Oxide perovskite crystals type $ABCO_4$: application and growth

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In the last year great interest appears to YBCO thin films preparation on different substrate materials. Preparation of epitaxial film is a very difficult problem. There are many requirements to substrate materials that must be fullfilled. Main problems are lattice mismatch (misfit) and similarity of structure. From paper [1] it follows that difference in interatomic distances and angles of substrate and film is more important problem than similarity of structure. In this work we present interatomic distances and angle relations between substrate materials belonging to $ABCO_4$ group (where A- Sr or Ca, B- rare earth element, C- Al or Ga) of different orientations and YBCO thin films.

There are many materials used as substrates for HTsC thin films. $ABCO_4$ group of compounds is characterized by small dielectric constants (it is necessary for microwave applications of HTsC films), absence of twins and small misfit [2]. Three most interesting compounds $CaNdAlO_4$, $SrLaAlO_4$ and $SrLaGaO_4$ were investigated. All these compounds are of pseudo - perovskite structure with space group I4/mmm. This structure is very similar to structure of YBCO. SLG substrate has the lowest misfit (0.3%) and dielectric constant.

For preparation of thin films on substrates of this group of compound plane of <100> orientation are mainly used. Good quality films of <001> orientations are obtained [3]. In this case not only a-a misfit play role, but c-3b misfit is very important too.

Sometimes, for preparation of thin films substrates of <001> and <110> orientations were used. On these substrates good films of YBCO with the same orientations were manufactured [3].

Different misfits for different YBCO faces have been analyzed. It has been found that the mismatching factor for (100) face is very similar to that for (001) face so there is possibility of preparation of thin films on both orientations.

$SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) crystals of general formula $ABCO_4$ have been grown by the Czochralski method. The quality of SLA and SLG crystals strongly depends on axial gradient of temperature and growth and rotation rates.

High quality crystals were obtained at axial gradient of temperature near crystal-melt interface lower than 50°C/cm, growth rate 1-3 mm/h and the rotation rate changing from 10-20rpm [4].

Strong anisotropy in morphology of SLA and SLG single crystals grown by the Czochralski method is clearly visible. On the basics of our considerations for $ABCO_4$ type of the tetragonal crystals there can appear {001}, {101} and {110} faces for ionic type model [5]. Morphology of these crystals depend on ionic-covalent character of bonding and crystal growth parameters. Point defects are observed in crystals and they are reflected in color changes (colorless, yellow, green). Point defects are detected in directions perpendicular to oxide planes and are connected with instability of oxygen position in lattice.

To investigate facets formations crystals were doped with Cr^{3+}, Er^{3+}, Pr^{3+}, Ba^{2+}. Chromium greater size ion which is substituted for Al^{3+} clearly induces faceting. There appear easy {110} faces and SLA crystals crack even then the amount of Cr is below 0.3at.%. SLG single crystals are not so sensitive to the content of chromium ions.

It was also found that if {110} face appears at the beginning of growth process the crystal changes its color on the plane {110} but it happens only on the shoulder part . The projection of {110} face has a great amount of oxygen positions which can be easy defected. Pure and doped SLA and SLG crystals measured by EPR in the <110> direction show more intensive lines than in other directions which allows to suggest that the amount of oxygen defects on the {110} plane is higher.

In order to find the origin of colors and their relation with the crystal stability, a set of SLA and SLG crystals were investigated using optical spectroscopy. The colored samples exhibit an absorption band stretching from the UV absorption edge of the crystal, from about 240 nm to about 550 nm. In the case of colorless sample, the absorption spectrum consists of a relatively weak band in the UV region. The spectral position and intensities of absorption bands of SLA are typical for imperfection similar to color centers which may be created in most of oxide crystals by UV and X-radiation.

It is pointed out that crystal growth process of polycomponent oxide crystals by Czochralski method depends on the preparation of melt and its stoichiometry, orientation of seed, gradient of temperature at crystal-melt interface, parameters of growth (rotation and pulling rate) and control of red-ox atmosphere during seeding and growth. Growth parameters have an influence on the morphology of crystal-melt interface, type and concentration of defects.

References:

1. Ruyan Guo, A.S. Bhalla, L.E.Cross and Rustum Roy, J.Mater.Res. 9 (1994) 1644

2. K.Mazur, J.Sass, A.Pajaczkowska, SPIE Liquid and Solid State Crystals 1845 (1992)103

3. S.Hotsu, J.Ishii, T.Kawai and S.Kawai, Appl. Phys. Lett. 59 (1991) 2886.

4. A. Gloubokov, R.Jablonski, W.Ryba-Romanowski, J.Sass, A.Pajaczkowska, R.Uecker and P.Reiche, J. Crystal Growth 147(1995)123.

5. E.Janssen, A.Gloubokov, A.Pajaczkowska and C.F.Woensdregt, "Growth Morphology of Tetragonal $ABCO_4$ Compounds: Theory and Observations on Czochralski Growth Crystals", submitted to ICCGXI' 95, in preparation.

OXIDE PEROVSKITE CRYSTALS TYPE $ABCO_4$: APPLICATION AND GROWTH

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CONTENTS:

Table 2. PEROVSKITE - TYPE SUBSTRATE MATERIALS FOR HTcS THIN FILMS

Material		$SrTiO_3$	$LaAlO_3$	$LaGaO_3$	$NdGaO_3$	Sr_2AlTaO_6	$SrLaAlO_4$	$SrLaGaO_4$
Unit Cell		Cubic[16,36]	Rhombo[16,20,36]	Ortho[16,36]	Ortho[18,20,36]	Cubic[33]	Tetra[16,22]	Tetra[32,34]
Lattice constants, nm	a	0.3905	0.5357	0.5519	0.5428	0.3895	0.3754	0.3843
	b		α=60°06'	0.5494	0.5498			
	c			0.777	0.711		1.263	1.268
Calculated parameter a_c*		0.3905	0.3788	0.3894	0.3863	0.3895	0.3754	0.3843
Lattice mismatch, % ***	YBCO[36]	1.0	2.0	0.7	0.07	0.74	3.0	0.6
	BSSCO[15,**]	2.3	0.7	2.2	0.6	2.0	1.6	0.7
	HBCCO[35]	1.5	1.5	1.2	0.4	1.3	2.5	0.08
Twins		+	+	+	±	-	-	-
Dielectric properies at Given Frequency Range, (GHz)****		10 - 300	10 - 700	10 - 500	10 - 300	10 - 100	10 - 500	10
Dielectric constant	ε'(300K)	310	20	26	22.8	11.9	17	22
	ε'(100K)	2200	21.5	25	22		16.7	
Loss tangents tan(δ)	(300K)	$3*10^{-2}$	$5*10^{-3}$	$8*10^{-3}$	$8*10^{-3}$	$1.7*10^{-3}$	$8*10^{-4}$	$5.7*10^{-5}$
	(100K)	$6*10^{-2}$	$1*10^{-3}$	$6*10^{-3}$	$6*10^{-3}$		$2*10^{-4}$	$2*10^{-5}$
Linear thermal coefficient expansion, α * 10^{-6} °C^{-1}		9.4	11	9	10		7.55	10.05
Melting point, °C		1920	2100	1750	1750	1900	1650	1520

* a_c calculated according to equatation: $a_c=\sqrt{(a^2+b^2)}/2$.

** a_{c1} calculated according to equatation: $a_{c1}=a_c*\sqrt{2}$.

*** Δ calculated accordning to equatation: $\Delta=|1-a_{film}/a_c|*100\%$.

**** All dielectric constants and linear thermal coefficient expansion are given along a axis.

SOME PROPERTIES OF $SrLaAlO_4$ AND $SrLaGaO_4$ SINGLE CRYSTALS

Properties	$SrLaAlO_4$	$SrLaGaO_4$
Structure (4I/mmm)		
a=b	0.3754 nm	0.3843 nm
c	1.263 nm	1.268 nm
Hardness		
on {001} planes	3512 MPa	7394 MPa
on {100} planes	6349 MPa	7119 MPa
Thermal conductivity (300K)		
along 'a' axis	7.078 W $m^{-1}K^{-}$	3.297 W $m^{-1}K^{-1}$
along 'c' axis	1.170 W $m^{-1}K^{-1}$	4.215 W $m^{-1}K^{-1}$
Claveage plane	{001}	?

CONCLUSIONS:

The Hartman-Perdok theory explains the form of the crystal-melt interface of SLA and SLG crystals grown from the melt by the Czochralski method.

The experiments confirm that (001) is the most stable face of the tetragonal $ABCO_4$ structure.

The appearance of {103} on SLG crystals can be explained by assuming that the Ga-O bonding is much weaker than the Al-O bonding especially at the conditions of superheating. This aspect has also be taken into account in the models with reduced effective oxygen charges.

The conclusion is that {110} and {103} facets should be avoided at the beginning of growth as they are not appropriate for crystal growth due to their association with coloring and point defects.

It was found that the best quality crystals are grown on {101} faces.

Point defects can be removed by fitting growth conditions relate to the crystal properties as well as their morphology.

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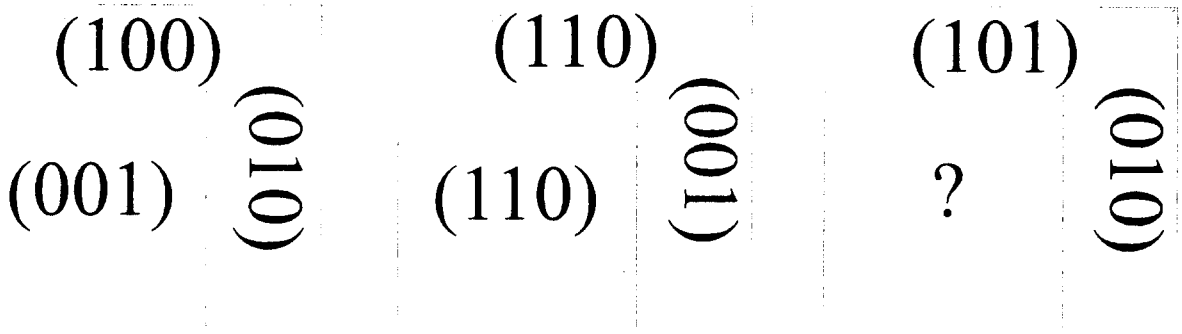
ELASTIC PROPERTIES - BRILLOUIN LIGHT SCATTERING

$SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) compounds crystallize in the perovskite-like, tetragonal K_2NiF_4 - type structure of I4/mmm space group. They have six independent elastic constants:
$C_{11} = C_{22}$, C_{33}, $C_{44} = C_{55}$, C_{66}, C_{12}, $C_{13} = C_{23}$.

Crystals of different geometry were measured:



The data for determination of the elastic constants, obtained from Brillouin spectra - Table 1. Using diferent scattering geometries the velocity of longitudinal (L) and transverse (T) modes were characterized by different polarization u. The velocity of acoustic phonons propagating along different directions in SLA and SLG single crystals was determined.

The velocity V_i of the transverse and longitudinal phonons were deduced from the measured frequency shifts $\Delta \omega_B$, using the Brillouin equation, which is in the case of 90^0 scattering geometry takes the from:

$$\Delta\omega_B = V_i \omega_i (n_i^2 + n_s^2 - 2n_i n_s \cos\theta)^{1/2} / c$$

where ω_i is the frequency of the incident light, n_i and n_s are the refractive indices for the polarization of incident and scattered light, respectively and θ is the angle between the incident and scattered beams.

The velocities were than used to estimate the elastic constants $C_{i,j}$
The elastic constants were determined from the solution of the equation of motion:

$$| C_{ijkl} q_j q_k - \rho V^2 \sigma ij |$$

Here q_j , q_k are the directions cosines of q, ρ is the density od the crystal, C_{ijkl} are the elastic constants.
The accuracy of calculations is no more than 2%.

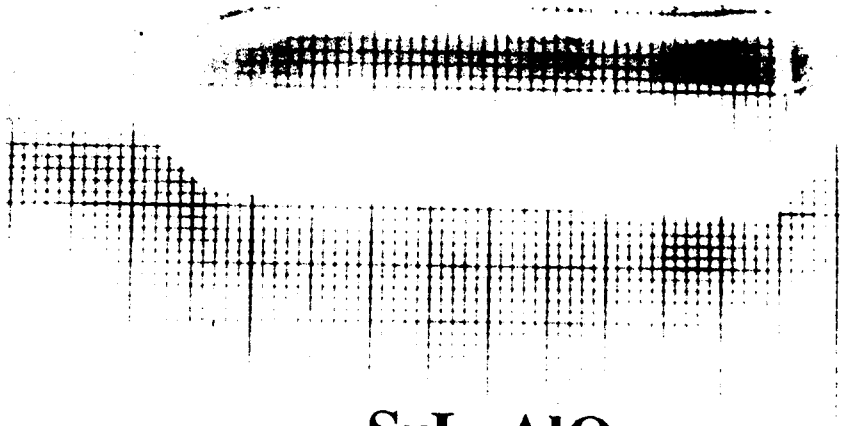
Results show that for SLG single crystals, the velocity of the longitudinal and transverse acoustic phonons propagating in (001) plane is different in a and b directions.

Lower value of the velocity in a direction can be probably caused by the damping of the elastic waves in this directions due to the existence of some kind of defects.

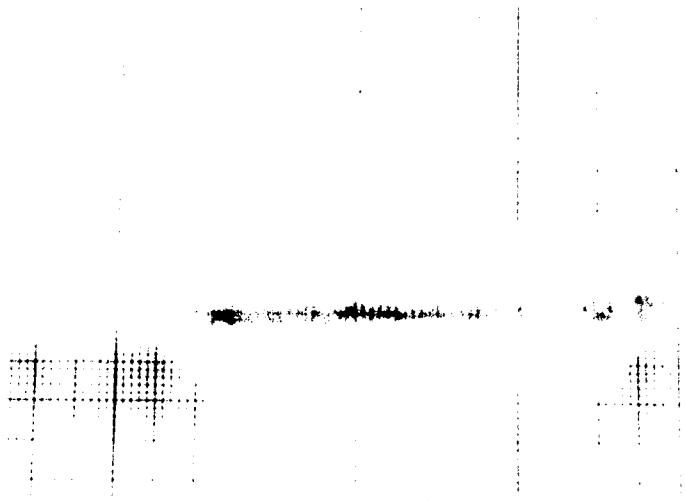
Table I. The data which served as a basis for the determination of the elastic constants C_{ij} of $SrLaAlO_4$ and $SrLaGaO_4$ single crystals.

No	q	u		ρV^2	SLA			SLG		
					$\Delta\omega_B$ [cm^{-1}]	V [m/s]	ρV^2 *10^{10} [N/m^2]	$\Delta\omega_B$ [cm^{-1}]	V [m/s]	ρV^2 *10^{10} [N/m^2]
1	[$\bar{1}01$]	[$\bar{1}01$]	QL	$\frac{(C_{11}+C_{33}+2C_{44})+\sqrt{(C_{11}-C_{33})^2+4(C_{13}+C_{44})^2}}{4}$	1,2879	6891	28,1	1,2590	6658	28,3
2	[$\bar{1}01$]	[101]	QT	$\frac{(C_{11}+C_{33}+2C_{44})-\sqrt{(C_{11}-C_{33})^2+4(C_{13}+C_{44})^2}}{4}$	0,6318	3381	6,8	0,5972	3159	6,4
3	[$\bar{1}01$]	[010]	T	$\frac{C_{44}+C_{66}}{2}$	0,8144	4358	11,2	0,731	3866	9,5
4*	[$0\bar{1}1$]	[$0\bar{1}1$]	QL	$\frac{(C_{11}+C_{33}+2C_{44})+\sqrt{(C_{11}-C_{33})^2+4(C_{13}+C_{44})^2}}{4}$	1,2803	6851	27,8	1,2349	6531	27,3
5*	[$0\bar{1}1$]	[011]	QT	$\frac{(C_{11}+C_{33}+2C_{44})-\sqrt{(C_{11}-C_{33})^2+4(C_{13}+C_{44})^2}}{4}$	0,6345	3395	6,8	0,5875	3107	6,2
6*	[$0\bar{1}1$]	[100]	T	$\frac{C_{44}+C_{66}}{2}$	0,8144	4358	11,2	0,7322	3873	9,6
7*	[$1\bar{1}0$]	[$1\bar{1}0$]	L	$\frac{C_{11}+C_{12}+2C_{66}}{2}$	1,3908	7442	32,8	1,2308	6510	27,1
8	[$1\bar{1}0$]	[001]	T	C_{44}	0,7794	4171	10,3	0,7202	3809	9,3
9*	[010]	[010]	L	C_{11}	1,2673	6781	27,2	1,2507	6615	28,0
10*	[010]	[001]	T	C_{44}	0,7611	4073	9,8	0,7284	3852	9,5
11	[100]	[100]	L	C_{11}	1,2709	6801	27,4	1,2158	6430	26,4
12	[100]	[001]	T	C_{44}	0,7566	4049	9,7	0,7092	3751	9,0
13*	[100]	[010]	T	C_{66}	0,8413	4501	12,0	0,6766	3579	8,2
14*	[001]	[001]	L	C_{33}	1,2778	6838	27,7	1,2002	6348	25,7
15	[001]	[010]	T	C_{44}	0,796	4259	10,7	0,6873	3635	8,4

(14). Therefore, for the calculations of the elastic constants, for both SLA and SLG single crystals, we have chosen only scattering geometries marked by asterisk.



$SrLaAlO_4$



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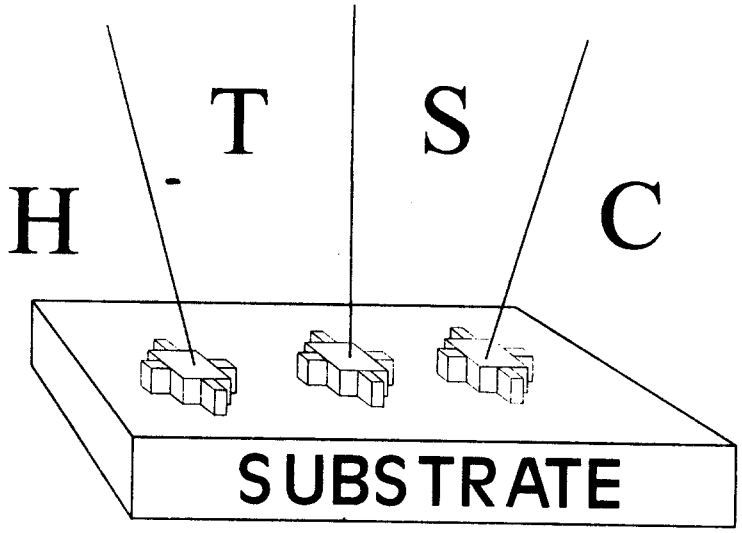

on Substrate Crystals and HTSC Films, ICSC-F '96,

Jaszowiec, Poland, September 16-20, 1996

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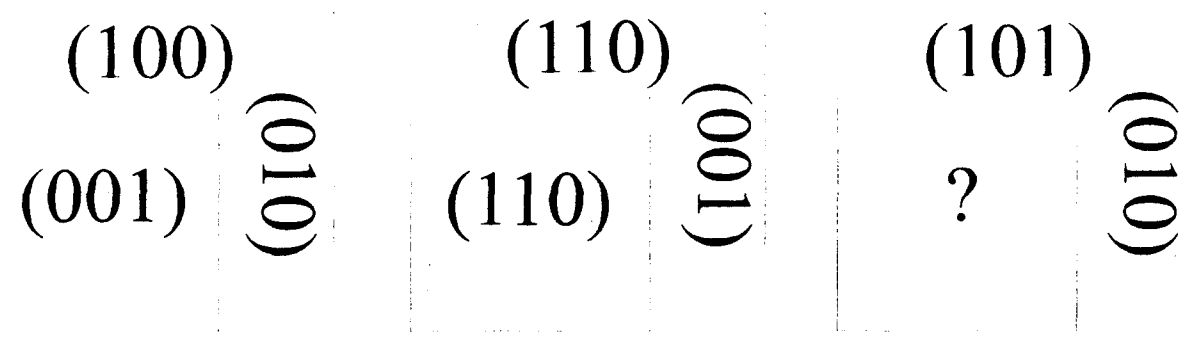

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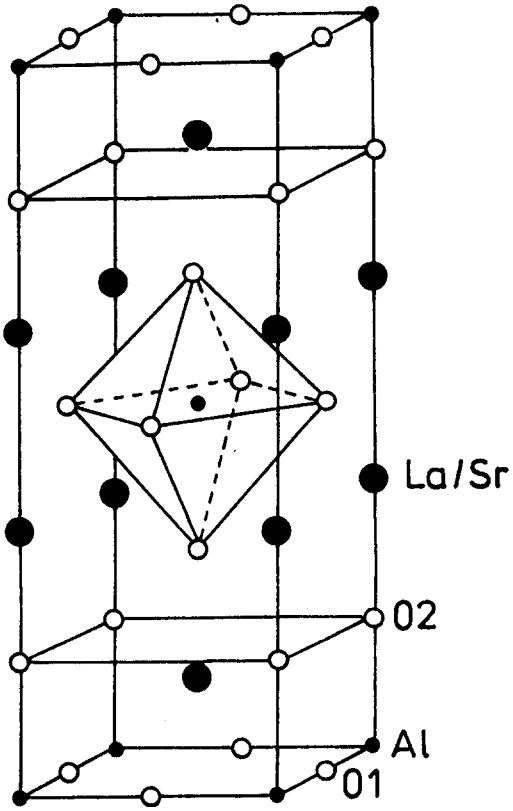
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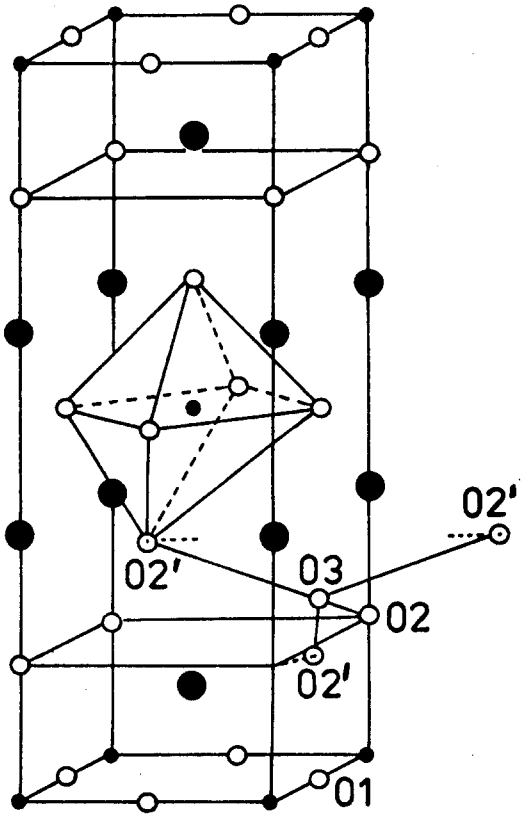
Al
01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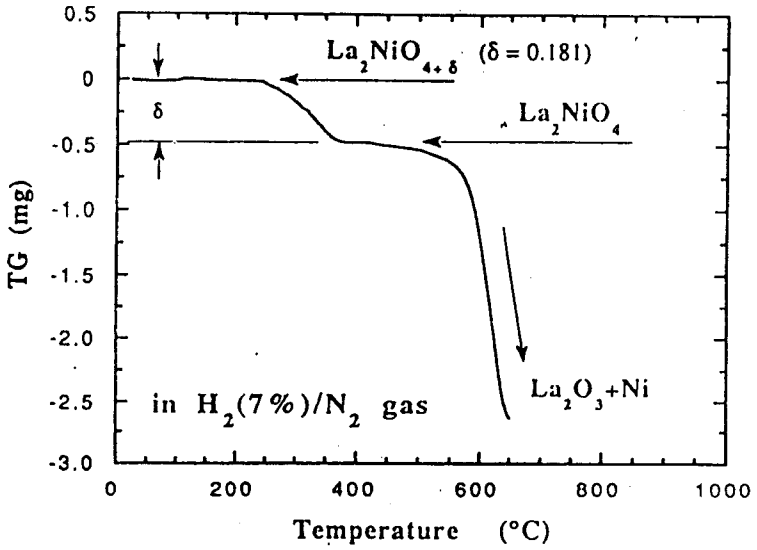
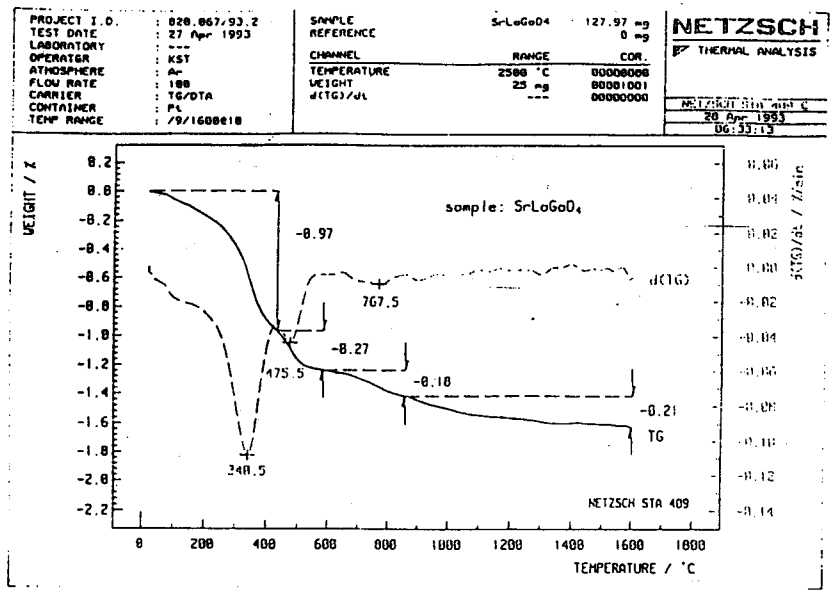
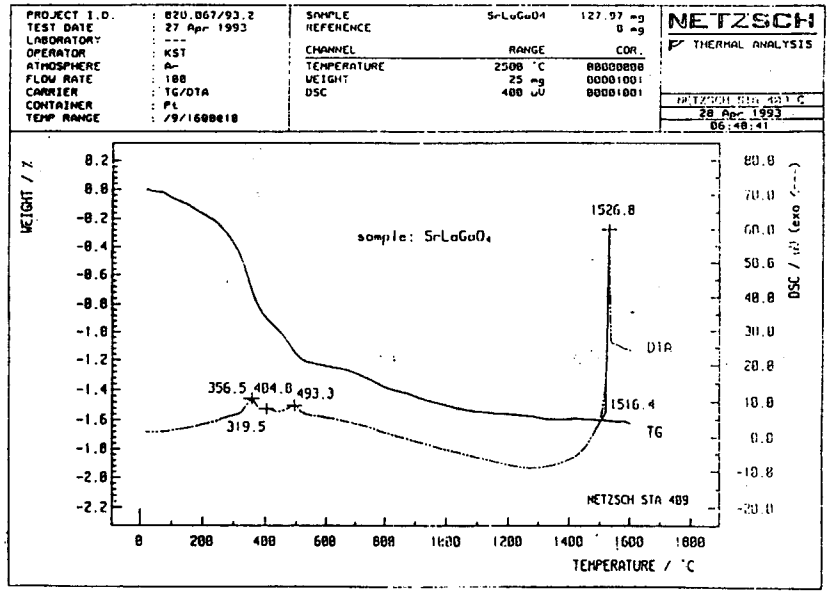
TG measurements of SLG and $La_2NiO_{4+\delta}$ compounds.

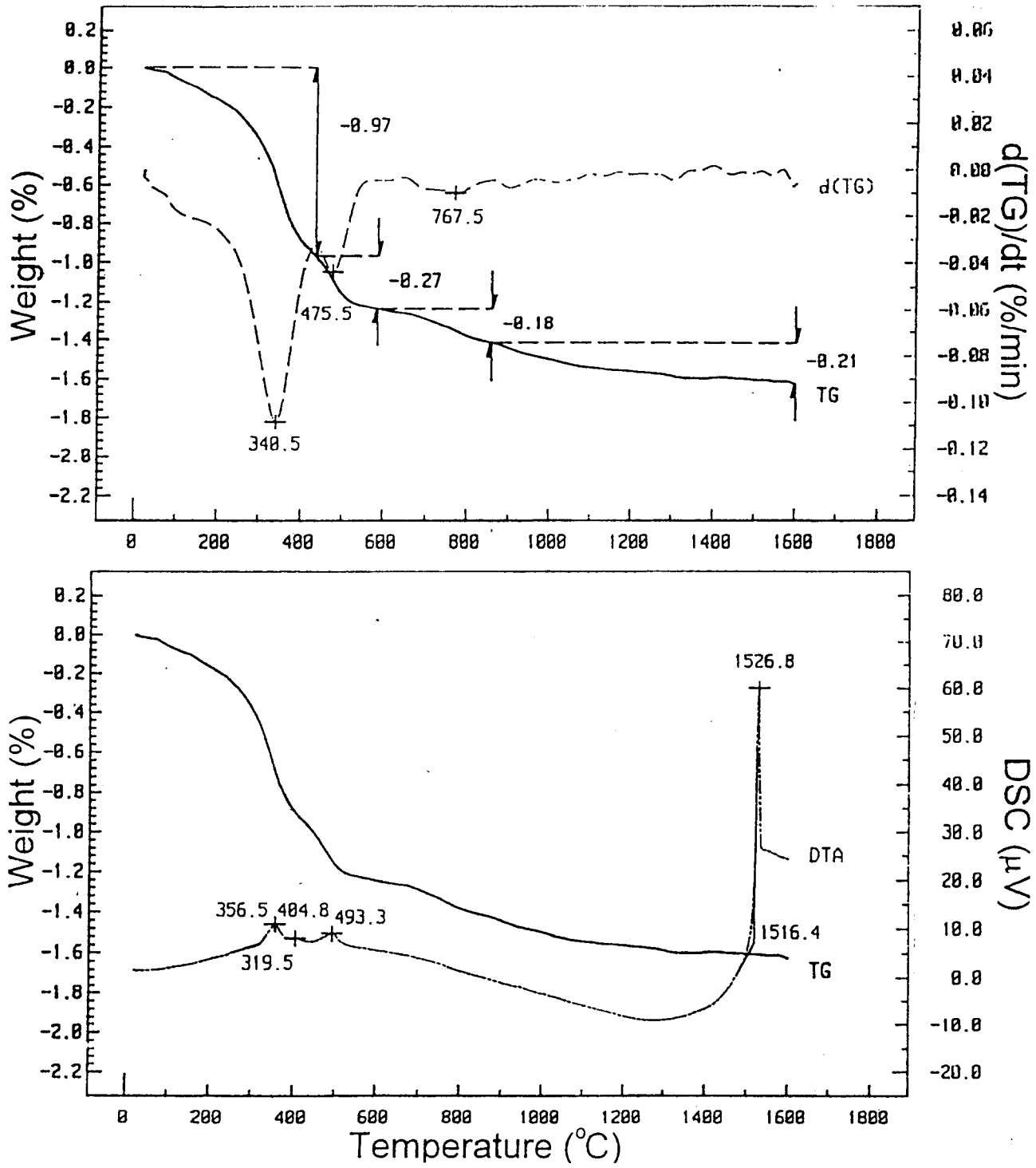


TG curve for the $La_2NiO_{4+\delta}$ crystal ($\delta = 0.18$) grown at $P(O_2) = 3$ atm. The first drop in the curve corresponds to the removal of excess oxygen δ, and the second one to the reduction of NiO to Ni.





THERMAL ANALYSIS OF SLG - synthesized



Auger electron spectroscopy (AES)

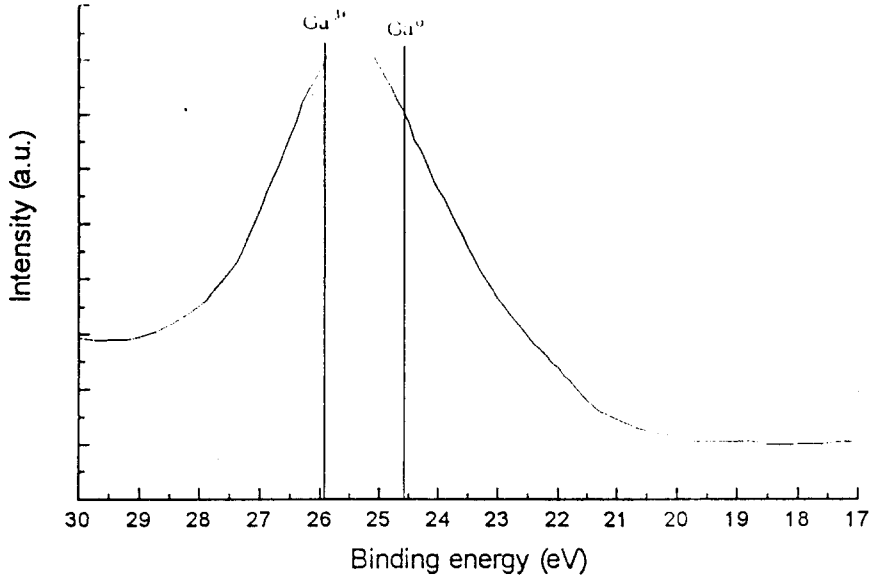
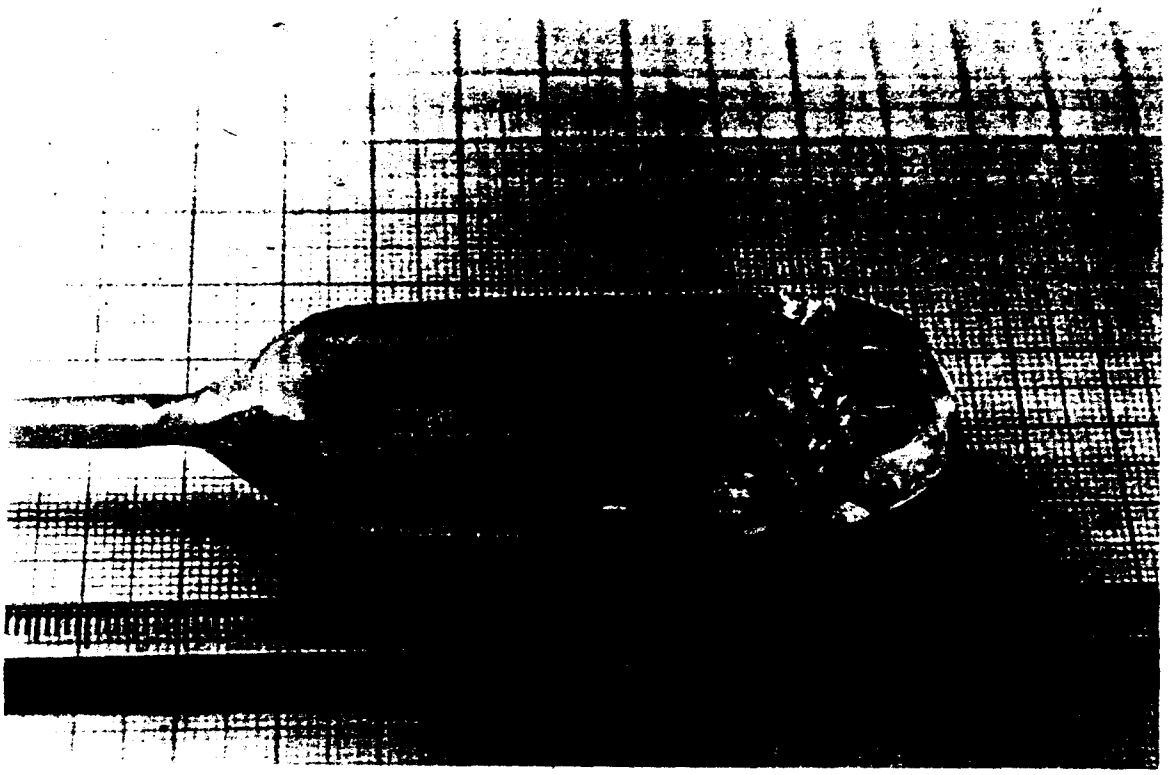
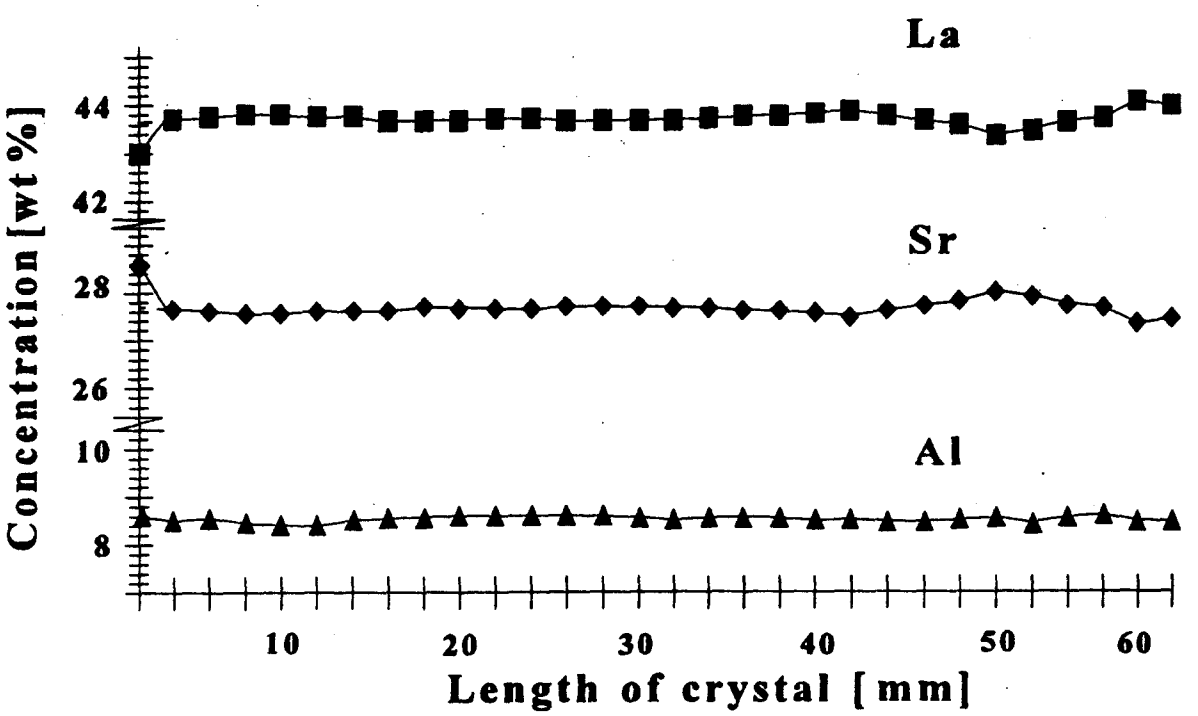


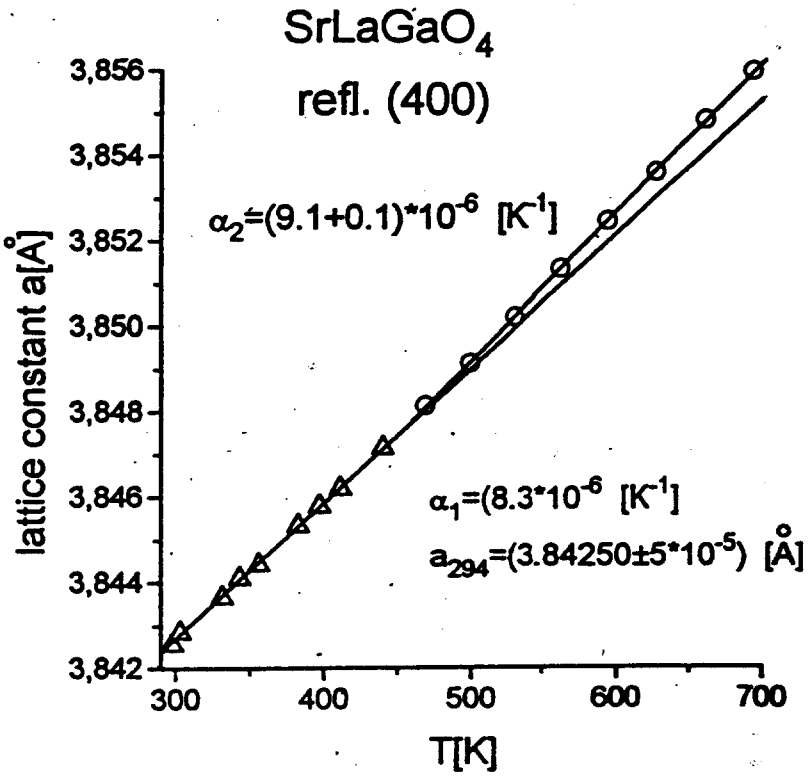
Figure 35. AES spectra of Ga ion (3d line, vacuum 10^{-9} mbar).

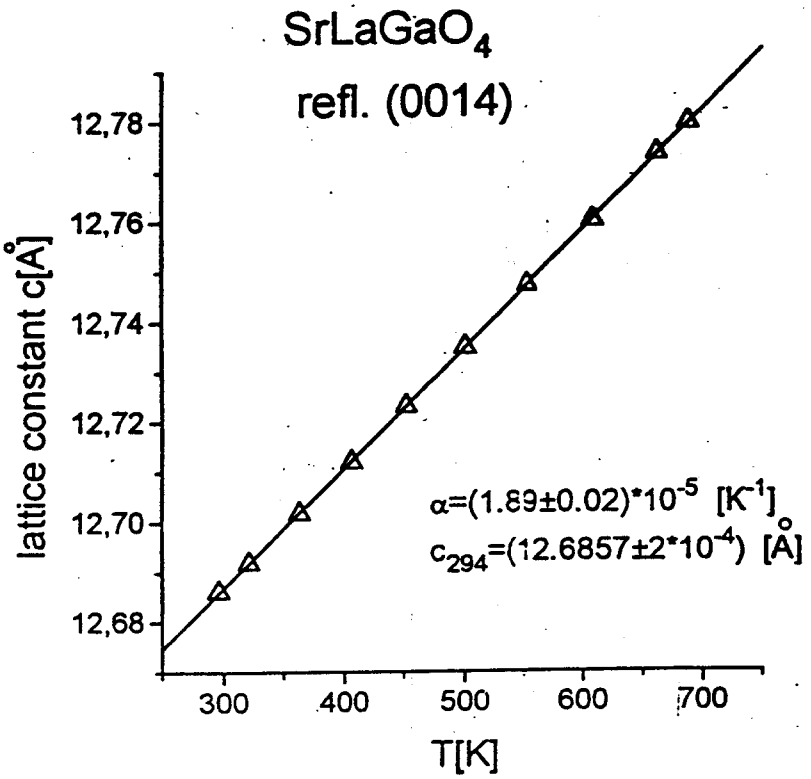
EPMA measurements





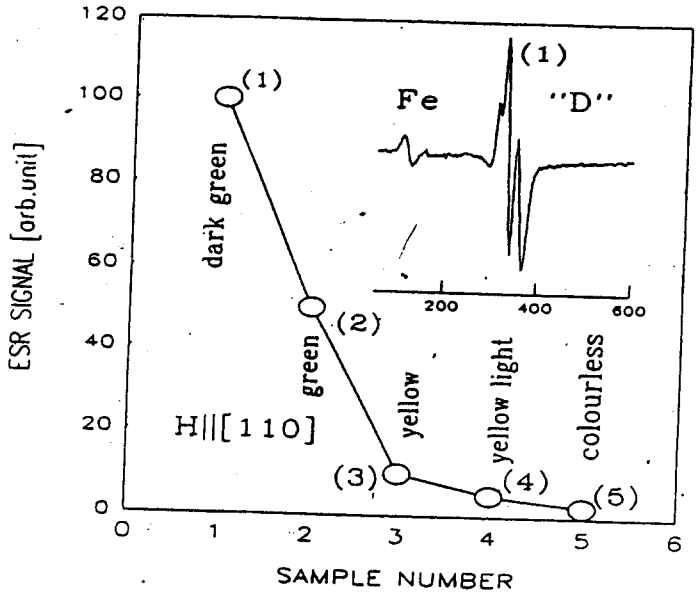
EPMA measurements of La, Sr and Al distribution along $SrLaAlO_4$ crystal



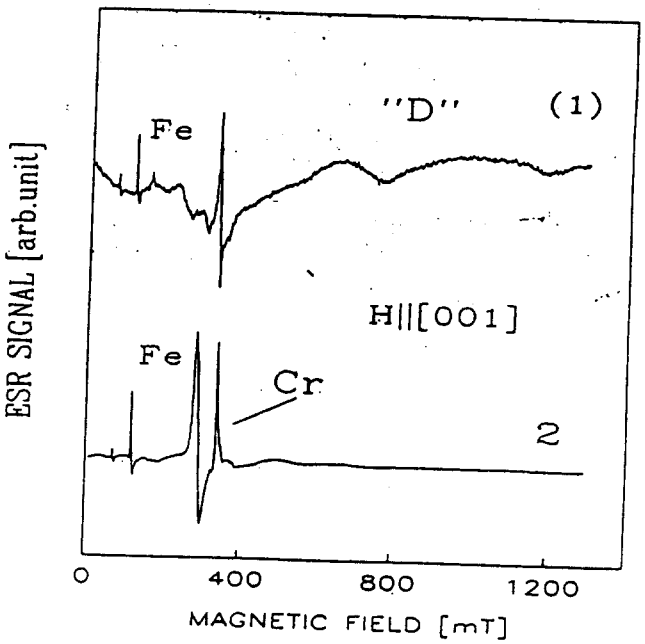


Temperature dependence of a and c lattice constants in $SrLaGaO_4$. The lattice constants at room temperature and thermal expansion coefficients are given.

4. ESR measurements



ESR intensivity signals for various colored crystals related to the intensivity of "D" line shown in the spectrum of the inset, presented for the dark green colored crystal (1). Signal of left side belongs to Fe impurity less 10^{-3} weight %. Spectra are given at 20 K and frequency $\upsilon = 9.423$ GHz, P= 2 mW.



ESR intensivity signals for H ∥ [001] of the dark green crystal (1), above Fig. and crystal doped Fe and Cr (1.5 *10^{-2} weight), curve 2. Spectra are given at 20 K and frequency $\upsilon = 9.423$ GHz, P= 2 mW.

A B S O R P T I O N S P E C T R A

SLA - single crystals - SLG

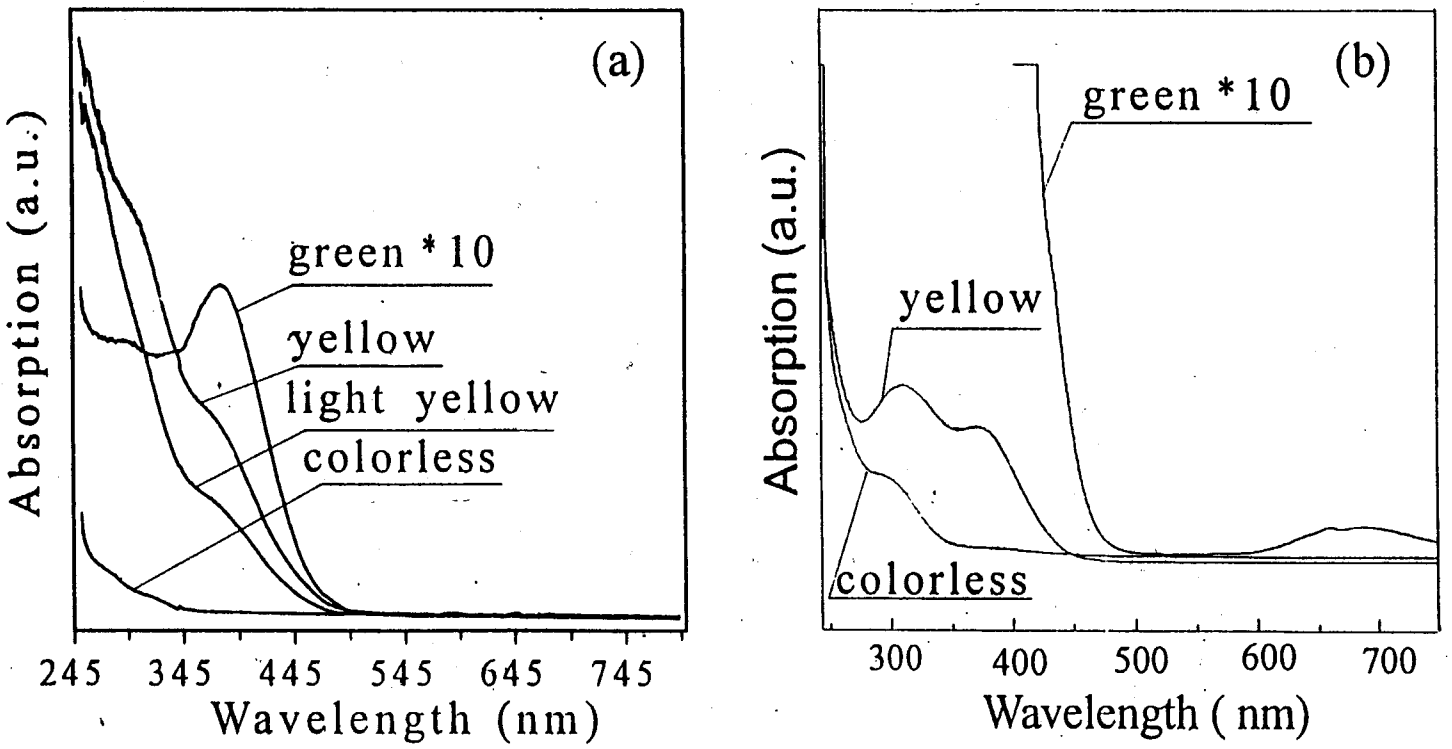
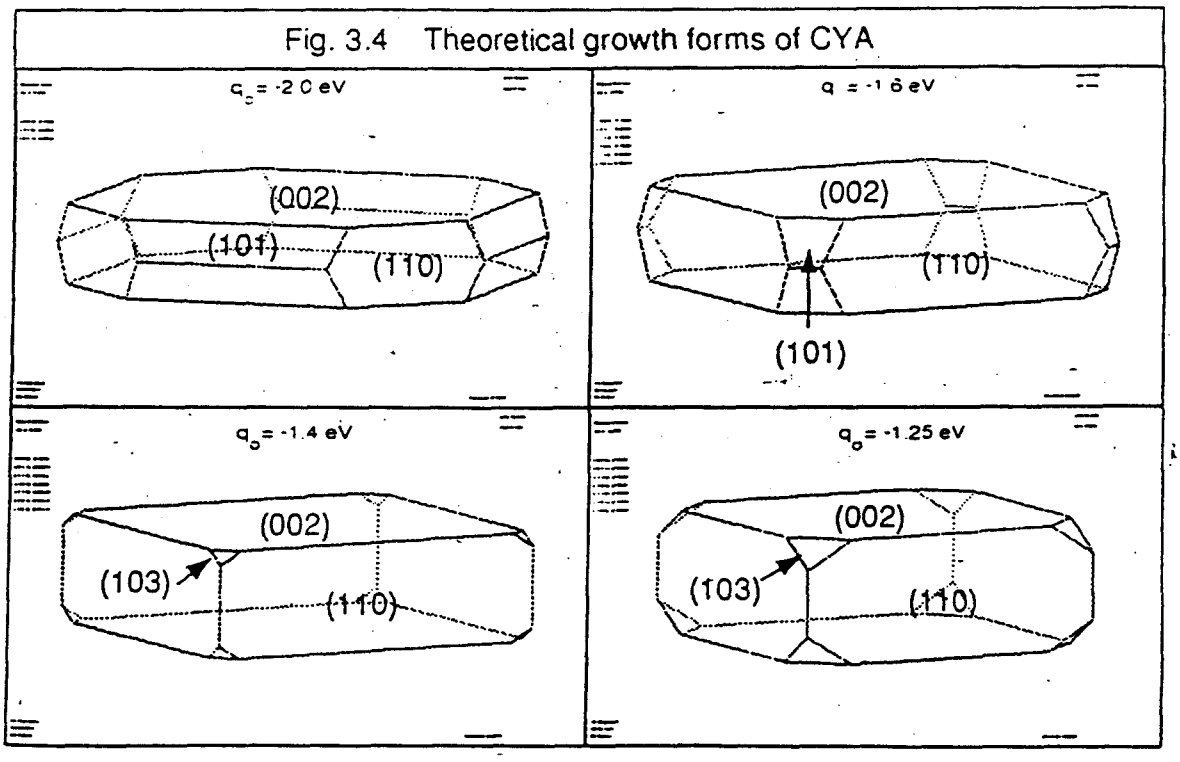
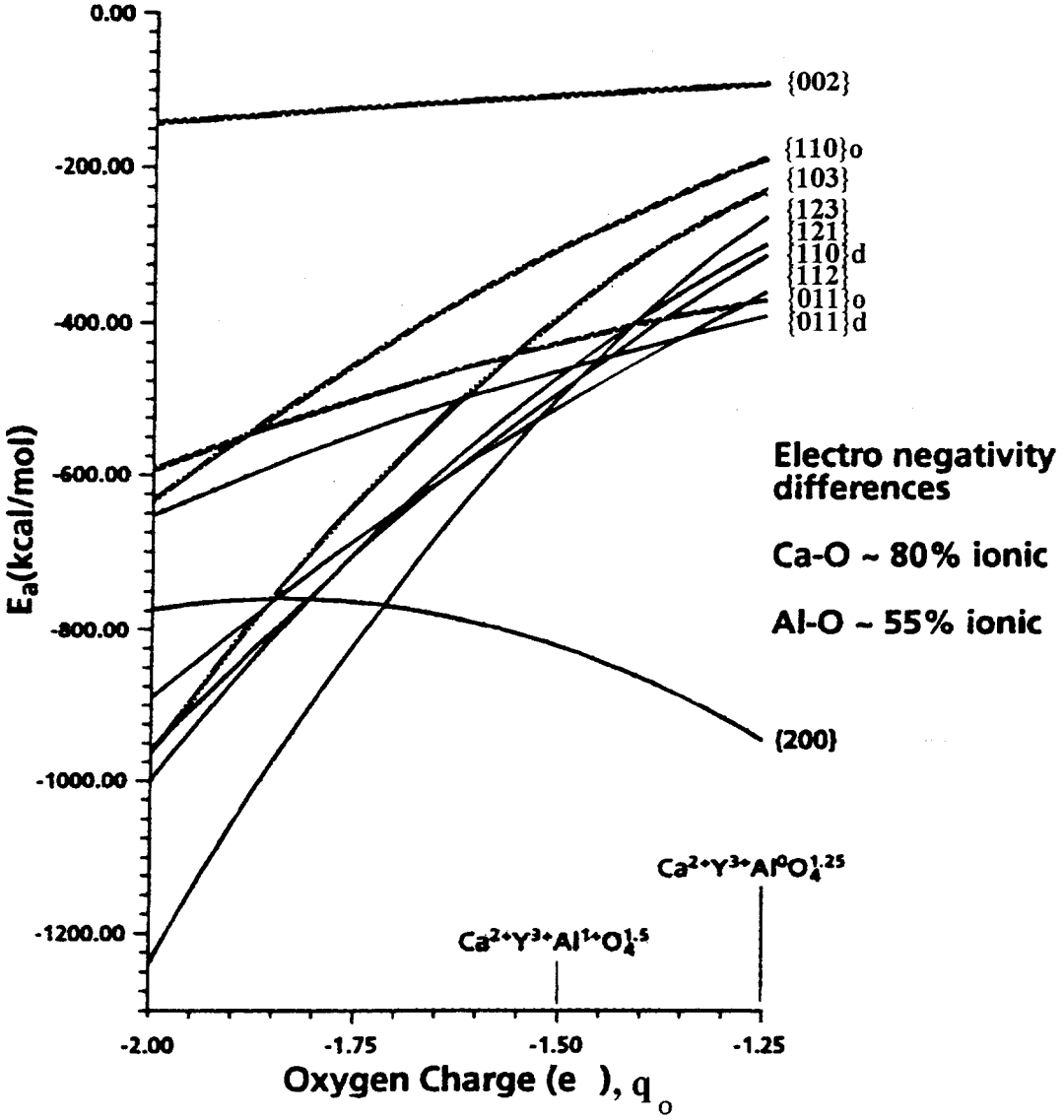


Fig. 3.4 Theoretical growth forms of CYA



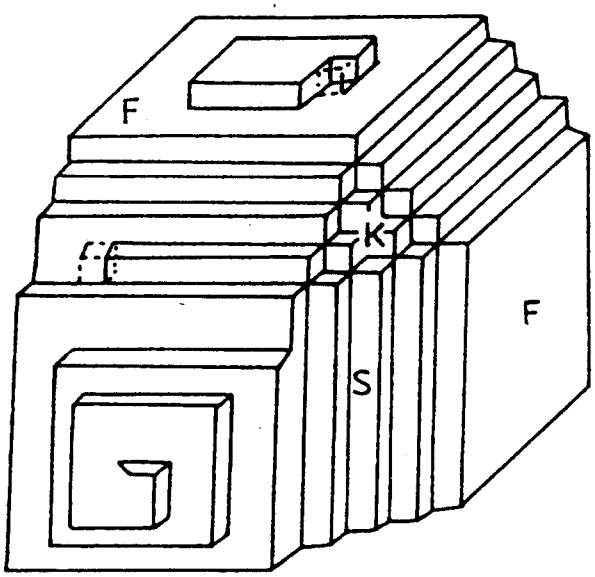

0.00
-200.00
-400.00
-600.00
-800.00
-1000.00
-1200.00
E_a(kcal/mol)
{002}
{110}o
{103}
{123}
{121}
{110}d
{112}
{011}o
{011}d
Electro negativity differences
Ca-O ~ 80% ionic
Al-O ~ 55% ionic
{200}
$Ca^{2+}Y^{3+}Al^{0}O_4^{1.25}$
$Ca^{2+}Y^{3+}Al^{1+}O_4^{1.5}$
-2.00
-1.75
-1.50
-1.25
Oxygen Charge (e), q_o

Hartman classifies the faces of a crystal into **F** (flat), **S** (stepped) and **K** (kinked) faces.

F - type faces possess at least two sets of chains of periodically bonded atoms, molecules or radicals (called Periodic Bond Chains, PBCs) **S** faces have one such PBC while **K** faces do not have any PBC.

Thus singular faces with minimum surface free energy are **F** faces, while **S** and **K** faces correspond to vicinal and nonsingular faces, respectively.

F - $CaYAlO_4$, $q_o = -2$ e, in order of decreasing d_{hkl} :
{002}, {101}, {103}, {110}, {112}, {200}, {123}



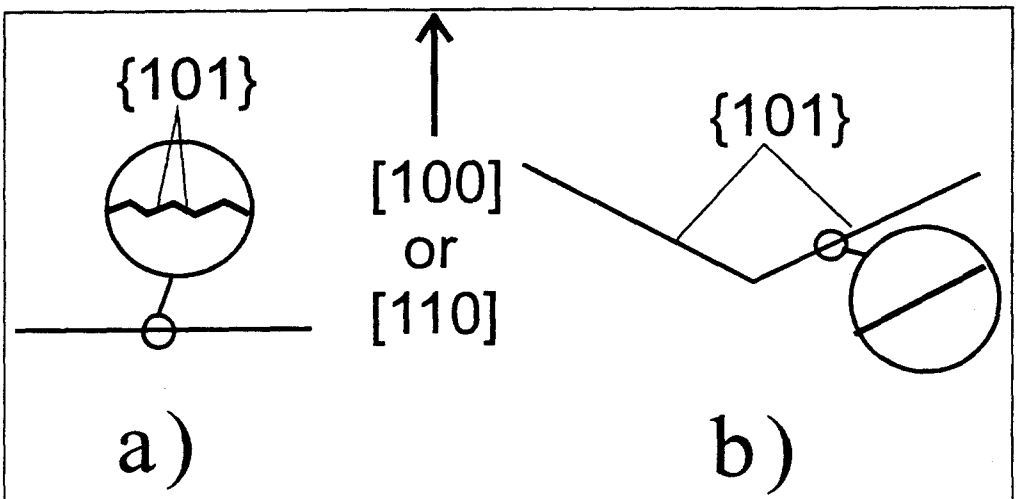
Classification of different types of faces of a simple cubic crystal according to the Periodic Bond Chains (PBC):
F (flat), **S** (stepped) and **K** (kinked).

$SrLaAlO_4$ (SLA) and $SrLaGaO_4$ (SLG) crystals of different colors, cracked and opaque have been found:

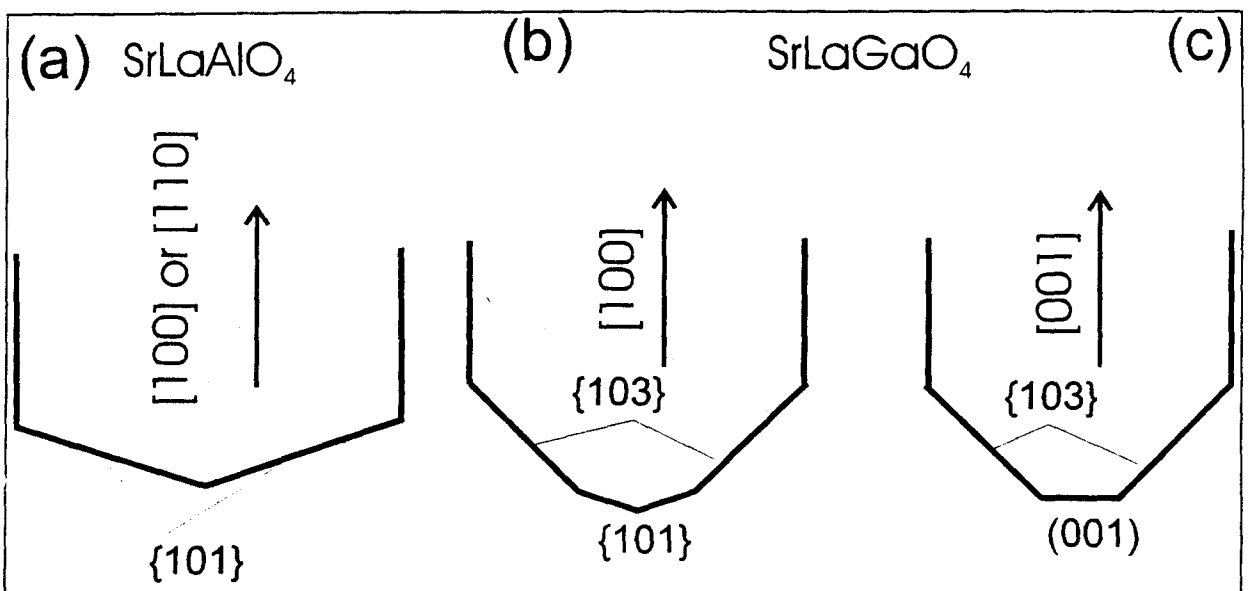
- good quality crystals (not cracked from top to bottom) are colorless-yellow,
- green color appears at the top of crystal if temperature gradient at the melt surface is high (higher than about 100 °C/cm), and oxygen content in nitrogen about 1 %vol.
- yellow/brown-amber color appears near opaque, cracking part, superheated parts

Investigations of various crystals by X-ray diffraction, ESR, optical measurements and chemicals by chemical analysis and DTA/TG have been performed:
- La_3O_3 chemical is sensitive to atmosphere of storage and reactive at temperature higher than 900 °C,
- in all crystals traces of Fe ions, less than 10^{-3} weight% has been identified by ESR,
- higher contents of Fe and Cr ions have been only found in the doped samples by optical measurements as well as ESR and chemical analysis,
- the defective structure 'D' found by ESR and optical measurements, the intensity of effect was lowered from green to yellow and colorless crystals,
- these defects are related to oxygen points defects, and some of these correspond to color center (the density of defects increases in UV light irradiation)
- fluctuation of Sr-La atoms appears at the top of crystal (near the seed and at the beginning of cracking). It can be explained as result of increasing of oxygen defects accompanied by the change of Sr^{2+} and La^{3+} ions ratio,
- any other phases e.g. La_2O_3, LaO(OH) compounds and transition elements have not been detected.

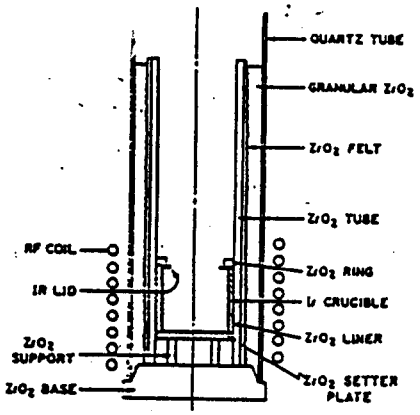
Crystals are colored depending on temperature gradient at the crystal-melt interface, melt composition and oxygen partial pressure. There is controversial discussion about the origin of color which is also related to the appearance of facets and may be caused by ordering of Sr/La and oxygen ions in the structure.
Growth morphology of SLA and SLG is strongly differed.

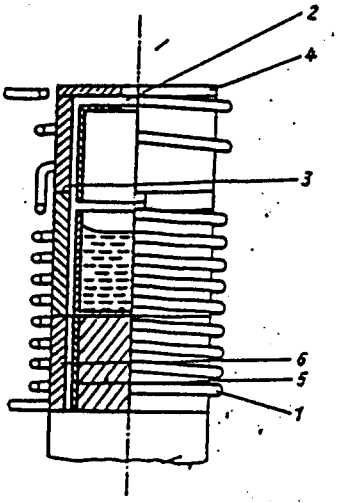


SLA crystal melt interface: (a) pseudo-flat; (b) conical smooth.



Conical crystal/melt interface: (a) SLA crystal, (b) and (c) SLG crystal seed orientations [100] and [001], respectively.





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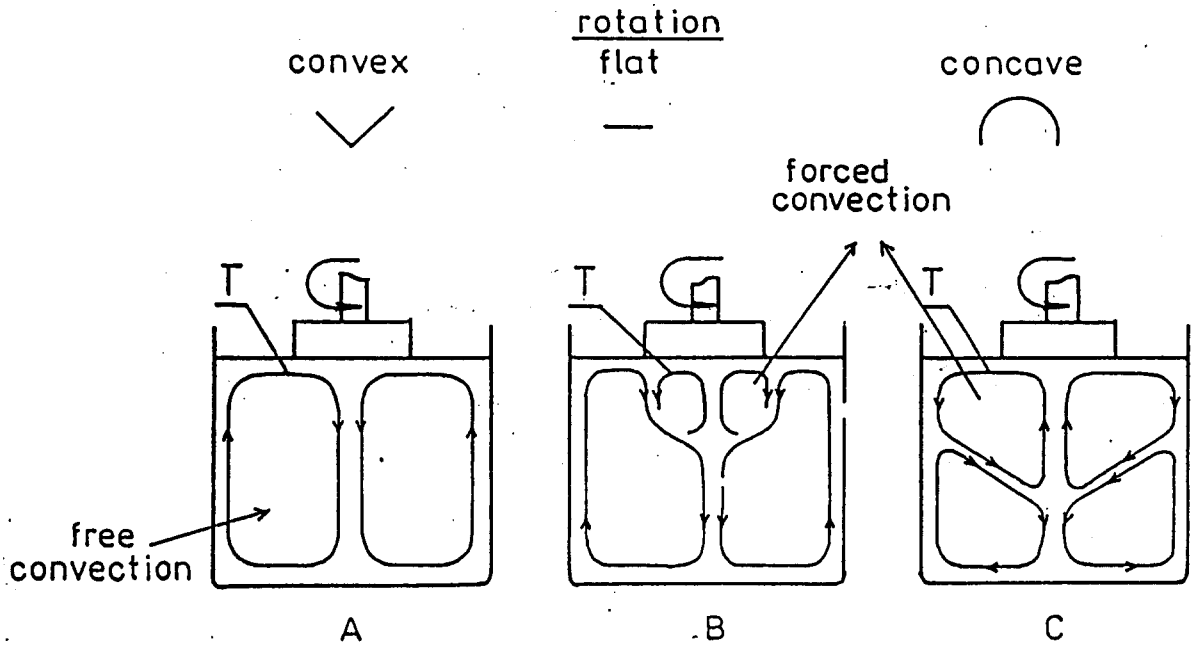
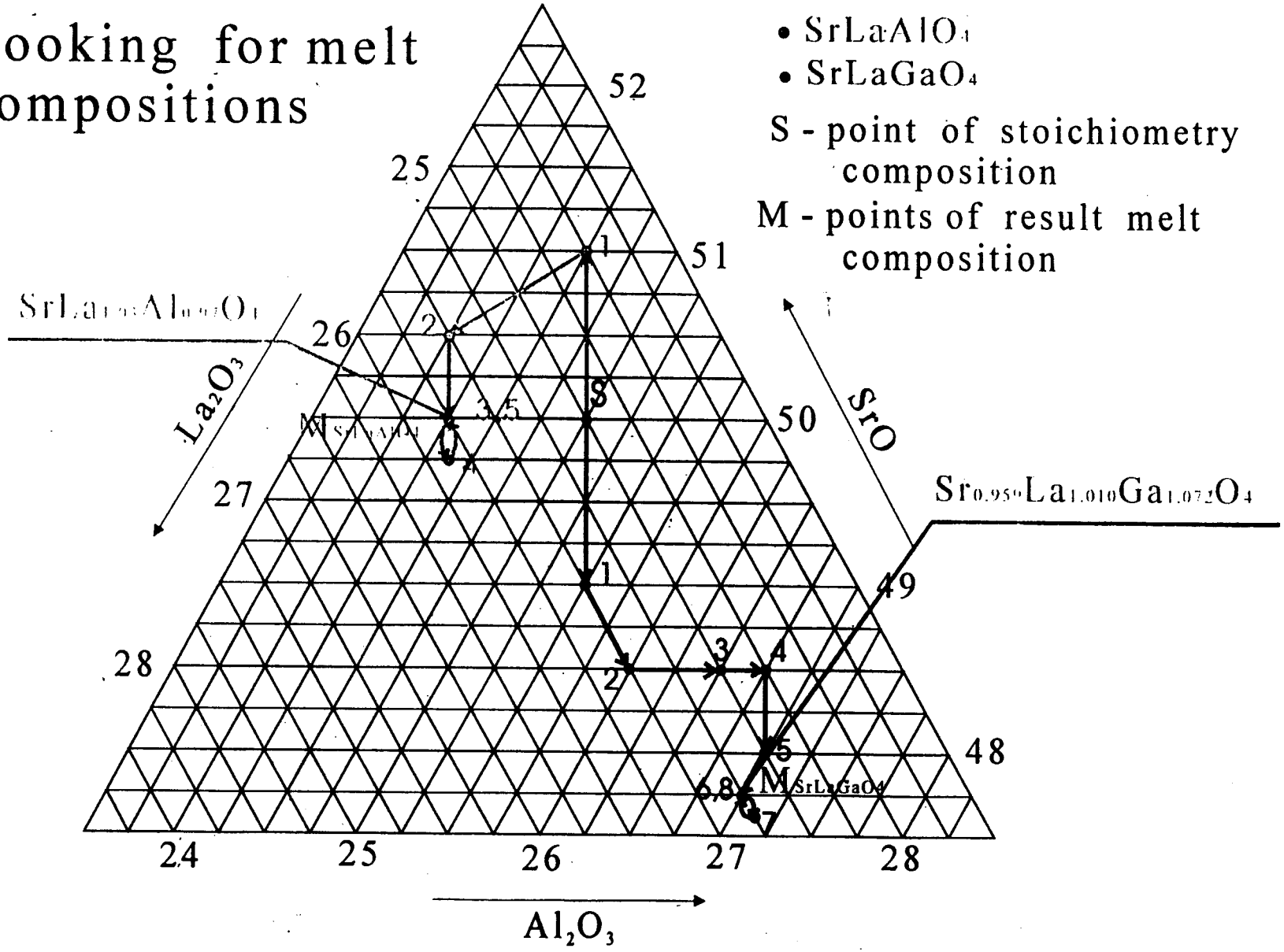


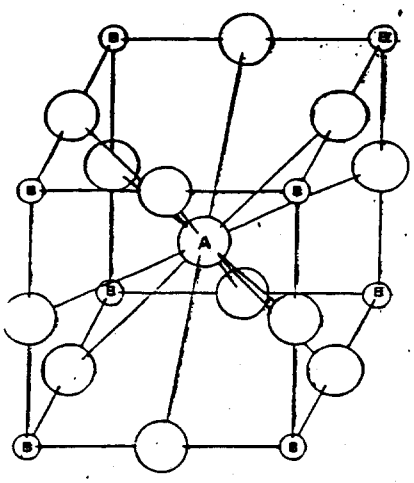
Looking for melt compositions

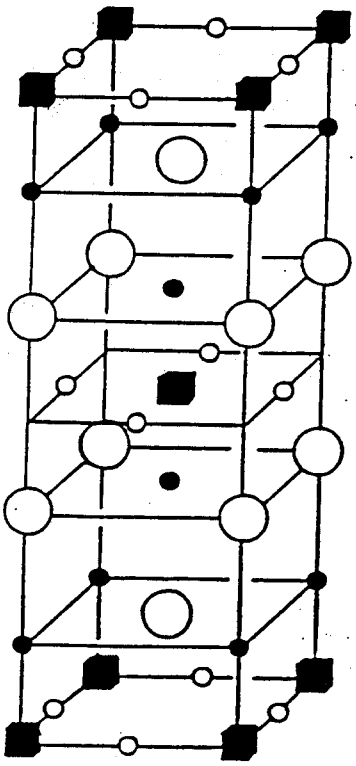


Pm$\bar{3}$m

($LaTiO_3$, $LaAlO_3$) $\alpha = \beta = \gamma = 90°$; $a = b = c$

R 3m $\quad a = b = c$, $\alpha \neq 90°$





$ABCO_4$

I 4/mmm $\quad K_2NiF_4$

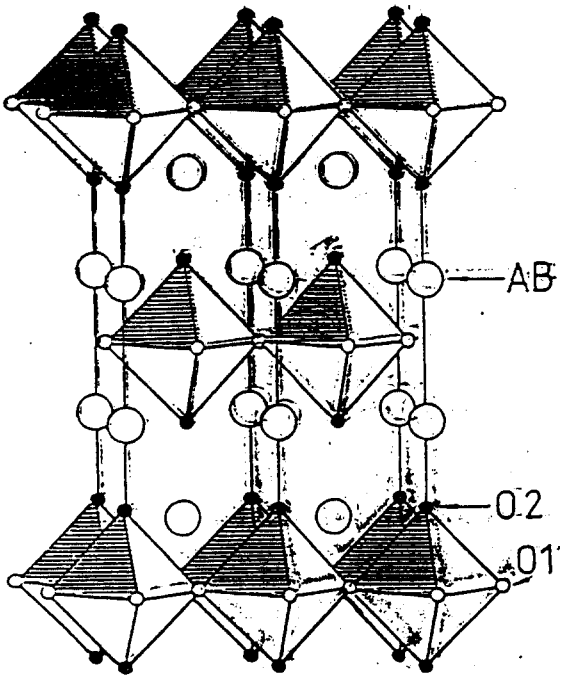
$c = 3a$

■ Al, Ga

●○ O

○ AB $\quad Sr^{2+}/La^{3+}$

$A_2B_2C_2O_8$



Al - 01 - unit cell dim. ½, 0, ½

Al - 02 - c - cell param.

variable z - positional param (0,0,z)

-depend on av. ionic rad. - A-B

$ABCO_4$ (A_2CO_4)

A = Ca, Sr
B = Y, rare earth
C = Al, Ga (0.5, 0.62)

$CaNdAlO_4$ -576 kcal/mol

$SrLaAlO_4$ -566 kcal/mol

$CaYAlO_4$

$SrLaGaO_4$ -497 kcal/mol