Crystal Growth of $Ca_3(Li,Nb,Ga)_5O_{12}$ Garnet Crystals

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Abstract

Various types of garnet compounds were synthsized by iso- and aliovalent substitutions and sintering method. Among them, fiber shapes of garnet crystals were grown from the $Ca_3Li_xNb_{(1.5+x)}Ga_{(3.5-2x)}O_{12}$ melt where x = 0 ~ 0.5 by modified micro-pulling down method in air using Pt crucibles. The measured lattice constants as a function of solidification fraction of grown fiber crystals are about 12.54 Å irrespective of x. It was found that the $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ garnet melts congruently at about 1450 °C based on the purities of garnet phase and variations of lattice parameter. Transparent and bubble-free crystals of x = 0.25 and 0.275 were grown by Czochralski techniques in air using Pt crucibles. An absorption spectrum is also reported.

1. Introduction

The Bi-containing iron garnet films $Ln_{(3-x)}Bi_x(Fe,Ga)_5O_{12}$, where Ln = rare-earth elements, have been shown to posses superior properties for uses as magneto-optic devices [1]. The magnitude of Faraday rotation and lattice parameter for these materials is proportional to the concentration of large Bi^{3+} cation. The incorporation of large Bi^{3+} cation into the garnet structure demands preparation of new non-magnetic garnet substrates. It is, therefore, of interest to obtain transparent garnet crystals with large lattice parameters which can be used as substrate material.

In the present report we try to prepare new garnet crystal which have following properties: (1) congruent melting, (2) low melting point (T_m < 1500 °C), (3) lattice parameter larger than 12.5 Å, and (4) low absorption in 400-1200 nm wavelength range.

2. Solid State Reactions

Using congruently melting composition of $Ca_3Nb_{1.6875}Ga_{3.1875}O_{12}$ (CNGG) and stoichiometric composition of $Ca_3Nb_{1.5}Ga_{3.5}O_{12}$ as basic material, we studied following substitutions shown by solid state reaction technique ; (1) $(Ca^{2+})_8 \rightarrow (Sr^{2+})_8$, (2) $(Ga^{3+})_6 \rightarrow (Ln^{3+})_6$, (3) $(Ga^{3+})_6 \rightarrow (In^{3+})_6$ and (4) $(Ga^{3+})_6 \rightarrow (Li^{+})_6 + (Nb^{5+})_6$.

In the types of substitution (1) and (2), total amount of non-garnet phase was very high. It is due to the large size of Sr^{2+}cation and the occupation of dodecahedral sites by rare-earth elements. In the types of substitution (3), $Ca_3In_{0.5}Nb_{1.5}Ga_3O_{12}$ garnet was impossible to grow crystal with Pt crucible because of high melting point of this mixture. The $Ca_3(Li,Nb,Ga)_5O_{12}$ garnets obtaining by substitution (4) was found to be best in accordance with requirements noted in the introduction of this report.

3. Fiber Crystal Growth by mm-PD Method

For more detailed investigation of congruency, fiber crystals with the various compositions of $Ca_3Li_xNb_{(1.5+x)}Ga_{(3.5-2x)}O_{12}$ (CLNGG), where x=0.0-0.5 were grown by mm-PD method using Pt/Rh crucible in air atmosphere. The grown crystals were transparent and well developed in crystal form. Bubbles and inclusions were not detected under the microscopic observation.

In all of the grown crystals, the non-garnet phases were not detected. It is necessary to note that in all experiments the amount of non-garnet phases in the solidified melt was much higher than that of raw materials, which is a result of segregation phenomena in the melts. In this experiment it appeared that the purity of garnet phase for raw material and remaining melt and the total crystallization fraction depends on the composition. Maximal growth rate which results in transparent single crystal growth depends on composition also. Lattice parameters of raw materials were widely distributed from 12.534 Å to 12.546 Å. But the variation of lattice parameter as a function of the solidification fraction of grown crystals were almost same for all compounds (12.539 Å < a < 12.542 Å). Therefore it was expected that the lattice parameter at congruent melting composition is 12.541 ± 0.001 A.

It was found that (1) growth rate resulting in high quality crystal, (2) purity of garnet phase and (3) total solidification fraction are maximum at the composition of $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ with the lattice parameter of 12.540 ± 0.001 Å. We conclude that within the compounds studied this compound is closest to congruently melting composition.

4. CZ single crystal growth

Transparent and slightly yellow color of single crystals were grown by CZ method from the $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$ and $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ melts. The pulling rate of 1 mm/hr, the rotation rate of 20 rpm and air atmosphere with flow rate of 0.6 l/min were used. Bubbles and inclusions were not detected.

The crystals had some cracks depending on melt composition. It was found that the density of cracks of crystals grown from $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ melt was lower than that from $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$. The variation of lattice parameter as a function of solidification fraction for CLNGG crystals is similar for both CZ and mm-PD grown crystals.

It was found that the phase purity of remaining $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ melt ($I_{(2nd)}/I_{(420)} = 0$) was higher than that of $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$ ($0.05 < I_{(2nd)}/I_{(420)} < 0.06$).

After the phase composition was studied, both of the remaining melts were recrystallized by slow cooling method. In the case of $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$ melt, many garnet crystals with about 1 mm size, which have mainly rhombododecahedral facets <111>, similar to that observed in ref. [2]. However, in $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ remaining melt, this phenomenon was not observed.

Judged from good faceting, the crystals were grown at relatively low growth rate as in the flux technique, with second phase compound acting as a flux.

No optical absorption was detected in 400-1200 nm wavelength range.

4. Conclusion

(1) Based on solid state reaction data it was found that in $Ca_3Li_xNb_{(1.5+x)}Ga_{(3.5-2x)}O_{12}$ system pure garnet phase formation was observed in the vicinity of stoichiometric composition of $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$.

(2) Single fiber crystals of CLNGG were grown by mm-PD method using melts with $0 < x < 0.50$. Highest growth rate (15 mm/h), highest solidification fraction (63 wt.%), lowest density of cracks and highest garnet phase purity of raw material and remain melt were observed for the crystals grown from $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ melt.

(3) Transparent and bubble-free single crystals of garnet with the lattice parameters of 12.540 Å were grown from $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$ and $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ melts by CZ method.

(4) It was found that $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ crystal melts congruently at 1450 °C in air atmosphere and can be grown using Pt crucible.

References

[1] P.Hansen and J.P.Krumme, Thin Solid Films 114(1984)69.

[2] V.I.Chani and A.M.Balbashov, J.Cryst.Growth 66(1984)616.

Crystal Growth of CLNGG

$Ca_3(Li,Nb,Ga)_5O_{12}$

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Bi^{3+} containing Rare Earth Iron Garnet

$Y_3Fe_5O_{12} \rightarrow (Bi_{3-3x}Y_{3x})Fe_5O_{12} \rightarrow Bi_3Fe_5O_{12}$

increase

a=12.38A a=12.61A

Faraday Rotation Coefficient

Lattice Parameter

[redacted]

Congruent Melting Garnets with a > 12.5 Å

#	Crystal Composition	a (Å)	Absorption	T_m	Method	Ref.
1	$Nd_3Ga_5O_{12}$	12.508	Yes	1550	CZ(Pt)	1
2	$Ca_3Nb_{1.6875}Ga_{3,1875}O_{12}$	12.510	No	1470	CZ(Pt)	2
3	$Ca_{0.92}Gd_{2.08}Gd_{0.05}Zr_{0.96}Ga_{0.99}Ga_3O_{12}$	12.527	No	-	CZ(Ir)	3
4	$Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$	12.540	No	1450	CZ(Pt)	4
5	$Sm_3Zr_{0.63}Mg_{0.63}Ga_{0.74}Ga_3O_{12}$	12.563	Yes	-	CZ(Ir)	3
6	$Gd_3Sc_2Ga_3O_{12}$	12.569	No	-	CZ(Ir)	5
7	$Gd_{2.4}Lu_{1.9}Ga_{3.7}O_{12}$	12.630	No	1730	CZ(Ir)	6
8	$Gd_{2.8}In_{1.8}Ga_{3.4}O_{12}$	12.667	No	1700	FZ	7
9	$Ca_{0.70}Nd_{2.24}In_{1.32}Mg_{0.98}Ga_{1.09}Ge_{1.67}O_{12}$	12.685	Yes	-	CZ(Ir)	3

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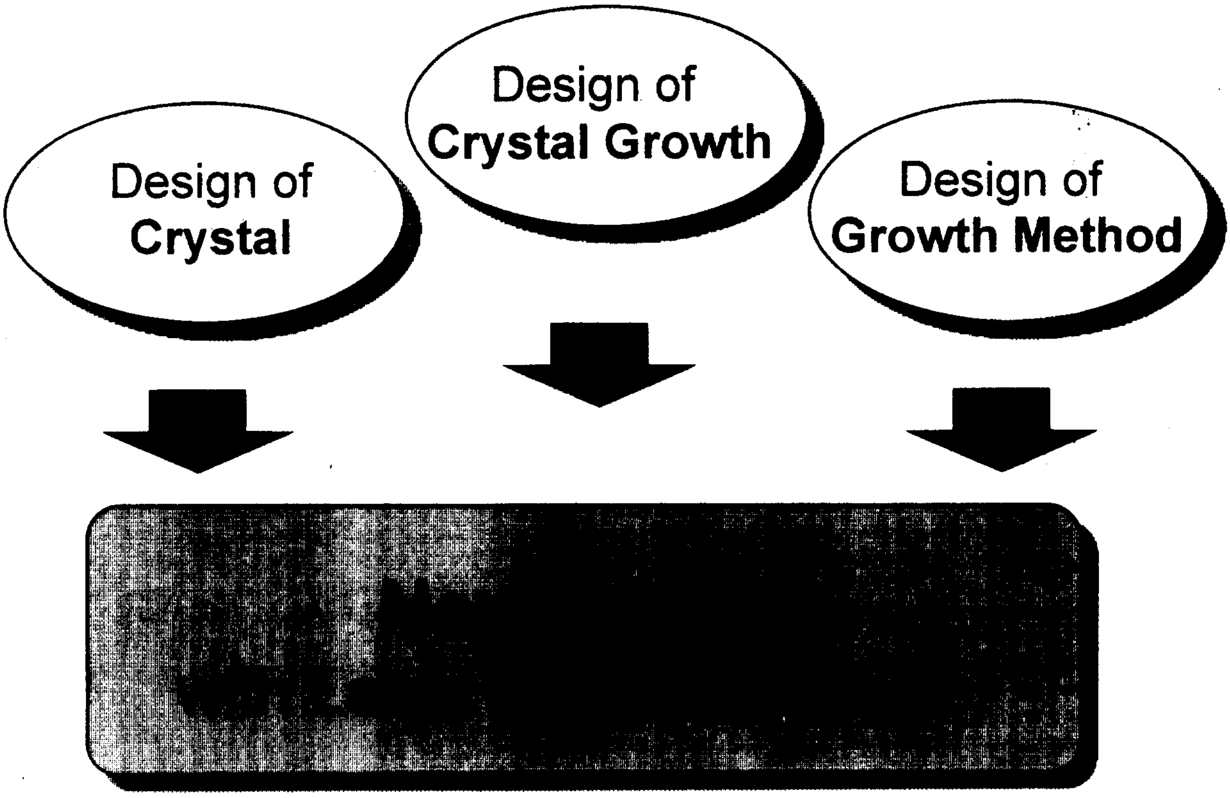
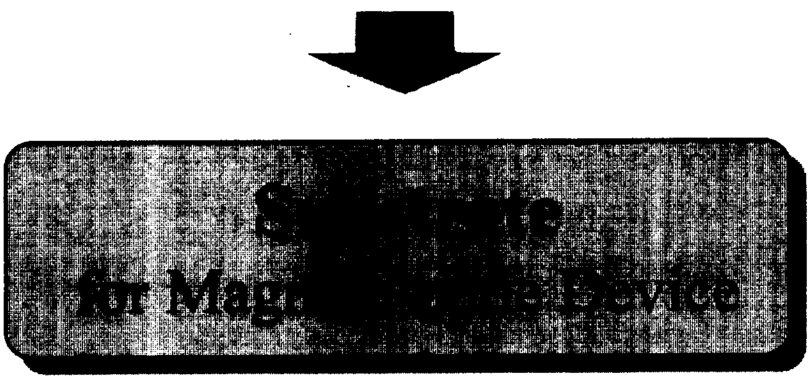
1 Markgraf et al.,1994
2 Shimamura et al.,1993
3 Mateika et al.,1990
4 this work, 1996
5 Kestigian et al.,1977
6 Miyazawa et al.,1990
7 Kawata at al.,1993



1. Large Lattice Parameter (>12.[illegible]5A)
2. Garnet Structure
3. Czochralski Growth
4. Low Melting Point (<1500°C)
5. High Transparency



Experimental Techniques

$\{C\}_3[A]_2(D)_3O_{12}$

C	K, Na, Ba, Sr, Ca, Pb, Rare Earth
A	Li, Mg, Zn, Ca, Rare Earth
D	V, Ga, Ge, Si, W, Sn

[redacted]

[redacted]

Phase Composition
Minor Non-garnet Phase Analysis
Lattice Parameter Measurement

[redacted]

Small Capillary Effect
Seggregation/Quasi-equiblium
Congruency Study

[redacted]

Confirm Congruency
Optical Properties

Basic Material

congruent **CNGG** $Ca_3Nb_{1.6875}Ga_{3.1875}O_{12}$

stoichiometric **CNGG** $Ca_3Nb_{1.5}Ga_{3.5}O_{12}$

Garnet structure

$\{C\}_3[A]_2(D)_3O_{12}$

Substitution

{C} site

Ca^{2+} ➡ Sr^{2+}

{A} site

Ga^{3+} ➡ Y^{3+}, Yb^{3+}, Gd^{3+}

Ga^{3+} ➡ In^{3+}

Ga^{3+} ➡ $Li^{+} + Nb^{5+}$

{D} site Ga^{3+} ➡ No Change

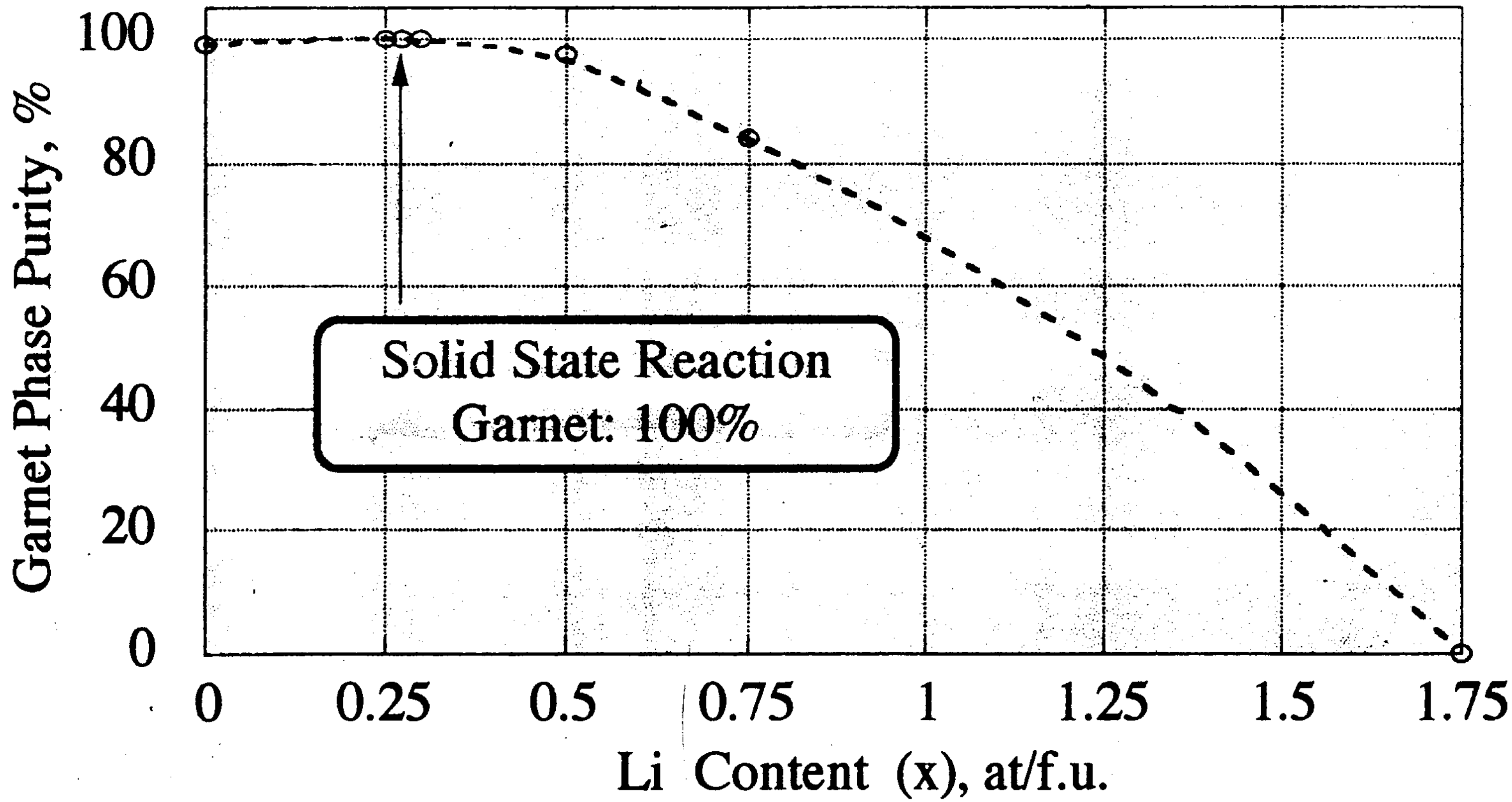
Solid State Reaction Experiments (1200-1450°C)

#	Composition	Phase Composition	a, (Å)	$I_{(2nd)}/I_{(420)}$
1	$\{Ca_{2.4}Sr_{0.6}\}Nb_{1.6875}Ga_{3.1875}O_{12}$	Garnet, 2nd Phase	12.55	0.14
2	$\{Ca_{1.8}Sr_{1.2}\}Nb_{1.6875}Ga_{3.1875}O_{12}$	Garnet, 2nd Phase	12.55	3.74
3	$\{Ca_{0.0}Sr_{3.0}\}Nb_{1.6875}Ga_{3.1875}O_{12}$	No Garnet	-	-
4	$Ca_3Y_{0.1875}Nb_{1.6875}Ga_{3.0}O_{12}$	Garnet, 2nd Phase	12.53	0.18
5	$Ca_3Yb_{0.1875}Nb_{1.6875}Ga_{3.0}O_{12}$	Garnet, 2nd Phase	12.53	0.08
6	$Ca_3Gd_{0.1875}Nb_{1.6875}Ga_{3.0}O_{12}$	Garnet, 2nd Phase	12.54	0.51
7	$Ca_3In_{0.50}Nb_{1.50}Ga_{3.0}O_{12}$	Garnet, 2nd Phase	12.58	0.03
	$Ca_3Li_xNb_{1.5+x}Ga_{3.5-2x}O_{12}$			
8	x=0	Garnet, 2nd Phase	12.51	0.01
9	x=0.2	Garnet, 2nd Phase	12.52	0.01
10	x=0.3	Garnet	12.54	0.00
11	x=0.5	Garnet, 2nd Phase	12.55	0.02
12	x=0.75	Garnet, 2nd Phase	12.55	0.19
13	x=1.75	No Garnet	-	-

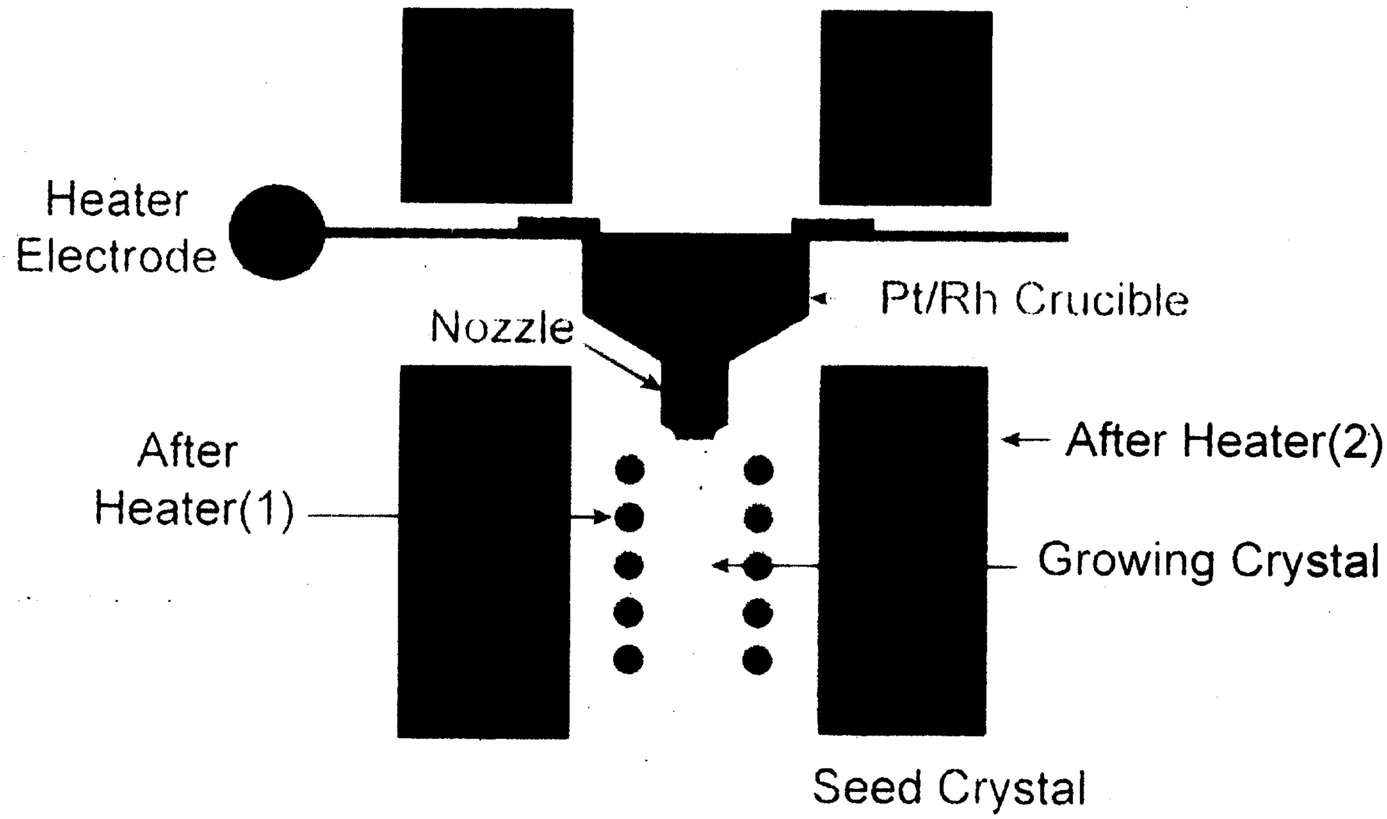
$I_{(2nd)}/I_{(420)}$ - amount of second phase was estimated as ratio between highest peak of second phase to highest peak of garnet (420)

Dependence of Garnet Phase Purity on Composition

$Ca_3Li_xNb_{1.5+x}Ga_{3.5-2x}O_{12}$ system



μ-PD Method



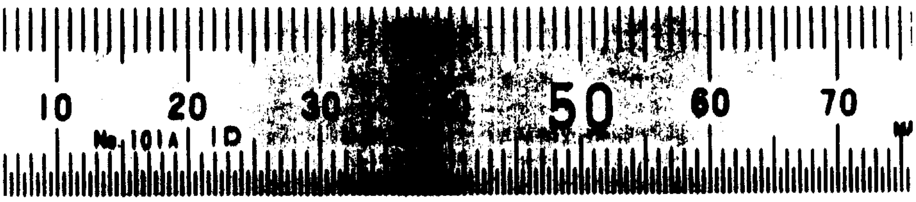
Composition	$Ca_3Li_xNb_{1.5+2x}Ga_{3.5-2x}O_{12}$
Pull Down Rate	3-18 mm/hr
Atmosphere	Air
Crucible	Pt or Pt/Rh 10mm x 5mm X 2mm
Nozzle	Pt 0.5 ~ 0.8mm in diameter

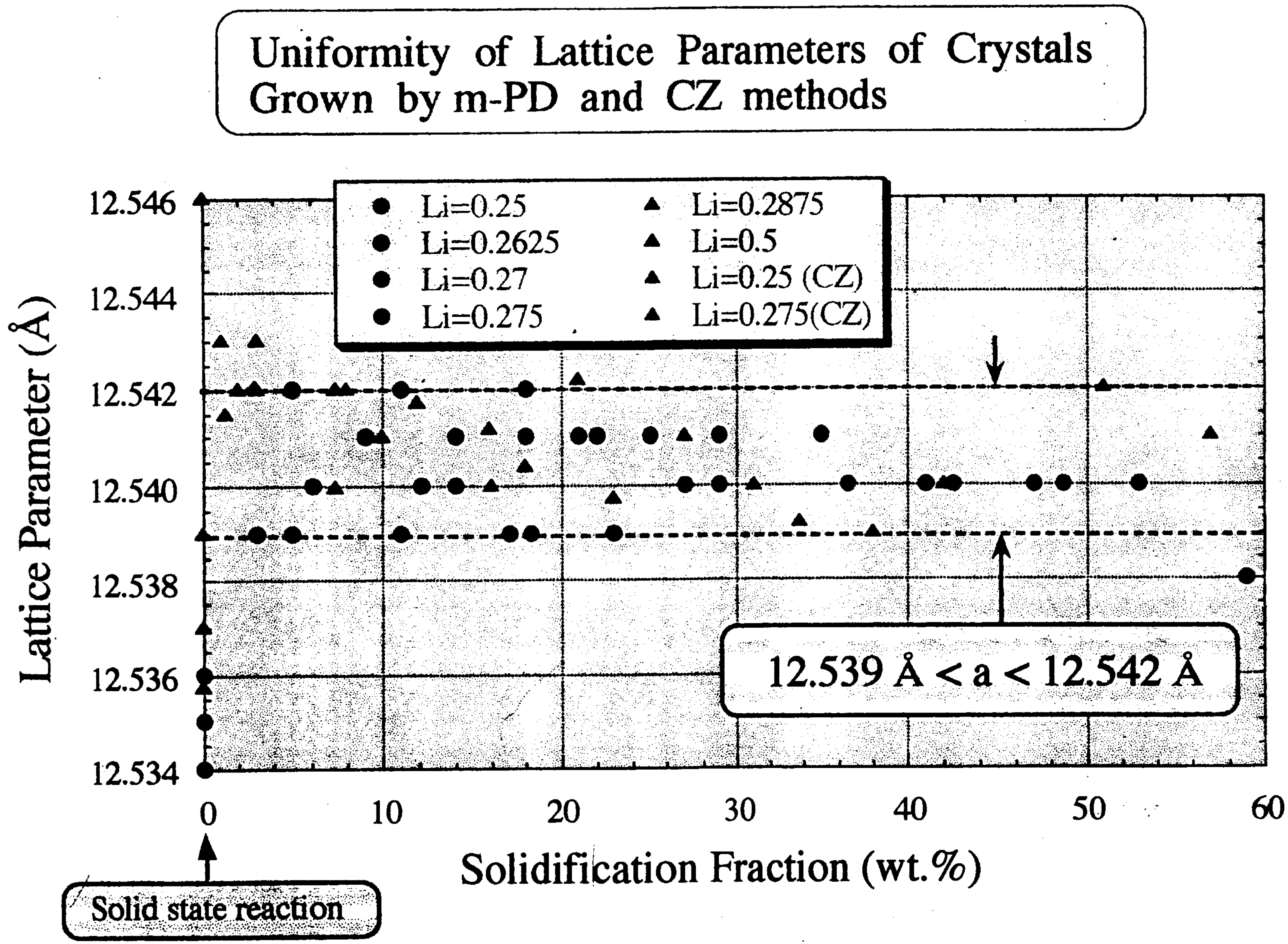
μ-PD Crystal Growth

Cracks at $x = 0$ Scales in mm No cracks at $x = 0.275$

μ-PD Growth Gallium Garnet

$Ca_3(Nb_{1.775}Li_{0.275})Ga_{2.95}O_{12}$



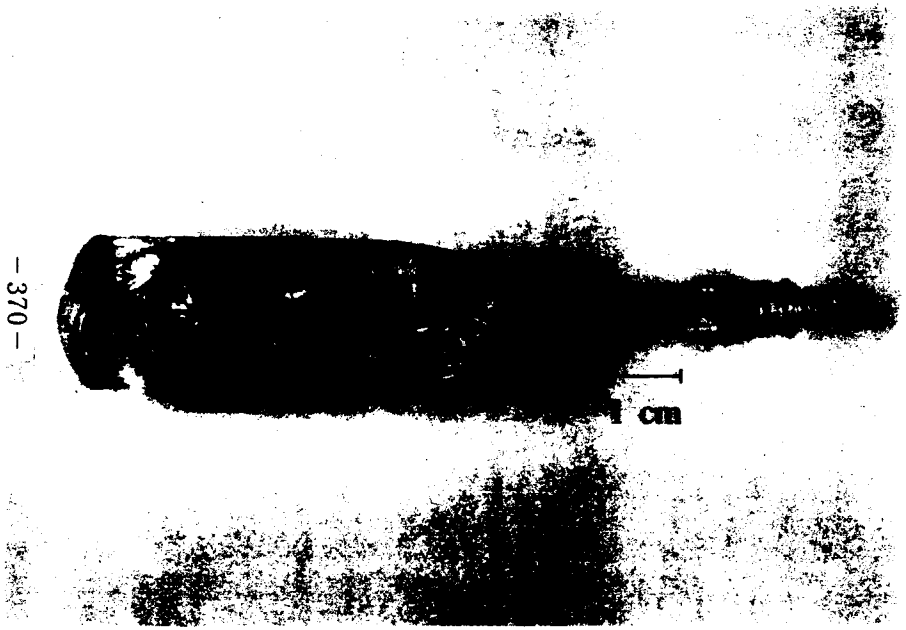


Uniformity of Lattice Parameters of Crystals Grown by m-PD and CZ methods
Li=0.25
Li=0.2625
Li=0.27
Li=0.275
Li=0.2875
Li=0.5
Li=0.25 (CZ)
Li=0.275(CZ)
Lattice Parameter (Å)
12.546
12.544
12.542
12.540
12.538
12.536
12.534
0
10
20
30
40
50
60
Solidification Fraction (wt.%)
12.539 Å < a < 12.542 Å
Solid state reaction

Melt composition, maximal growth (pulling) rate f (mm/h), density of crack D, total crystallization fraction C (wt.%), average lattice parameter of grown fiber crystal a (Å) and relative intensity ratio $r = I_{(2nd)}/I_{(420)}$ for X-ray pattern the raw materials r(RM) prepared by solid state reaction and solidified melts r(SM) after μ-PD process

#	Melt composition	*f*	D	C	a	r(RM)	r(SR)
	$Ca_3Li_xNb_{1.5+x}Ga_{3.5-2x}O_{12}$:						
1	x=0.25	12	High	27	12.541	0.01	0.01
2	x=0.2625	12	Low	37	12.542	0.00	-
3	x=0.27	12	Low	51	12.541	-	0.01
4	x=0.275	15	Very low	63	12.540	0.00	0.01
5	x=0.2875	12	High	27	12.541	-	0.13
6	x=0.3	12	Low	16	12.540	0.00	-
7	$Ca_{3.06}Li_{0.21}Nb_{1.74}Ga_3O_{12}$	12	Very high	23	12.544	-	-
8	$Ca_{2.95}Li_{0.2875}Nb_{1.7625}Ga_3O_{12}$	12	High	50	12.537	1.41	-

CZ Crystal Growth

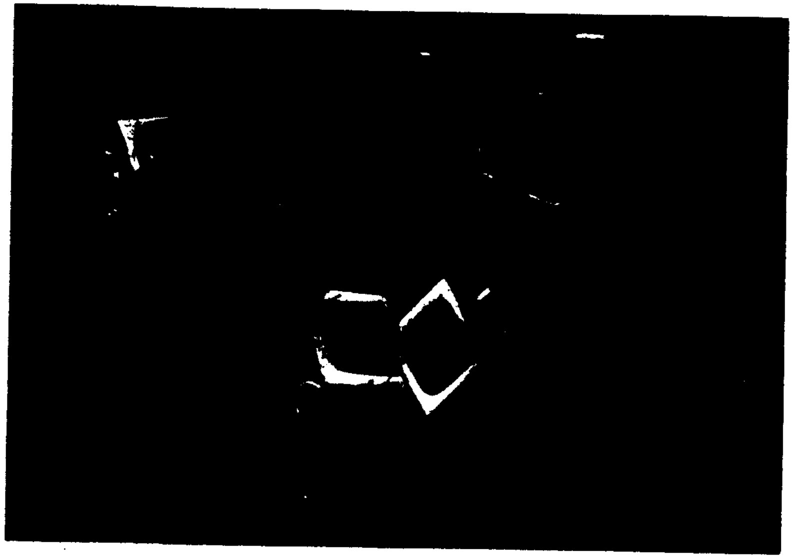


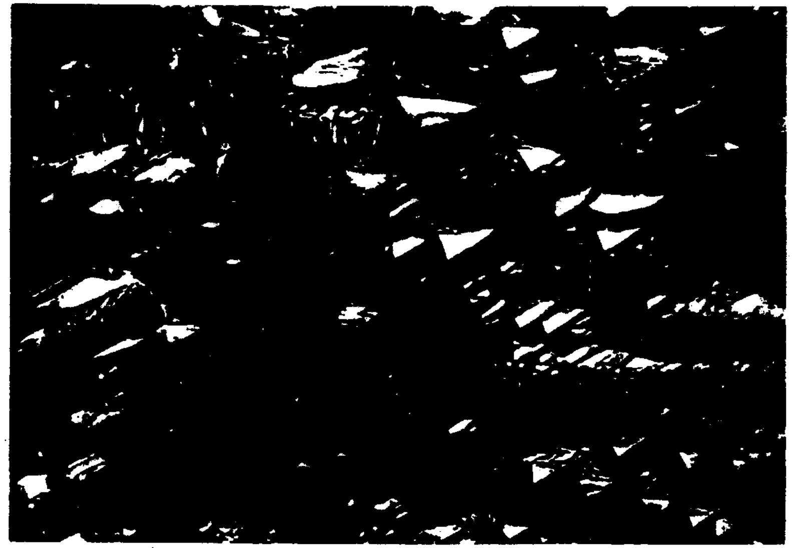
pulling rate	1mm/hr
Rotation rate	20rpm
Atmosphere	Air
Crucible	Pt

$x = 0.25$

$x = 0.275$

Phase purity of remain melts was studied by heating of melts just above melting point (1460 °C) and slow (about 5°C/h) solidification



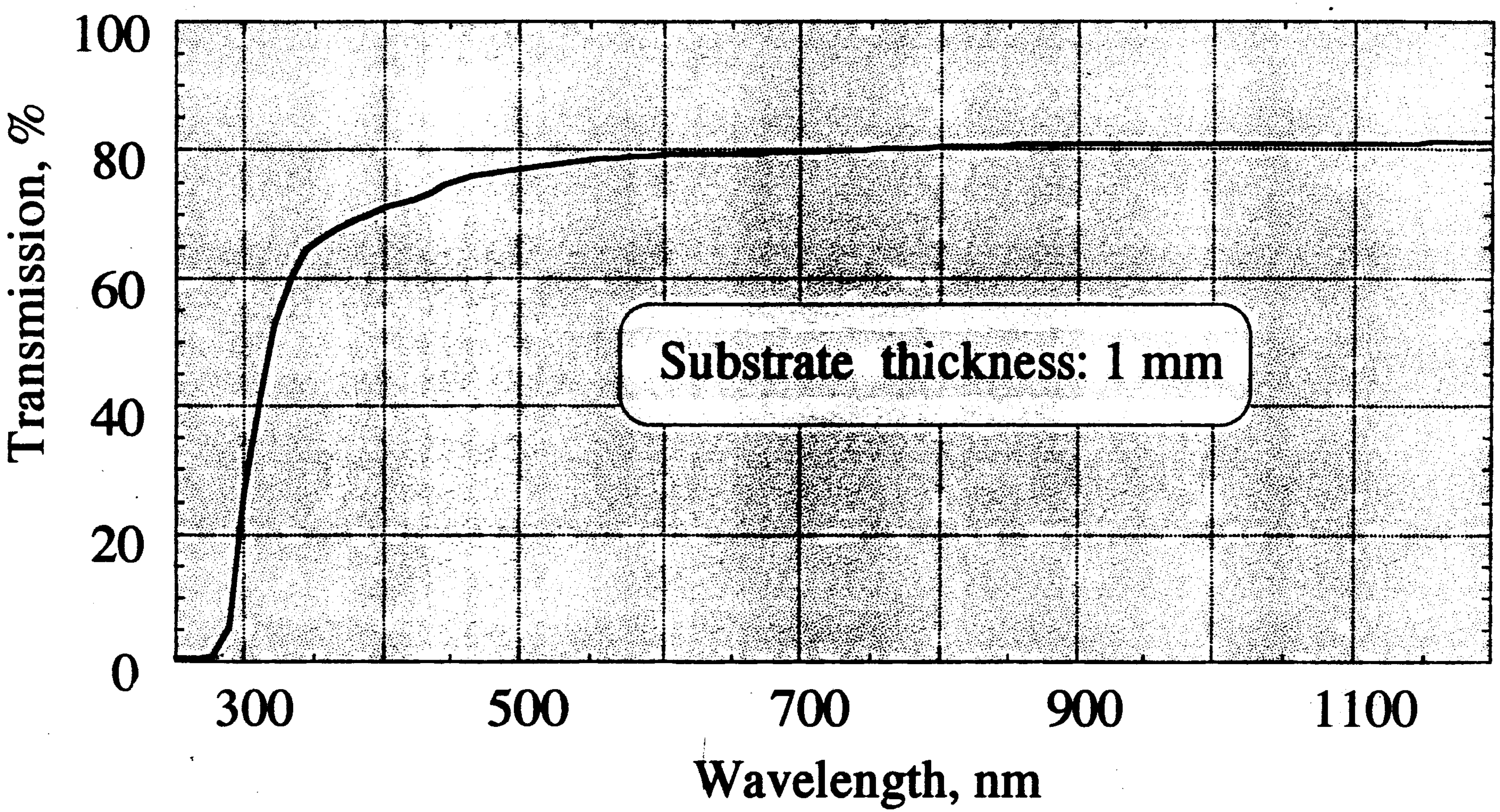


$x = 0.25$
(Second phase as flux)

1 mm

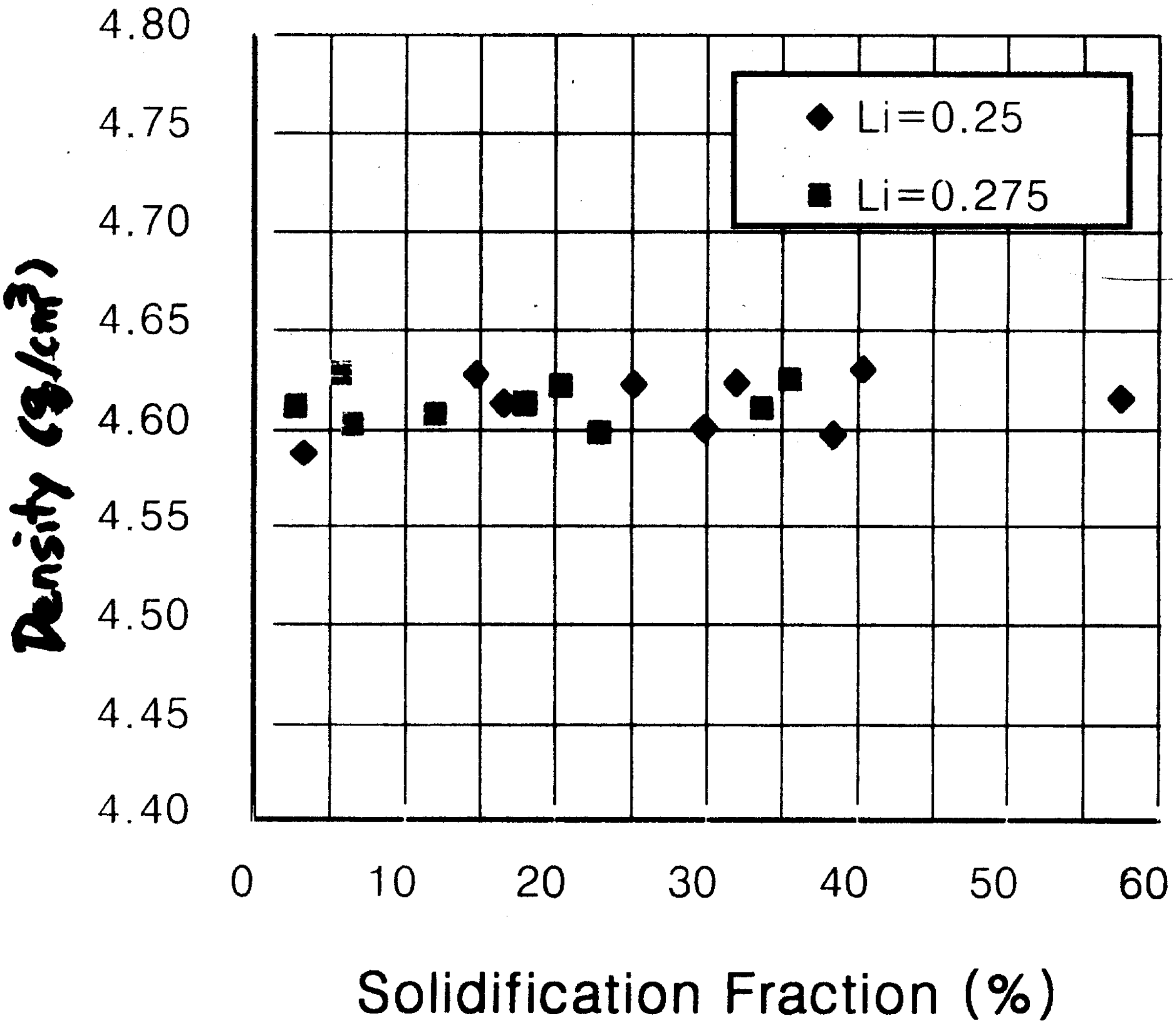
$x = 0.275$
(Single garnet phase)

Optical Spectrum of $Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$ CZ Single Crystal



Density of Grown Crystals

	Measured Density	Calculated Density
$Ca_3Nb_{1.6875}Ga_{3.1875}O_{12}$	4.6687	4.6920
$Ca_3Li_{0.25}Nb_{1.75}Ga_3O_{12}$	[illegible]	4.[illegible]200
$Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$	4.6[illegible]5	4.6144



Summary

1. We have shown that $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ garnet crystals (a = 12.540 Å) melt congruently at about 1450°C.

2. Crystals of $Ca_3Li_xNb_{1.5+x}Ga_{3.5-2x}O_{12}$, (x = 0.25 and x = 0.275) were grown by both CZ and μ-PD technique using Pt crucibles.

3. No optical absorption was detected at a wavelength range between 400 and 1200 nm in the crystals grown.

4. $Ca_3Li_{0.275}Nb_{1.775}Ga_{2.95}O_{12}$ crystals seems to be one of the best substrates for the Bi-containing iron garnet films.