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Investigations of $BaFe_{0.5}Nb_{0.5}O_3$ nano powders prepared by a low temperature aqueous synthesis and resulting ceramics

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ABSTRACT

A facile method to prepare nanoscaled $BaFe_{0.5}Nb_{0.5}O_3$ via synthesis in boiling NaOH solution is described herein. The nano-crystalline powder has a high specific surface area of 55 $m^2\,g^{-1}$ and a crystallite size of 15 nm. The as-prepared powder does not show any significant crystallite growth up to 700 °C. The activation energy of the crystallite growth process was calculated as 590 $kJ\,mol^{-1}$. Dense ceramics can be obtained either after sintering at 1200 °C for 1 h or after two-step sintering at 1000 °C for 10 h. The average grain sizes of ceramic bodies can be tuned between 0.23 μm and 12 μm. The thermal expansion coefficient was determined as $11.4(3)\cdot 10^{-6}\,K^{-1}$. The optical band gap varies between 2.90(5) and 2.63(3) eV. Magnetic measurements gave a Néel temperature of 20 K. Depending on the sintering regime, the ceramic samples reach permittivity values between 2800 and 137,000 at RT and 1 kHz.

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1. Introduction

Perovskite materials with high relative permittivities (dielectric constants) are of interest because of their potential applications in advanced technology e.g. as memory devices, sensors, and capacitors [1–4]. Many of the corresponding materials, such as $Pb(Ti,Zr)O_3$ contain lead, therefore it is of importance to examine more eco-friendly materials like $BaFe_{0.5}Nb_{0.5}O_3$ that shows high dielectric constants over a wide temperature and frequency range with dielectric relaxation [5]. Patel et al. [6] reported that grain boundary effects are causal for the high permittivity values, whereas investigations by Wang et al. [7] suggest an oxygen defect induced dielectric behaviour. A possible ferroelectric nature of $BaFe_{0.5}Nb_{0.5}O_3$ is discussed controversially. Several authors suggest that $BaFe_{0.5}Nb_{0.5}O_3$ is a relaxor ferroelectric material [8–13], whereas other investigations show that $BaFe_{0.5}Nb_{0.5}O_3$ is a non-ferroelectric [6,7,14–17]. Additionally, structural investigations by Tezuka et al. [18], Galasso and Darby [19] as well as Bhagat and Prasad [20] point to a non-ferroelectric characteristic. In addition to its dielectric properties, $BaFe_{0.5}Nb_{0.5}O_3$ is an antiferromagnet with a Néel temperature of about 25 K [18] and also shows interesting catalytic activities. Voorhoeve et al. [21] used $BaFe_{0.5}Nb_{0.5}O_3$ for both the catalytic reduction of NO and the oxidation of CO. Recently, Pan et al. [22] and Chung et al. [23] reported on the dry reforming of methane with CO_2 to form syngas in the presence of $BaFe_{0.5}Nb_{0.5}O_3$. Usually $BaFe_{0.5}Nb_{0.5}O_3$ is synthesized by the conventional mixed-oxide method leading to coarse-grained powders [13,15,17,18,24–27]. In addition, fine-grained powders for ceramics with small and tuneable grain sizes have been prepared. For this purpose, several wet-chemical syntheses have been reported, such as sol-gel and co-precipitate routes [6,12,28]. A microwave assisted synthesis was developed by Charoenthai et al. [29]. A nanoscaled $BaFe_{0.5}Nb_{0.5}O_3$ powder via a biosynthesis using Lactobacillus was reported by Jha et al. [30], which surprisingly showed a ferromagnetic behaviour.

The aim of this paper is to describe a fast and facile synthesis route for obtaining nanoscaled $BaFe_{0.5}Nb_{0.5}O_3$ with a high specific surface area. The reaction was carried out in boiling aqueous NaOH solution and the influence of the NaOH concentration on the particle growth kinetic was investigated. Furthermore, the sintering behaviour, phase evolution and microstructure of resulting ceramic bodies have been studied. Magnetic and dielectric measurements were carried out on samples obtained from different sintering regimes and the thermal expansion coefficient and the optical band gap were determined with respect to the particle size.

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2. Experimental

2.1. Material preparation

$BaFe_{0.5}Nb_{0.5}O_3$ samples were prepared by reaction of Ba^{2+}-, Fe^{3+}-, and Nb^{5+}-reactants in boiling NaOH solutions with different concentrations. The reactions were carried out in PFA (perfluoroalkoxycoplomyer) round bottom flasks under argon atmosphere to avoid the formation of carbonates and silicon contaminations from glass.

$NbCl_5$ (0.01 mol, Alfa Aesar) was dissolved in 15 ml 2-methoxyethanol yielding a clear solution. In a separate solution $FeCl_3$ (0.01 mol, Alfa Aesar) and $BaCl_2{\cdot}2H_2O$ (0.02 mol, Fluka) were dissolved in 20 ml deionized water. 150 ml of an 8 M NaOH solution was heated up to about 70 °C and both the Nb- and the Fe/Ba-solutions were added slowly. The unified solution was refluxed for 5 h under vigorous stirring. Afterwards the resulting orange-ochre precipitate was filtered, washed with deionized water several times until no chloride ions were detectable and the pH value of the filtrate was about 7. The washed powder was dried at 120 °C for 2 h in air.

The synthesis was also carried out in 2 M, 6 M, 10 M, and 14 M NaOH solutions. The resulting as-prepared powders are donated as BFN-2M, BFN-6M, BFN-8M, BFN-10M, and BFN-14M in the following.

To obtain ceramic bodies, the as-prepared powder BFN-8M was mixed with 5 wt% of a saturated aqueous polyvinyl alcohol (PVA) solution as pressing aid and was uniaxially pressed (50 MPa) into pellets (green density 2.6 g cm^{-3}). These pellets were placed on a ZrO_2 fibre mat and sintered under conditions specified below.

2.2. Characterization

X-ray powder diffraction patterns were collected at room temperature on a *Bruker D8-Advance* diffractometer, equipped with a one-dimensional silicon strip detector (LynxEye^{TM}) and operating with Cu-K_α radiation. A counting time of 1 s per data point and a step size of 0.01° were used. Crystallite size and the strain parameter were determined from the XRD line broadening (integral peak breadth) using the Scherrer and Wilson equation (software suite WinXPOW [31]). Dilatometric investigations were performed in flowing synthetic air (50 ml min^{-1}) in a *Setaram* TMA 92-16.18 dilatometer. Scanning electron microscope images were recorded with a *Phenom* ProX SEM in backscattered electron mode (BSE). TEM images were recorded with a *FEI* Titan 80–300 using an acceleration voltage of 300 kV. For magnetic measurements a *Quantum Design* PPMS 9 was used. Hysteresis loops were obtained with magnetic field cycling between −90 and +90 kOe. In addition, the temperature dependent magnetic moments were measured in the temperature range of 3–300 K under field-cooled (FC) and zero-field-cooled (ZFC) conditions. An Impedance Analyzer 4192A (*Hewlett Packard*) was used for permittivity measurements up to 10 MHz. Gold electrodes were sputtered onto the ceramic bodies in a *Cressington* Sputter Coater 108auto. Diffuse reflectance spectra were recorded at room temperature using a *Perkin Elmer* UV–Vis spectrometer Lambda 19. $BaSO_4$ was used as white standard.

3. Results and discussion

3.1. Synthesis and powder characterization

The reactions were carried out in boiling NaOH solutions with various molarities (2, 6, 8, 10, and 14 M). The patterns of the as-prepared powders show reflections of $BaFe_{0.5}Nb_{0.5}O_3$ and traces of $BaCO_3$ (Fig. S1, Supporting information). The volume-weighted average crystallite sizes (size of a coherent scattering domain) of the as-prepared powders are 15 – 17 nm and do not differ significantly between the various samples. Additionally, the specific surface areas of the as-prepared powders are larger than 50 $m^2\,g^{-1}$ and do not vary significantly. Therefore, the NaOH concentration during the synthesis process has no significant influence on neither the crystallite size nor the specific surface area of the as-prepared powders (as illustrated in Fig. 1). However, an increasing NaOH concentration causes an increase of the strain parameter as seen from graph b in Fig. 1. After calcination of the as-prepared powders at 1000 °C for 2 h the XRD patterns show only reflections of the perovskite phase (Fig. S1, Supporting information). Only the samples prepared with 2 M and 6 M NaOH solution show a weak peak at $2\theta \approx 34°$ from traces of $BaFe_{12}O_{19}$. The crystallite size from the XRD line broadening after heating at 1000 °C rises with increasing NaOH concentration and accounts to 29 nm for sample BFN-2M and increases to 108 nm for BFN-14M (Fig. 1, Graph d). The reason for the increasing crystallite sizes most likely lies in the increase of the strain parameter in the as-prepared powders with rising NaOH concentration. The strain parameter reflects the amount of crystal lattice defects, which promote particle growth. As a conclusion a NaOH concentration less than 8 mol l^{-1} results in samples with trace impurities after calcination at 1000 °C, while a NaOH concentration above 8 mol l^{-1} leads to phase pure samples with a considerable increase of the particle size after thermal treatment, caused by the larger amounts of lattice defects in the as-prepared powders.

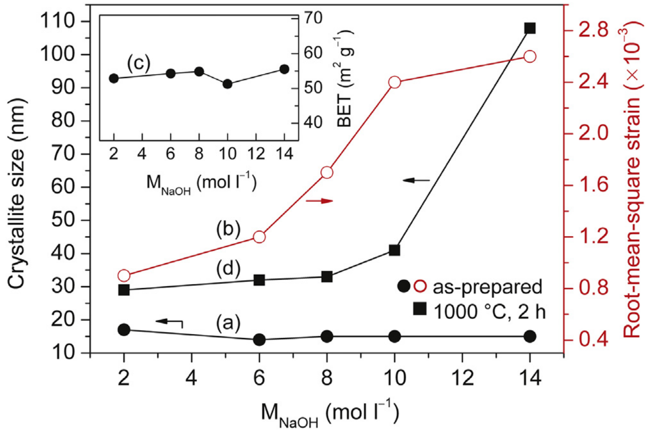

Fig. 1. Development of (a) volume-weighted average crystallite size, (b) root-mean-square strain, and (c) specific surface area of as-prepared powders depending on the initial NaOH concentration. Graph (d) shows the crystallite size of the powders after heating at 1000 °C for 2 h versus NaOH concentration.

To obtain phase pure samples with a reduced particle growth during thermal treatment we use the as-prepared powder BFN-8M for further investigations. The as-prepared powder BFN-8M has a specific surface area of 54.8 $m^2\,g^{-1}$, corresponding to an equivalent particle size of 17 nm. The volume-weighted average crystallite size was calculated to be 15 nm and the root-mean-square strain was found to be $1.7{\cdot}10^{-3}$ from the XRD line broadening. TEM images show spherical particles in the range between 9 and 25 nm as seen from Fig. 2. XRD patterns of the powder BFN-8M after thermal treatment at various temperatures for 2 h is shown in Fig. 3. The small amount of $BaCO_3$ disappears after calcination above 800 °C and the peak widths decrease with rising temperature.

Fig. 4 shows the evolution of the crystallite size depending on the thermal treatment. Above 700 °C the crystallite size increases with rising temperature up to 57 nm, whereas the strain parameter decreases to $0.24{\cdot}10^{-3}$ at 1100 °C. Remarkably, we do not observe any significant crystallite growth up to 700 °C.

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