Proceedings of the ICSC–F'96 Jaszowiec '96

$SrLaGaO_4$–$SrLaAlO_4$ SOLID SOLUTIONS — SUBSTRATE MATERIALS WITH TUNEABLE LATTICE PARAMETER FOR VARIOUS HTSC COMPOUNDS

M. Berkowski, J. Fink-Finowicki and E. Mojaiskaia
Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

The increase in T_c for high temperature superconductors can be realized, among others, by appropriate substrate/film combinations. $SrLaGaO_4$–$SrLaAlO_4$ solid solutions were grown by the Czochralski method. The already achieved results allow to obtain single crystals of $SrLaAl_{1-x}Ga_xO_4$ with lattice constant a in the range from 0.3754 to 0.3775 nm, and $SrLaGa_{1-x}Al_xO_4$ crystals with lattice constant a in the range from 0.3843 to 0.3826 nm. Electron-probe microanalysis along obtained single crystals was used for determination of segregation coefficient between aluminum and gallium ions.

PACS numbers: 61.16.–d, 61.50.Nw, 81.10.Fq, 64.75.+g

1. Introduction

Single crystals with K_2NiF_4 structure such as $SrLaAlO_4$ (SLA), $SrLaGaO_4$ (SLG) are very attractive substrate materials for the epitaxy of superconducting layers: $SrLaGaO_4$ has more favorable mismatch than $LaAlO_3$ for epitaxial growth of YBaCuO and 1212 and 1223 phases of IIg based superconductors. Mukaida and Miyazawa [1] have demonstrated a-axis growth of YBaCuO with in-plane alignment on the (100) orientation of $SrLaGaO_4$ making this substrate attractive for Josephson junction device applications. These compounds have no phase transitions which would lead to twinning in the temperature range between the melting point and the application temperature. Materials with K_2NiF_4 structure have low dielectric constant and microwave losses [2] and therefore they are appropriate for electronic applications. Large single crystals can be grown by the Czochralski method. Their melting points are located in reasonable region.

It is known that T_c of the bulk materials can be increased by applying external pressure to a sample. Sato et al. [3] reported that LaSrCuO thin films deposited on $SrLaAlO_4$ exhibit higher T_c than this of bulk material with the same composition. Similar or even better results should be possible to obtain on substrates prepared from solid solutions $SrLaGaO_4$–$SrLaAlO_4$. The materials engineering allows, in principle, to tune the lattice parameter and therefore to control the internal stresses by choosing appropriate substrate/film combinations.

2. Crystal growth

Both those materials and their solid solutions are obtained by the Czochralski method. Chemical composition of single crystals $SrLaAlO_4$ and $SrLaGaO_4$ obtained by the Czochralski method slightly differs from the stoichiometric composition.

Although $SrLaAlO_4$ is slightly non-stoichiometric it melts congruently. In this material at its melting temperature evaporation and dissociation of constituent oxides is negligible and for this reason properly chosen starting composition is practically the same as the crystal composition. Thus, the melt composition remains unchanged during the crystal growth. The optimum starting melt composition was found as: 50 mol.% of SrO, 25.3 mol.% of La_2O_3 and 24.7 mol.% of Ga_2O_3.

$SrLaGaO_4$ melts incongruently at the temperature of about 1520°C [4]. In this case, the growth of $SrLaGaO_4$ crystal should be considered on a basis of phase diagram for the system $LaGaO_3$–SrO. Below the melting temperature the melt decomposes into Sr_2LaGaO_5 remaining in a solid phase and the melt with composition corresponding to the peritectic point i.e. deficient in SrO. Therefore, it is necessary to start crystal growth process from the composition with lower SrO concentration than that at the peritectic point composition. Composition of single crystals obtained by the Czochralski method is slightly (about 1%) enriched with Ga_2O_3 as compared to the stoichiometric composition. During crystal growth the melt composition shifts toward lower SrO concentrations. The crystal composition changes in the same direction but much slower. Good quality crystals of $SrLaGaO_4$ with reasonable dimensions can be obtained by the Czochralski method only due to the small difference between the composition of the single crystal and the peritectic point.

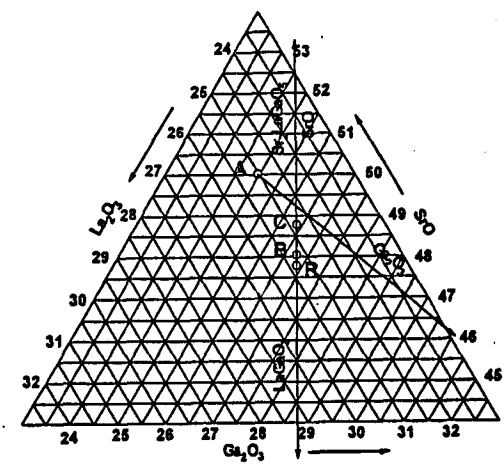

Fig. 1. Fragment of the Gibbs diagram for $SrLaGaO_4$. *A* — stoichiometric composition, *B* — optimum starting composition, *C* — expected single crystal composition, *R* — composition of the melt which remains after crystal growth process.

Figure 1 shows the fragment of the Gibbs diagram for $SrLaGaO_4$. The stoichiometric composition is denoted as A, whereas the optimal starting composition as B. The expected composition of $SrLaGaO_4$ single crystal is denoted as C, and the composition of the melt which remains after crystal growth process as R. The composition of the crystal and the melt which remains after crystal growth process, studied by comparative electron-probe microanalysis (EPMA) method, reveals that the crystal contains about 1 mol.% SrO more than the remaining melt.

3. Results and discussion

$SrLaGaO_4$–$SrLaAlO_4$ solid solutions allow to obtain single crystals with the lattice constant which can be controlled in a relatively broad range. Although the growth rate for the solid solutions is lower than that of the constituent single crystals, nevertheless all the factors responsible for the improvement of the crystal quality are still valid. The already achieved results allow to grow single crystals of $SrLaAl_{1-x}Ga_xO_4$ (x up to 0.27) and $SrLaGa_{1-x}Al_xO_4$ (x up to 0.2) crystals with lattice constants change as shown in Fig. 2. The concentrations range of solid

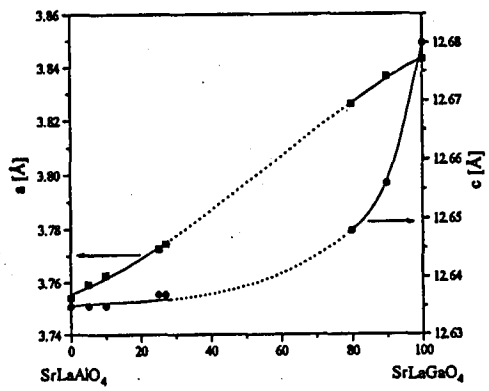

Fig. 2. Lattice constants a and c of solid solutions of $SrLaGaO_4$–$SrLaAlO_4$ as a function of the second component concentration.

solutions investigated up to now allows to draw the following conclusions:

— both admixtures: gallium in SLA and aluminum in SLG build into the crystals isomorphically,

— the lattice constant a is practically a linear function of the second component concentration.

The segregation between aluminum and gallium ions in obtained crystals was studied with EPMA analysis. Concentrations of Ga and Al, measured on slices cut along growth direction from single crystals of solid solutions, versus parameter g describing the part of crystallized material are shown in Fig. 3. It is seen that the admixture concentration along the growth direction in the case of gallium doped SLA increases whereas in aluminum doped SLG decreases. The admixture

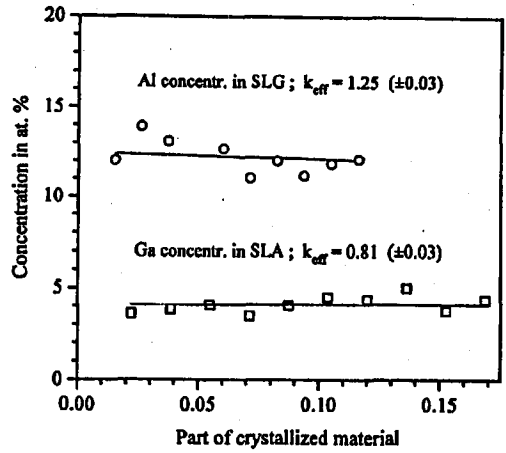

Fig. 3. Concentrations of Ga and Al in at.% along the growth direction, versus parameter g describing the part of crystallized material.

concentration during the conservative single crystal growth process according to [5] is given by Eq. (1):

$$C(g) = k_0 C_{0l}^{i}(1-g)^{k_0-1}, \tag{1}$$

where k_0 is the segregation coefficient; C_{0l}^{i} is the starting admixture concentration in the liquid, on the liquid solid interface; g is the ratio of the crystal mass at any chosen part to the total starting mass in a crucible.

In the case of good stirring, the following equation can be used [6]:

$$C(g) = k_{\mathrm{ef}} C_{0l}(1-g)^{k_{\mathrm{ef}}-1} \tag{2}$$

where k_{ef} is the effective distribution coefficient, and C_{0l} is the starting admixture concentration in the melt.

The effective segregation coefficients, calculated on the basis of Eq. (2) and EPMA measurements are for gallium in SLA — $k_{\mathrm{efGa/Al}} = 0.81$ (± 0.03) and for aluminum in SLG — $k_{\mathrm{efAl/Ga}} = 1.25$ (± 0.03). Let us note that $k_{\mathrm{efGa/Al}} \approx 1/k_{\mathrm{efAl/Ga}}$ although the measurements were performed on the samples with different admixture concentrations.

4. Summary

$SrLaAl_{1-x}Ga_xO_4$ solid solutions were grown by the Czochralski method in relatively broad range. These single crystals allow to tune the lattice parameter and therefore to control the internal stresses by choosing appropriate substrate/film combinations. The already achieved results allow to obtain single crystals of $SrLaAl_{1-x}Ga_xO_4$ with lattice constant a in the range from 0.3754 to 0.3775 nm, and from 0.3843 to 0.3826 nm. It is worth noting that the solid solution with $a = 0.378$ nm has a zero mismatch to LaSrCuO, whereas that with $a = 0.382$ nm to b-axis of YBaCuO.

The segregation coefficients for gallium in SLA ($k_{\mathrm{efGa/Al}} = 0.81$) and for aluminum in SLG ($k_{\mathrm{efAl/Ga}} = 1.25$) are close to 1, and the obtained results prove

that the crystals with the homogeneous admixture concentration and with the lattice constant that does not change along the crystal, can be obtained. Thus, it appears that solid solutions of $SrLaAl_{1-x}Ga_xO_4$ have essential advantages over other substrate materials.

Acknowledgments

This work was partially supported by the Commission of the European Communities under contract CIPA-CT93-0032.

References

[1] M. Mukaida, S. Miyazawa, *Appl. Phys. Lett.* **63**, 999 (1993).

[2] R.D. Shanon, R.A. Oswald, J.B. Pareise, B.H.T. Chai, P. Byszewski, A. Pajączkowska, R. Sobolewski, *J. Solid State Chem.* **98**, 90 (1993).

[3] H. Sato, M. Naito, to be published, 1996.

[4] K. Nakamura, R. Katuno, I. Aoyama, *Phase Transit.* **42**, 99 (1993).

[5] R.A. Laudise, *The Growth of Single Crystals*, Prentice Hall, Englewood Cliffs 1974, p. 74.

[6] A. Dąbkowski, M. Berkowski, G. Jasiołek, *J. Cryst. Growth* **71**, 371 (1985).