectric permittivity of the phase assemblage or to a contribution to the diffuseness from the mixing of the two cations (Pb

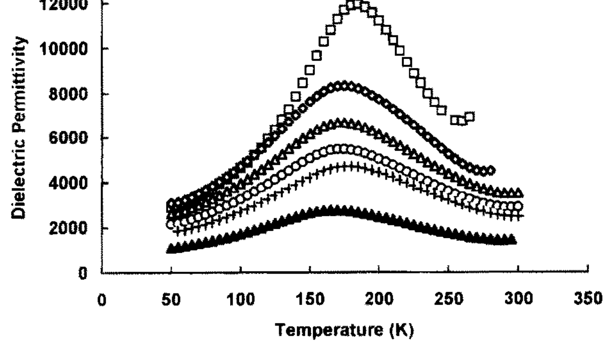

Fig. 5. Dielectric permittivity as a function of temperature, at 10 KHz, for $Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ compositions.

and Na) on the A sites, which could somehow counterbalance the contribution from the B site ordering.

5 Conclusion

Both X-ray and TEM diffraction patterns of Na doped PFW ceramics exhibited superlattice reflections indexed as $h+\frac{1}{2}, k+\frac{1}{2}, l+\frac{1}{2}$, which were associated with 1:1 ordering of Fe^{3+} and W^{6+} cations on B sites. The ordering degree was observed to be enhanced by Na doping when $Na \leq 8$ at%, but weakened when $Na > 8$ at%.

$Pb_{1-x}Na_x[Fe_{(2-x)/3}W_{(1+x)/3}]O_3$ ceramics are not monophasic. Besides the perovskite PFW phase, a second phase, $PbWO_4$, was also observed and its amount increases with the increase of the Na content.

The dielectric permittivity decreases with increasing the Na content, while the diffuseness increases and the transition temperature is almost unchanged, in all the Na doping range.

The enhancement of the ordering of PFW ceramics by sodium doping is suggested to be due to the weakening of the charge imbalance between the ordered and disordered regions, caused by the monovalent ions substituting divalent ions. The competition between the enhancement of ordering and the formation of the $PbWO_4$ phase is suggested to be responsible for the decrease of ordering, when $Na > 8$ at%.

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