Growth and structure of strontium doped $LaGaO_3$

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ABSTRACT

A series of $La_{1-x}Sr_xGaO_3$ solid solution single crystals with x = 0, 0.04 and 0.12 were grown by the Czochralski method and with x = 0.01, 0.06 and 0.1 by the floating zone method. The segregation coefficient of Sr in $LaGaO_3$ has been found to be k_{eff} (Sr) = 1.25 (± 0.01). The crystals were grown from the melt with stoichiometric Ga_2O_3 amount at a growth rate ranging from 2.5 mm/h for pure $LaGaO_3$ to 1.2 mm/h for $La_{0.88}Sr_{0.12}GaO_3$.

The structure of these crystals was investigated by X-ray powder diffraction technique using CuK_α radiation. The diffraction patterns were analyzed by Rietveld refinement method. Crystals with strontium concentrations from x = 0 to 0.1 crystallizes adopting Pbnm structure. It was found that deviation from the ideal perovskite structure decreases with rising strontium concentration, finally reaching centrosymmetric Ibmm structure at x = 0.12. Orthorombic unit cell parameters *c* and *b* decreases whereas *a* increases with x.

Thermal analysis proved that the temperature of the first order phase transition observed in pure $LaGaO_3$ at 150 °C falls to 126 °C at x = 0.01 and remains almost constant at higher x.

Keywords: crystal growth, doping, Czochralski method, high temperature superconductor epitaksy.

1. INTRODUCTION

$LaGaO_3$ crystallizing in the space group Pbnm[1-3] would be an attractive substrate material for YBCO epitaxial films[4], because of a small lattice mismatch and good chemical stability resulting from its relatively high melting point of 1710 °C were it not for the fact that a structural phase transition occurs at ~150 °C [5]. The phase transition is the most serious drawback of many lanthanide gallates and aluminates[5] for it can cause formation of twins and roughness of the substrate surface[6]. We have previously investigated the $La_{1-x}Nd_xGaO_3$ $La_{1-x}Pr_xGaO_3$ systems[7,8] and found crystals with the lattice parameters suitable as substrates for High Temperature Superconductors (HTSc) epitaxy.

The thermal analysis proved that the temperature of the first order phase transition observed in $LaGaO_3$ rises linearly with Nd and Pr concentration *x* at the rate of 20.5 °C/Nd mol % and 13.3 °C/Pr mol % respectively. Apart from Pr and Nd we have also investigated other isomorphous rare earth elements including Sm, Eu and Er in $LaGaO_3$ single crystal. Substitution of Sm, Eu and Er increases the phase transition temperature at the rate higher than Pr and Nd. It shows that the phase transition temperature increases at higher rate for smaller ions. This results suggest possibility of using larger ions like Sr that should decrease the phase transition temperature.

It is interesting to note that the volume of GaO_6 octahedron increases in both systems despite decrease of the unit cell volume. The ratio of the perovskite unit cell to the octahedron volume linearly decreases with *x* from 5.73 in $LaGaO_3$ to 5.55 in $PrGaO_3$ and 5.57 in pure $NdGaO_3$, while in the ideal perovskite lattice it equals 6. This ratio indicates that La, Pr and Nd ions are too small to form the cubic lattice but Sr might be sufficiently large in order to remove the distortion.

It has been found that only Pr and Nd galates form solid solutions in the whole concentration range with $LaGaO_3$. The solubility limit of other rare earth elements decreases rapidly with decreasing radii of ions smaller than La. Nonisomorphic substitution should be possible in a limited range of concentration lowering phase transition temperature and decreasing unit cell distortion.

2. GROWTH OF $La_{1-x}Sr_xGaO_3$ SINGLE CRYSTALS

A series of $La_{1-x}Sr_xGaO_3$ solid solution single crystals with *x* = 0, 0.04, 0.12 were grown by the Czochralski method and with *x* = 0.01, 0.06, 0.1 by the floating zone method. The growth processes by the floating zone method were carried out in the ambient atmosphere at 2mm/h growth rate using rods sintered at 1340 °C.

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The floating zone method allows growing mixed crystals with constant concentration of the admixture along the growth direction, apart from the relatively short regions at the beginning and the end of the grown crystal. Thus, the crystals obtained by the floating zone method can be used not only for investigation but also as a reference with well defined composition for future comparison with crystals grown by the Czochralski method. Quality of the crystals grown by this method decreases with increasing strontium concentration; therefore we employed the Czochralski method to grow crystals with high Sr concentration.

In order to grow solid solution single crystals by the Czochralski method with a definite composition, the segregation coefficient of the admixture in the host lattice has to be known. The segregation coefficient can be derived from both ions concentration varying along the crystal in the growth direction. The details of the derivation procedure are described in[7].

The admixture concentration in solid solution single crystals along the crystal growth directions was measured by the Electron Probe Microanalysis (EPMA) method. The accuracy of this method depends on the type of reference sample, therefore we used crystals grown by the floating zone method as the reference. The effective segregation coefficient of strontium in $LaGaO_3$ $k_{eff}(Sr) = 1.25$ ($\pm$ 0.01) was determined from the crystal grown by the Czochralski method from the melt containing 3.2 Sr at. %. Because of Sr segregation, the crystals contained 4 Sr at.%.

It has been found that the concentration of Ga_2O_3 in $LaGaO_3$, $La_{1-x}Sr_xGaO_3$ single crystals grown by the Czochralski method is slightly lower than that corresponding to the stoichiometric composition. Consequently, if the process is started from the melt of stoichiometric composition, the concentration of Ga_2O_3 in the melt increases with time. The increase in Ga_2O_3 concentration is compensated to a substantial degree by thermal dissociation of Ga_2O_3 followed by evaporation of dissociation products. This process can be controlled by partial pressure of oxygen in the growth chamber atmosphere. The best crystals were grown when they were pulled from the melt with the stoichiometric Ga_2O_3 concentration in a nitrogen atmosphere containing 1 vol. % of oxygen, at the pulling rate from 2.5 mm/h (for pure $LaGaO_3$) to 1.2 mm/h (for $La_{0.88}Sr_{0.12}GaO_3$).

3. ANALYSES OF THE $La_{1-X}Sr_xGaO_3$ STRUCTURE

The structure of $La_{1-x}Sr_xGaO_3$ solid solution crystals was investigated by means of precise X-ray powder diffraction technique using Cu K_α radiation. Since these crystals exhibit a distinct tendency to twinning, it is difficult[2], to prepare a single domain sample necessary for single crystal diffraction technique. We preferred to rely on the powder X-ray diffraction because twins does not interfere with this technique. The diffraction was measured in a $\theta/2\theta$ scanning mode in the angle range $19° < 2\Theta < 150°$ with a step of 0.02° and averaging time of 10 s/step.

Table 1. Crystallographic data of $La_{1-x}Sr_xGaO_3$ solid solutions.

Atom sites	Para-meters	$La_{1-x}Sr_xGaO_3$						
		Pbnm						Ibmm
		x=0	0.01	0.04	0.06	0.1	0.12	0.12
	a, Å	5.52469	5.52479	5.5248	5.52723	5.52872	5.529	5.52898
	b, Å	5.49259	5.49062	5.49062	5.4901	5.48911	5.48772	5.48771
	c, Å	7.7744	7.77121	7.7712	7.77095	7.77033	7.77032	7.77031
	V,Å^3	235.91	235.74	235.74	235.81	235.81	235.76	235.76
La(Sr) 4c	x	-0.0033	-0.00369	-0.00408	-0.00238	-0.00514	-0.003	-0.00363
	y	0.0176	0.01508	0.01526	0.01240	0.00906	0.00491	0
	z	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Ga 4b	x	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	y	0	0	0	0	0	0	0
	z	0	0	0	0	0	0	0
O1 4c	x	0.07070	0.07349	0.07306	0.09483	0.07114	0.10565	0.10874
	y	0.508	0.50046	0.50091	0.46691	0.49851	0.50316	0.5
	z	0.25	0.25	0.25	0.25	0.25	0.25	0.25
O2 8d	x	-0.28	-0.26771	-0.26814	-0.25538	-0.26412	-0.2738	0.25
	y	0.269	0.27154	0.27379	0.25741	0.28073	0.27099	0.25
	z	0.039	0.04167	0.04119	0.05817	0.02848	0.03222	0.02626

The diffraction patterns were analyzed by the Rietveld refinement method, using the DBWS-9006PC package[9]. This package allows one to take into account positional and thermal corrections, scaling factor, zero shift, background parameter, Bragg-peak profile parameter and extinction correction. The diffraction patterns were analyzed in 44° <2Θ <150° range only, in order to avoid experimental errors that might arise from misalignment of the samples particularly at low diffraction angles. There are 480 reflections within this angle range for Cu $K_{\alpha 1}$ and Cu $K_{\alpha 2}$ lines, number sufficient for Rietveld analyzes. The structure was measured for following compositions x=0, 0.01, 0.04, 0.06, 0.1, 0.12. The lattice structure has been analyzed in Ibmm and Pbnm space groups, parameters and atom positions in both structures are listed in Table 1.

The diffraction patterns in the angle range 44° < 2Θ < 71° for Sr concentration x=0, 0.04, 0.06, 0.1, 0.12 is shown in Fig. 1. The plots are shifted vertically for clarity. There is evident decrease of intensity of some reflections with odd sum of h, k, l indices. At x=0.12 these reflections disappear completely. That is characteristic for higher space group symmetry: Ibmm. Thus, it ought to be concluded that lattice of Pbnm symmetry at 0<x<0.12 adopts the Ibmm space group at x=0.12.

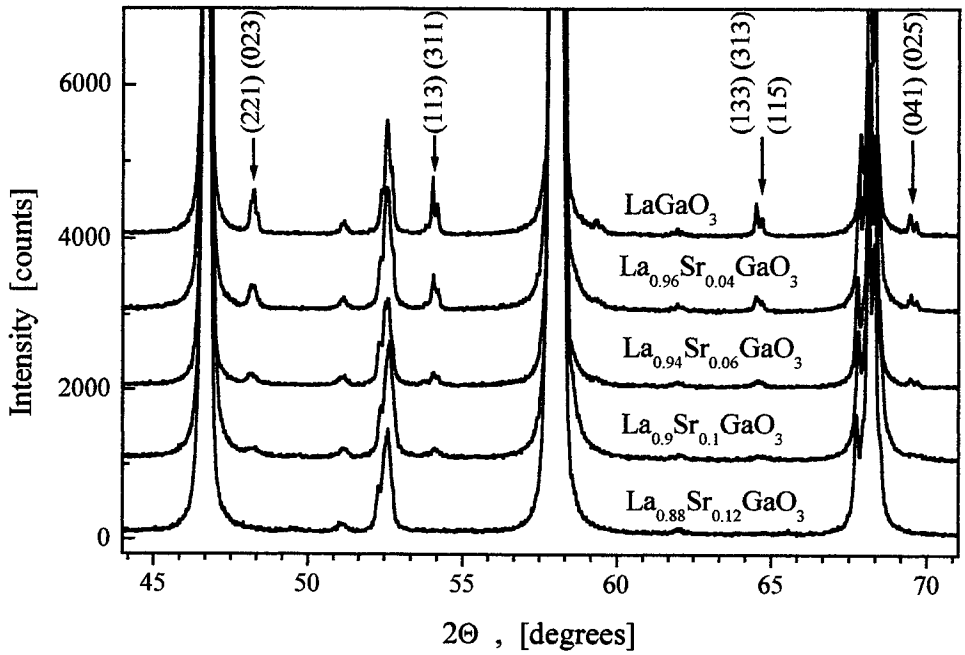

Figure 1. X-ray powder diffraction patterns of $La_{1-x}Sr_xGaO_3$ crystals. The plots are shifted vertically for clarity. The reflections characteristic for the Pbnm symmetry are indexed.

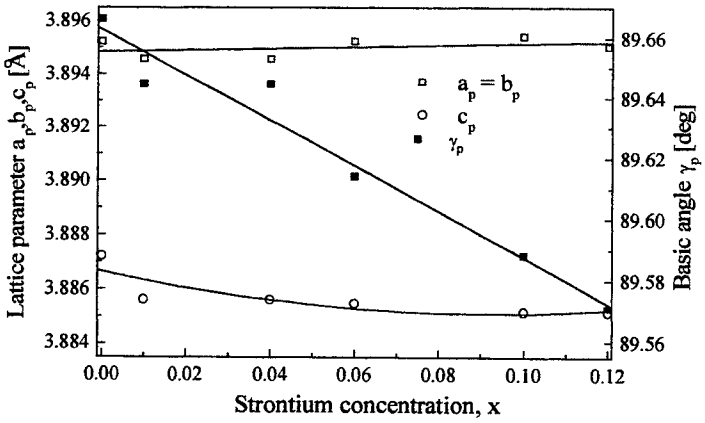

Figure 2. Perovskite-like unit cell parameters

The orthorhombic unit cell parameters *a*, *b* and *c* determined by Rietveld analyzes were used to calculate the parameters of a perovskite-like unit cell using the formulas: $a_p = \sqrt{(a^2 + b^2)}/2$, $c_p = c/2$ and $\gamma_p = 2^*$ arctg(b/a). The perovskite-like cell parameters of the $La_{1-x}Sr_xGaO_3$ crystals versus Sr concentration *x* are presented in Fig. 2. The lattice parameter a_p increases and c_p decreases with increasing Sr concentration though range of a_p change is smaller than of c_p, the angle γ_p at the base of the perovskite unit cell changes from 89.7° to 89.6°.

The projection of the unit cells along <001> and <010> directions of $La_{0.88}Sr_{0.12}GaO_3$ in Ibmm and Pbnm space groups are depicted in Fig. 3 in order to visualize the differences in

the atoms arrangement. There are evident differences between the unit cells: projections of the GaO_6 octahedra are rectangle in the Ibmm structure.

4. THERMAL ANALYSES

The temperature of the first order phase transitions was measured for following compositions x=0, 0.01, 0.04, 0.1, 0.12. The dependence of the first order phase transition temperature T_c on Sr concentration is presented in Fig. 4. The temperature changes nonlinearly with the composition, it may be assumed that in the range from x=0 to slightly above 0.01 the phase transition temperature changes at the rate of -23.3 °C/Sr mol %, at higher concentrations x≤0.12 the rate decreases to about 2 °C/Sr mol %.

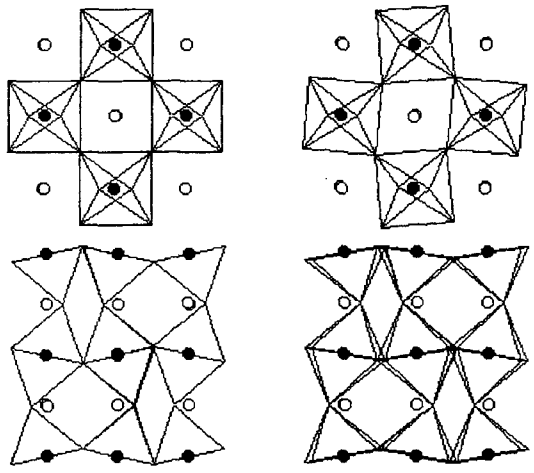

Figure 3. Projections along <001> (top) and <010> (bottom) of the unit cell in Ibmm (left) and Pbnm (right) space groups.

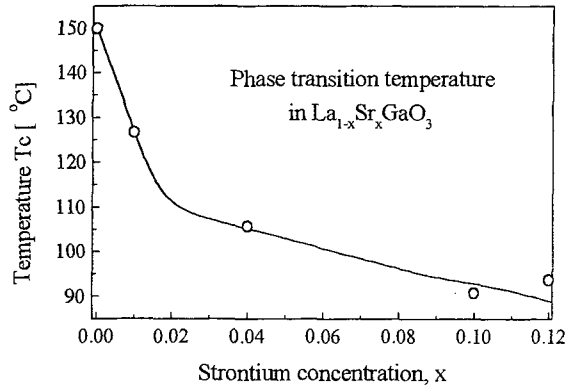

Figure 4. Phase transition temperature dependence on Sr concentration.

5. CONCLUSIONS

Large single crystals of $La_{1-x}Sr_xGaO_3$ solid solutions were grown by the Czochralski method in the concentration range from 0 to 0.12. The Sr segregation coefficient in $LaGaO_3$ has been determined to be $k_{ef}(Sr) \approx 1.25$. The solubility limit for nonisomorphic substitution of La by Sr is about 12 mol.% while up to about 1.5 mol.% the introduced admixture behaves as isomorphic substitute. The unit cell volume hardly changes with Sr concentration, it probably results from oxygen vacancies introduced by nonisomorphic doping.

It is interesting to note that with Sr concentration x=0.12 crystal adopts space group Ibmm not the expected Pbnm.

The first order phase transition temperature decreases linearly from ~150 °C at the rate of approximately 23.3°C/Sr mol % in concentration range from x=0 to 0.01 and 2 °C/Sr mol % in concentration range from x=0.04 to x=0.12.

The (110) oriented plane of the crystal with x = 0.04 has the perovskite - like unit cell parameters a_p = 3.8946 Å (3* a_p = 11.6838 Å) and c_p = 3.8856 Å which are very close to the YBCO lattice constants c = 11.6827 Å and b = 3.8836 Å respectively.

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