Materials Research Bulletin 48 (2013) 1934–1938

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Structure and dielectric properties of $Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$ tungsten bronze ceramics

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ARTICLE INFO

Article history:
Received 11 July 2012
Received in revised form 21 December 2012
Accepted 23 January 2013
Available online 8 February 2013

Keywords:
A. Ceramics
C. X-ray diffraction
D. crystal structure
D. dielectric properties

ABSTRACT

A new type of tungsten bronze ceramic $Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$ has been prepared by a conventional solid-state reaction technique. Its structural, dielectric properties were investigated. Rietveld analysis shows that $Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$ has a single-phase tetragonal (space group *P4bm* and lattice constants $a = b = 12.4961(4)$ Å, $c = 3.9426(8)$ Å, $V = 615.66(4)$ Å^3) tungsten bronze structure. The occupations of sites A and B are quite interesting. A1 sites are fully disordered occupied by Ba ions and Nd ions and A2 sites for Ba ions only, while B-sites are equal for both Cu and Nb ions to occupy. This material exhibits an obvious relaxation behavior in the 213–573 K temperature range. The dielectric constants have been fitted by the modified Curie–Weiss law and all the estimated γ values are close to 2, confirming the typical relaxor ferroelectric behavior. The disorders of Ba^{2+} or Nd^{3+} in A1 sites and Nb^{5+}, Cu^{2+} in B sites induced by the oxygen vacancies may contribute to this dielectric behavior.

1. Introduction

Because of the fascinating physics and their potential applications, considerable research effort has been spent on dielectric materials [1]. Promising applications of these composites include magnetic field sensors, transducer, filters, oscillators, phase shifters, memory devices, and so on [2,3]. In most of these applications, high dielectric constant and low dielectric loss are generally required together with a small temperature coefficient of dielectric constant [4]. In recent years, a large majority of dielectric ceramics have been reported in various systems, including CCTO [5], $BiFeO_3$ [6,7], $LnMnO_3$ [7,8], $BaTiO_3$ [9], $Pb(Zr,Ti)O_3$ [10–12], $LuFe_2O_4$ [13], etc. However, there are no materials combined with high dielectric constant and low dielectric loss to fulfill the miniaturization of electric devices, and new dielectric materials with both high permittivity and low dielectric loss continue to remain a hot area of scientific research.

As one kind of important dielectric ceramics, the structure and dielectric properties of some materials which possess tetragonal tungsten bronze (TTB) structure have been extensively investigated [14–16]. The tetragonal tungsten bronze structure with a general chemical formula $(A1)_2(A2)_4(C)_4(B1)_2(B2)_8O_{30}$ is composed by a complex array of distorted BO_6 octahedral sharing corners with three different types of interstices (square A1, pentagonal A2, and trigonal C) being available for cations substitution that can tailor physical properties of materials for device applications. Generally, A1 and A2 sites are filled by divalent or trivalent cations, B1 and B2 sites by tetravalent or pentavalent cations and C site being small, often keeps vacant. Thus, the general formula can be expressed as $A_6B_{10}O_{30}$ for the tungsten–bronze structure [17–22]. The abundant cationic sites of tungsten bronze structure result in extended substitution opportunities which can induce magnetic interactions [23]. Moreover, the magnetic crystals of TTB compound are known to reveal incommensurate polar state, which may favor a coupling between magnetic and ferroelectric order [24,25]. Levin et al. [26] and Stennett et al. [27] indicated the relationship between the ferroelectric behavior in TTB structure and the modulation of commensurate/incommensurate driven by the A2 cation size. When the A2 cation size is less than 1.32 Å, the compounds display ferroelectric phase transitions; otherwise, the compounds exhibit a relaxor behavior with an incommensurate phase [28]. According to some recent studies, most of the TTB tantalites are paraelectric at room temperature, while the niobates, having a relatively high Curie temperature, tend to display ferroelectric or relaxor ferroelectric nature. Some compounds in this family such as $M_4R_2Ti_4Nb_6O_{30}$ [28,29], $M_5RTi_3Nb_7O_{30}$ [17], and $M_4R_2Ti_4Ta_6O_{30}$ [30] (M = Ba and Sr, R = La, Nd, Sm, and Y) have been investigated as dielectric materials, and the dielectric properties of rare earth/iron substituted TTB have been studied.

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http://dx.doi.org/10.1016/j.materresbull.2013.01.044

However, the effect of copper ion substitution in Ti sites is unknown, and much less information is available on TTB compounds in the $BaO–Nd_2O_3–CuO–Nb_2O_5$ system. In the present work, the dielectric characteristics of tungsten bronze $Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$ ceramic were evaluated over a broad temperature (213–573 K) and frequency (1 kHz–1 MHz) range, and its crystal structure was discussed.

2. Experimental

2.1. Sample preparation

A polycrystalline sample of $Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$ (BNCN) was prepared by the high-temperature solid-state reaction method using high purity $BaCO_3$, Nd_2O_3, CuO, Nb_2O_5 as starting materials. The weighted raw materials were mixed by ball milling with ZrO_2, ethanol for 24 h, and then the dried mixture was pre-calcined at 1200 °C for 10 h to yield desired material. The calcined powder was pulverized with approximately 5 wt% polyvinyl alcohol. The screened powder was pressed into pellet of 11 mm in diameter and approximately 1 mm in thickness under a pressure of ~200 MPa. The samples were heated at 400 °C for 3 h to burn out the organic binder and then a final sintering at 1380 °C continued for another 10 h. The pellets were ready for electroding with a post fire silver paste on both sides.

2.2. Characterization

The phase purity and crystallinity of the calcined powder were examined using X-ray diffraction (XRD) (Cu Kα, λ = 0.1541 nm) operated at 30 kV and 30 mA. The XRD data for Rietveld analysis were collected in the 2θ range of 10–90° in 0.01° steps. Rietveld structure refinement of the diffraction pattern was carried out using the Fullprof Suite 2009 software.

The impedance analyzer (Agilent 4980A) was used to characterize the dielectric properties in the temperature range of 213–573 K.

The polarization–electric field (*P–E*) hysteresis loop of BNCN was measured by Ferroelectric test system (Radiant WS-2000, USA).

3. Results and discussion

3.1. The structure analysis

The tolerance factor (*t*) for TTB structure has been discussed by Wakiya et al. [31], which is a parameter to estimate the stability of the crystal structure. As reported in Ref. [4], when the value of *t* is bigger than 0.95, stable TTB structure composites such as $Ba_3La_3Ti_5Ta_5O_{30}$ have been formed. According to the general formula of TTB, two kinds of A sites are present, one is A1 site with 12-fold coordination which is identical to that in perovskite structure, while the other is A2 site which occupies pentagonal site with 15-fold coordination. Thus, the value of *t* can be calculated by the following equation [31]:

$$t_{A1} = \frac{r_{A1} + r_O}{\sqrt{2}(r_B + r_O)} \quad (1)$$

$$t_{A2} = \frac{r_{A2} + r_O}{\sqrt{23 - 12\sqrt{3}}(r_B + r_O)} \quad (2)$$

where t_{A1} and t_{A2} represent the tolerance factor of A1 and A2 sites, r_A, r_B and r_O are the ionic radii at A sites, B sites, and oxygen, respectively. In order to better understand the relationship between tolerance factor and stability of TTB structure, combination of these two kinds of tolerance factor can be expressed as:

$$t = \frac{t_{A1} + 2t_{A2}}{3} \quad (3)$$

Based on this equation, and using the oxidation state ionic radii reported by Shannon [32], the calculated tolerance factor of BNCN is 1.0131, which suggests that BNCN has a stable TTB structure.

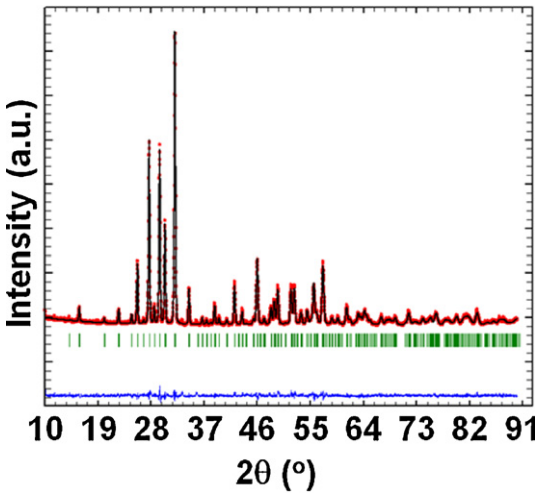

Fig. 1. X-ray diffraction patterns of tungsten bronze BNCN (experimental data are indicated by dots in the figures, and the refined pattern is shown by the continuous line on the same axes. The difference between the experimental data and the refined pattern is shown by the lower continuous line. The marks between two continuous lines indicate positions of the Bragg reflections).

X-ray diffraction pattern of BNCN ceramic at room temperature is shown in Fig. 1. All peaks were indexed and there was no evidence of any second phase present, which indicated that the composite was phase-pure. Rietveld refinements were performed using an averaged model with a tetragonal symmetry (space group *P4bm*, no. 100). A total of 55 parameters including scale factor, lattice parameter, full width at half maximum (FWHM), preferred orientation, site occupancy and isotropic thermal parameters were refined. The refinement result indicates that BNCN ceramic crystallizes in a tetragonal structure with the space group *P4bm*. The good agreement is obtained between the calculated and observed pattern and the pattern factor R_p, the weighted pattern factor R_{wp} and the expected pattern factor R_{exp} are 6.13, 8.54 and 3.05, respectively. The refined unit cell parameters *a*, *c*, *V* for BNCN are 12.5052(3) Å, 3.9450(1) Å, and 616.92(4) Å^3.

Table 1 shows the refined structural parameters. It can be concluded from Table 1 that two B sites are equal for both Cu and Nb ions to occupy. The situation of A sites is quite interesting, Ba ions occupy the A2 sites fully, while A1 sites are occupied by either

Table 1
Details of the atoms, their refined equivalent positions and thermal factors.

Atoms	Wyckoff positions	*x*	*y*	*z*	B_{iso} (Å^2)
Nd1	2a	0.0000(0)	0.0000(0)	0.0000(0)	2.651(3)
Ba1	2a	0.0000(0)	0.0000(0)	0.0000(0)	2.651(3)
Ba2	4c	0.1612(3)	0.6794(5)	1.0086(3)	1.300(2)
Nb1	2b	0. 0000(0)	0.5000(0)	0.4764(4)	1.244(2)
Cu1	2b	0.0000(0)	0.5000(0)	0.4764(4)	1.244(2)
Nb2	8d	0.072(0)	0.2144(2)	0.5128(1)	1.387(2)
Cu2	8d	0.072(0)	0.2144(2)	0.5128(1)	1.387(2)
O1	2b	0.0000(0)	0.5000(0)	0.0211(5)	0.066(9)
O2	4c	0.7922(9)	0.7498(0)	0.5667(6)	0.066(9)
O3	8d	0.0816(4)	0.2046(6)	−0.0900(1)	0.066(9)
O4	8d	0.3493(0)	0.0010(4)	0.44921(3)	0.066(9)
O5	8d	0.1386(2)	0.0701(6)	0.3995(9)	0.066(9)