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Preparation of $Sb_3Nb_3O_{13}$ powders using molten salt method

**Di Zhou · Hong Wang · Huanfu Zhou · Xiaojun Xie ·
Xi Yao · Yonghong Cheng**

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Abstract The powders of pure cubic phase of $Sb_3Nb_3O_{13}$ were obtained using molten salt method at 1,100 °C with incubation time of 3 h. The formation of a kind of compound with hydroxyl restrains the volatilization and oxygenation of antimony oxides. The powder of cubic $Sb_3Nb_3O_{13}$ shows octahedral shape and its size lies between 1 μm and 20 μm. Densified ceramic was obtained using the $Sb_3Nb_3O_{13}$ powders. The microstructure of ceramic samples was studied by XRD and SEM analysis. And the dielectric properties as a function of frequency and temperature were measured between 25 °C and 550 °C and 100 Hz~1 MHz.

Introduction

Synthesis of antimony niobate by conventional mixed oxide method is complicated because of the volatilization, oxidation and decomposition [1, 2]. Solid state reaction could be accomplished by mixing Sb_2O_3 and Nb_2O_5 and annealing between 900 °C and 1,000 °C. Considering Sb_2O_3 being easily oxidized to Sb_2O_4 above 500 °C, vacuum or inert atmosphere environment is necessary. However, vacuum annealing might result in oxygen deficient in materials. In addition, antimony-based compounds become volatile above 1,040 °C. Unfortunately, the above conditions make it difficult to obtain dense, crystalline specimens. Some novel processing technology for ceramic powder preparation such as sol–gel method, molten salt method [3, 4], and high-energy ball milling method [5, 6] have been utilized. The $Sb_3Nb_3O_{13}$ $[Sb(^{3+})_2Sb(^{5+})Nb(^{5+})_3O_{13}]$ phase having a defect pyrochlore structure has been prepared by heating a sol–gel derived powder in oxygen [7]. The X-ray powder diffraction results indicate that $Sb_3Nb_3O_{13}$ has a face-centered cubic structure, S.G. Fd3m (227), with a unit cell parameter a = 10.4965(1) Å. And it is isostructural with the defect pyrochlore phase Sb_6O_{13} reported by Stewart et al. [8].

In present work, the $Sb_3Nb_3O_{13}$ was prepared employing the molten salt method at 1,100 °C. The densified ceramic with pure phase of cubic $Sb_3Nb_3O_{13}$ were obtained after being sintered at 1,180 °C for 2 h. The dielectric properties as a function of frequency and temperature were measured and discussed.

Experimental

Proportionate amounts of reagent-grade starting materials of Sb_2O_3 (>99%, Shu-Du Powders Co., Ltd., China) and Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co., Ltd., China) were mixed with the ratio of Sb:Nb = 1:1 and ball-milled for 2 h with alcohol in a nylon container with ZrO_2 balls. Then the salts (NaCl–KCl with mol ratio 1:1) with the same weight of oxide materials were added and the total milling time was about 5 h. The mixtures were dried and then calcined between 900 °C and 1,100 °C for 3 h. After cooling, the salt was eliminated by washing with deionized water and $AgNO_3$ solution was used for the titration to insure the absolute elimination of salt. Then the obtained

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D. Zhou · H. Wang (✉) · H. Zhou · X. Yao
Electronic Materials Research Laboratory, Key Laboratory
of the Ministry of Education, Xi'an Jiaotong University,
Xi'an 710049, China
e-mail: hwang@mail.xjtu.edu.cn

X. Xie · Y. Cheng
State Key Laboratory of Electrical Insulation for Power
Equipment, Xi'an Jiaotong University, Xi'an 710049, China

compounds were re-milled for 5 h to get powders with small sizes. After drying, the powders with 5 wt% PVA binder was uniaxially pressed into pellets in a steel die. Then the green samples were sintered at 1,180 °C for 2 h.

The crystalline structures of powders and ceramics samples were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). To investigate the morphology of the samples, the dispersed powders and the broken surface of densified ceramic after being eroded by HF solution were observed by scanning electron microscopy (SEM) (JEOL JSM-6460, Japan). The dielectric properties of ceramic as a function of frequency (100 Hz~1 MHz) and temperature (25–550 °C) were carried out with a precision LCR meter (HP, 4284, USA). The temperature coefficient of permittivity α_ε was calculated by the following formula:

$$\alpha_\varepsilon = \frac{\varepsilon_T - \varepsilon_{25}}{\varepsilon_{25} \times (T - 25)} \tag{1}$$

where ε_{25} is the permittivity at 25 °C, and ε_T is the permittivity at measuring temperature T.

Results and discussion

The X-ray diffraction patterns of powder and ceramic samples are shown in Fig. 1. For the powders prepared by molten salt method at 900 °C and 1,000 °C for 3 h, just a mixture of a little amount of $Sb_3Nb_3O_{13}$ phase, a large amount of $Sb_2O_{4.4}(OH)_{1.2}$ and the remnant Nb_2O_5, Sb_2O_3 were revealed as shown in Fig. 1a and b. After being heated at 1,100 °C for 3 h, the pure cubic phase of $Sb_3Nb_3O_{13}$ was obtained. Comparing with the results by heating pure oxides, the volatilization was prevented and the oxygenation was reduced with only one-third part of the Sb^{3+} being oxygenated to Sb^{5+}. Both of these two preconditions ensure the synthesis of pure $Sb_3Nb_3O_{13}$ phase and it might be attributed to the formation of $Sb_2O_{4.4}(OH)_{1.2}$ compound and the molten-salt environment. The XRD patterns of ceramic sample also show pure phase of $Sb_3Nb_3O_{13}$ and this compound seemed not easy to decompose by heating in air. The cell structure of $Sb_3Nb_3O_{13}$ $[Sb(^{3+})_2Sb(^{5+})Nb(^{5+})_3O_{13}]$ was shown in Fig. 2a. In a cell, the intact formula is Sb_8(16d)–(Sb_4Nb_{12})(16c)–O_{48}(48f)–O_4(8b). The so-called multiplied substitution and occupation factor (SOF) for every kind of ions were also shown in Fig. 2a in the parentheses. The calculated XRD patterns matched well with the measured ones as shown in Fig. 2b. The Rwp factor is less than 20% and the results are believable.

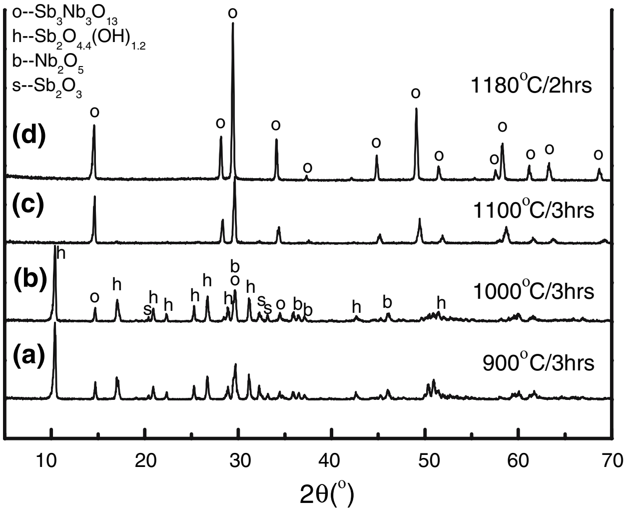

Fig. 1 XRD patterns of samples prepared at different temperatures

The SEM photos of powders prepared by molten salt method and ceramics sintered at 1,180 °C for 3 h were shown in Fig. 3. Almost all the crystal grains show an octahedral shape as shown in Fig. 3a. The crystal size changes between 1 μm and 20 μm and the size distribution is wide. After being re-milled for 5 h, the crystal size could be reduced and the distribution could become more even. Subsequently, the sintering of ceramics becomes easy. As shown in Fig. 3b, the ceramics samples of $Sb_3Nb_3O_{13}$

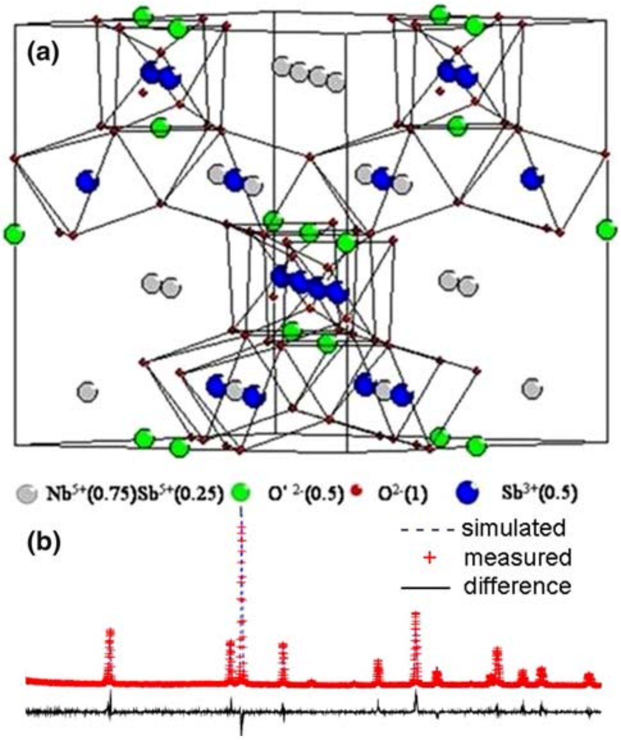

Fig. 2 The cell structure (**a**) for $Sb_3Nb_3O_{13}$ and the comparing between simulated and experimental XRD (**b**)

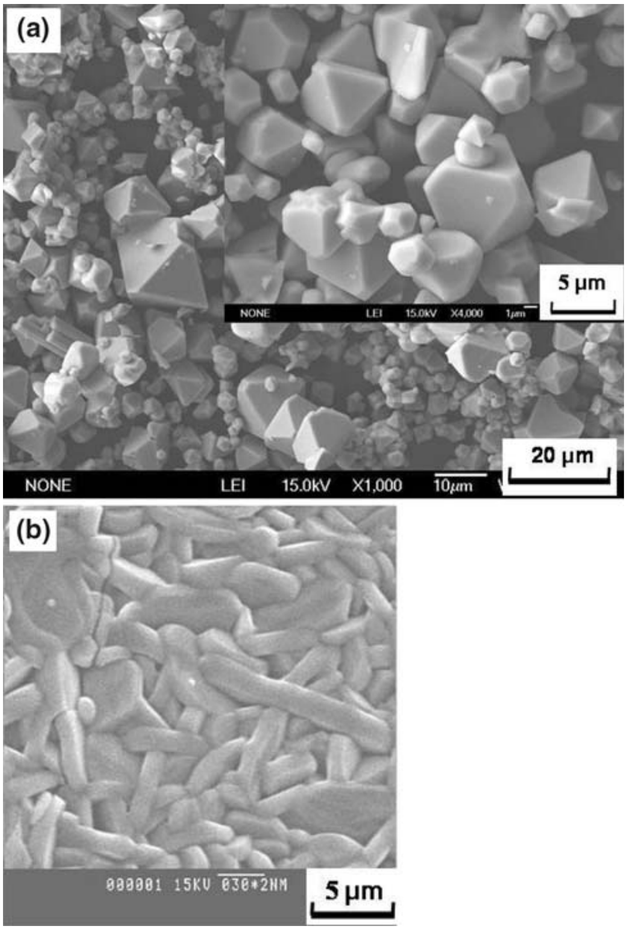

Fig. 3 SEM photos for powders (**a**) prepared by molten salt method and ceramics (**b**) sintered at 1,180 °C for 3 h

could be densified well at 1,180 °C for 3 h. The grains shape is like flake with thickness about 1 μm and length about 1–10 μm.

Figure 4 shows the dielectric properties of $Sb_3Nb_3O_{13}$ ceramics as a function of frequencies. As the frequency increasing from 100 Hz to 1 MHz, the permittivity decreased slowly from 33.3 to about 31.8 and the dielectric loss (tanδ) decreased from 0.03 to 0.005. The decrease of permittivity and dielectric loss could be generally explained as followings. As the frequency increasing, more and more polarizations could not respond to the changing of the electric field and the contribution to losses from conduction weakened.

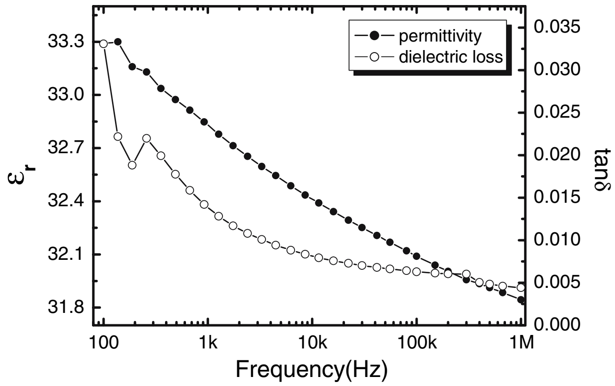

Fig. 4 Dielectric properties of $Sb_3Nb_3O_{13}$ ceramic as a function of frequency

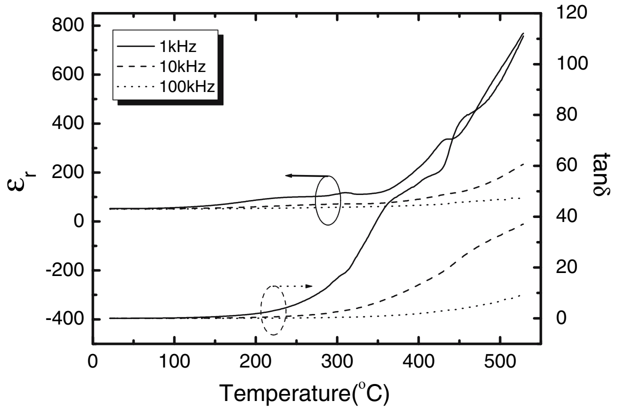

Fig. 5 Dielectric properties of $Sb_3Nb_3O_{13}$ ceramic as a function of temperature

Figure 5 shows the dielectric properties of $Sb_3Nb_3O_{13}$ ceramics as a function of temperatures between 25 °C and 550 °C. Both the permittivity and dielectric loss increased as the temperature increasing. At the three frequencies 1, 10 and 100 kHz, the change trends were similar to each other. And both of the permittivity and dielectric loss decreased with the frequency increasing with the same results as shown in Fig. 4, which means the leakage conductance dominates in low frequency range. The α_ε at 85 °C were +573, +179 and +72 ppm/°C, respectively at the frequencies 1, 10 and 100 kHz.

Conclusion

The powders of pure cubic phase of $Sb_3Nb_3O_{13}$ were obtained using molten salt method at 1,100 °C with incubation time of 3 h. The crystal grain showed an octahedral shape with size lying between 1 μm and 20 μm. The densified ceramic of pure $Sb_3Nb_3O_{13}$ could be got after being sintered at 1,180 °C for 3 h. The permittivity changed between 33.3 and 31.8 at frequency region 100 Hz~1 MHz with the dielectric loss (tanδ) lying between 0.03 and 0.005. And the temperature coefficient of permittivity at 100 kHz was +72 ppm/°C between 25 °C and 85 °C.

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References

1. Roth RS, Waring JL (1963) Am Mineral 48:1348
2. Ayyub P, Palkar VR, Multani MS, Vijayaraghavan R (1987) Ferroelectrics 76:93
3. Yoon KH, Cho YS, Lee DH, Kang DH (1993) J Am Ceram Soc 76:1373
4. Nagata K, Okazaki K (1985) Jpn J Appl Phys 24:812
5. Kong LB, Zhu W, Tan OK (1999) Ferroelectrics 230:281
6. Zhou D, Wang H, Yao X (2007) J Am Ceram Soc 90(1):327
7. Blanton TN, Barnes CL, Eichorst DJ (1993) Powder Diffract 8(3):188
8. Stewart D, Knop O, Ayasse C, Woodhams F (1972) Can J Chem 50:690