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Synthesis of Lead Metaniobate Template Particles with Needle-like Morphology by Molten Salt Synthesis Process

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Abstract

Lead metaniobate $PbNb_2O_6$ (PN) is a material with tungsten bronze type crystal structure. PN crystallizes in three different crystal structures, but only the metastable low temperature orthorhombic crystal structure shows ferroelectric properties. Due to its high Curie temperature PN is deemed suitable for high temperature piezoelectric transducer applications. However, most important problems with lead metaniobate are; difficulty in densification of PN ceramics through conventional methods, stabilization of the ferroelectric phase, and its low ferroelectric properties. In this study, lead metaniobate was produced as single crystal template particles with needle-like morphology using molten salt synthesis process to both stabilize the ferroelectric phase, as was as to increase the ferroelectric and piezoelectric properties through crystal anisotropy. Lead oxide (PbO) and niobium oxide (Nb_2O_5) were used as starting powders and molten salt synthesis process was applied in a sodium chloride – potassium chloride salts mixture. X-Ray diffraction analysis showed that heat treated powders have orthorhombic crystal structure. Scanning electron microscopy examinations proved that lead metaniobate particles were grown with a needle-like morphology. Heat treatment temperature was found to be critical in obtaining a pure PN phase and particles with higher aspect ratios. Lead metaniobate aspect ratios were found to depend on heat treatment temperature and determined to be 10x3µm, 13x2 µm & 15x1,5 µm for temperatures of 850°C, 950°C & 1050°C, respectively.

Ergimiş Tuz Sentezi Süreci ile İğnesel Morfolojide Kurşun Metaniyobat Şablon Parçacıklarının Sentezi

Özet

Kurşun metaniyobat $PbNb_2O_6$ (PN), tungsten bronz tipi kristal yapıya sahip bir malzemedir. PN üç farklı kristal yapıda kristalleşir, ancak yalnızca düşük sıcaklıktaki yarı kararlı ortorombik kristal yapı ferroelektrik özellikler gösterir. Yüksek Curie sıcaklığı nedeniyle PN, yüksek sıcaklık piezoelektrik dönüştürücü uygulamaları için ideal bir malzeme olarak kabul edilmektedir. Kurşun metaniobat ile ilgili en önemli sorunlar; PN seramiklerinin geleneksel yöntemlerle yoğunlaştırılmasındaki zorluk, ferroelektrik fazın stabilizasyonu ve düşük ferroelektrik özellikleri şeklinde sıralanabilir. Bu çalışmada, hem ferroelektrik fazı stabilize etmek hem de kristal anizotropi yoluyla ferroelektrik ve piezoelektrik özellikleri arttırmak için ergimiş tuz sentez yöntemi kullanılarak iğnesel morfolojiye sahip tek kristal kurşun metaniyobat şablon partiküller olarak elde edilmiştir. Başlangıç tozları olarak kurşun oksit (PbO) ve niyobyum oksit (Nb_2O_5) kullanılmış ve sodyum klorür-potasyum klorür tuz karışımında ergimiş tuz sentez işlemi uygulanmıştır. X-Işını kırınım analizi, ısıl işlem görmüş tozların ortorombik kristal yapıya sahip olduğunu göstermiştir. Taramalı elektron mikroskobu incelemeleri, kurşun metaniobat parçacıklarının iğnemsi bir morfoloji ile büyüdüğünü kanıtlamıştır. Saf bir PN fazı ve daha yüksek en-boy oranlarına sahip partiküller elde etmede ısıl işlem sıcaklığının kritik olduğu saptanmıştır. Kurşun metaniyobat tozlarının en-boy oranlarının ısıl işlem sıcaklıklarına bağlı olarak değiştiği gözlenmiştir ve 850°C, 950°C & 1050°C sıcaklıkları için sırasıyla 10x3 µm, 13x2 µm ve 15x1.5 µm olarak belirlenmiştir.

1. INTRODUCTION

Ferroelectricity and piezoelectricity in lead metaniobate was discovered by Goodman in 1953 as one of the first non-perovskite ferroelectrics.[1] The Curie temperature (T_c) was reported to be 570°C.[1,2] Above the Curie temperature, the paraelectric lead metaniobate $PbNb_2O_6$ (PN) phase assumes a tetragonal-tungsten–bronze type crystal structure[2-5], whereas below T_c, the ferroelectric phase was reported to assume orthorhombic symmetry with ferroelectric polarization along the [010] and [100] axes.[2] The general chemical formula for materials with tungsten bronze structure can be given as $[(A1)_2(A2)_4(C)_4][(B1)_2(B2)_8]O_{30}$, where the A site is generally occupied by mono-trivalent cations, and the B sites are occupied by Nb^{5+}, Ta^{5+} or V^{5+} atoms. Tungsten bronze structure contains corner sharing BO_6 octahedral creating three interstitial sites. The C site is the smallest interstice in this structure and it is usually empty, thus the general chemical formula of tungsten bronze structure can be rewritten as $A_6B_{10}O_{30}$ for materials with all the other sites filled.[6] Lead metaniobate is known to crystallize in two stable and one metastable crystal structure. These are low temperature rhombohedral, high temperature tetragonal and low temperature meta-stable orthorhombic structures. The tetragonal phase is stable above 1200°C and paraelectric rhombohedral phase is stable below 1200°C.[7] However, it was reported[8,9] that the low temperature orthorhombic metastable phase cannot be obtained through conventional ceramic processing. Either rapid heating the rhombohedral phase from low temperatures[8] or quenching the tetragonal structure from high temperatures[7,9] was required. Since only the metastable orthorhombic crystal structure shows piezoelectric and ferroelectric properties in lead metaniobate ceramics, it is imperative to obtain and stabilize this phase.[9-11] Ferroelectric lead metaniobate has a high Curie temperature (570°C) therefore it is suitable for high temperature transducer applications. Additionally, the electromechanical quality factor depends on crystallographic direction, indicating a high anisotropy. Low dielectric constant and low mechanical quality factor are other electrical properties of lead metaniobate which may be advantageous for electroacoustic applications.[12-13]

Dense ferroelectric PN ceramics were cited[8] to be difficult to obtain through conventional sintering techniques due to the appearance of secondary phases, exaggerated grain growth and resultant cracking that is related to the aforementioned phase transitions. Thus, special ceramic processing procedures[8-11] are required to obtain dense PN ceramics with ferroelectric character. However, an additional technique is also known to yield the ferroelectric phase with the metastable orthorhombic structure, namely, growth of anisometric single crystalline particles by molten salt synthesis process.[8] Anisometric single crystalline particles, by definition, have either one dimension that is much larger than the other two, as in the case of a needle-like or rod-like particles, or two dimensions that are much larger compared to the third one, as in the case of particles with plate-like morphology. The growth morphology is usually closely related to the crystal structure of the material. The anisometric growth morphologies arise due to the differences of growth rates along various crystallographic directions, or by the modification of growth conditions. These particles are specifically synthesized in an anisometric morphology for specialized applications. Inducing the formation of a crystallographically textured polycrystalline ceramic body through templated grain growth process is one such application, where anisometric single crystalline particles are indispensable.[10,14] Crystallographically textured ceramics were developed to enhance the piezoelectric and ferroelectric properties of PN ceramics by accessing the crystalline anisotropy.

This study reports the synthesis of lead metaniobate - PN ($PbNb_2O_6$) particles with needle-like morphology by molten salt synthesis (MSS) method for use in another novel anisotropic structure, namely a piezocomposite with oriented needle-like PN particles embedded in a polymer matrix.

In this study, effect of processing conditions with a focus on the heat treatment temperature on the morphology of lead metaniobate ceramic powders during their synthesis by molten salt synthesis was investigated. This process was chosen to obtain needle shaped single crystal lead metaniobate template particles with inherently ferroelectric properties.

2. MATERIALS & METHODS

Lead Oxide (PbO, 99.9% Alfa Aesar) and Niobium Oxide (Nb_2O_5, 99.9% Alfa Aesar) were used as starting powders. Starting powders were weighed in equimolar ratios, and then they were mixed with equal weight sodium chloride (NaCl, 99.5% Merck) and potassium chloride (KCl, 99.5% Merck) solid solution in isopropanol media. The mixture was ball milled for 48 hours and dried in an oven for 24 hours after milling. Dried powders were filled into alumina crucible and the cover of the crucible was sealed with calcined alumina. The powder mixture was heat treated at various temperatures for 1 hour and samples were named according to the following naming convention (PN1:750°C, PN2:850°C, PN3:950°C and PN4:1050°C). After heat treatment, the mixture was washed with hot DI water and salt was separated from the mixture by dissolving. The washing step was repeated several times, after which the powders were dried and prepared for structural analysis. Crystal phases of ceramic powders were determined using on X-Ray Diffractometer (XRD; Rigaku DMax 2200, Japan). The microstructural features and average dimensions of the particles were determined using scanning electron microscopy (SEM-Philips FEI XL 30 SFEG, USA).

3. RESULTS AND DISCUSSION

3.1. Phase Analyses

X-Ray Diffraction (XRD) analyses were done for all of the lead metaniobate ceramic powders obtained by the molten salt synthesis process. The XRD patterns are presented in Figure 1. PN1 sample has secondary phases. The XRD peaks were matched with two different phases: namely lead metaniobate ($PbNb_2O_6$) - PN (JCPDS Card #: 00-050-0122) and sodium niobate ($Na_2Nb_4O_{11}$) - NN (JCPDS Card #: 00-044-0060). This was believed to be due to the Sodium (Na) from the NaCl salt reacting with the Niobium source (Nb_2O_5) at low temperatures. The PN2, PN3, and PN4 ceramic powders, on the other hand were found to have crystallized in the single lead metaniobate phase within the detection limits of the XRD equipment. The XRD peaks were indexed according to the orthorhombic symmetry.

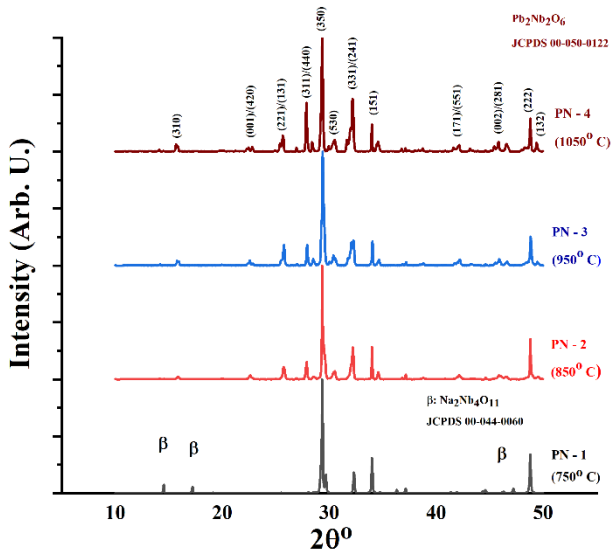

Figure 1. XRD patterns of lead metaniobate powders synthesized at 750°C, 850°C, 950°C, 1050°C for 1 hour.

3.2. Microstructural Features

Scanning electron microscopy of the PN particles were undertaken to determine the microstructural features of the particles synthesized at different temperatures. The SEM image of PN1 given in Figure 2a indicated the presence of particles with two distinctly different morphologies.

Particles marked with red rings showed the initial growth of rod-like lead metaniobate particles. Single crystals with tetragonal tungsten bronze (TTB) structure are known to grow in needle-like or rod-like morphology with c-axis of the tetragonal structure along the long axis of needles.[15] Our previous studies have supported this finding where we have obtained needle-like single crystal particles in the $KSr_2Nb_5O_{15}$ (KSN) based TTB system[16] and rod-like particles in the $Ba_2NaNb_5O_{15}$ (BNN) based TTB system.[17] But the aspect ratios in Figure 2(a) for the PN particles clearly showed that particles have not grown enough in length. This was thought be due to the insufficient driving force for crystal growth at low temperatures (PN1: 750°C). The presence of small, sub-micron particles with equaxial, near-spherical morphology on the larger rod-like particles, on the other hand, was a proof that the growth process proceeded through Oswald ripening, where larger particles grow at the expense of smaller particles due to the drastic differences between the surface energies of large and small particles. According to the Ostwald–Freundlich equation given in Eq (1):[18]

$$S = S_0 exp\frac{4\gamma_{SL}V_m}{RTd} \quad (1)$$

solubility (S) of a particle with size (d) depends on the solid-liquid interface energy (γ_{SL}), molar volume (V_m) of the solid, gas constant (R), temperature (T) and solubility of a flat surface (S_0). Thus, it is expected that smaller particles will have a higher solubility compared to the larger ones, and that larger particles will grow by the sacrificial dissolution of smaller particles and their recrystallization on the surfaces of the larger particles.

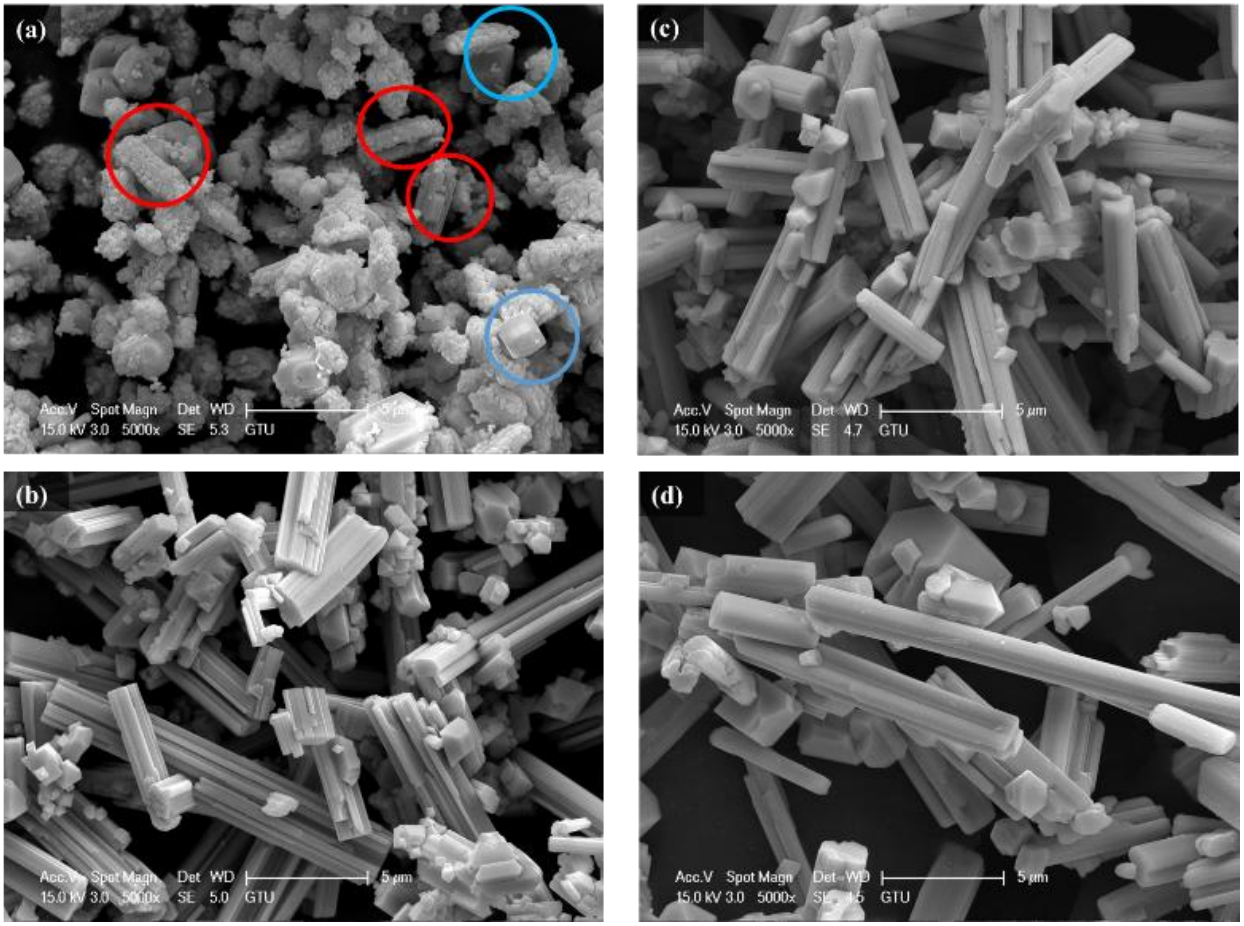

Figure 2. Scanning electron micrographs of lead metaniobate powders synthesized at (a) 750°C, (b) 850°C, (c) 950°C, (d) 1050°C for 1 hour.

Particles marked with blue rings, on the other hand, were found to have a cubic-like morphology. Considering the observation of a secondary phase in XRD analysis belonging to sodium niobate ($NaNbO_3$) particles, this cubic morphology was expected, because materials with cubic perovskite structure tend to grow with a cubic morphology under equilibrium conditions.

Increasing the synthesis temperature to 850°C was found to cause a clear formation of particles with needle-like morphology, as shown in Figure 2(b). Considering the XRD and SEM study together, this temperature was thought to be the relatively lowest level to synthesize phase-pure PN with needle-like morphology. Further increase in the synthesis temperature, especially to 1050°C, was found to lead to a slight increase in the aspect ratio of the particles. The morphology of the PN particles synthesized in this study did not have a smooth side surface with a cross-section of simple geometrical shape, but instead they were observed to have a step-wise surface and complex cross-sections, as was previously reported by Zhao et al.[19] and was also observed by our group in the MSS growth of needle-like KSN particles.[16,20] This step-wise morphology was reported to have arisen due to two-dimensional nucleation starting at crystal surfaces centers or corners.[19]

4. CONCLUSIONS

Lead metaniobate ceramic particles with needle-like morphology were successfully prepared using molten salt synthesis method. 750°C was found to be insufficient to obtain pure PN phase with NN appearing as a secondary phase. Increasing synthesis temperature up to 1050°C was determined to be not only enough for synthesis of pure PN phase, but it was also found to lead to an increase in the aspect ratios of the particles. A step-wise growth behavior was observed at high temperatures. Lead metaniobate aspect ratios were found to depend on heat treatment temperature and determined to be 10x3µm, 13x2 µm & 15x1,5 µm for temperatures of 850°C, 950°C & 1050°C, respectively.

- Lead metaniobate particles with needle-like morphology were synthesized using MSS method.
- Increasing synthesis temperature was determined to be sufficient for synthesis of pure PN phase and led to an increase in the aspect ratios of the particles.

Competing Interests

The authors declare no competing interests.

Author Contributions

Author H.A. Sarı conducted the experimental work. Author S. Alkoy conceived and supervised the project and evaluated the results.

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