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Second-harmonic generation in nano-structured $LiTaO_3$- and $LiNbO_3$-xerogels with randomly oriented ferroelectric grains

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ABSTRACT

Second-harmonic generation (SHG) in polycrystalline and porous $LiTaO_3$- and $LiNbO_3$-xerogels is reported. The ferroelectric xerogels are synthesized via the sol–gel method and sintered at different temperatures of 700 °C, 900 °C, 1100 °C and 1150 °C, respectively for 48 h. The nano-structured materials (grain size of 250–1760 nm) are characterized by scanning electron microscopy, thermogravimetry, X-ray diffraction and piezoresponse force microscopy. The ferroelectricity of the grains is determined with piezoresponse force microscopy measurements. While the SHG efficiency grows with increasing grain size, the SHG output energy increases with a higher grade of stoichiometry and increases quadratically as a function of the input energy.

1. Introduction

Disordered materials with nonlinear optical properties receive currently much attention due to their potential for applications, e.g., second-harmonic generation (SHG) [1] or difference frequency mixing [2,3], without phase matching conditions present only in single crystals. To combine the potential of random systems with nonlinear optical properties, materials with high nonlinear optical coefficients have to be selected. Suitable materials for this challenge are lithiumniobate ($LiNbO_3$) and lithiumtantalate ($LiTaO_3$) due to their large nonlinear optical coefficients [4,5]. In this contribution we report on the preparation of $LiNbO_3$- and $LiTaO_3$-xerogels via the sol–gel procedure. Xerogels are solid materials with a three dimensional network of colloidal particles, derived from a dried gel body [6,7]. It is characteristic for xerogels to exhibit a high porosity around 50% and very small pores (1–10 nm) [8]. The pore and grain sizes can be adjusted in a controlled manner by varying the pH-value, the aging time and medium, the drying conditions, and the sintering temperature. The advantage of the sol–gel technique is the opportunity to design materials by varying these parameters.

We synthesized porous lithiumtantalate and lithiumniobate xerogels to study the influence of grain size and composition ratio of Li:Ta or Li:Nb on the SHG efficiency. The $LiTaO_3$- and $LiNbO_3$-xerogels prepared consist of a large number of single-crystalline grains with random orientation of the polarization, which was investigated by piezoresponse force microscopy.

2. Experimental section

2.1. Material preparation

$LiTaO_3$- and $LiNbO_3$-xerogels were prepared using the sol–gel method [9–11]. As starting materials for stoichiometric $LiTaO_3$ gels we used 0.5 g lithiumethoxide powder (Sigma Aldrich) and 3.9 g liquid tantalumethoxide (Fluka). In order to prepare a complex alcoxide solution with a ratio of Li:Ta = 1:1 we added 1 g ethanol (VWR), 5.75 g acetic acid (99.8%) (Sigma Aldrich) and stirred the solution for 1 h in a argon glove box. After 24 h the liquid formed a wet gel at 50 °C and was dried at the same conditions for 2 weeks. The resulting xerogels were sintered at 700 °C, 900 °C, 1100 °C, 1150 °C for 48 h under atmospheric conditions. The furnace was heated up to the final temperature with a heating rate of 0.25 K/min for LTO1, LTO2 and 5 K/min for LTO3–LTO5. The $LiNbO_3$-xerogels were prepared in the same manner as the $LiTaO_3$-xerogels, but lithiumethoxide and niobiumethoxide were

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Table 1
Chemicals and their amount used for the preparation of $LiTaO_3$ and $LiNbO_3$ gels. EtOH stands for ethanol and HAc stands for acetic acid.

No.	LiO–C_2H_5 (g)	TaO_5–$(C_2H_5)_5$ (g)	HAc (g)	EtOH (g)
LTO1	0.5	3.9	5.75	1
LTO2	0.21	2.5	2.46	1.5
LTO3	0.5	3.9	5.75	1
LTO4	0.5	3.9	5.75	1
LTO5	0.5	3.9	5.75	1
No.	LiO–C_2H_5 (g)	NbO_5O–$(C_2H_5)_5$ (g)	HAc (g)	Ethanol (g)
LNO1	0.5	3.06	5.75	1
LNO2	0.07	0.8	0.79	0.14
LNO3	0.5	3.06	5.75	1

Table 2
Stoichiometric ratio between Li and Ta respectively Nb and sinter temperature used for the materials prepared.

No.	Ratio Li:Ta	T (°C)
LTO1	1:1	700
LTO2	1:1.5	700
LTO3	1:1	900
LTO4 1	1:1	1100
LTO5	1:1	1150
No.	Ratio Li:Nb	T (°C)
LNO1	1:1	700
LNO2	1:1.9	700
LNO3	1:1	900

used as precursors. Non-stoichiometric xerogels were prepared by adding a higher amount of tantal- or niobiumethoxide to the solutions, as listed in detail in Tables 1 and 2. All xerogels prepared had a thickness of 0.4 mm.

2.2. Material characterization

The dried and sintered xerogels were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetry (TGA), and piezoresponse force microscopy (PFM) [12]. The sample surfaces were analyzed by using a scanning electron microscope of type Leo 1530 VP to evaluate the grain size and shape. The SEM pictures in Fig. 1 show the microstructure of $LiTaO_3$ (LTO1 in Table 1) and $LiNbO_3$ (LNO1) xerogels. All grains exhibit a polyhedral shape. In both samples the grains have built sinter necks at their point of contact. These grains enclose pores. 42% of the pores in LTO1 are larger than 80 nm in diameter, 32% are between 20 nm and 80 nm, and 36% are smaller than 20 nm. For $LiNbO_3$-xerogels (LNO1) 10% of the pores exhibit a diameter over 80 nm, 40% are between 10 nm and 80 nm, and 50% are smaller than 10 nm. The specific surfaces are 4 m^2/g for LTO1 and 5 m^2/g for LNO1. The size of individual grains was determined from the SEM pictures by the analySIS 5.0 software [13] by marking all individual grains and measuring their area equivalent circle diameter. The grain size distribution of LTO1 exhibits a maximum at about 250 nm and the distribution is symmetric between 100 nm and 400 nm (Fig. 1a). The $LiNbO_3$ (LNO1) grain distribution is slightly asymmetric with a maximum between 250 nm and 300 nm and a certain over representation of smaller grains (Fig. 1b). In both cases the grain sizes are around a factor of 10 smaller than the coherence length for SHG known from the corresponding single crystalline materials. The coherence length for SHG of 1.06 μm in $LiTaO_3$ is about 3.9 μm and in $LiNbO_3$ 2.9 μm [22,23].

As can be inferred from Table 3 the grain sizes can be adjusted by varying the sintering temperature. Increasing the sintering temperature leads to a growth of the grains. Notably the $LiTaO_3$ grains

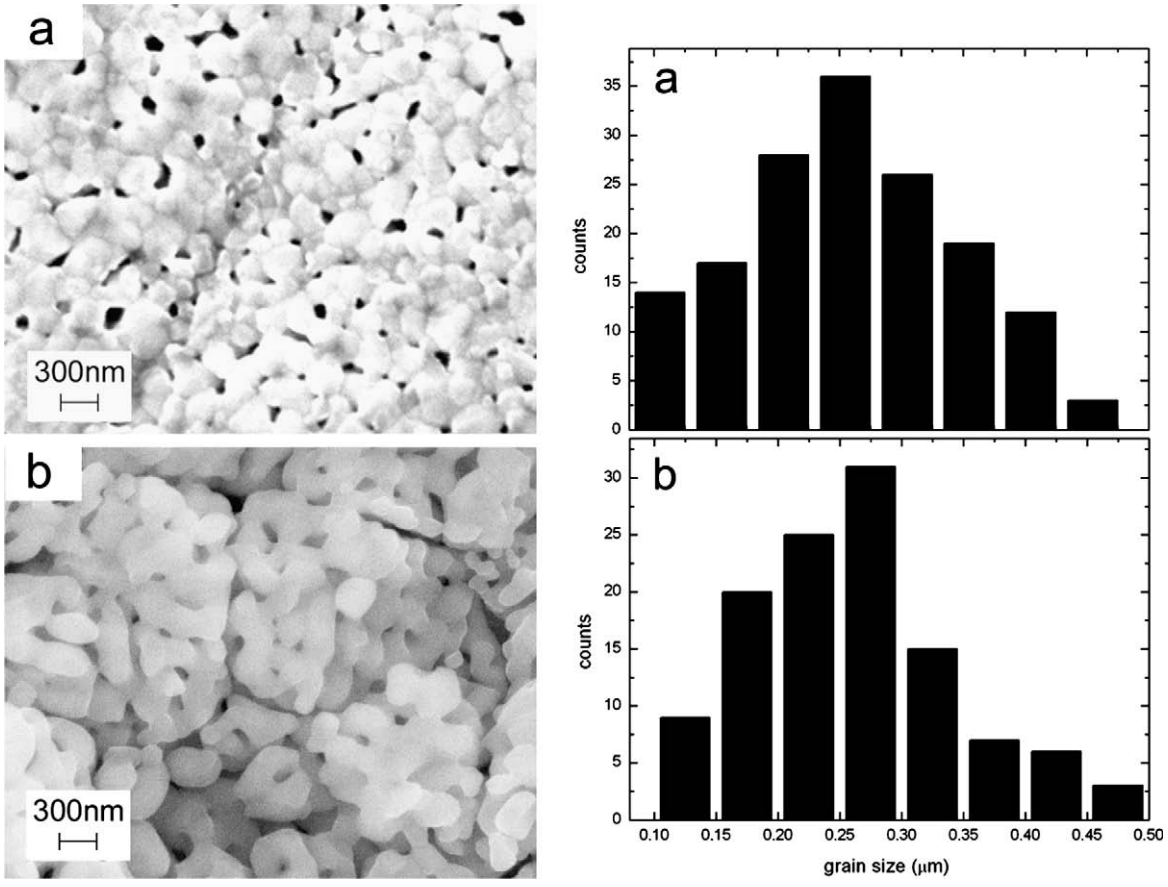

Fig. 1. SEM images (left) and grain size distribution (right) of the stoichiometric xerogels LTO1 (a) and LNO1 (b) (see Table 1).