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Dielectric and ferroelectric characteristics of $Ba_4Pr_2Fe_2Nb_8O_{30}$ tungsten bronze ceramics

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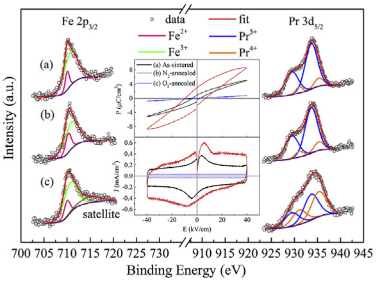
HIGHLIGHTS

- Dielectric and ferroelectric properties of $Ba_4Pr_2Fe_2Nb_8O_{30}$ are investigated.
- Ferroelectric hysteresis loop is observed in $Ba_4Pr_2Fe_2Nb_8O_{30}$ ceramics.
- The ferroelectric properties are closely related to the valences of Pr ions.
- The ferroelectric transition temperature is dominated by the radius difference between A1-and A2-site.

GRAPHICAL ABSTRACT



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ABSTRACT

$Ba_4Pr_2Fe_2Nb_8O_{30}$ tungsten bronze ceramics have been prepared by a standard solid-state sintering method, and the electrical, dielectric and ferroelectric properties have been determined together with the structure. The structure dependence of ferroelectricity has been investigated by comparing the as-sintered, N_2-annealed and O_2-annealed samples. The typical relaxor ferroelectric nature is generally indicated in the present ceramics, where the broaden dielectric constant and dielectric loss peaks with strong frequency dispersion feature are observed. The peak temperatures for both dielectric constant and dielectric loss are significantly increased together with the much stronger frequency dispersion by N_2-annealing, while the O_2-annealing results in the decreased peak temperatures and the suppressed frequency dispersion. These phenomena are closely related to the valences of Fe and Pr ions. The hopping between Fe^{2+} and Fe^{3+} inside the grains causes the dielectric relaxation in as-sintered and N_2-annealed samples. The enhanced ferroelectricity near room temperature is attributed to the increased ion radius difference between A1 and A2 ions because of the “substitution” Pr^{4+} for Pr^{3+} after N_2-annealing.

1. Introduction

Recently, materials with filled tungsten bronze structure have attracted much attention due to their unique structure features and interesting characteristics [1–5]. Among them, $Ba_4R_2Fe_2Nb_8O_{30}$ (R=Nd–Gd) compounds become the subject of intense investigation because of their room temperature multiferroic properties, which are considered to have great potential applications in multifunctional devices [6–10]. Josse et al. [6] and Castel et al. [8] investigated the ferroelectric properties of tungsten bronze $Ba_4Pr_2Fe_2Nb_8O_{30}$, and found that it behaves as a relaxor below 170 K. The ferroelectric characteristics of filled tungsten bronze $M_{6-p}R_pTi_{2+p}Nb_{8-p}O_{30}$ ($p = 1, 2$; M = Ba or Sr; R = rare earth or Bi) have been intensively investigated [1–5]. Generally, a ferroelectric transition is indicated together with up to three low-

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temperature dielectric relaxations in these materials. The ferroelectric transition is determined as 4/mmm→4 mm, and the low-temperature dielectric relaxations are deeply concerned with the structure modulations due to the order/disorder of ions in A1-and A2-sites, their random cross occupancy, and the order/disorder of B-site ions. Both the ferroelectric transition and low-temperature dielectric relaxations are dominated by the composition and radius difference between A1-and A2-site ions (Δr) [1] and the degree of size mismatch (variance) of the A-cations [11,12]. In tungsten bronze ferroelectrics, the dipoles originated from the displacement of B1 cations in the c axis are stabilized by the large tetragonality of the unit cell [13]. However, the physical understanding on the ferroelectric characteristics of $Ba_4R_2Fe_2Nb_8O_{30}$ (R = rare earth elements) is still limited. Since B-site is partially occupied by non-ferroelectric active Fe, $Ba_4R_2Fe_2Nb_8O_{30}$ is expected more relaxor with a decreased ferroelectric transition temperature (T_m) compared with those for $Ba_{6-p}R_pTi_{2+p}Nb_{8-p}O_{30}$ with the same rare earth element. Moreover, the possible mixed valent structure will lead to the more complex situation in $Ba_4R_2Fe_2Nb_8O_{30}$. The mixed valent structure at B-site will result in the more relxor behavior, while the mixed valent structure at A-site will change the radius difference between A1-and A2-site ions which will subsequently modify the features of ferroelectric transition and low-temperature dielectric relaxations. However, the tungsten bronze structure has a limited ability to accommodate rare earths with small ion radius [6,12]. This limitation causes the disorder distribution of A-site ions over both pentagonal and square tunnels, which leads to abnormal changes of dielectric maximum temperature and cell volume [6].

On the other hand, ions' valence change has been paid considerable attention for decades in many perovskite oxides owning to its close link to material structure and properties [14,15]. For tungsten bronzes, Liu et al. [9] investigated the effect of oxygen vacancies induced by the Fe valence change between Fe^{2+} and Fe^{3+} on the ferroelectric properties of $Ba_4Nd_2Fe_2Nb_8O_{30}$. However, the related physical understanding is still lack. $Ba_4Pr_2Fe_2Nb_8O_{30}$ is a unique case in tungsten bronze $Ba_4R_2Fe_2Nb_8O_{30}$, where both Pr and Fe have variable valences. Though the nominal valance structure of Pr^{3+} and Fe^{3+} are expected, Pr^{4+} and Fe^{2+}, which have different ion radius to those of Pr^{3+} and Fe^{3+}, may also be obtained according to the sintering and annealing atmospheres. Therefore, it should be possible to modify the ferroelectric characteristics by tailoring the valent structure of Pr and Fe through varying the sintering or annealing atmosphere, and subsequently the physical understanding on the ferroelectric characteristics of tungsten bronze $Ba_4R_2Fe_2Nb_8O_{30}$ is expected to be deepened.

In the present work, dense $Ba_4Pr_2Fe_2Nb_8O_{30}$ tungsten bronze ceramics are prepared by sintering in air and subsequently annealed in O_2 or N_2 atmosphere. The effects of valence fluctuation of Fe and Pr ions on electrical, dielectric and ferroelectric properties are thoroughly investigated, and the structural origin of the ferroelectricity is discussed.

2. Experimental details

$Ba_4Pr_2Fe_2Nb_8O_{30}$ ceramics were prepared by a standard solid-state sintering method from high-purity powders of $BaCO_3$ (99.99%), Fe_2O_3 (99.9%), Nb_2O_5 (99.99%) and Pr_6O_{11} (99.9%). The stoichiometric raw materials were ball milled for 24 h and calcined at 1623 K in air for 3 h. The calcined powders were re-ground and added with 5% PVA (Polyvinyl alcohol) as binders. The pressed pellets were sintered at 1673 K in air for 3 h. Two sets of $Ba_4Pr_2Fe_2Nb_8O_{30}$ ceramic samples were then annealed in N_2 and O_2 at 1423 K and 1523 K for 3 h, respectively.

The crystal structures of sintered samples were identified by X-ray powder diffraction analysis with Cu K_α radiation (Empyrean, PANalytical, Holland). The microstructures were evaluated for the polished and thermal-etched surfaces of the present ceramics with a field emission scanning electron microscopy (SEM, SU70, Hitachi Co., Tokyo, Japan). The mixed-valent structure of Fe and Pr ions were evaluated by X-ray photoemission spectroscopy (ESCALAB 250Xi; Thermo Fisher Scientific Inc., Waltham, MA) with Al K_α radiation ($h\nu = 1486.6$ eV). The dielectric characteristics of the present ceramics were evaluated with a broadband dielectric spectrometer (Turnkey Concept 50, Novocontrol Tech., Hundsangen, Germany). Ferroelectric P-E hysteresis loop were measured using a precision materials analyzer (Premier II, Radiant Tech., Albuquerque, NM) at 253 K.

3. Results

3.1. XRD and SEM measurements

Fig. 1 shows the XRD patterns of the as-sintered and annealed $Ba_4Pr_2Fe_2Nb_8O_{30}$ ceramics. All the diffraction peaks can be indexed as a tetragonal tungsten bronze structure in space group *P*4*bm* at room temperature, and no evident diffraction peaks of secondary phase can be observed. The lattice parameters of the present ceramics are calculated from the powder XRD data by the least-squares method: a = b = 12.4552 Å, c = 3.9227 Å, and V = 608.53 $Å^3$ for the as-sintered sample, a = b = 12.4620 Å, c = 3.9228 Å, and V = 609.22 $Å^3$ for the N_2-annealed sample, and a = b = 12.4809 Å, c = 3.9274 Å, and V = 611.78 $Å^3$ for the O_2-annealed sample. As shown in Fig. 2, the dense ceramics with columnar grain morphology are obtained, and there is no apparent change in grain morphology and size is observed for the as-sintered and annealed samples.

3.2. Dielectric and electrical properties

Fig. 3(a)–(c) give the frequency dependence of *ac* conductivity (σ_{ac}) for all the samples in the temperature range of 370–570 K. The *dc* conductivity (σ_{dc}) becomes dominate below the frequency range mentioned above. The σ_{ac} drops with the decrease of frequency until a frequency-independent plateau appears. The σ_{dc} is obtained by fitting the σ_{ac} data using the well-known Jonscher's relation:

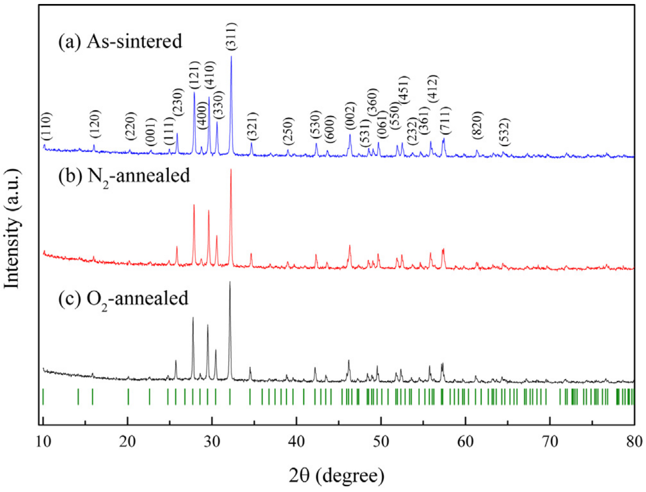

Fig. 1. XRD patterns of $Ba_4Pr_2Fe_2Nb_8O_{30}$ ceramics.

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