New Oxide Crystals as Substrates for GaN-based Blue Light Emitting Devices

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We have successfully grown <111>-oriented (La,Sr)(Al,Ta)O_3 (LSAT) mixed-perovskite single crystals and <0001>-oriented $Ca_8La_2(PO_4)_6O_2$ (CLPA) single crystals with the apatite structure by the Czochralski method. The compositional and lattice parameter uniformity of the crystals are discussed in relation to the growth conditions. Since LSAT and CLPA single crystals have excellent lattice matching with GaN, they are promising as new substrates for the growth of high quality GaN epitaxial layers.

KEYWORDS : (La,Sr)(Al,Ta)O_3, $Ca_8La_2(PO_4)_6O_2$, GaN, Czochralski method, Substrate, Lattice matching

1. Introduction

Due to its wide direct bandgap and high thermal stability, GaN is a promising material for optoelectronic devices such as diodes and lasers emitting in the blue and ultraviolet wavelength regions, as well as for electronic devices operating at high temperatures. It has been reported that GaN layers could be successfully grown on sapphire substrates by MOCVD, and blue light emitting diodes and lasers have been realized [1-5]. However, dislocation densities in these layers are very large, as high as 10^8 to 10^{10} cm^{-2}, because of the large lattice mismatch between the epitaxial layer and the substrate [6,7]. These dislocations have recently been shown to strongly affect the lifetime of continuous wave blue laser diodes [8].

While sapphire is widely used as a substrate for GaN epitaxial growth, its large lattice mismatch with GaN (14 - 16 %) is a limiting factor for the quality improvement of the grown epilayers [8]. Although other materials such as GaAs, SiC, MgO and ZnO have also been studied as substrates, high quality epilayers could not be obtained because of their large lattice mismatch and/or decomposition under the reducing atmosphere used for epitaxial growth [9]. Since high quality bulk GaN single crystals are not yet available, it is very important to find appropriate substrates for GaN heteroepitaxy.

We have found new candidates, $(La,Sr)(Al,Ta)O_3$ (LSAT) and $Ca_8La_2(PO_4)_6O_2$ (CLPA), as substrates for GaN epitaxial growth. LSAT and

CLPA are expected to have a fairly small lattice mismatch (< 0.1 %) with GaN.

The use of LSAT mixed-perovskite crystals as substrates for high-T_c superconductors was first reported by Mateika et al. [10]. LSAT belongs to the cubic crystal system, while GaN belongs to the hexagonal crystal system, having the space group $P6_3mc$ of the wurtzite-type structure. Although materials belonging to the hexagonal crystal system are preferable as substrates, those belonging to the cubic system may also be candidates, since the (111) face of cubic crystals has hexagonal symmetry.

It is known that single crystals with the apatite structure (space group $P6_3/m$) are effective host materials for luminescent and laser applications [11,12]. Moreover, the existence of a variety of synthetic apatites, compounds of the rare-earth oxyapatite family such as $Ca_8RE_2(PO_4)_6O_2$ (RE=La-Lu) and $Ca_2RE_8(SiO_4)_6O_2$, permits a variety of lattice parameter. This means that the rare-earth oxyapatite family has high potential for substrate materials as well.

In the present work, we demonstrate the successful growth of LSAT and CLPA single crystals. We have also investigated uniformity of the chemical composition and lattice parameter, and optical transmission of the crystal.

2. Experimental procedure

Single crystals were grown in a conventional Czochralski (CZ) furnace driven by a 60 kW RF generator with an iridium crucible (50 mm in diameter and height). Oxide powders of 99.99 % purity were used as raw materials. The La_2O_3, $SrCO_3$, Al_2O_3 and Ta_2O_5 powders of 99.99 % purity were used as raw materials for LSAT. Starting material was prepared by mixing these powders to the composition of $La_{0.294}Sr_{0.706}Al_{0.647}Ta_{0.353}O_3$ [10]. Starting material for CLPA was prepared by mixing of 99.99% $CaCO_3$ and La_2O_3 powders and 98% $CaHPO_4$ powder at the stoichiometric ratio of $Ca_8La_2(PO_4)_6O_2$.The crystals were grown under Ar atmosphere with a gas flow rate of 1.0 *l*/min.

The phase identification and determination of the lattice parameter of the grown crystals were carried out by X-ray powder diffraction analysis. The chemical composition was analyzed by electron microprobe analysis. Transmittance was measured in the wavelength region from 200 to 2500 nm for two polished specimens.

3. Results and Discussion

3.1.Crystal growth

The CZ growth of LSAT single crystals was performed using an iridium rod as a seed. Since the grown crystal was oriented to the <011> direction, the preferred growth orientation of LSAT is supposed to be

<011>. However, <111>-oriented single crystals are most appropriate to prepare <111>-oriented substrates to realize lattice matching with GaN <0001> epitaxial layers. Therefore, <111>-oriented seed crystals were prepared from the crystal grown along <011>.

Fig.1 shows an as-grown LSAT single crystal 22 mm in diameter and 100 mm in length, pulled along the <111> direction. Pulling and rotation rates were 1mm/h and 10 rpm, respectively. This crystal was red-brown in color. The solidification fraction, g (weight ratio of crystal to starting melt), for the crystal shown in Fig.1 was 0.42. When the value of g exceeded 0.6, spiral growth occurred.

The growth interface of crystals grown with a rotation rate 10 rpm, was fairly convex towards the melt. At 40 rpm, although the growth interface was still convex towards the melt, the core observed in the crystal grown at 10 rpm disappeared, and the shape of the growth interface became smooth. This suggests that a higher crystal rotation speed is preferable in order to decrease the stress in the grown crystals.

The red-brown color of the LSAT specimen changed to pale yellow after annealing at 1650 °C for 6 hours under Ar:0.2%H_2 gas mixtured atmosphere. Fig.2 shows a typical transmission spectrum of the LSAT as-grown specimen compared with that of the annealed one. The as-grown specimen had a broad absorption peak, while the annealed one did not. The

existence of the broad absorption peak is the cause of red-brown coloring of as-grown crystals.

Annealing at 1780 °C for 24 hours under the same atmosphere made the LSAT specimen black. We attributed this black coloration to the valence change of Ta^{5+}, that is, Ta^{4+} or Ta^{3+} appeared by reduction of Ta^{5+} at high temperatures. Although Ta^{3+} and Ta^{4+} cations cannot exist at the site coordinated by 8 oxygens, they can exist at the site coordinated by 6 oxygens [13]. These results, together with Fig.2, indicate that a growth atmosphere with a lesser amount of H_2, such as 0.1% or 0.05 %, is better for the growth of colorless LSAT crystals.

In Ar atmosphere, the final melting of the synthesized oxyapatite was observed at 1650±10 °C. However, if we merely held the melt at this temperature, even for a long time, we did not succeed in growing transparent crystals. Although crystals were observed to be transparent during the growth process, after cooling they became cloudy and white in color, with many small cracks along the boule. This behavior was observed under both inert (Ar) and slightly oxidizing (Ar + 1 vol. % O_2) atmosphere. It has been reported that in the case of phosphate apatites, the formation of poorly reactive intermediate phases like $Ca_4P_2O_9$ is possible [14]. However, according to the result of powder X-ray diffraction analysis, our crystals grown as described always had a single $Ca_8La_2(PO_4)_6O_2$ phase. Better results were obtained by overheating the melt to 1730 °C and holding it at this

temperature for 2 hours. Then, the melt was super-cooled to around 1550 °C, and the growth process was started. In this case, the crystal remained transparent without cracks after cooling.

Fig.3 shows a photograph of a typical CLPA crystal grown from an overheated melt with super-cooling before growth. Pulling and crystal rotation rates were 1mm/h and 20rpm, respectively. The optical transmission spectrum is shown in Fig.4. No absorption peaks were observed from 250nm to 2300nm.

We note that there were some inclusions inside the crystals, and their distribution along the boule depended on the growth conditions. Crystals pulled at rates exceeding 2.5 mm/h always had particles with size about ~10μm collected mainly in the core region. Moreover, these crystals were usually clear at the top, but the concentration of precipitate increased towards the bottom. According to the local composition measurement by EPMA, the inclusions contained La_2O_3. However, crystals pulled at a rate of 1.5 mm/h had no detectable inclusions along the boule. With rates lower than 1.5 mm/h, the crystal quality was not significantly further improved.

3.2.Lattice parameter and uniformity

The lattice parameter of the LSAT single crystal was 7.735 Å. Fig.5 shows the dependence of the lattice parameter on the solidification fraction. The lattice parameter was almost constant along the growth axis. Fig.6 shows

the variation in concentration of each cation composing LSAT with the solidification fraction. Each cation was distributed almost uniformly along the growth axis. This agreed well with the uniformity of the lattice parameter.

The (111) plane of the LSAT crystals is a close-packed plane of the anion framework, which forms the primitive cubic lattice, and thus the <111> direction is the body-diagonal direction of this cubic cell. The surface structure, therefore, has hexagonal symmetry. The lattice parameter " a_{hex} " of the LSAT (111) plane, considered as a 2-dimensional hexagonal crystal, is given by

$$a_{hex} = \sqrt{6}/3 \cdot a_{cub} ,$$

where a_{cub} is the conventional lattice parameter of the cubic crystal. Since the measured a_{cub} of LSAT was 7.735 Å, a_{hex} was calculated to be 6.316 Å, which was close to twice the corresponding lattice parameter of GaN (3.160 - 3.190 Å). The lattice mismatch was calculated to be 0.06 - 1.00 %.

The chemical composition and lattice parameter along the pulling direction of the CLPA crystal grown at 1.5 mm/h, are shown in Fig.7 and Fig.8, respectively. The lattice parameter is almost uniform along the growth axis. In accordance with this, the chemical composition of all cations is also almost constant.

Lattice parameter of CLPA were measured to be a=9.446 Å and c=6.922 Å. The lattice mismatch between GaN and CLPA is calculated as follows when a_{GaN} is 3.16 Å ;

$$\frac{a_{GaN} - a_{CLPA}/3}{a_{GaN}} = 0.003586\text{L} \qquad \text{i.e.} \quad 0.36\%$$

where a_{CLPA} is a lattice parameter of CLPA. Since the reported lattice parameter of GaN ranges from a=3.16-3.19 Å, the lattice mismatch of CLPA with GaN was calculated to be 0.36 - 1.3 %.

4. Summary

LSAT single crystals of the cubic crystal system and CLPA single crystals with apatite structure were successfully grown by the conventional Czochralski method. The growth orientation of LSAT and CLPA was controlled to be <111> and <0001>, respectively, so that the crystals could serve as substrates for the growth of <0001> GaN epitaxial layers. The lattice parameter of LSAT and CLPA was constant along the growth axis. This agreed with the uniformity of the chemical composition. Because of the small lattice mismatch with GaN, LSAT and CLPA single crystals have high potential as substrates for the growth of high quality GaN epitaxial layers with low dislocation density.

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Figure captions

Fig.1. As-grown LSAT single crystal pulled along the <111> orientation.

Fig.2. Transmission spectrum of the as-grown LSAT single crystal and of the annealed crystal.

Fig.3. Typical CLPA single crystal grown from overheated melt.

Fig.4. Optical transmission spectrum of CLPA.

Fig.5. Lattice parameter of LSAT as a function of the solidification fraction. Error bars are within the size of the symbols.

Fig.6. Dependence of concentration of each cation composing LSAT on the solidification fraction, where C_0 and C_s are the initial concentration and the concentration at each solidification fraction, respectively. Error bars are within the size of the symbols.

Fig.7. Lattice parameter of CLPA as a function of the solidification fraction. Error bars are within the size of the symbols.

Fig.8 Dependence of concentration of each cation composing CLPA on the solidification fraction, where C_0 and C_s are the initial concentration and the concentration at each solidification fraction, respectively. Error bars are within the size of the symbols.

Fig.1 Fukuda et

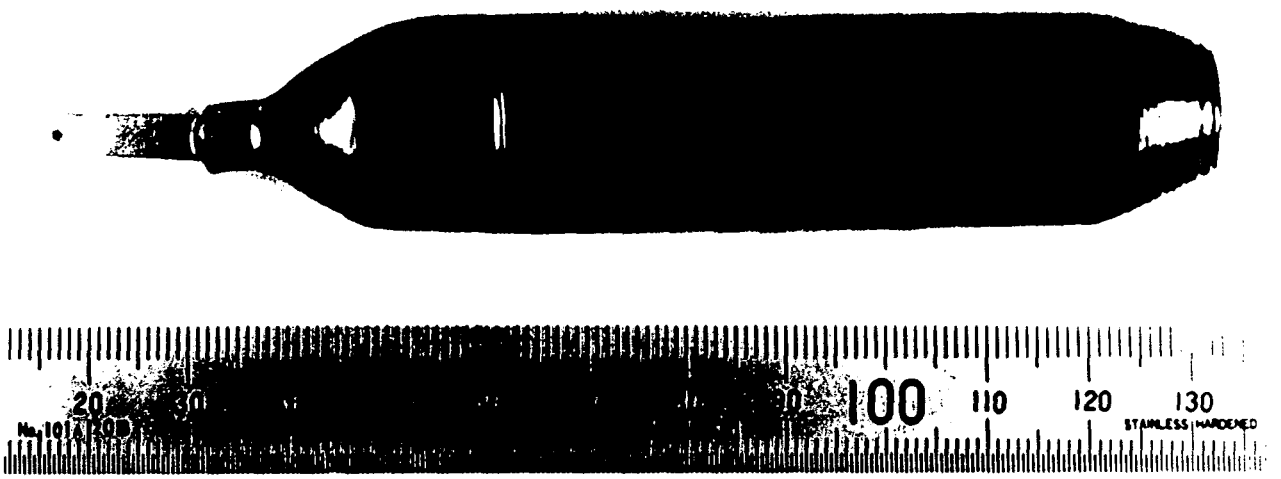


Fig.2 Fukuda et

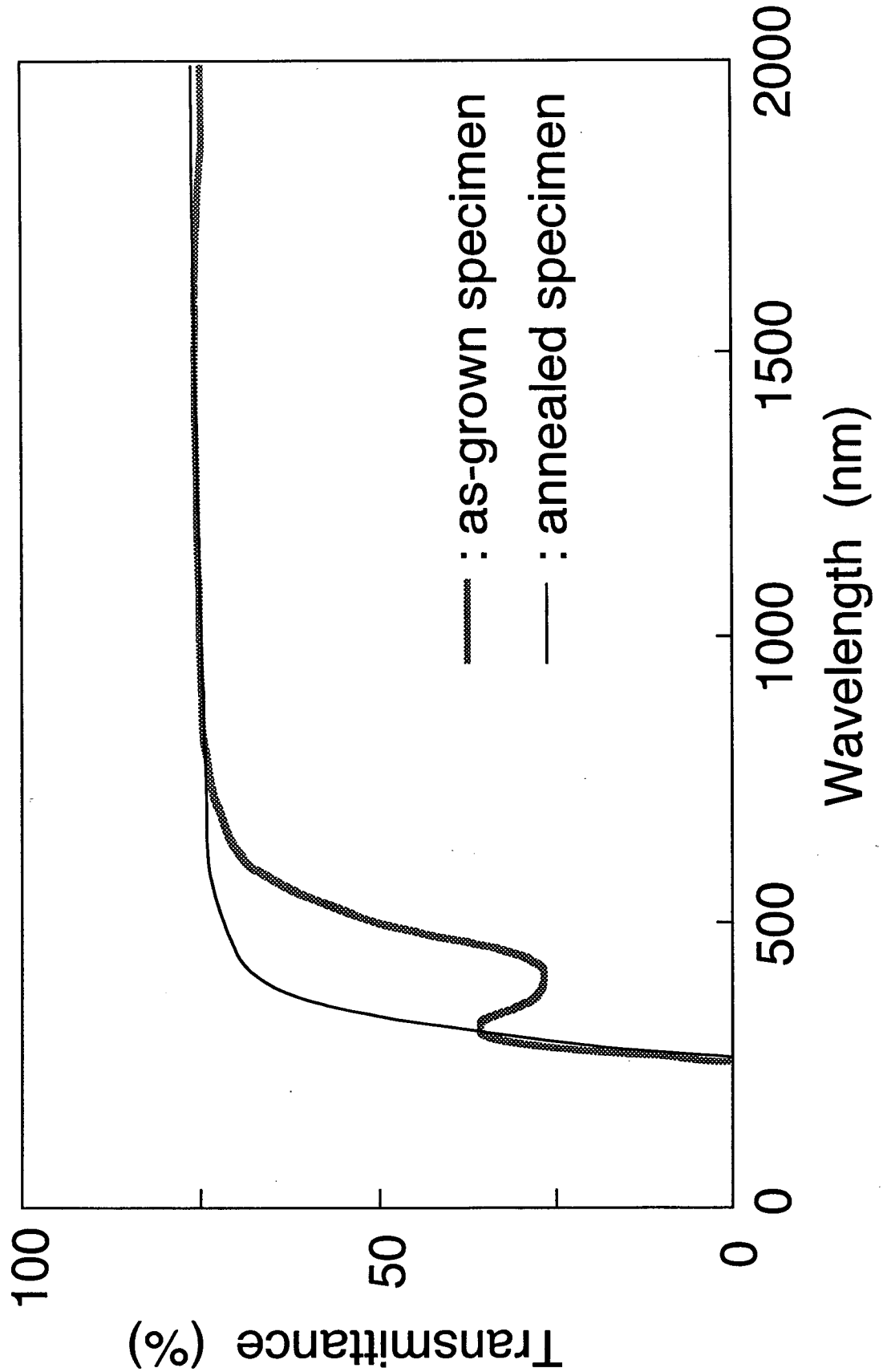


Fig.3 Fukuda et

Fig.4 Fukuda et

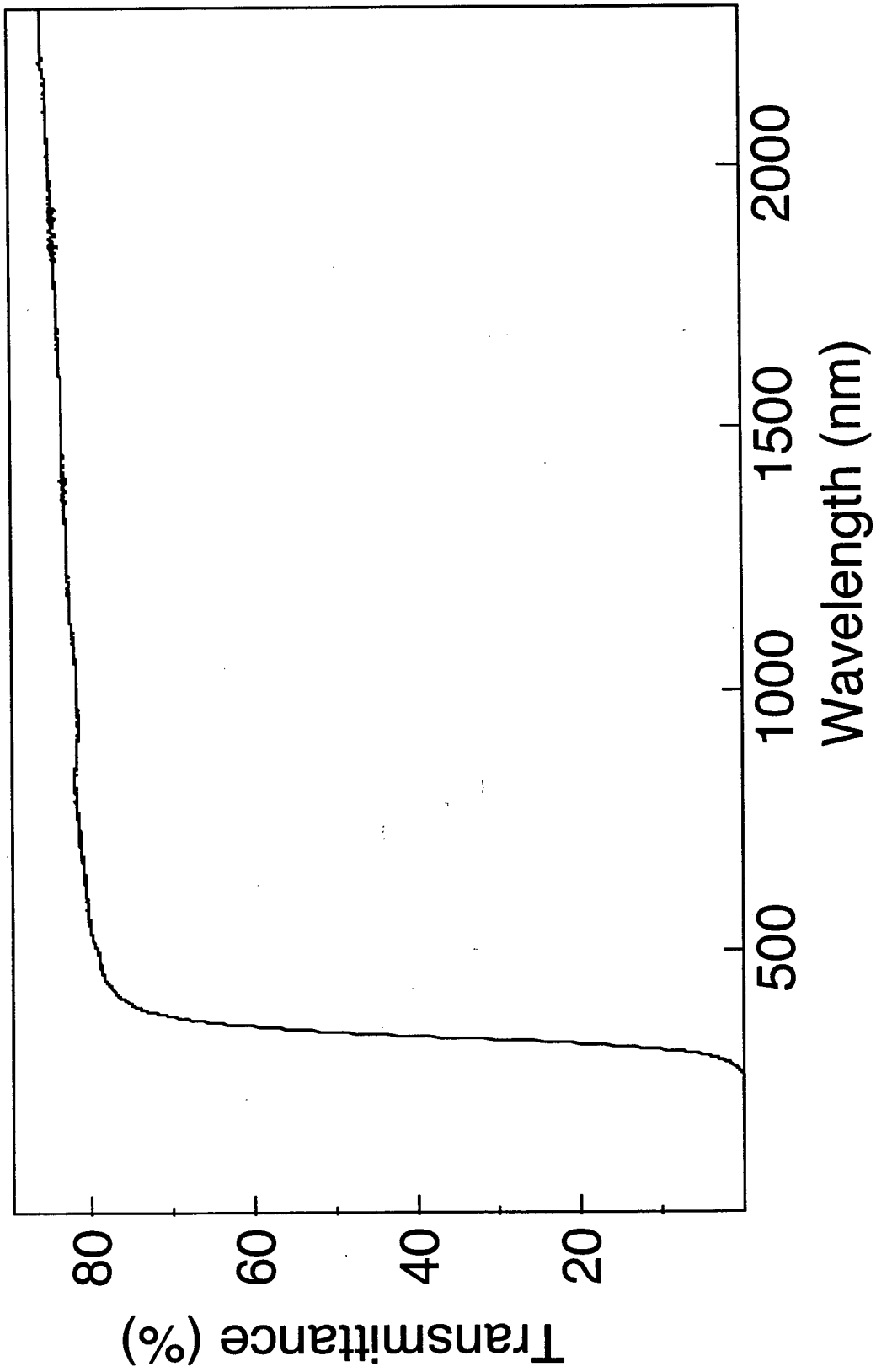


Fig.5 Fukuda et

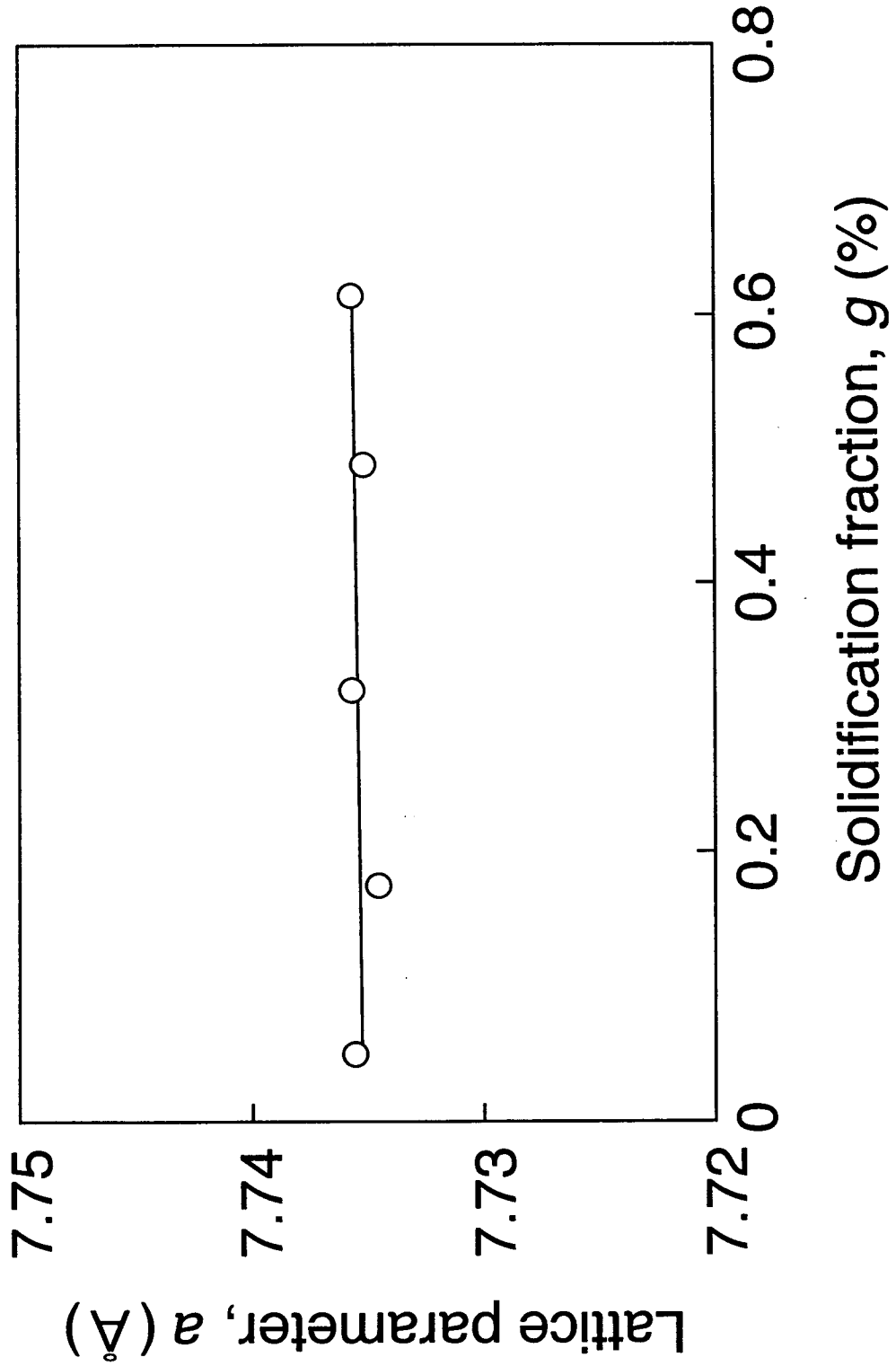


Fig.6 Fukuda et

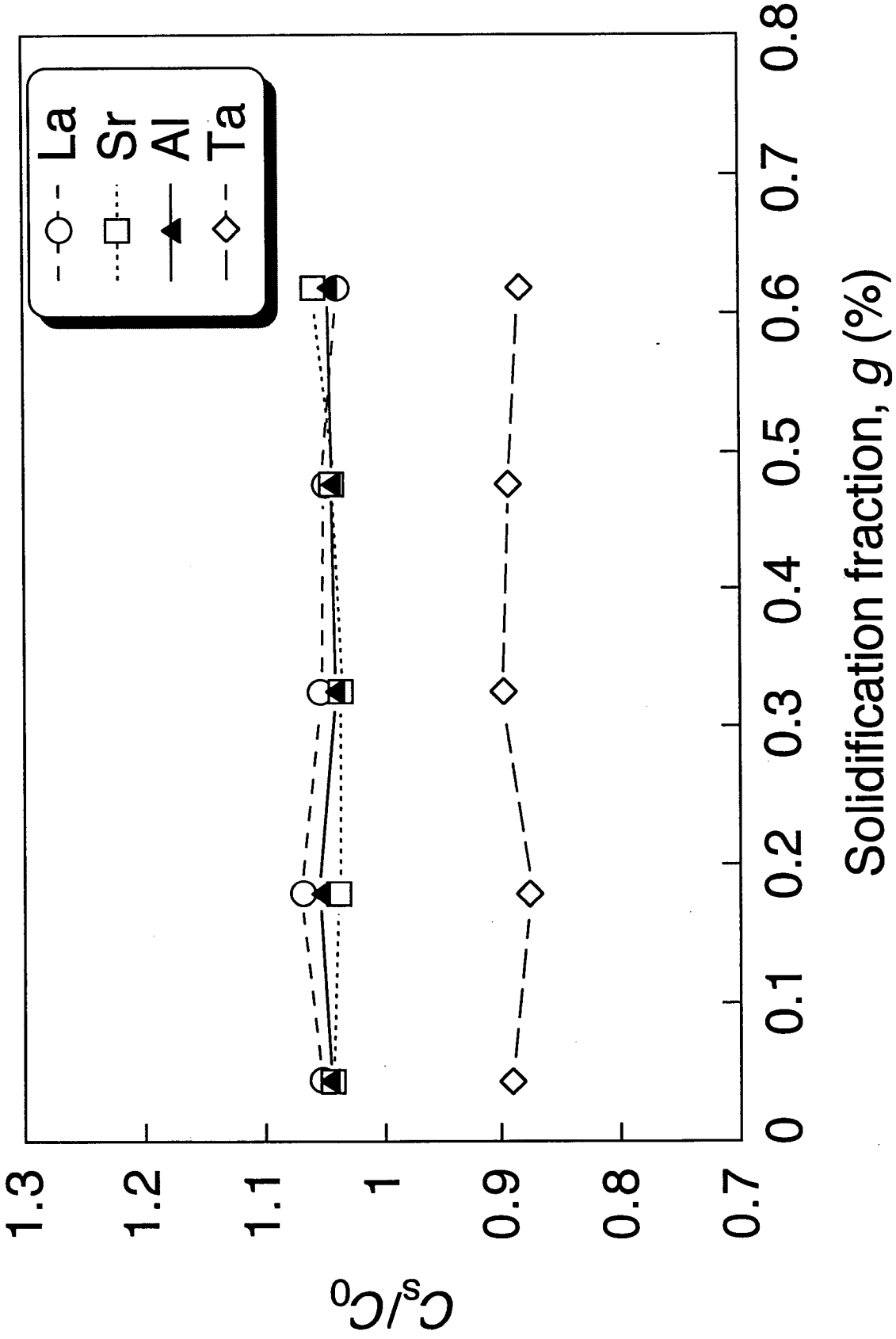


Fig.7 Fukuda et

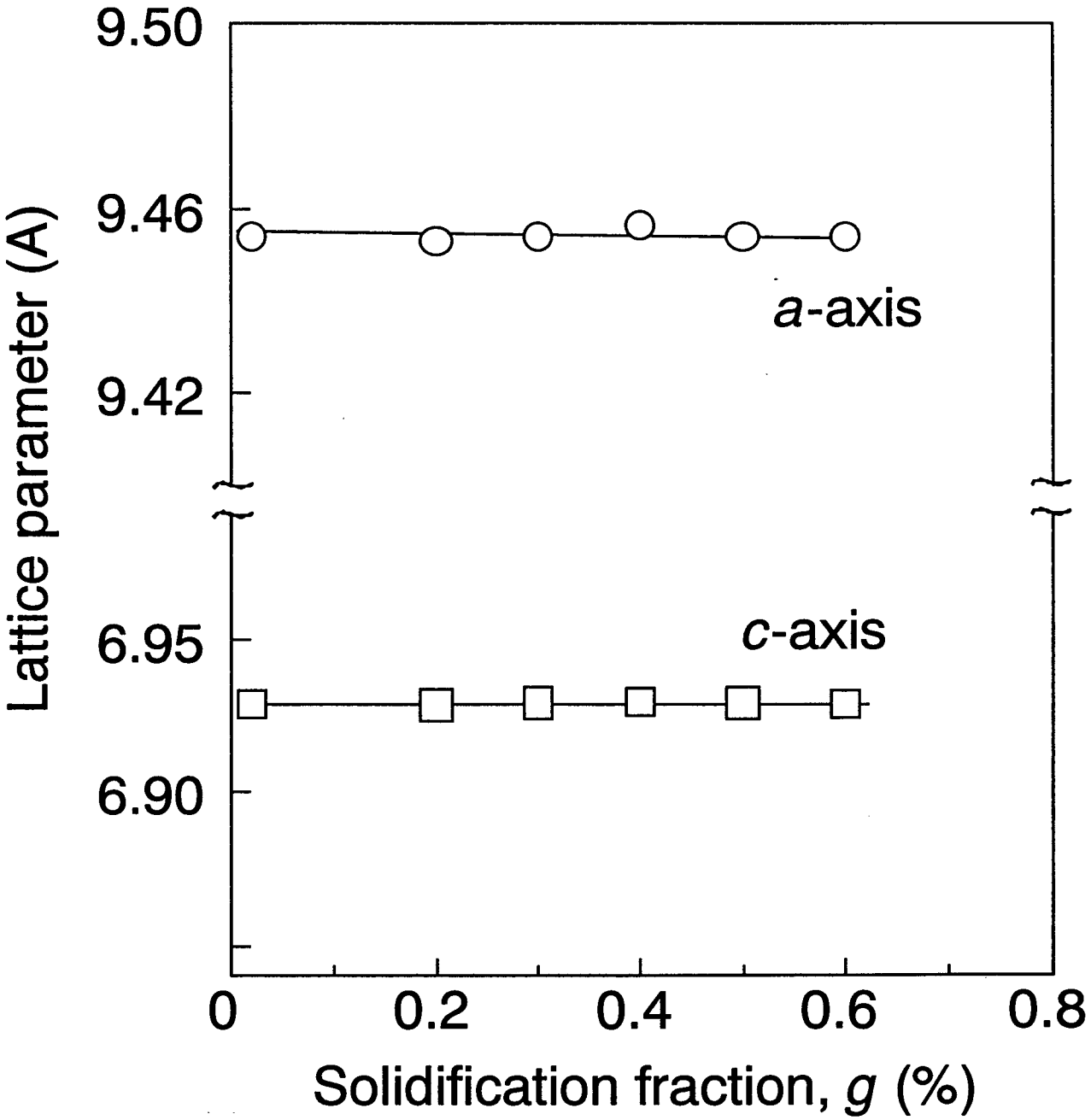
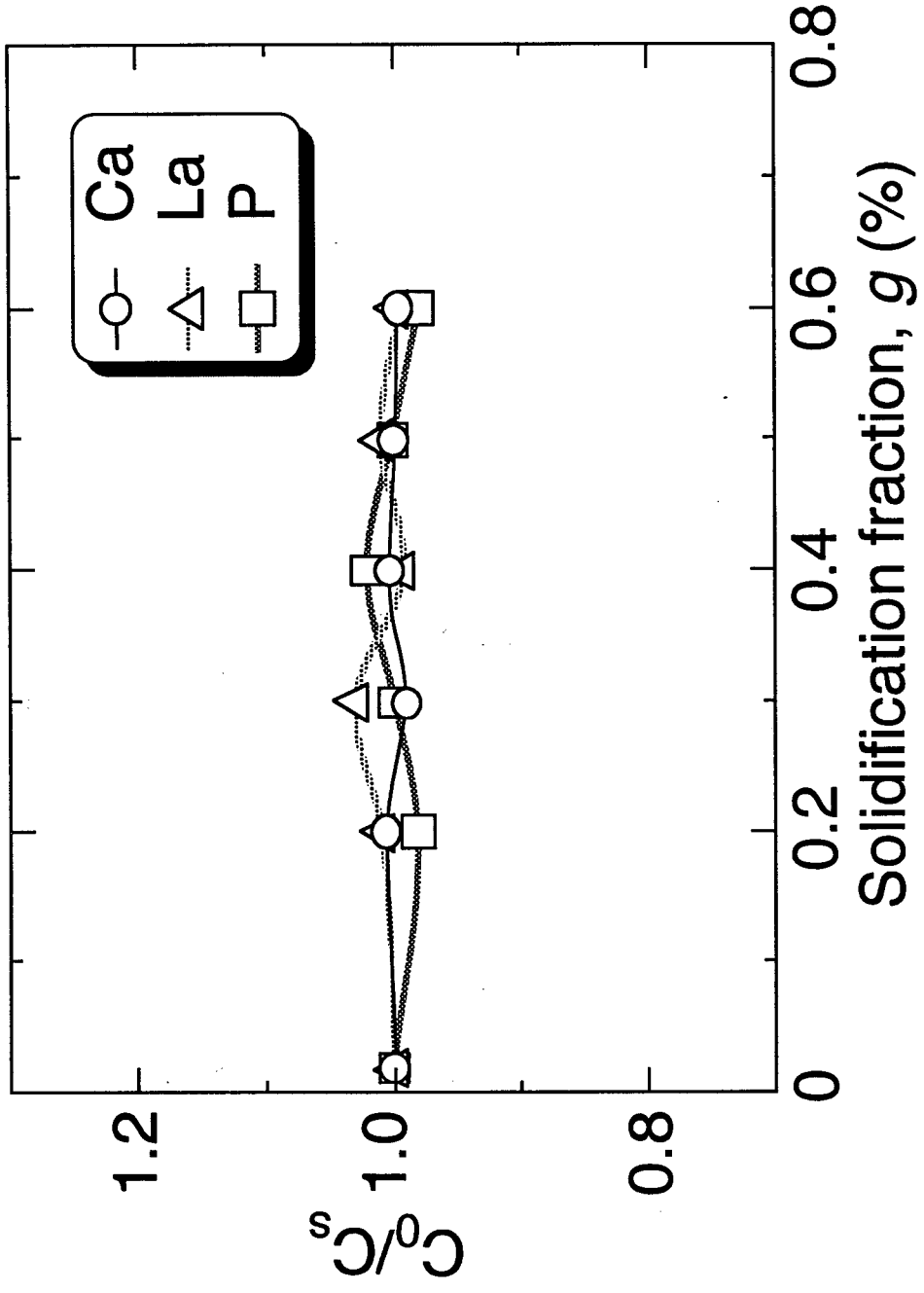
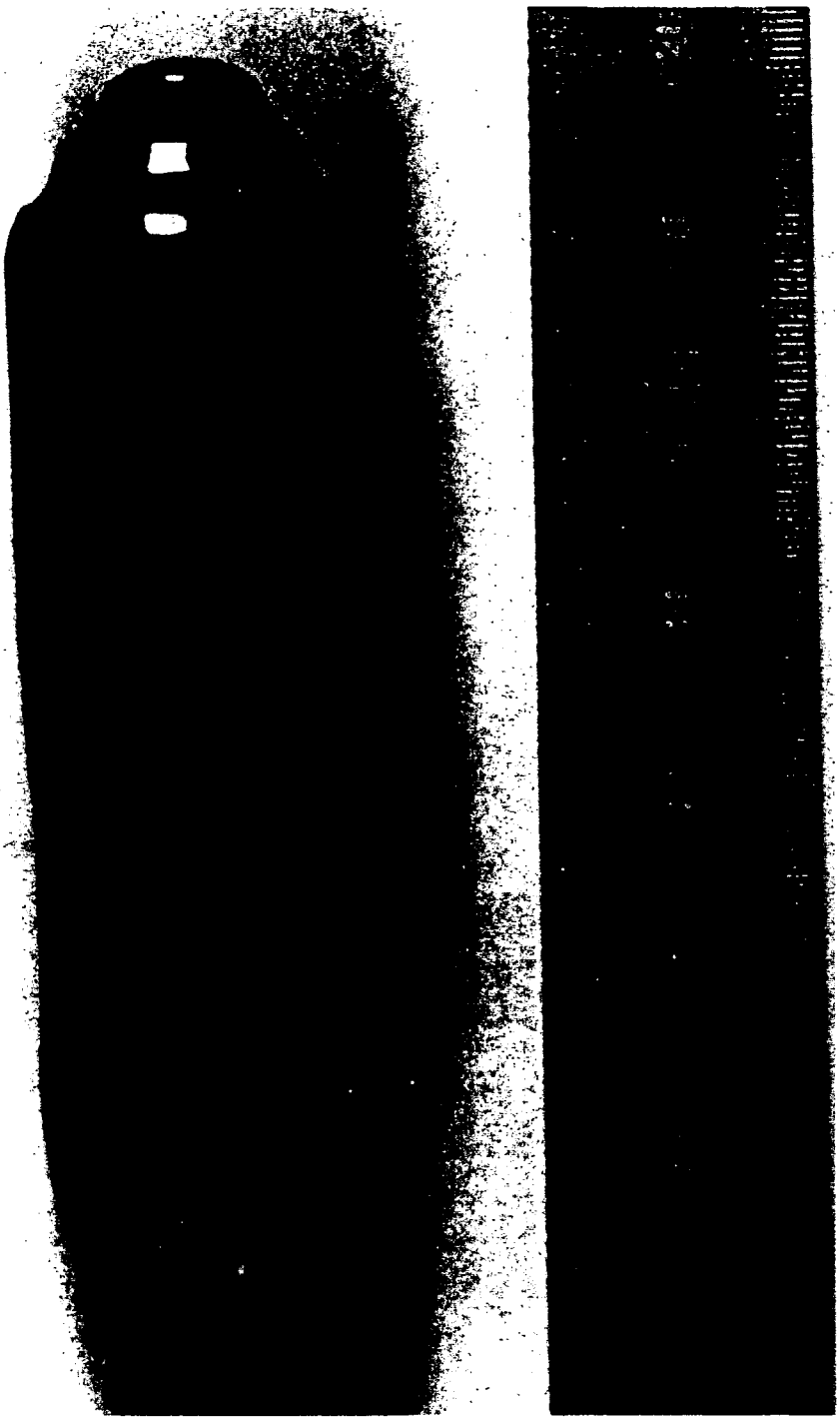


Fig.8 Fukuda et

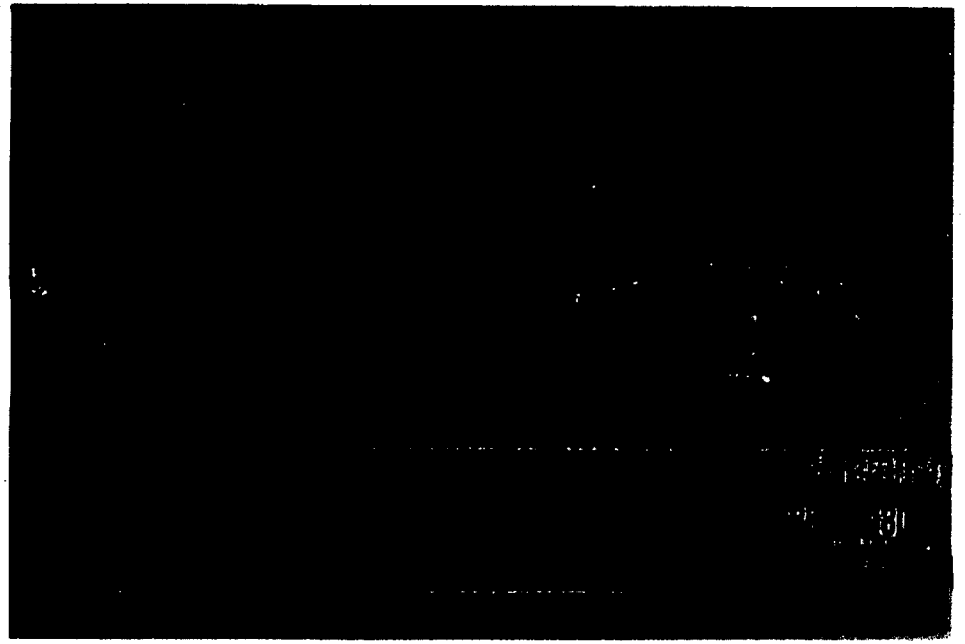




$La_{0.294}Sr_{0.706}Al_{0.647}Ta_{0.353}O_3$ Single Crystal
(LSAT Seed)

○Change of crystal growth atmosphere

$Ar+H_2$ (0.2vol%)



high purity Ar (6N)