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INVESTIGATION OF PHASE TRANSITION IN $La_{1-x}Pr_xGaO_3$ AND $La_{1-x}Nd_xGaO_3$ CRYSTALS

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Abstract

The solid solution crystals, $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ have been studied by differential scanning calorimetry method; the crystals exhibit the first order phase transition, the temperature of the transition linearly increases with the concentration of Pr or Nd. The structure of the crystals has been determined by X-ray diffraction. The correlation between the phase transition temperature and crystalline structure at the temperature of the phase transition in both solid solution families is discussed.

Keywords: differential thermal analysis, perovskites, phase transition, structural investigation

Introduction

The model compounds adopting perovskite structure are $CaTiO_3$ and silicates $MSiO_3$ (M=Mg, Fe) [1]. The ideal perovskite structure has cubic symmetry (space group Pm3m) yet there exist distorted perovskite lattices like rhombohedral (R3c), orthorhombic (Pbnm) or tetragonal (14/mcm). In $CaTiO_3$ Ti cations are located inside O_6 octahedra and Ca cations occupy sites inside oxygen O_{12} polyhedra. Various structures result from deformation and tilting of the O_6 octahedra [2, 3]. The ideal perovskite structure in many cases is reached at high temperatures above a first order phase transition e.g. in $SrZrO_3$ at 1167°C [4], $BaCeO_3$ ~900°C [2], $PrAlO_3$ ~1300°C [5]. Above the phase transition temperature, the oxygen octahedra regain their symmetry; then in many perovskites the octahedra are aligned with the crystal axes. $LaGaO_3$ undergoes the phase transition to a structure of higher symmetry at approximately 150°C [6] yet octahedra remain tilted. Unfortunately, there are only few publications devoted to the enthalpy change at the phase transitions because of the difficulties in precise calorimetric measurements at high temperatures.

We have investigated solid solution single crystals $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$. Information on crystal growth conditions, structure of the solid solutions and some information on the phase transition are published in ref. [7, 8]. All three compounds: $LaGaO_3$, $NdGaO_3$ and $PrGaO_3$ have the orthorhombic structure of

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the Pbnm space group symmetry at room temperature [9]. $LaGaO_3$ and the solid solutions undergo the first order phase transition. The enthalpy change at the phase transition has been measured as a function of Nd or Pr concentration using differential scanning calorimetry (DSC) method.

The $LaGaO_3$, $PrGaO_3$ and $NdGaO_3$ gallates are interesting as potential substrates for YBCO epitaxial films [10, 11]. However, the structural phase transition may have negative influence on the properties of deposited film [12]. It could be expected that with addition of Nd or Pr the phase transition could be moved to temperature higher than epitaxial growth temperature.

Experimental results

Solid solution single crystals $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ have been grown by the Czochralski and floating zone methods, the technology has been described in details in [7, 8]. Concentration of the admixture in solid solution single crystals has been determined from the technological process; in a few crystals used later as the reference ones, composition has been determined by the electron probe microanalysis (EPMA).

X-ray diffraction results

The structure of single $La_{1-x}Pr_xGaO_3$ crystals was investigated by X-ray powder diffraction technique using Siemens D5000 diffractometer with CuK_α radiation and Si(Li) semiconductor detector. The single crystals were powdered to avoid effects arising from twinning. Data were collected from 20 to 150° in $\theta/2\theta$ mode with a step size of 0.02°and averaging time of 10 s/step. The X-ray diffraction patterns were analyzed with the use of Rietveld refinement method in order to determine the lattice constant and position of atoms in the unit cell precisely. For the $La_{1-x}Pr_xGaO_3$ system, we use the lattice parameters published in [7]. The lattice parameters change with Nd or Pr concentration is listed in Table 1.

Table 1 Lattice parameters of $La_{1-x}Nd_xGaO_3$ [7] and $La_{1-x}Pr_xGaO_3$ solid solutions [8]

	$LaGaO_3$	$La_{1-x}Nd_xGaO_3$ solid solutions	$NdGaO_3$
a_{ort}/Å	5.52267	$a_{ort}=5.5239-0.1140x+0.0178x^2$	5.42761
b_{ort}/Å	5.49048	$b_{ort}=5.4904-0.0051x+0.0131x^2$	5.49791
c_{ort}/Å	7.77131	$c_{ort}=7.7735-0.0429x-0.0235x^2$	7.70782
V_{ort}/Å^3	235.64	$V_{ort}=235.76-6.38x+0.629x^2$	230.005
	$LaGaO_3$	$La_{1-x}Pr_xGaO_3$ solid solutions	$PrGaO_3$
a_{ort}/Å	5.5229	$a_{ort}=5.5229-0.599x-0.0051x^2$	5.4579
b_{ort}/Å	5.4913	$b_{ort}=5.4913-0.0047x+0.0046x^2$	5.4912
c_{ort}/Å	7.7723	$c_{ort}=7.7723-0.0122x-0.0301x^2$	7.7300
V_{ort}/Å^3	235.72	$V_{ort}=235.72-3.13x-0.92x^2$	231.67

The same structure has been found in the whole $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ series. It has been found that, the orthorhombic lattice parameters a_{ort} and c_{ort} decrease whereas b_{ort} is almost constant with increasing Nd or Pr concentration in solid solution crystals, it results in a decrease of the unit cell volume.

In the orthorhombic lattice of the Pbnm symmetry there are 4(b) positions at (1/2, 0, 0) lattice sites occupied by Ga^{+3}, the 4(c) positions at (X, Y, 1/4) occupied by La or Pr ions and octahedra apical oxygen O(1) and 8(d) positions at (X, Y, Z) occupied by equatorial oxygen O(2). X, Y and Z are normalized atom positions along the respective lattice axes. The results of Rietveld analyses were used to find formulas describing variation of the position of atoms *vs*. Nd/Pr concentration.

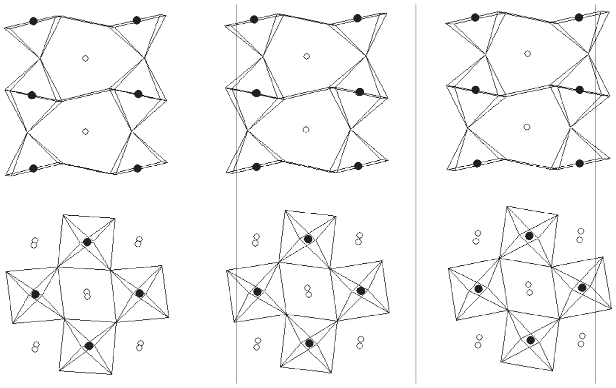

Fig. 1 View along y-axis (top) and along z-axis (bottom) of the unit cell of $LaGaO_3$, $La_{0.5}Pr_{0.5}GaO_3$ and $PrGaO_3$, full circles represent rare earth ions, open gallium ions; oxygen ions are connected to visualize the octahedra

The main component of the distortion from ideal cubic structure corresponds to the tilting of the GaO_6 octahedra. The octahedra are rotated only around b_{ort} and c_{ort} orthorhombic axes. The rotation may be denoted as $a^{0}_{ort}b^{+}_{ort}c^{+}_{ort}$ [9] applying Glazer notation [13] to the orthorhombic axes. The symbols denote angle and +(–) superscript indicates rotation in the same direction (opposite) direction of the successive octahedra around a_{ort}, b_{ort} and c_{ort} axes. The effect of substitution of La by Pr on the rotation of the octahedra is schematically shown in Fig. 1. The rotation of the octahedra around b_{ort} axis changes linearly from 5.5 to 9.3° and around c_{ort} axis from 12.6 to 11.5°.

The feasibility of formation perovskite lattice is measured by the tolerance factor defined as ratio of the rare earth (R)–oxygen, d_{R-O}, average distance in RO_{12} polyhedron to the Ga–oxygen, d_{Ga-O}, average distance in octahedra: $t=d_{R-O}/\sqrt{2}d_{Ga-O}$. In the ideal perovskite lattice t equals 1, however if R ions built into the lattice have too small radius then t decreases below 1 and the lattice undergoes a distortion. The value of t, calculated from the positions of atoms determined by Rietveld analyses, decreases in $La_{1-x}Pr_xGaO_3$ from 0.98837 at $x=0$ to 0.98267 at $x=1$. Rotation of the GaO_6 octahedra increases with decreasing of the tolerance factor t in agreement with previously published results [9]. It is worth mentioning that the volume of GaO_6 octahedra increases with concentration *x* despite the unit cell volume decrease.

Thermal investigation

Thermal analyses were carried out in the temperature range from 25 to 600°C using a DuPont Instruments 910 DSC and at temperatures up to 1400°C using Netzsch STA 409 apparatus. The experiments were performed at a heating rate of 10 deg min^{-1} using samples 6 mm in diameter, weighing 100–200 mg. Empty pans or pans filled with Al_2O_3 were used as reference. Filling the pans had an influence only on the base line not on the integrated heat flow at the phase transition. The DSC instrument was calibrated with In, Sn, Pb, Zn, Li_2SO_4, Al and Ag.

The phase transition in $LaGaO_3$ at ~150°C connected with the structural transformation from orthorhombic (Pbnm) to rhombohedral (R3c) phase [6, 9] is observed in thermal analyses as the endothermic effect. With increasing Nd/Pr concentration the temperature of the phase transition (T_{tr}) increases linearly. The T_{tr} temperature increase follows the formula T_{tr}=145.4+2104x in $La_{1-x}Pr_xGaO_3$ crystals up to x=0.53, whereas in $La_{1-x}Pr_xGaO_3$ formula T_{tr}=147.84+1331x up to x=0.81. The expected phase transition temperature at higher concentration *x* in both series exceeds temperature accessible in our equipment.

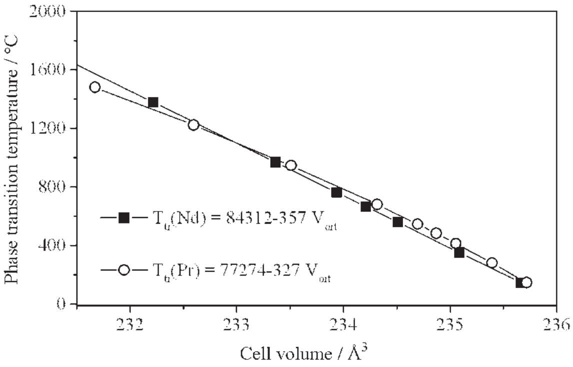

Fig. 2 Temperature of the phase transition in solid solutions of $La_{1-x}Pr_xGaO_3$ and $La_{1-x}Nd_xGaO_3$ *vs*. unit cell volume measured at *RT*

The phase transition temperature T_{tr} increases linearly while orthorhombic unit cell volume V_{ort} almost linearly decreases with Nd/Pr concentration *x*. It implies that T_{tr} linearly descends with increasing V_{ort}. The $T_{tr}(V_{ort})$ dependence for the two series of the crystals is shown in Fig. 2. It is astounding that both plots are almost identical. We have searched for the tentative explanation of the dependence on the basis of the unit cell dimensions at approaching the phase temperature that are being modified by substituting La by smaller Pr or Nd ions.

Table 2 Thermal expansion coefficients in pure compounds after [9] in K^{-1}

	a	*b*	*c*
$LaGaO_3$	$12.15 \cdot 10^{-6}$	$9.7 \cdot 10^{-6}$	$11.0 \cdot 10^{-6}$
$NdGaO_3$	$12.5 \cdot 10^{-6}$	$5.6 \cdot 10^{-6}$	$11.6 \cdot 10^{-6}$
$PrGaO_3$	$11.1 \cdot 10^{-6}$	$6 \cdot 10^{-6}$	$10.6 \cdot 10^{-6}$

Published information on the thermal expansion coefficient of $LaGaO_3$, $PrGaO_3$ and $NdGaO_3$ [9, 14, 15] may be used to evaluate the variation of the unit cell parameters at the phase transition temperature still in the orthorhombic Pbnm structure. As first approximation, it may be assumed that the thermal expansion coefficient of solution crystals is a weighted linear combination of both components. We use the room temperature lattice parameters of the solution crystals listed in Table 1 and thermal expansion coefficients of pure components listed in Table 2. Variation of the lattice parameters $a_n=2^{-1/2}a_{ort}$, $b_n=2^{-1/2}b_{ort}$ and $c_n=c_{ort}/2$, in $La_{1-x}Pr_xGaO_3$ with x at 1040 K is shown in Fig. 3. The calculated parameters agree sufficiently well with the only available experimental data obtained from high temperature measurements performed on solid solution crystal $La_{0.63}Nd_{0.37}GaO_3$ of the orthorhombic structure [16].

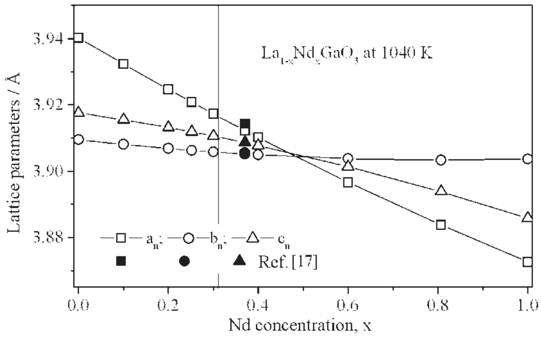

Fig. 3 Comparison of calculated orthorhombic lattice parameters in $La_{1-x}Nd_xGaO_3$ at 1040 K with the experimental value for x=0.37 published in [16]. The vertical line indicates the lowest Nd concentration at which the compound exists in the orthorhombic structure at 1040 K

The thermal expansion coefficients listed in Table 2 have been used to calculate unit cell parameters $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ at the phase transition temperature in the orthorhombic structure (Fig. 4).

It results from the comparison of the lattice parameters over wide range of x and T that the unit cell has to reach similar dimensions in both compounds for the phase transition to occur (compare also range of *Y*-axes in Fig. 4 with data in Table 1). Therefore, a $La_{1-x}Nd_xGaO_3$ crystal with a small unit cell has to be heated to relatively high temperatures in order to enlarge the unit cell to enable rotation of the GaO_6 octahedra and transform the crystal from Pbnm to the R3c symmetry. In contrast, the 'appropriate' size of the unit cell in $LaGaO_3$ crystal is reached already at low temperature.

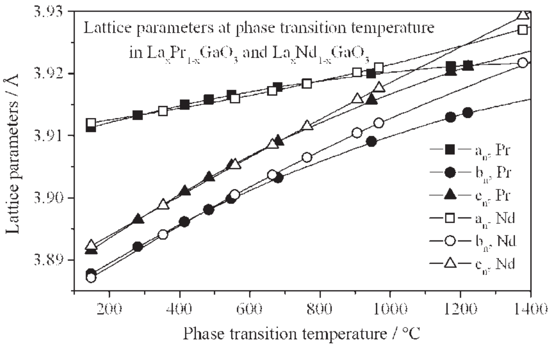

Fig. 4 Calculated normalized lattice parameters of $La_{1-x}Pr_xGaO_3$ and $La_{1-x}Nd_xGaO_3$ at the phase transition temperature

The substitution of lanthanum by neodymium or praseodymium leads to non-monotonic enthalpy change at the phase transition. It increases from approximately ΔH=1.23 J g^{-1} (315.7 J mol^{-1}) at x=0 to 2.33–2.45 J g^{-1} at x=0.20÷0.25, then at higher concentrations x, falls down. The phase transition in crystals with high concentration of Nd is difficult to register because it extends over wide temperature range (Fig. 5).

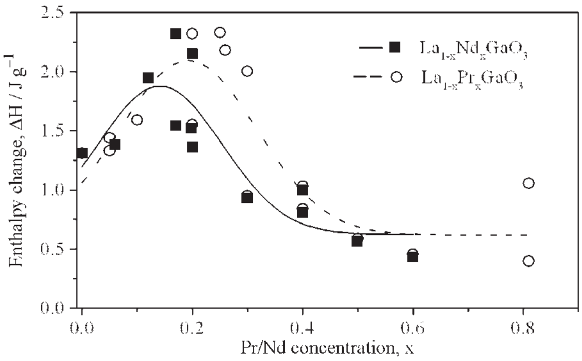

Fig. 5 Enthalpy change at the phase transition in $La_{1-x}Pr_xGaO_3$ and $La_{1-x}Nd_xGaO_3$ crystals

The Clapeyron–Clausius law $dT/dp=T_{tr}\Delta V/\Delta H$ connects the variation of the molar enthalpy $-\Delta H$ during phase transition with the change of the molar volume $-\Delta V$. It is plausible that the molar volume change is the largest at the intermediate x values.

Conclusions

The unit cell volume decreases almost linearly with increasing concentration of praseodymium or neodymium in the $La_{1-x}Nd_xGaO_3$ and $La_{1-x}Pr_xGaO_3$ mixed crystals. The first order phase transition is observable in these crystals in wide concentration range of the admixture. The temperature of the phase transition in both systems increases linearly with increasing the concentration of Pr or Nd. The variation of the phase transition temperature in both solid solution types may be presented as a common linear function of the unit cell volume. It indicates that the rotation of GaO_6 octahedra and consequently the phase transition may only occur when the unit cell reaches sufficient size. The enthalpy change at the phase transition varies non-monotonically with praseodymium or neodymium concentration.

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