



# Influence of antimony substitution on spontaneous strain and thermodynamic stability of lanthanum orthoniobate

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## Abstract

Analysis of the influence of antimony substitution on the temperature dependence of unit cell distortion in lanthanum orthoniobate has been performed. The values of spontaneous strain and Landau order parameter for three different antimony contents have been calculated. The monoclinic–tetragonal phase transition occurring for antimony substituted lanthanum orthoniobate was found to be of the second order. High temperature oxide melt solution calorimetry has shown that antimony substitution has little influence on the stability of the monoclinic phase. The average value of enthalpy of formation of antimony substituted lanthanum orthoniobate with fergusonite structure is  $-132.0 \pm 0.8$  kJ/mol, and that of scheelite structure is  $-126.4 \pm 1.5$  kJ/mol, implying greater stability for the former polymorph.

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## 1. Introduction

Lanthanide orthoniobates,  $\text{LnNb}^{5+}\text{O}_4$  (Ln=La–Yb), are interesting materials with properties depending on the lanthanide element. They are potentially technologically interesting because of their wide spectrum of possible use as ferroelectrics, phosphors and laser materials. These materials have also been proposed as potential ionic conductors, especially while acceptor-doped on the lanthanide site [1–3]. They exist in a number of polymorphs of different structure type and arrangement of  $\text{NbO}_x$  polyhedra. The high temperature polymorph of lanthanum niobate with the scheelite structure contains isolated  $\text{NbO}_4$  tetrahedra. In the low temperature fergusonite phase, the edge-sharing  $\text{NbO}_x$  polyhedra have the shape of hemidodecahedra [4–6]. The phase transition from the high temperature tetragonal scheelite structure (space group  $I4_1/a$ ) to the low temperature monoclinic fergusonite (space group  $I2/c$ ) occurs at approximately 500 °C in the undoped lanthanum niobate [7]. Substitution of niobium by tantalum leads

to an increase [8] whereas substitution by vanadium or antimony results in a decrease of the transition temperature [9,10]. On the other hand, substitutions of lanthanum by calcium or magnesium, with appropriate charge balancing by oxygen vacancies do not influence the transition temperature significantly [11–13]. For undoped material and the Ca or Mg doped material, this transition is of the second order. In the tetragonal to monoclinic phase transition the symmetry is reduced, therefore in the monoclinic phase two energetically equivalent but orientationally different states form. Consequently, in the monoclinic phase a spontaneous strain forms. An analysis of the spontaneous strain and Landau order parameter for magnesium doped lanthanum orthoniobate has been presented recently [13]. The same approach has been applied in the current study to analyze the antimony substituted material.

Several works showing the influence of isovalent doping on the niobium site on the phase transition have been published [8–10]. However, there are no reports related to the effect of doping and structural phase transition on the thermochemical properties of the compounds.

In this work, spontaneous strain and Landau order parameter of antimony substituted lanthanum orthoniobate have been

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analyzed. In addition, the influence of antimony substitution on the thermodynamic stability of lanthanum orthoniobate has been investigated by drop solution calorimetry.

## 2. Experimental methods

Powders of  $\text{LaNb}_{1-x}\text{Sb}_x\text{O}_4$ , where  $x=0.05\text{--}0.30$ , were prepared by a standard solid state synthesis method using  $\text{La}_2\text{O}_3$  (Alfa-Aesar, Germany, 99.9% preheated at  $900^\circ\text{C}$ ),  $\text{Nb}_2\text{O}_5$  (Alfa Aesar, Germany, 99.9985%) and  $\text{Sb}_2\text{O}_3$  (POCH, Poland, 99%) as reagents. Stoichiometric amounts of reagents were ball milled in a zirconia milling cup with zirconia balls for 12 h in ethanol. No contamination of the sample by zirconia was detected. The powders were uniaxially pressed into pellets and calcined at  $1200^\circ\text{C}$  for 8 h. Following the calcination the samples were again milled and pressed. The pellets were then sintered at  $1400^\circ\text{C}$  for 8 h. The sintered samples were ground in an agate mortar and examined by powder X-ray diffraction using a Phillips X'Pert Pro MPD with  $\text{CuK}\alpha$  radiation. High temperature XRD analysis was carried out between  $50$  and  $700^\circ\text{C}$ . Panalytical High Score Plus software was used to perform Rietveld analysis. As an initial point of the analysis, unit cell parameters of the Fergusonite (space group no. 15,  $I2/c$ ) [14] and Scheelite (space group no. 88,  $I4_1/a$ ) [15] crystal structures of  $\text{LaNbO}_4$  were used. The pseudo-Voigt profile function was applied. The calculations of spontaneous strain and Landau order parameter have been done on the theoretical basis explained in our previous research on doped lanthanum orthoniobates [13].

Differential scanning calorimetry (DSC) and thermogravimetry (TGA) were conducted in a Setaram LABSYS evo thermoanalyzer (Setaram, Cailure, France) using lidded platinum crucibles with heating/cooling rate of  $10^\circ/\text{min}$  up to

$1000^\circ\text{C}$ . The enthalpies of formation from binary oxides of the investigated compounds were measured by high temperature oxide melt drop solution calorimetry in a Tian-Calvet type twin calorimeter Setaram AlexSys [16,17]. Pressed pellets weighing 3.8 to 5.7 mg of the initially powdered samples were dropped from room temperature ( $25^\circ\text{C}$ ) into a molten sodium molybdate ( $3\text{Na}_2\text{O}\text{--}4\text{MoO}_3$ ) solvent held in a platinum crucible in the calorimeter at  $800^\circ\text{C}$ . Oxygen was bubbled through the solvent at 5 ml/min. and flushed over the solvent at 60 ml/min. The calorimeter was calibrated using the heat content of corundum. The methodology is the same as used previously for sodium niobate [18].

## 3. Results and discussion

Fig. 1 presents the high-temperature X-ray diffraction (HT-XRD) data collected up to the temperature of the phase transition. At room temperature all the reflections can be indexed in the monoclinic fergusonite-type structure ( $I2/c$ ), whereas above a certain temperature depending on the substitution level, ( $100^\circ\text{C}$  for 30 mol% and  $400^\circ\text{C}$  for 5 mol% substitution), the patterns correspond to the tetragonal body-centered scheelite structure ( $I4_1/a$ ). The gradual change from the fergusonite to the scheelite structure confirms previous results for lanthanum orthoniobates [11–13]. Fig. 2 presents the temperature evolution of unit cell parameters, obtained by Rietveld refinement of HT-XRD patterns for samples with different antimony content for the purpose of our previous research [10]. For all investigated samples, a reorientation of the unit cell characteristic for  $\text{LaNbO}_4$  occurs, in which the  $a$  and  $c$  parameters of the monoclinic unit cell evolve to the  $a$  parameter of the tetragonal structure. In addition, the  $b$  parameter evolves to the parameter  $c$  in the tetragonal structure and the monoclinic angle decreases to  $90^\circ$  with temperature

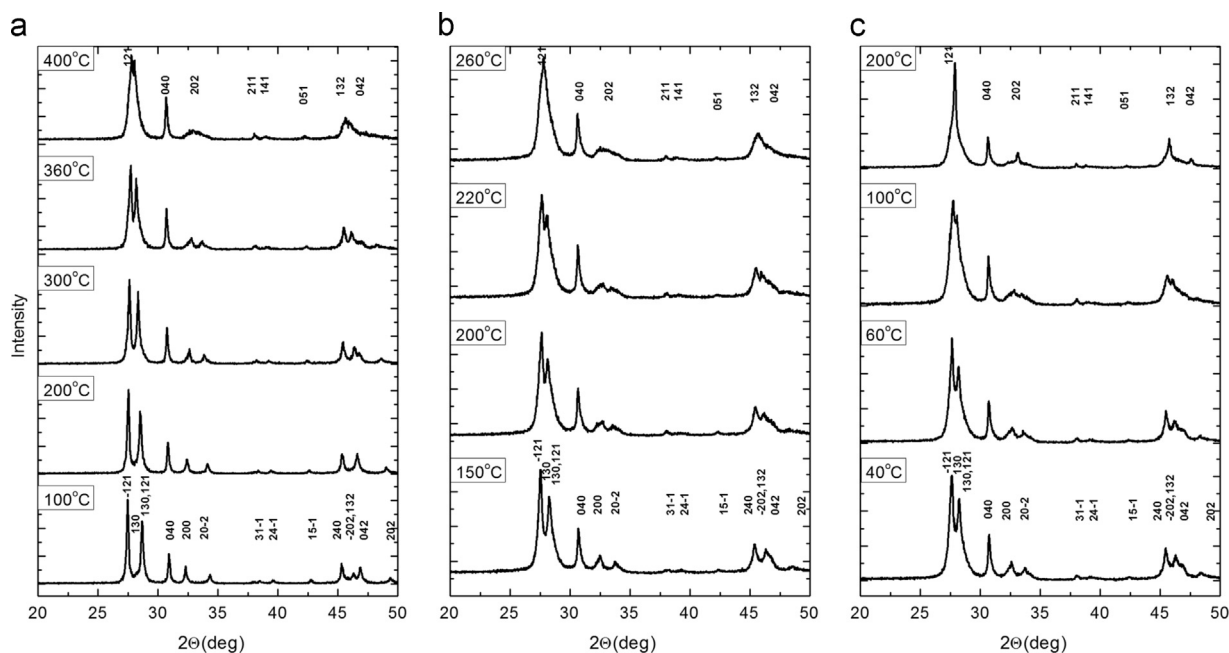


Fig. 1. High temperature X-ray diffractograms of samples with (a) 5, (b) 15 and (c) 25 mol%. The Miller indices for fergusonite ( $I2/c$ ) – bottom spectra and scheelite ( $I4_1/a$ ) – upper spectra phases of lanthanum orthoniobate are given.

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