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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 ± 0.8 kJ/mol, and that of scheelite structure is 126.4 ± 1.5 kJ/mol, implying greater stability for the former polymorph.

Keywords: Lanthanum orthoniobate; Spontaneous strain; Landau order parameter; Enthalpy of formation

1. Introduction

Lanthanide orthoniobates, $LnNb^{5+}O_4$ (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 NbO_x polyhedra. The high temperature polymorph of lanthanum niobate with the scheelite structure contains isolated NbO_4 tetrahedra. In the low temperature fergusonite phase, the edge-sharing 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 $LaNb_{1-x}Sb_xO_4$, where x=0.05–0.30, were prepared by a standard solid state synthesis method using La_2O_3 (Alfa-Aesar, Germany, 99.9% preheated at 900 °C), Nb_2O_5 (Alfa Aesar, Germany, 99.9985%) and Sb_2O_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 °C for 8 h. Following the calcination the samples were again milled and pressed. The pellets were then sintered at 1400 °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 CuKα radiation. High temperature XRD analysis was carried out between 50 and 700 °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, *I*2/*c*) [14] and Scheelite (space group no. 88, $I4_1/a$) [15] crystal structures of $LaNbO_4$ 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°/min up to 1000 °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 °C) into a molten sodium molybdate ($3Na_2O–4MoO_3$) solvent held in a platinum crucible in the calorimeter at 800 °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 (*I*2/*c*), whereas above a certain temperature depending on the substitution level, (100 °C for 30 mol% and 400 °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 $LaNbO_4$ 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° with temperature

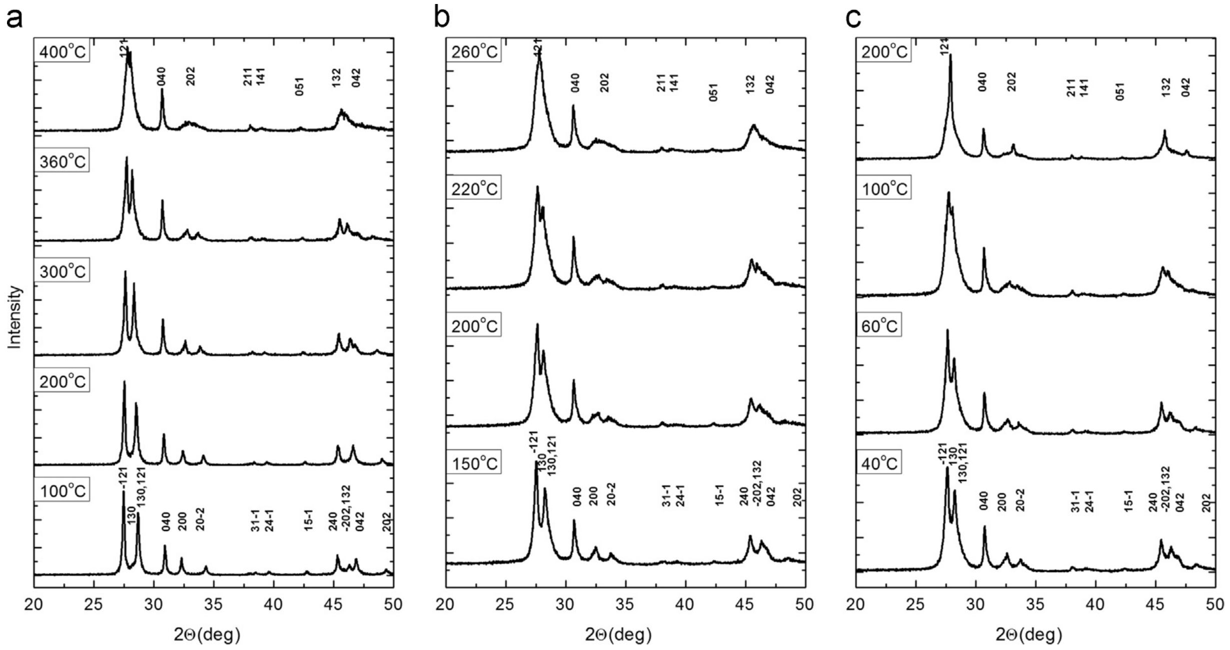

Fig. 1. High temperature X-ray diffractograms of samples with (a) 5, (b) 15 and (c) 25 mol%. The Miller indices for fergusonite (*I*2/*c*) – bottom spectra and scheelite ($I4_1/a$) – upper spectra phases of lanthanum orthoniobate are given.

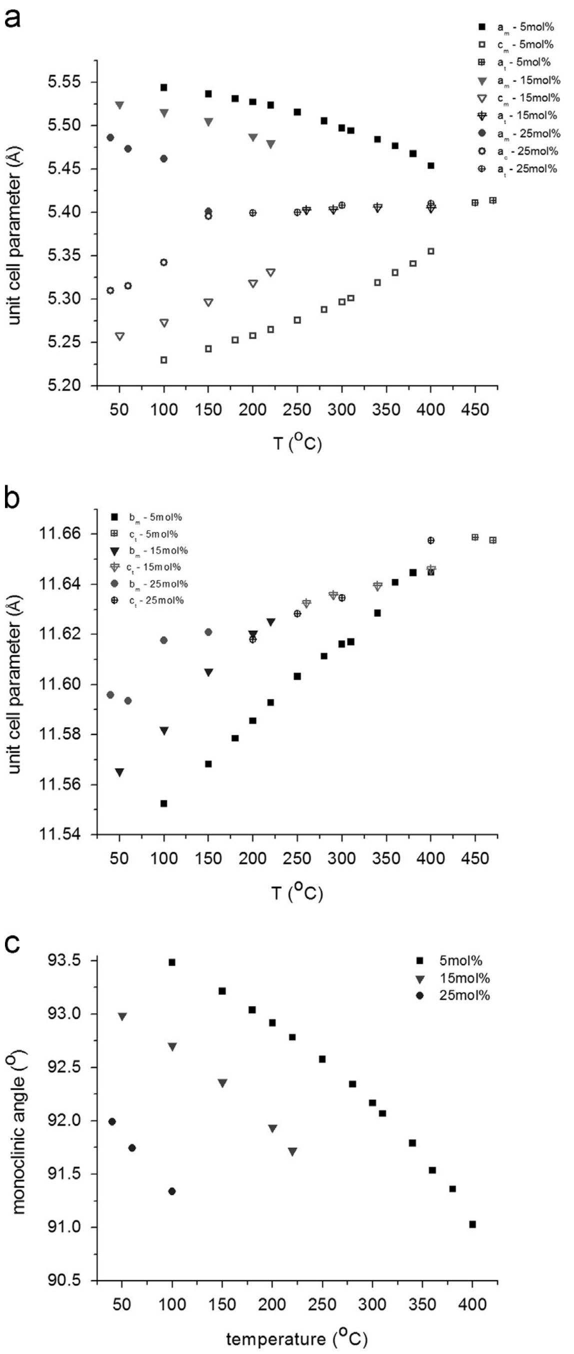

Fig. 2. Temperature evolution of unit cell parameters on the basis of Ref. [10]. The Rietveld refiment patterns are presented in S1–3.

increase. Fig. 2 shows that increasing antimony content does not influence the type of temperature dependence of the unit cell parameters, but it affects their values and shifts the plots towards lower temperature. This shift corresponds to a decreasing structural phase transition temperature. Our previous research shown that the temperature of phase transition decreases as the antimony content increases. The transition temperature of $LaNb_{1-x}Sb_xO_4$ for $x=0.05$, 0.15 and 0.25 is 404, 254 and 125 °C, respectively, whereas $LaNb_{0.7}Sb_{0.3}O_4$ is tetragonal at room temperature [10]. The influence of antimony content on the values of unit cell parameters, seen in Fig. 2, is relatively small. For instance, the relative differences between unit cell volumes at room temperature and at temperatures corresponding to $T/T_0 \approx 0.8$ are 1.02 and 0.38% for the $LaNb_{0.75}Sb_{0.25}O_4$ and $LaNb_{0.95}Sb_{0.05}O_4$ samples, respectively. Similarly, unit cell parameters of the tetragonal structure do not change much with increasing antimony content. The small variations in unit cell parameters indicate a relatively small cell distortion resulting from substitution of antimony on the niobium site. Our previous work also shows that substitution of pentavalent cations, including antimony, on the niobium site, the atom coordinates also do not vary much in comparison with unsubstituted material [10].

The structural distortions resulting from the change of lattice parameters can be estimated through the magnitude of the spontaneous strain. Values of scalar spontaneous strain calculated on the basis of Aizu formula [19] are collected in Table 1. Fig. 3a shows the temperature dependence of the spontaneous strain scalar values for samples with different antimony content. The scalar values of spontaneous strain have similar temperature characteristics for all samples. The values of spontaneous strain for $T/T_0 \approx 0.8$ decrease with antimony content increase. These indicate that smaller distortion of unit cell occurs during the phase transition with increasing antimony content, consistent with the lower transition temperature. It should be noted that the value of the strain for antimony substituted samples is smaller than that reported by Jian and Wayman for lanthanum orthoniobate (5.199×10^2 at 300 °C) [20].

The observation that the spontaneous strain in the antimony substituted lanthanum orthoniobate is lower than for the unsubstituted material suggests that the antimony is present in this compound as Sb^{5+} rather than Sb^{3+}. The ferroelastic phase transition in rare earth orthoniobates is associated with reorientation of niobium polyhedra and thus the change in the niobium sublattice is crucial for both phase transition and unit cell distortion [4–6,11–13]. The ionic radii of Sb^{3+}, Sb^{5+} and Nb^{5+} in six-fold coordination are 0.76 Å, 0.62 Å and 0.64 Å, respectively [21]. Therefore, it could be expected that the presence of significantly larger cation in the position of niobium, which is six coordinated in m-$LaNbO_4$, should cause a significant change in both unit cell parameters and spontaneous strain.

Fig. 3b shows scalar spontaneous strain values correlated with the values of Landau order parameter calculated from the expression $\eta = \sqrt{\frac{(T_o - T)}{(T)}}$ where T_0 is the phase transition temperature obtained by dilatometry measurement by Wachowski et al. [10]. The relation between the Landau order parameter and the spontaneous strain is linear within experimental error. This linear relation can be expressed as $\eta = k e_s$ where k is 18.86 ± 0.56, 32.5 ± 1.4 and 36.8 ± 3.8 for samples substituted with 5, 15 and 25 mol percent antimony, respectively. The values of k for antimony substituted $LaNbO_4$ are higher than that for undoped ($k = 10.52$) and magnesium doped $LaNbO_4$ ($k = 11.191 \pm 0.002$) [13,20]. In the case of tantalum substitution, Vullum et al. [8] obtained values of 10.0 and 9.1 for $LaNb_{0.80}Ta_{0.20}O_4$ and $LaNb_{0.60}Ta_{0.40}O_4$, respectively. Additionally, tantalum substitution results in a transition temperature increase in comparison with the undoped material [8].

Fig. 4 shows the enthalpy of drop solution and the enthalpy of formation from oxides versus antimony content. The enthalpy

Table 1
Spontaneous strain for antimony substituted samples at different temperatures.

T (°C)	T/T_0	$e_s \times 10^2$
$LaNb_{0.95}Sb_{0.05}O_4$, $T_0 = 404$ °C		
100	0.55	5.928
150	0.62	5.508
180	0.67	5.212
200	0.70	5.024
220	0.73	4.806
250	0.77	4.457
280	0.82	4.048
300	0.85	3.738
310	0.86	3.587
340	0.90	3.085
360	0.93	2.690
380	0.96	2.356
400	0.99	1.807
$LaNb_{0.85}Sb_{0.15}O_4$, $T_0 = 254$ °C		
50	0.62	3.952
100	0.72	3.588
150	0.81	3.137
200	0.91	2.572
220	0.95	2.286
$LaNb_{0.75}Sb_{0.25}O_4$, $T_0 = 125$ °C		
40	0.82	2.654
60	0.87	2.336
100	0.97	1.792

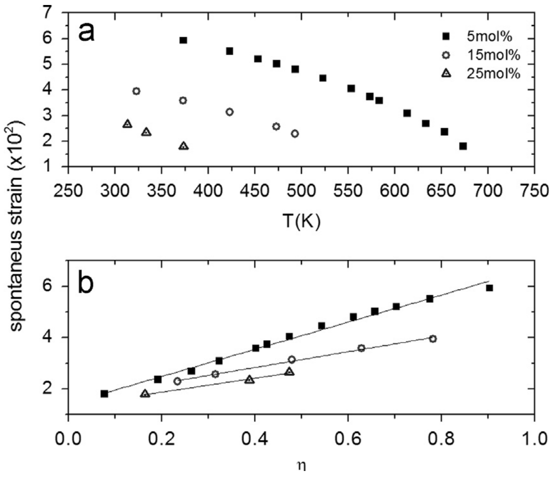

Fig. 3. Spontaneous strain versus (a) temperature and (b) Landau order parameter dependency.

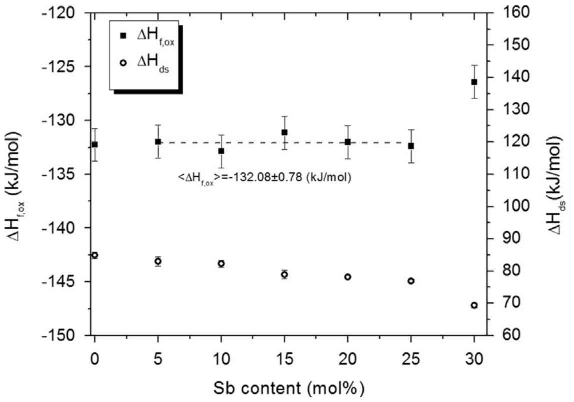

Fig. 4. Enthalpies of drop solution and formation from binary oxides of antimony substituted lanthanum orthoniobates vs antimony content. The line represents the average value of antimony doped samples in the 5–25 mol% range. The error is two standard deviation of the mean.

of formation was calculated using the thermodynamic cycle in Table 2. Values of the enthalpy of drop solution of the binary oxides and the orthoniobates are summarized in Table 3. The values for binary oxides are in a good agreement with previous work at 700 °C [22,23] when one takes the heat content difference between 700 and 800 °C into account.

The values of the enthalpy of formation from oxides obtained for samples substituted with 5–25 mol% of antimony, having monoclinic fergusonite structure at room temperature, are the same within experimental error. In their work Vullum et al. suggested that, in the case of substitution of niobium by tantalum, stabilization of monoclinic phase occurs due to the six coordination of tantalum in $LaTaO_4$ [8]. The calorimetric results show that in the case of antimony substitution there is no evidence of stabilization of the monoclinic phase though the antimony six-fold coordination in $ASbO_4$-type compounds [24].

The average enthalpy of formation for these samples, (−132.0 ± 0.8 kJ/mol) is more negative than that of the compounds with tetragonal scheelite structure (−126.4 ± 1.5 kJ/mol). The enthalpy of formation from oxides of the unsubstituted sample (−132.3 ± 1.5 kJ/mol) is the same, within experimental error, to the average value for the antimony doped ones and is equal to. The less negative enthalpy of formation from oxides of the tetragonal lanthanum orthoniobate, $LaNb_{0.70}Sb_{0.30}O_4$, than those of the samples containing 5–25 mol% of antimony shows that at room

Table 2
Thermodynamic cycles used to determine the enthalpies of formation from oxides.

$LaNb_{1-x}Sb_xO_4$ (s, 298 K)$\rightarrow\frac{1}{2}La_2O_3$ (dis, 1073 K)$+\frac{x}{2}Sb_2O_5$ (dis, 1073 K)$+\frac{1-x}{2}Nb_2O_5$ (dis, 1073 K)	ΔH_{ds}
La_2O_3 (s, 298 K)$\rightarrow La_2O_3$ (dis, 1073 K)	ΔH_1
Sb_2O_5 (s, 298 K)$\rightarrow Sb_2O_5$ (dis, 1073 K)	ΔH_2
Nb_2O_5 (s, 298 K)$\rightarrow Nb_2O_5$ (dis, 1073 K)	ΔH_3
$\frac{1}{2}La_2O_3$ (s, 298 K)$+\frac{x}{2}Sb_2O_5$ (s, 298 K)$+\frac{1-x}{2}Nb_2O_5$ (s, 298 K)$\rightarrow LaNb_{1-x}Sb_xO_4$ (dis, 1073 K)	ΔH_4
$\Delta H_{f,ox}=-\Delta H_{ds}+\frac{1}{2}\Delta H_1+\frac{x}{2}\Delta H_2+\frac{1-x}{2}\Delta H_3$	

Table 3
Enthalpies of drop solution of binary oxides measured in sodium molybdate at 800 °C. The values in brackets represent the number of experiments. The error is two standard deviations of the mean.

Binary oxide	ΔH_{ds} (kJ/mol)
La_2O_3	-221.81 ± 2.25 (7)
Nb_2O_5	127.48 ± 0.80 (10)
Sb_2O_5	62.73 ± 0.91 (8)

temperature the tetragonal phase is less stable than the monoclinic one. This difference in enthalpy is consistent with the tetragonal phase being the high temperature polymorph of lanthanum orthoniobate. A relatively small difference in the enthalpies of these phases also explains the DSC results, in which there is no weight change and no discernible heat effect at temperatures near the phase transition for any of the samples studied. The difference between the average value for the fergusonite structure and the value for scheelite namely (5.7 ± 2.3 kJ/mol), can be used as an estimate of the average enthalpy difference between the two structures. Such a small difference, spread out over the temperature range of the second order transition, would be hard to detect in the DSC scan.

All formation enthalpies of the orthoniobates are less exothermic than the formation enthalpy of $LaPO_4$ ($\Delta H_{f,ox}=-321.4\pm1.6$ kJ/mol [23]) which reflects the lower acidity of Nb_2O_5 and Sb_2O_5 relative to P_2O_5. The similar values regardless of the degree of antimony substitution suggest that the acidity of Nb_2O_5 and Sb_2O_5 is similar.

4. Conclusion

The influence of antimony substitution on temperature dependence of unit cell distortion has been investigated. The values of spontaneous strain and Landau order parameter are given. The fergusonite – to – scheelite phase transition in antimony substituted lanthanum orthoniobate is of second order, with a small total enthalpy change of about 5.7 kJ/mol. Substitution of antimony does not influence the energetic stability of the monoclinic fergusonite phase.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2014.10.010.

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