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in

"Surface Treatments for Industrial Applications"

HIGH TEMPERATURE METATHESIS FOR THE PREPARATION OF Nb₃GaAl SUPERCONDUCTORS

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Abstract

This works deals with the A15 compound synthesis on niobium samples and over the internal surface of niobium cavities by means of induction heating. Specifically, three compounds were studied: Nb₃Ga, Nb₃Al and Nb-Al-Ga. As for the preparation of the niobium samples, they were treated with BCP solution in order to polish the surface. The niobium cavities were treated with centrifugal tumbling, BCP solution and high pressure water rising. Subsequent, the samples, or cavities, were placed into an inductor controlling the voltage, time, sample position, temperature, type and pressure of gas used. The highest critical temperature obtained was 18 K and Δ Tc 0,35 K, in Nb-Al-Ga#1 sample by inductive measurement. Mapping analysis showed the uniform diffusion of aluminum into the niobium, and the gallium diffuses creating channels into niobium. The composition was measured by EDS obtaining (82±1)% wt. Niobium, (11,3±0,9)% wt. Gallium, (4,7±0,2)% wt. Aluminum and (1,9±0,1)% wt. Oxygen. Finally, RF test confirmed that the cavities obtained after the annealing were normal conductive indicating that the preparation parameters must still be optimized.

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INTRODUCTION

Nowadays, technological advances in particle accelerators are focus according to the physical needs, such as nuclear physics, free- electron lasers, high energy particles physic and neutron spallation sources, which allows solving human needs related to medicine, space exploration and electronic technology.^[1]

Superconducting radio frequency (SRF) technology is based on bulk niobium cavities that allow higher acceleration gradients compared to conventional copper cavities because of lower electrical losses. SRF properties are inherently a surface phenomenon because it is shallow the penetration depth of the radio frequency fields: less than one micron of thickness. For this reason, and for the high cost of niobium, the thin film coating technique is a great benefit to fabricate superconducting cavities. ^[2]

The development of different deposition techniques for thin films and superconducting materials are on the top of the technological revolution in this field. Therefore, the general objective is to implement the methodology for performing thin films of A15 compounds on the internal walls of the 6 GHz niobium dummy cavities by means of induction heating.

Within the specific objectives there are the following:

- Performing preliminary studies of Nb₃Ga, Nb₃Al and Nb-Al-Ga samples before initiating the studies with 6 GHz niobium cavities, in order to observe the feasibility of obtaining good results.
- Ensuring the optimal parameters of heat treatment by the inductor, so that it is reproducible.
- Characterizing the samples and cavities with a thin film of A15 compound, specifically, determine the critical temperature, the Q value, chemical composition, crystal structure and microscopic properties of the coatings.

Finally, it will be shown the study performed with the work group of superconductivity lab -INFN illustrating the possible parameters to continue this research project and achieve the goal of increasing the performance of the cavities for particle accelerators, employing a new technique and A15 compounds without the need of ultra-high vacuum system.



CHAPTER 1. LITERATURE REVIEW

I.1. Particle Accelerators

In cavities, electromagnetic fields are excited by coupling in an RF source with an antenna. When a cavity is excited at the fundamental mode, a charged particle bunch, passing through cavity apertures, can be accelerated by the electric fields, supposed that the resonant frequency is matched with the particle velocity. In our lab, at LNL of INFN, the resonant frequencies in SRF cavities are in the range from 200 MHz to 3 GHz but depend on the particle species to be accelerated. ^[3]



Fig.1. Sketch of SRF cavity in helium bath with RF coupling and passing particle beam.^[3]

SRF cavities demand high performance and for this reason they are necessary chemical facilities for harsh cavity treatments, clean room for assembling the components, high pressure water rising and complex cryomodule vessel. ^[3]



Fig.2. Collection of SRF cavities.^[3]

I.2. Superconducting Radio Frequency Resonant Cavities

The technology of superconducting radio frequency (SRF) involves the application of superconducting materials to radio frequency devices, where the ultra-low electrical resistivity allows the obtainment of high quality factor (Q) values in RF resonator. This event means that the resonator stores energy with very low loss. For example, for 1,3 GHz niobium cavity at 1,8 K was obtained a Q factor of 5×10^{10} . ^[4]

The most common application of superconducting RF is in Particle Accelerators, where usually the resonant cavities are made of bulk niobium and, in a few cases, with bulk copper coated with niobium.^[4]

I.3. Physical basis SRF cavities

The physics of superconducting RF can be complex; however the principal parameters will be defined.

A resonator's quality factor is defined by the following expression: ^[5]

Where:

- ω is the resonant frequency [rad/s]
- U is the energy stored [J]
- Pd is the power dissipated in the cavity [W]

The energy stored in the cavity is given by the integral of field energy density over its volume: ^[5]

— eq. 2

Where: H is the magnetic field in the cavity and μ_0 is the permeability of free space.

The power dissipated is given by the integral of resistive wall losses over its surface:

Where: Rs is the surface resistance.

The integrals of the electromagnetic field in the above expressions are generally not solved analytically; therefore, the calculations are performed by computer programs that solve for non-simple cavity shapes. Another alternative is determinate Geometry Factor (G) which is given by the following expression: ^[5]

_____ eq.4

Then, the Q factor can be obtained by:

eq.5

eq.3

In the superconducting RF cavities for particle accelerators, the field level in the cavity should be as high as possible to most efficiently accelerate the beam passing through it. The Qo values tend to degrade as the fields increase, showed in "Q vs E" curve, where "E" refers to the accelerating electric field. Ideally, the cavity Qo would remain constant as the accelerating field is increased up to the point of a magnetic quench field (Hc2), but in reality, is quenching before due to impurities, hydrogen contamination and a rough surface finish.^[5]



Fig.3. SRF cavity Qo vs. the accelerating electric field Ea.^[5]

I.4. Surface resistance in superconductors

When the current flowing in the superconductor is a DC current (direct current) or a low frequency Alternating Current (AC), the superconducting electrons shield the normal conducting electrons from the electromagnetic field so that the power is not dissipated. However, this is not the case when in the superconductor flows alternating current at radio or microwave frequencies because the shielding is not perfect due to the inertia of the Cooper pairs which prohibits them to follow immediately with the change of electromagnetic fields. This event provides a surface resistance known as **BCS resistance** which depends on the square of the frequency of the AC current and the number of normal conducting electrons. The surface resistance can be obtained with the following expression: ^[6]

eq.6

 R_{res} is the residual resistance and R_{BCS} is the BCS resistance.

The R_{BCS} can be approximated to the following expression:

eq. 7

Where:

- S is the strong coupling factor (~2).
- ρ_n is the normal state resistivity in DC.
- Tc is the critical temperature.
- T is the operational temperature.

Then Equation 7 tells us that a low R_{BCS} loss superconductor must have a high critical temperature and the most metallic behavior in the normal state.

I.5. A15 compounds

The A15 materials are an intermetallic compounds, brittle where generally occurring close to the A₃B stoichiometric ratio. The "A" is a transition metal and "B" can be any element. The crystal structure is the β -W or Cr₃Si type. ^[7]



Fig.4. Unit cell of the A₃B compound showing "B" atoms at the apical and body center positions while "A" atoms in pairs on the faces of the cube. ^[8]

In 1933 it was discovered the first intermetallic compound with the typical A_3B composition. It was Cr_3Si , but without any interest. However, few years later Hardy and Hulm found a superconducting transition in V3Si at 17,1 K. Consequently, many A15 compounds were studied in the coming years, as shown below. ^[9, 8]

In the below table, we can see different values of Tc which is strongly influenced by the degree of Long-Range crystallographic Order (LRO). In compounds with B atoms are not a transition metal, the highest Tc value is obtained when all the A atoms are on the A sites and all the B atoms are on the B sites. This order is quantified through the *S* parameter and this parameter reaches the unit, means it has been achieved the Long Range Order. On the other hand, when the B atoms are not a metal transition, the compound does not have the same sensitivity to order. ^[7]

B/A3	Ti	Zr	V	Nb	Та	Cr	Mo
	4	4	5	5	5	6	6
Al 3			11,8	18,8			0,6
Ga 3			16,8	20,3			0,8
In 3			13,9	9,2			
Si 4			17,1	19			1,7
Ge 4			11,2	23,2	8	1,2	1,8
Sn 4	5,8	0,9	7	18	8,4		
Pb 4		0,8		8	17		
As 5			0,2				
Sb 5	5,8		0,8	2,2	0,7		
Bi 5		3,4		4,5			
Tc 7							15
Re 7							15
Ru 8						3,4	10,6
Os 8			5,7	1,1		4,7	12,7
Rh 9			1	2,6	10	0,3	
Ir 9	5,4		1,7	3,2	6,6	0,8	9,6
Pd 9			0,08				
Pt 10	0,5		3,7	10,9	0,4		8,8
Au 11		0,9	3,2	11,5	16		

Table 1. Superconducting transition temperatures Tc of some A15 compound. The number of valence electrons is given for each element. ^[10]



Fig.5. A15 type structure of a system A_3B with different occupation of the $6c \ (\circ)$ and the $2a \ (\circ)$ sites by the two atomic species. ^[11]

I.5.1. Nb₃Ga

This compound is formed by a peritectic reaction at 1860 °C and 21 at. % Ga. as shown in the phase diagram below. Stoichiometric Nb₃Ga is well known to have the second highest Tc among A15 compounds after Nb₃Ge. ^[12]



Fig.6. Niobium- Gallium phase diagram.^[12]

The critical temperature value for A15 compounds depends on the Long Range Ordering, as mentioned before, but specifically depends on the heat treatment applied. Below the Tc annealing history in Nb₃Ga is showed. ^[13]



Fig. 7. Tc annealing history: ^[12,14]

Range I: T<750°C. No segregation occurs but increases Tc after three days caused by long-range ordering (LRO) effects.

Range II: 750<T<1100 °C. Segregation occurs, resulting in a shift of "frozen" phase limit of 22,5 at.% Ga obtained from the arc—melting process. The annealing times for reaching thermal equilibrium at temperatures below 1000°C are prohibitively long. After two months at 1100°C, the composition was 20,8 at.% Ga, while the lattice constant value increased which corresponding the lowest Tc value (9°C).

Range III. 1100<T<1740 °C. The composition of A15 phase follows the phase limit indicated in the phase diagram. The rapid quenching is necessary in order to prevent a shift of the phase limit during the cooling process.



Fig. 8. Lattice parameter obtained as function of Critical temperature for Nb_3Ga . ^[12, 14]

Table 2. Nb₃Ga properties. ^[15]

Critical temperature	20 [K]
High $H_{c2}(4,2 \text{ K})$	Above 30 [T]
Max. Jc (4,2 K) on wires	280 [A/mm ²]
Lattice parameter	5,163 [Å]

I.5.2. Nb₃Al

This compound is obtained by the peritectic reaction at 2060 °C and 22,5 at.% Al. The stoichiometric composition is metastable at room temperature and is only stable at 1940 °C. The homogeneity range is found at 1000°C between 19 and 22 at.% Al.^[16]



Fig. 9. Niobium- Aluminum phase diagram. ^[17]

Table 3.	Nb ₃ Al	properties.	μ	17	1	
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Critical temperature	18,8 [K]
High $H_{c2}(4,2 \text{ K})$	Above 30 [T]
Max. Jc (4,2 K) at 20 T	$10^{5} [A/cm^{2}]$
Lattice parameter at 18,2 K	5,183 [Å]



Fig.10. Critical magnetic fields (H_{c2}) as a function temperature for three materials.^[14]

High temperature process around 1800°C and 2000 °C consists of continuous heating and quenching, then retransformed from BCC to A15 at 850 °C, as shown in the figure bellow. ^[18,19]



RHQT (Rapidly-Heating/Quenching & Transformation) Process

Fig. 11. Heat treatment for Nb₃Al compound. ^[19]

I.5.3. Nb₃GaAl

The superconducting properties of alloys in the Nb₃Al-Nb₃Ga system have been studied by Otto who reported a *Tc* about 18,4 K for Nb₃Al sample, increased up to 18,7 K when Otto added gallium obtaining Nb₃Al_{0,65}Ga_{0,35}. In this system it was observed the A15 phase. ^[20]



Fig.12. Nb-Al-Ga system a	t 1000°C. ^l	20]
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 Table 4. Summary of the lattice parameters and superconducting transition temperatures of

 Nb-Al-Ga alloys.

Sample No.	Nominal composition, at %		at %	Heat Phases		Latt	Loe para	meters, 1	Superconducting
	ND	A1	Gen	ment *		A15	or T	1 ND 5 Ga 3	temperature, K
	AU		va			a	a	0	
1	85	10	5	(1)	ND, A15	5.194			11 ± 1
2	82+5	12.5	5	(1)	No trace, 415	5+193			14±1
				(2)	Nb trace, A15	5.193			11.1±0.1
3	80	15	5	(1)	A15	5.188			17.8±0.1
				(2)	▲1 5	5.190			13.00±0.05
4	77.5	17.5	5	(1)	A15,6 trace	5.187	9-97	5.17	18.65 [±] 0.05
				(2)	15, 5 trace	5.187	9•97	5.17	16.50± 0.05
5	75	20	5	(1)	A15,5	5.183	9+972	5.162	18.65±0.05
				(2)	A15,0	5.187	9.974	5.165	16.95±0.05
6	73	22	5	(1)	≜ 15,σ				18.5-0.1
				(2)	415, σ	5.187	9.972	5.165	15.4-0.5
7	70	25	5	(1)	A15, o	5.183	9+963	5.162	17.35±0.05
				(2)	A15, 6	5.187	9.966	5.166	13.40:0.05
8	68	27	5	(3)	A15 trace, 5	5.185	9.957	5.165	11.0±0.1
9	66.5	28.5	5	(1)	A15 trace, €				14.8 [±] 0.1
				(3)	۵.		9.939	5.167	**

10	82.5	10	7.5	(1)	No trace, A15				15.0±0.5
				(2)	No trace, A15	5.192			12.0±0.2
11	80	12.5	7.5	(1)	A15	5.187			16.7±0.2
				(2)	∆ 15	5.187			14.0±0.1
12	77.5	15	7.5	(1)	A15,5 trace	5.187	9.96	5.16	18.1±0.1
				(2)	A15,5 trace	5.185	9.96	5.16	15.90±0.05
13	75	17.5	7.5	(1)	A15, C	5.184	9.96	5.16	19.00±0.05
				(2)	A15,6	5.185	9.966	5.160	16 .5 0±0.05
14	72.5	20	7.5	(1)	A15,0	5.181	9.974	5.157	18.6±0.1
				(2)	▲ 15, 0	5.186	9.967	5.162	15.50±0.05
15	70	22.5	7.5	(1)	A15, 5	5.181	9.964	5.165	18.65±0.05
				(2)	A15, 5	5.186	9.965	5.164	15.0±0.5
16	66.5	26	7•5	(1)	6		9•943	5.170	**
				(3)	G		9.944	5.166	**
17	85	5	10	(1)	Nb, A15, 5 trace	5,192		:	
				(2)	No, A15	5.193			9.8±0.5
18	82.5	7.5	10	(1)	No, 115				17.1±0.5
				(2)	Nb trace, A15	5.191			13.2±0.2
19	80	10	10	(1)	No, A1 5, e	5.189	9+933	5.159	17•4 [±] 0•1
				(2)	A15	5,185			15.1±0.1
20	77.5	12.5	10	(1)	115, €	5.185	9.936	5.164	18.0±0.1
				(2)	▲15, •	5.185	9.962	5.168	15.3*0.1
21	7 5	15	10	(1)	115, or				18.85±0.05
				(3)	A15, o	5.184	9.956	5.163	15.7±0.1
22	72.5	17.5	10	(1)	▲ 15, 6°	5.185	9.949	5.167	18.85±0.05
				(2)	A15,6	5,185	9.962	5.162	15.60±0.05
23	70	50	10	(1)	A15,6	5.183	9.946	5.166	17 ,1± 0,1
				(3)	A15,6	5.185	9.956	5.162	15.5 ± 0.2
24	80	5	1 5	(1)	A15, 6 trace	5.183			16.85±0.05
				(2)	A15	5.183			13 . 5±0.1
25	75	10	15	(1)	A15,6	5.181	9.944	5.150	17.5±0.1
26	77•5	2.5	20	(1)	A15, Nb and T1 traces				16.5 [±] 0.1
				(3)	A15, 6	5.177	10.31	5.07	13.2 [±] 0.1
27	75	5	20	(1)	A15,6	5.181	9.936	5.174	16.40±0.05
				(3)	▲ 15 ,6 ,11	5.178	9.944	5.161	15.6±0.1
							10.320	5.057	
28	72	8	20	(1)	A15,6,T1 trace	5.181	9.940	5.159	17.40±0.05
29	70	10	20	(1)	A15,6,T1 trace	5.180	9.920	5.166	17.8±0.1
	-					-			-

* (1) at 800°C for 1 month; (2) at 1600° for 6 hrs, and then at 1000°C for 2 weeks;
 (3) at 1500°C for 6 hrs, and then at 1000°C for 2 weeks.

★★ not superconducting down to 4.2 K.



Fig.13. Lattice parameters and critical temperatures of the ternary A15 phase vs. composition of Nb-Al-Ga alloys for the section of the phase diagram at 7,5 at.% gallium. 1) Tc after low-temperature annealing. 2) Tc after high-temperature annealing. 3) Lattice parameter "a" of the A15 phase after high temperature annealing. ^[21]

CHAPTER 2. EXPERIMENTAL PROCEDURE

II.1. Induction Heating System

In order to develop RF superconducting A15 cavities was used induction heating which allows direct heating on samples (or cavities) reaching temperatures higher than 2500°C. This system has the following advantages compared to the infra-red heating in ultra-high vacuum system:

- Clean quartz tube, where is not found contaminations from chamber or alumina crucible.
- Short time of treatment (few seconds or fractions) instead of hours.
- Very high temperatures around 3000°C. On the contrary, the infra-red heating reaches no higher than 1100°C.

The complete system was assembled for the induction heat treat as shown in the figure below, in order to get the coating of A15 compounds, as the first experimental proof on niobium samples and then, on niobium cavities.



Fig.14. Sketch of the induction system.

The induction system consists of a quartz tube where on the bottom part it is fluxed argon or helium. The chamber is sealed with Viton o-ring to the aluminum flanges. The sample or cavity is centered on the coil and this, in turn, is connected to the work head AMERITHERM model. Subsequent, the work head is connected with the power supply EKOHEAT brand, where it can control the time and the voltage. The maximum power allowed is 15 kW. Using a pyrometer IRtec P-200 model it can read the temperature in the (250-3000)°C range.



Fig.15. Induction heating for samples.



Fig.16. Induction heating for cavities.

In the figures 15 and 16 it can be observed the induction system; however, it can be noticed that for cavities the coil and the quartz tube have larger diameter than sample system.



Fig.17. Left side: Viton o-ring to seal the tube. Right side: Plastic tube on the bottom part which transports the helium or argon from the bottle into the chamber.



Fig.18. Left side: Power supply where it can set up the voltage and time for the annealing. Right side: Pyrometers.

II.2. Samples and cavities preparation

Before coating the niobium samples with A15 compound, these were chemically etched with BCP (Hydrofluoric acid 40%, Nitric acid 65% and Phosphoric Acid 85%) solution with a 1:1:2 relation, in order to increase the purity of the sample surface. High rate reaction was observed when the samples were introduced into the solution as well as brown gas was observed (NO_3).

Nitric acid is an oxidizing agent on niobium surface. Hydrofluoric acid reduces the niobium pentoxide into a salt that is soluble in water. Phosphoric acid acts as a moderator for the chemical reaction giving rise to a less turbulent and more controllable reaction.

$$6Nb_{(s)} + 10HNO_{3(aq)} \rightarrow 3Nb_2O_{5(s)} + 10NO_{(gas)} + 5H_2O_{(l)}$$
 eq. 8

$$Nb_2O_{5(s)} + 6HF_{(aq)} \rightarrow H_2NbOF_{5(aq)} + NbO_2F_{(s)} \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O_{(l)}$$
 eq. 9

$$NbO_2F_{(s)} \cdot \frac{1}{2}H_2O + 4HF_{(aq)} \rightarrow H_2NbOF_{5(aq)} + \frac{3}{2}H_2O_{(l)}$$
 eq. 10



Fig.19. Left side: a) Without treatment. b) After chemical etching. Right side: BCP solution system.

On the other hand, 6 GHz niobium cavities were used to evaluate the surface resistance of the treatment trough the Q value measurement. 6 GHz cavities are made through spinning technology (seamless). These are used instead of 1,5 GHz resonators to simulate the real conditions with new superconducting materials. This process is done at low cost due to reduction of: material, energy in heat treatments, and spending cryogenic.

Before coating the cavities, it was needed to polish the internal surface. For this, mechanical treatment was performed through a centrifugal tumbling. The 6 GHz cavities were filled with abrasive agent pieces (silicon carbide) and Yttria Stabilized Zirconium oxide spheres, plugged up and fixed to the machine. The tumbler makes the cavity rotate, so that the pieces can erode the metal surface in a uniform way reducing the scratches according a satellite motion.



Fig.20. Centrifugal tumbling system.

After tumbling process, the cavities were rinsed with DI water, then with ultrasonic around 60 minutes, rinsing with acetone or alcohol and drying with nitrogen. Subsequently, chemical treatment was performed. Equally, the BCP solution was used with the same ratio 1:1:2. However, the solution circulated in a closed circuit. In the pulsed system, the acid flux is directed from the bottom to the top of the cavity in order to evacuate the hydrogen, produced during the process.



Fig.21. BCP system for cavities.

Once completed the chemical treatment, the cavity was rinsed with DI water, then with ultrasonic around 60 minutes, rinsing with high pressure water, acetone or alcohol and drying with nitrogen.



Fig.22. High pressure water rinsing with a water jet.

II.3. A15 preparation

In order to perform the coating on niobium samples it was used:

- 1) Liquid gallium with 99,99% of purity for Nb₃Ga samples.
- Commercial foil, high purity sheet or powder of 200 mesh and 99% purity of aluminum for Nb₃Al samples.
- 3) For Nb-Al- Ga samples:
 - a) Liquid gallium + Aluminum sheet.
 - b) Paste 1: liquid gallium + Aluminum powder.
 - c) Paste 2: liquid gallium + Aluminum foil.



Fig.23. Aluminum forms used: a) Sheet. b) Commercial foil. c) Powder.

The first way to apply the materials mentioned above was the sandwich structure which consists in placing the gallium or/and aluminum between two niobium samples. The second configuration performed was a surface layer without the volume of gallium or aluminum enclosed. The last system used was a drop of liquid gallium on the niobium surface. For these three methodologies we used hands, with the appropriated protective gloves, together with chemical tools as shown in the figure below.



Fig.24. Structures to prepare the samples: a) Sandwich. b) Surface layer. c) Drop of gallium.



Fig.25. Chemical tools used on the samples preparation process.

To make the coating in the cavities, it was used liquid gallium and gallium-aluminum paste 2. The first way consisted in filling the cavity with gallium, plugging it up and placing in the rotor in order to try obtaining a uniform gallium coat. After half an hour in which the cavity is turning, the residual gallium is evacuated.



Fig.26. Rotor system to perform the cavity coating.

The second way was to hand-shake the cavity instead of using the rotor, so to evacuating the residual gallium.



Fig.27. Gallium coating performed shaking by hand the cavity.

The third form was to fill completely the cavities with gallium and after perform the heat treatment without evacuating the gallium, as shown in the figure below.



Fig.28. Third way in order to perform Nb₃Ga.

The fourth way was put the liquid gallium with Yttria- stabilized Zirconium oxide inside the niobium cavity, plug it up and agitate it with both hands. Later, the residual gallium and Yttria- stabilized Zirconium oxide spheres were evacuated.



Fig.29. Fourth way to coat the cavity with gallium.

Last way was using hands with the respective protection gloves i.e. using the fingers to spread the paste 2 on the internal niobium surface.



Fig.30. Fifth way: coating with Nb-Al-Ga paste 2.

Table 5. Summary of the	e methodology	used in cavities to	o obtain the A1:	5 compound.
2	0,			1

Method	Result
Rotor method (with gallium)	The coating is not uniform
Hand-shake (with gallium)	The coating is not uniform
Heat treatment without evacuate the residual gallium	Cavities melted
Gallium with Yttria-stabilized Zirconium spheres	The coating is not uniform
Paste 2 coating with fingers	Uniform coating

Once obtained the coating of gallium, aluminum, or both, on the niobium surface, it is necessary the heat treatment with the inductor. We raise the cavity or the sample at high temperatures close to the melting point, in order to promote the diffusion of these elements within the niobium, and so to obtain the desired A15 phase. Therefore, the next procedure carried out was setting the heat treatment profile, specifically the voltage and the time through the display located on the power supply. However, there are other parameters to control, such as sample or cavity position, pressure of gas, temperature and type of gas.



Fig.31. Time profile of the induction heating system.

CHAPTER 3. RESULTS AND DISCUSSION

In total we performed 51 samples with different parameters and 7 cavities by means of induction heating, distributed as shown below.



Fig.32. Heat treatment by induction.



Table 6. Samples and cavities treated by induction heating.

Performed on	Materials	Number of samples	Total
	Nb-Ga	10	
Samples	Nb-Al	6	51
	Nb-Al-Ga	45	
Covition	Nb-Ga	6	7
Cavities	Nb-Ga-Al	1	/

After the annealing process, we have to evaluate if we reach the A15 compounds i.e. the superconducting state. For this, it was used an inductive measurement in order to define the critical temperature (Tc). The inductive measurement is based on the principle of the Meissner- Ochsenfeld effect. The superconducting material is placed under a primary coil that generates an oscillating magnetic field. A secondary coil induces an AC current from the oscillating field. However, when the superconducting state is reached the material expels the magnetic field lines that pass through it and the measure phase shift is carried out. Samples were cooled down with the liquid helium, by dipping the whole set up into the helium tank.



Fig.33. Inductive measurement system.

III.1. Nb3Ga samples

Below the results obtained for niobium gallium system are shown, indicating the parameters used in the process.

Sample	Tc	ΔTc	Temperature Treatment	Time	Power	Voltage
#	[K]	[K]	[° C]	[min]	[kW]	[V]
			Max		Max	Max
0-A	11,73	1,57	1666	8,2	5	-
0-B	11,24	1,26	1666	8,2	5	-
1	11,7	1,56	1664	6,3	5	-
2	10,84	1,19	1727	13,3	6	-
3	Only Nb	-	1100	10	3,6	333
4	Only Nb	-	1190	10	4,1	357
5	Only Nb	-	1250	10	6,2	451
6	Only Nb	-	1200	10	2,8	342
7-pre	Only Nb	-	900	60	0,9	84
7-post	12,32	0,44	1500	6,6	-	-
8-sand1	Only Nb	-	2150	3	Max	Max
9_wires	16,27	0,49	1930	1,1	Max	600

Table 7. Summary of the results for the Nb-Ga system.

The critical temperature (Tc) reported on the before table was determined from the graphs of the inductive method. These values were calculated from the following expressions:

_____ eq. 11 eq. 12

Where T $_{(90\%)}$ is the temperature in which the resistance has a value equal to 90% of the transition, T $_{(10\%)}$ is the temperature at which the resistance is 10% of the transition. Δ Tc is an indication of how sharp is the transition.



Fig.34. Phase Shift vs Temperature of the most important transitions obtained by the sandwich Nb-Ga structure.



Fig.35. Phase Shift vs Temperature for Nb-Ga system where the A15 phase was not found.

According to the figure 34, the highest critical temperature was obtained on the sample called Nb₃Ga_wires (the black one) with a Tc of 16,27 K and Δ Tc 0,49 K. The conditions used were: maximum temperature of 1930 C°, maximum voltage (600 V) and 1,1 minutes. The temperature read by the pyrometer is not accurate due to the sensibility i.e. the temperature on the sample changes faster than the time in which the pyrometer takes the measure. Also because the camber walls of the induction system were metalized due to the gallium vapor.

The behavior of the Nb₃Ga_wires curve is unusual due to the presence of two superconducting transitions and between them the resistance increases. The first one at 16,27 K as it was mentioned before and the second one at 13,71 K. This means the presence of the two different superconducting phases. However, this hypothesis can be corroborated by analysis of composition and review of the microstructure. Nevertheless, these tests were not conducted because the sample with highest Tc value was the only thoroughly analyzes and it was found in the Nb-Al-Ga system.

On the other hand, the Nb₃Ga_wire sample and the other samples with transitions between 10 and 12 K (see figure 34) indicate that obtaining a single phase, specifically the A15 phase is almost impossible because the region where the phase is stable is very narrow according to the phase diagram of Nb-Ga system (see figure 6). In addition, when heat treatment was carried out, we note that the gallium evaporated. The consequence of this fact is we can't control the stoichiometry on Nb-Ga samples. As well, we are not certain from the beginning about how much gallium diffuses into the surface of niobium. Figure 35 shows the samples of Nb-Ga in which did not precipitate any superconducting phase. Only the niobium transition was observed. It could be for several reasons:

- 1) Complete evaporation of gallium due to the long heat treatment around 10 minutes.
- 2) The gallium volume was not enclosed since these samples were made with surface layer and gallium drop configurations.
- 3) The low wettability of gallium on niobium surface makes the liquid gallium fall as droplets within the chamber system and it is worse when the temperature is increasing since the viscosity decreases.

In addition, the gallium handling process was difficult due to the fact that it does not wet the niobium surface, so not allowing to do the procedure for sandwich arrangement, gallium drop or surface layer structure (see figure 24) in simple way. Notwithstanding, the best structure for working at high temperature is the sandwich model because it encloses the gallium volume decreasing the amount evaporated.



Fig.36. Gallium drop configuration.



Fig.37. Best configuration for samples.



Fig.38. Nb-Ga samples obtained after annealing.

Figure 38 shows how the niobium gallium samples look after the heat treatment with the inductor. In some cases, oxidized samples were found, indicating that it should be improved or adjusted the sealing system of the chamber. Also, samples showed dark spots and the surface a little melted as the temperature of the annealing was very high. The control of the temperature was difficult and very small changes of the time around milliseconds or on the voltage approximately 5 volts made an important different whether the sample was melted or not. This implies that the induction system is very sensitive to changes on voltage and time implemented through the power supply.



Fig.39. Profile of temperature vs. time for Nb₃Ga samples.

Figure 39 shows the time at which the sample was subjected to a certain temperature. According to these profiles and the results of the critical temperature, it can concluded that long
time of heat treatment is not recommended because the A15 phase does not precipitate and if it does the critical temperature was found in a low range between 10 and 12 K compared to 20 K reported in the literature ^[14]. On the other hand, the trend of the results is that when the temperature of annealing does not exceed 1500°C the superconducting phase is not found.

It was also determined the cooling rate of the samples obtained when the gas flow into the chamber, either helium or argon. The average speed is 50 K/s and in comparison with rates reported in literature (5000 K/s) is very slow ^[13]. This parameter is crucial for A15 compound as a high cooling rates prevents the destruction of the superconducting phase because the time spent in the range of (800- 1100) °C is lower.

In order to increase the Tc, it was performed a post-annealing in high vacuum system at 700°C for Nb-Ga samples 1 and 2 but the difference in the value (Tc) with respect to the obtained without post-annealing was negligible in both cases (see table 8). The idea of the post- annealing at low temperature is promote the long range ordering according to reports in the literature ^[14]. An important aspect for this purpose is not exceeding 800 °C because otherwise the A15 phase will be destroyed and long time of treatment around weeks are recommended to note significant changes in the critical temperature. ^[12]

Sample	Previous Tc	Tc	ΔTc	Temperature Treatment	Time	Pressure
#	[K]	[K]	[K]	$[^{\circ}C]$	[h]	[mbar]
1	11,7	11,8	1,4	700	24	2,3E ⁻⁷
2	10,84	11	1,13	700	6,5	1,3E ⁻⁷

Table 8. Post- annealing parameters.

The X-ray diffraction analysis allows us to have information about the material crystal structure and plane orientations also detect the presence of undesired species. During the scanning process the incident beam is fixed at as small angle while the detector rotate depending on the parameters chosen through the software, mainly start and stop angles and acquisition time.

The equipment used for this purpose is a Bragg diffractometer X'Pert-Pro model produced by the Philips Company with a X-ray beam wavelength of 1,5405 Å (Cu K α 1). The angular range used was from $2\theta = 20$ to $2\theta = 120$.



Fig.40. XRD spectrum for Nb₃Ga_wire sample.

Table 9.	Peak	list repo	orted on	Xpert	HighScore®	analyzer	for Nb ₃ Ga.
				-	0		

No.	hkl	d [A]	2Theta [deg]	I [%]
1	110	3,6628	24,280	3,8
2	200	2,5900	34,605	26,7
3	210	2,3166	38,843	100
4	211	2,1147	42,723	55
5	220	1,8314	49,746	0,4
6	310	1,6381	56,101	0,5
7	222	1,4953	62,013	8,2
8	320	1,4367	64,847	16,1
9	321	1,3844	67,616	20,4
10	400	1,2950	73,000	9
11	410	1,2563	75,633	0,1
12	411	1,2209	78,234	0,3
13	420	1,1583	83,370	4,5
14	421	1,1304	85,915	11,6
15	332	1,1044	88,453	3,7
16	422	1,0574	93,524	0,1
17	430	1,0360	96,066	0,1
18	431	1,0159	98,622	0,3
19	432	0,9619	106,415	9,9
20	521	0,9457	109,076	4,3
21	440	0,9157	114,537	4,8
22	530	0,8884	120,247	0,2
23	531	0,8756	123,227	0,1
24	442	0,8633	126,312	2,1
25	610	0,8516	129,525	2,6
26	611	0,8403	132,893	4,9
27	620	0,8190	140,272	0,1
28	621	0,8090	144,421	0,1
29	541	0,7993	149,042	0,2

According to the X-ray measurement showed in the figure 40 and the software analyzer Xpert HighScore[®], the principal planes of diffraction match with Nb₃Ga compound. The lattice parameter obtained from this measurement was 5,1811 Å and the standard value is 5,1800 Å but the lattice parameter changes according to long range ordering in the crystal structure, i.e. the disorder involves greater distortion in the unit cell and this in turn is reflected in the critical temperature (decreasing Tc).^[12]

III.2. Nb₃Al samples



The inductive measurement results for the critical temperature on Nb-Al system shown below.

Fig.41. Phase shift vs. temperature for Nb-Al system.

After analyzing the above graphs, it was obtained the critical temperature and ΔTc reported on the table 10, as well as the parameters used during the annealing process. Niobium aluminum samples were realized with sandwich configuration. In the figure 41, are denominated as Nb₃Al the samples made of aluminum sheet and Nb₃Al (AF) the samples made of commercial aluminum foil. On the other hand, we didn't observed an important transition because the only superconducting transition detected was that of Nb₃Al_1 that however is very broad.

Sample	Tc	ΔTc	Temperature Treatment	Time	Power	Voltage
#	[K]	[K]	[° C]	[min]	[kW]	[V]
			Max	Max	Max	Max
1	Many transitions	-	1700	5	5,9	-
2	17,34	0,1	1520	8,7	2,3	171
3	Only Nb transition	-	2060	1,5	Max	Max
4 (AF)	Only Nb transition	-	2061	0,65	-	
5 (AF)	16,58	0,35	1738	0,63	-	580
6 (AF)	Only Nb transition	-	1739	0,6	-	

Table 10. Critical temperature and parameters used in the annealing process for Nb-Al

system.

Also, it was evidenced evaporation problems of aluminum at high temperatures, which metalized the camber walls. As a result, the temperature reading is not accurate, as well as the contribution due to the pyrometer sensibility. These temperature values are indicated in the table 10 with red color.

One of the advantages of using aluminum as compared to the gallium is easier to manipulate, therefore, the process to assemble the sandwich structure was faster. On the contrary, it was observed that the gallium reacts more than aluminum with the niobium. This may be due to the corrosive property of the gallium and hence the diffusive process is better.

Over time, we understood that the long time annealing does not form the desired phase. Consequently, we changed the time of annealing from minutes (around 10 min.) to few seconds. However, when the annealing process is too short, it is very difficult to control the temperature switch on/off manually. As a result, we began to configure the times and voltages for each sample in automated way. Thus, the results can be more reproducible between samples. The following table shows the set up parameters.

Sample	Stage	Time	Voltage
#		[s]	[V]
	R1	0,5	120-250
	A1	4	250
	D1	0,5	250-0
	B1	4	0
	R2	0,5	0-550
4_AF	A2	2	550
	D2	0,5	550-0
	B2	4	0
	R3	0,5	0-580
	A3	2	580
	D3	0,5	580-0
	R1	0,5	120-250
	A1	4	250
	D1	0,5	250-0
	B1	4	0
	R2	0,5	0-540
5_AF	A2	2	540
	D2	0,5	540-0
	B2	4	0
	R3	0,5	0-580
	A3	2	580
	D3	0,5	580-0
	R1	0,5	120-250
	A1	4	250
	D1	0,5	250-0
	B1	4	0
	R2	0,5	0-545
6_AF	A2	2	545
	D2	0,5	545-0
	B2	4	0
	R3	0,5	0-580
	A3	2	580
	D3	0,5	580-0

Table 11. Voltage and time for Nb₃Al (AF) samples (see figure 31).

These treatment profiles are showed to understand how fast is the annealing. For example, in the Nb₃Al_5 sample we remain at 580 V only 2 seconds. After setting the inductor with the above parameters, in the following way looks the temperature vs. time profile.



Fig.42. Temperature vs. time profile for Nb₃Al samples.



Fig.43. Temperature vs. time profile for Nb_3Al (AF) samples.

XRD analysis was carried out on the Nb₃Al_2 sample, which it had a very short transition but a high critical temperature. The idea is to determine the presence of A15 phase. X-ray beam wavelength was 1,5405 Å (Cu K α 1) and the angular range used was from $2\theta = 20$ to $2\theta = 120$.



Fig.44. XRD spectrum for Nb₃Al_2 sample.

No.	hkl	d [A]	2Theta [deg]	I [%]
1	110	3.6614	24.290	25.4
2	200	2,5890	34,618	14,9
3	210	2,3157	38,859	100
4	211	2,1139	42,741	30,5
5	220	1,8307	49,766	2,7
6	310	1,6374	56,125	3,5
7	222	1,4948	62,040	11,8
8	320	1,4361	64,875	16
9	321	1,3839	67,645	11,4
10	400	1,2945	73,033	6,9
11	410	1,2559	75,667	0,1
12	411	1,2205	78,270	1,5
13	420	1,1578	83,409	2,6
14	421	1,1299	85,957	11,6
15	332	1,1040	88,496	2,2
16	422	1,0570	93,571	0,6
17	430	1,0356	96,116	0,1
18	431	1,0155	98,673	1,5
19	432	0,9615	106,474	9,8
20	521	0,9454	109,138	2,5
21	440	0,9154	114,605	3,9
22	530	0,8880	120,324	0,7
23	531	0,8752	123,309	0,1
24	442	0,8630	126,400	1,3
25	610	0,8513	129,619	2,6
26	611	0,8400	132,995	3
27	620	0,8187	140,395	0,3
28	621	0,8087	144,560	0,1
29	541	0,7990	149,202	0,7

The Xpert HighScore[®] analyzer indicates that the main diffraction planes match with the reported for Nb₃Al compound. The lattice parameter obtained from this measurement was 5,1971 Å and the standard value is 5,1780 Å. This means that probably this sample has low range ordering in the crystal structure i.e. low value of "S", increasing the distortion in the unit cell and the lattice parameter.

III.3. Nb₃AlGa samples

First, they will be shown the results of liquid gallium with aluminum sheet called as Nb-Al-Ga and the paste 1 (liquid gallium with aluminum powder) denominated Nb-Al-Ga_P.



Fig.45. System for the first group of Nb-Ga-Al samples.



Fig.46. Phase shift vs. temperature with important transition for Nb-Al-Ga system (first

group).



Fig.47. Phase shift vs. temperature for Nb-Al-Ga system with the presence of only niobium transition (first group).

After analyzing the figure 46 and 47, the values of critical temperatures was calculated for each sample with its corresponding ΔTc .

Sample	Tc	ΔTc	Temperature Treatment	Time	Voltage
#	[K]	[K]	[°C]	[min]	[V]
			Max	Max	Max
1	18,01	0,35	1420	2,6	600
2	14,54	1,42	1420	4	84
3	17,18	0,63	1860	1,5	-
4	Only Nb transition	-	2200	1,6	600
5	Only Nb transition	-	2118	1,8	560
6	15,2	1,15	1600	2,9	600
7	17,61	0,28	2134	1,3	600
8	Only Nb transition	-	2080	1,3	550
P1	17,48	0,71	2040	1,2	520
P2	16,15	0,74	1860	1,3	520
P3	14,15	0,82	1440	1,2	550

Table 13. Critical temperature and parameters used in the annealing process for the Nb-Al-Ga system (first group).

Table 13 shows that the highest critical temperature was 18 K with the Δ Tc of 0,35 K indicated with black curve in figure 46. Also, all the temperatures are highlighted in red color because they are not accurate for the same reasons before mentioned. The former reason is the metallization of the chamber walls during the treatment, and the latter, the sensitivity of the pyrometer.



Fig.48. Physical appearance of some Nb-Al-Ga samples.

In the figure 48 it is pointed out that some samples were melted and oxidized. This is because the temperature control is difficult on samples despite the voltage and time parameters were set on computer. A small variation of voltage or time involved to reach temperatures above of 2000°C thus, the liquid phase was reached. After obtaining a high

critical temperature in one sample, trying to change a little the voltage or time, three things happen:

- 1) The sample is melted.
- 2) The critical temperature value decreases.
- 3) It is not present a superconducting phase.

As for the oxidation process was continually reinforced the sealing system of the chamber in order to avoid this problem.

For the highest critical temperature the parameters established on the power supply were not recorded. However, the Nb-Al-Ga_1 sample gave us the indication that the annealing process must be done in a short time. The second highest critical temperature was obtained for Nb-Al-Ga_7 sample with a value of 17,61 K and 0,28 Δ Tc with the following parameters.

Sample	Stage	Time	Voltage
#		[s]	[V]
	R1	0,5	120-250
	A1	4	250
	D1	0,5	250-0
	B1	4	0
	R2	0,5	0-600
NbGaAl_7	A2	1	600
	D2	0,5	600-0
	B2	4	0
	R3	0,5	0-600
	A3	1,2	600
	D3	0,5	600-0

Table 14. Voltage and time set for NbGaAl_7 sample (see figure 31).

From the table 14 it is important to note that the maximum power was used for 1,2 seconds and the temperature reached with these parameters was 2134 °C. It is here showed how the temperature looks vs. time profile for the two higher critical temperatures.



Fig.49. Temperature and time profile for Nb-Ga-Al samples 1 and 7.

The parameters set for the other samples and the temperature - time profiles are presented in the annexes. In a second opportunity, the post- annealing was conducted in order to enhance the critical temperature. Unlike last time, it was done with the induction system without using UHV system.



Fig.50. Effect of the post-annealing.

Sample	Tc	ΔTc	Temperature	Time	Voltage
#	[K]	[K]	[°C]	[min]	[V]
P3_base	14,15	0,82	1440	1,2	550
P3_post1	13,81	0,91	700	60	81
P3_post2	14,24	0,67	800	60	93
P3_post3	14,36	1,12	800	60	93
P3_post4	14,67	1,1	800	60	93

Table 15. Parameters used in post- annealing process.

From figure 50 and table 15, it is observed that initial critical temperature decreases and then increases but subtly, so the changes are not expected and even they can be considered negligible. These can be caused by several reasons:

- Oxidation problem because the system used was the induction heating and this fact is worse when the annealing is performed for long time. Actually, the sample changes to dark color.
- 2) Nb, Al, Ga percentages are farther away from the desired stoichiometry lower the effect of post-annealing.
- 3) The annealing time was not sufficient to promote the long range ordering.

The second group of Nb-Ga-Al samples were made with the paste 2 (liquid gallium and aluminum foil) applied as a surface layer (without enclosing the volume of the paste). These samples were denominated as Nb-Al-Ga_C as shown in the figure below.



Fig.51. Simple surface layer method for Nb-Al-Ga system.



Fig.52. Phase shift vs. temperature for Nb-Al-Ga system group 2 with an important transition.



Fig.53. Phase shift vs. temperature for Nb-Al-Ga system group 2 with only niobium transition.

The following table shows the respective values of Tc, Δ Tc and the parameters used.

Table 16. Critical temperature, Δ Tc and parameters used for second group Nb-Al-Ga system.

Sample	Tc	ΔTc	Temperature Treatment	Time	Voltage
#	[K]	[K]	$[^{\circ}C]$	[min]	[V]
C1	14,86	0,75	-	-	550
C2	16,71	0,84	-	-	550
C3	Only Nb transition	-	-	-	550
C4	14,16	1,22	-	-	550
C5	13,96	1,29	-	-	550
C6	Only Nb transition	-	1838	0,9	580
C7	15,88	1,39	-	-	580
C8	Only Nb transition	-	2060	1,2	600
C9	Only Nb transition	-	1860	1,2	550
C10	Only Nb transition	-	2137	1,1	500
C11	Only Nb transition	-	1827	0,4	500
C12	13,74	2,14	1640	0,5	50
C13	16,56	1,37	1860	0,7	500
C14	Only Nb transition	-	1138	0,3	500
C15	11,77	1,9	1224	0,3	570
C16	15,57	1,26	1842	0,5	580

From figure 52 and table 16 it can be observed that the highest critical temperature was found for Nb-Al-Ga_C2 sample with 16,71 K and Δ Tc 0,84. Although this value is good for the final goal (superconducting cavities), but the fact that the paste volume was not enclosed between niobium pieces implied big amounts of paste evaporated, bringing as a result an error in the temperature measurement and no control on the stoichiometry. For this reason, the procedure for preparing the paste according to the composition ratio was not done with a rigid procedure.

Sample	Stage	Time	Voltage
#		[S]	[V]
	R1	1,5	84-250
	A1	4	250
	D1	0,5	250-0
	B1	4	0
	R2	0,5	0-550
Nb-Al-Ga-C2	A2	1	550
	D2	0,5	550-0
	B2	4	0
	R3	0,5	0-550
	A3	1	550
	D3	0,5	550-0

Table 17. Voltage and time set on power supply for Nb-Al-Ga_C2 sample.

Unfortunately, due to problems with the pyrometer, it was not obtained the temperature vs. time profile for C1, C2, C3, C4, C5 and C7 samples. The profiles for the others samples from the second group are present in the annexes section.

Given that it was a problem the fact that the paste 2 evaporated, we proceeded to make samples with the same paste but using the sandwich structure to see if the key of the problem lays in enclosing the paste to obtain higher critical temperature.



Fig.54. Third group of Nb-Al-Ga sample with sandwich structure.

The inductive measurements for the third group of Nb-Al-Ga samples were indicated as NbAlGa_CS and they are showed in the figure 55 y 56.



Fig. 55. Phase shift vs. temperature with the highest critical temperature for the third group of Nb-Al-Ga samples.



Fig. 56. Phase shift vs. temperature for Nb-Al-Ga_CS samples.

The critical temperature and ΔTc calculated with the parameters used for the third group of Nb-Al-Ga samples are showed below.

Sample	Тс	ΔTc	Temperature Treatment	Time	Voltage
#	[K]	[K]	[°C]	[min]	[V]
CS_1	Only Nb transition	-	-	-	570
CS_2	15,72	1,66	1454	1,2	570
CS_3	12,34	1,44	1421	0,8	570
CS_4	12,28	1,46	1488	2,9	570
CS_5	11,65	0,97	1398	0,5	570
CS_6	12,22	1,12	1484	2,2	580
CS_7	17,24	0,74	1421	1,6	580
CS_8	17,55	0,42	1858	0,6	580
CS_9	16,76	1,07	1722	0,7	580
CS_10	17,47	0,55	1697	1,9	586
CS_11	14,65	1,97	1773	1,8	586
CS_12	15,83	1,57	1944	1,6	588
CS_13	Only Nb transition	-	1832	1,6	588
CS_14	Completely melted	-	1755	1,5	588
CS_15	17,71	0,31	1956	1,1	550
CS_16	15	0,85	1621	0,6	550
CS_17	Many transitions	-	1176	1,1	550
CS_18	15,87	1,69	1803	0,6	550

Table 18. Critical temperature, Δ Tc and parameters used for of Nb-Al-Ga samples.

Figure 55 and table 18 shows that the highest critical temperature it was obtained for CS15 sample, highlighted with blue color with a Tc of 17,71 K and Δ Tc 0,31. This means that the transition was very important because the value of Tc is high and the Δ Tc low, so the transition was very sharp indicated that probably the present of only one phase (A15). These samples were performed with a maximum temperature treatment of 1950°C and the following profile of voltage and time.

Sample	Stage Time		Voltage
#		[s]	[V]
	R1	0,5	120-180
	A1	6	180
	D1	0,5	180-0
	B1	3	0
	R2	0,5	0-350
CS_15	A2	5,5	350
	D2	0,5	350-0
	B2	5	0
	R3	0,5	0-550
	A3	1	550
	D3	0,5	550-0

Table 19. Voltage and time profile for CS15 sample.

After set the profile above, in the following way looks the temperature and time profile.



Fig.57. Temperature and time profile for CS15 sample.

The other profiles such temperatures vs. time as voltage vs. time are showed in an informative way in the appendix section.

In this group of sample, although the paste was enclosed by niobium sheets (sandwich structure), it was still evaporating but to lesser degree. After an entire series of samples performed, it can be concluded that the sandwich structure is the best one because the paste is forced to diffuse into niobium due to it has no other way. The paste handling process was better since it wets the niobium surface and also it was adherent. One hypothesis about these better results is that the Nb-Ga and Nb-Al are complementary systems. It was observed that aluminum has low reaction with niobium so the gallium can corrode first the niobium surface for example reducing the amount of oxide allowing greater diffusion of aluminum. On the other hand, the aluminum increases the wettability of gallium over niobium hence the samples preparation is less cumbersome.

Newly, the post- annealing treatment was realized for Nb-Ga-Al_7 and Nb-Ga-Al_C2 samples under vacuum system at 6×10^{-7} mbar, 790°C and 6 hours. Nevertheless, we can see in figures 58 and 59 that the change in the critical temperature value is negligible and this may be due to the treatment time. In fact, reports in the literature recommends at least two weeks or more in order to perceive changes in the long range ordering. ^[13]



Fig.58. Phase shift vs. Temperature for NbAlGa#7 sample after post-annealing.



Fig.59. Phase shift vs. Temperature for NbAlGa_C2 sample after post-annealing

Nonetheless, from all the samples collected, the sample 1 of the first Nb-Al-Ga group it was obtained the highest Tc at 18 K with Δ Tc 0,35 which means that the transition phase is very sharp. Thus, it was analyzed the chemical composition and morphologies by means of Scanning Electron Microscopy (SEM) "XL-30" model produced by Philips Company with an electron source of W filament. The interaction between electrons and the atoms of sample make up signals that contain the following showed below.



Fig.60. Chemical composition and morphology on the red point.

Figure 60 shows that the sample was prepared with epoxy resin and it was analyzed through the cross section. On the red point, the gallium and aluminum are present and this is due to the paste viscosity decreases flowing to the outside walls of the sandwich structure when the temperature is so high during the annealing process. Also in this point can be formed the A15 phase. According to the composition without taking into account the presence of oxygen (70,23 % at. Nb, 13,69 % at. Ga and 16,06 % at. Al.) and the phase diagram the phases precipitated are A15 and σ .



Fig.61. Chemical composition and morphology on the red point.

Figure 61 shows the morphology on the sandwich structure where the niobium part looks lighter shade than Nb-Al-Ga zone. The photomicrograph shows a crack on the superconducting layer and this may be due to typically brittle behavior of A15 compound. As expected in the zone with the red point is almost pure niobium. But aluminum traces were found with 0,19% wt. and 2,38% wt. of oxygen. The oxygen presence is mainly to the induction chamber does not work with vacuum system.



Fig.62. Chemical composition and morphology on the red zone.

To obtain the chemical composition on the superconducting layer, it was measured 5 different points around the red cross showed on figure 62, and then these values were averaged. However, recalculating the composition without taking into account the presence of oxygen was obtained: $(73\pm1)\%$ at. Nb, $(13,3\pm0,9)\%$ at. Ga and $(14,2\pm0,4)\%$ at. Al. According to these values and the phase diagram the precipitated phases are A15 and A2.



Fig.63. Interfaces morphology for Nb-Al-Ga_1 sample.

By observing the morphology with higher magnification (6400X) in the niobium and NbAlGa interfaces, it was noted that the superconducting layer looks flatter than niobium alone. This may be due to the corrosive action of gallium acting as polish.



Fig.64. Microphotographs of the Nb and NbAlGa interface obtained with BSE and SE.

Figure 64 shows the Nb and NbAlGa interface obtained with back scattered electrons and secondary electrons. The microphotograph by SE affirms that the niobium morphology looks rougher than the superconducting layer. While the microphotograph by BSE shows dark spots related the chemical information, specifically, the light elements look dark and this case can be an inclusions.

In the same area a mapping was performed to observe how the distribution of the elements in the interface is.



Fig.65. Mapping of the Nb and NbAlGa interface.

According to the following table, the brighter pixel of the mapping corresponds to the higher X-rays counts. Thus, it indicates that gallium diffuses in such way that creates channels and this behavior is due to its corrosive property. The aluminum diffuses uniformly but the brighter pixel is also located is the same place that brighter place of gallium. This means that the gallium helps to aluminum in the diffusive process. The oxygen is completely uniform and combinations of these elements were represented such as Ga-Nb, Al-Nb, Ga-Al and O-Nb.

		Total Counts X-Rays			
Element	Color	Smin	Smax		
O K	Red	11	99		
Ga L	Green	17	405		
Al K	Blue	19	296		
Nb L	Yellow	151	2805		
Ga K	Purple	21	366		

Table 20. X- ray counts obtained from mapping measurement.

XRD analysis was not performed for Nb-Al-Ga_1 sample because the sandwich structure would not allow it and also it could not open because this was embedded in epoxy resin.

III.4. Cavities

After making a long study on samples and knowing that it is possible to obtain good superconducting layer preferentially on NbAlGa system, we began to do preliminary testing of 6GHz niobium cavities. The results were the following.



Fig.66. Results of the tests with the cavities.

Cavity	Flux	Time [min]	Annealing Max. Temperature [°C]	Power [kW]	Voltage [V]	Notes
1	He	1,3	2000	7,2	-	Melted
2	Не	14,4	1731	5,2	371	Cavity with a small hole
3	Ar	2,2	1770	5,6	-	Melted
4	Ar	3	1200	2,4	-	Normal conductor
5	Ar	10	1091	2,7	245	Normal conductor
6	Ar	6,1	2031	-	670	Normal conductor
7*	Не	1,4	1830	-	670	Normal conductor

Table 21. Parameter used during the annealing and results for cavities obtained RF- test.

Note *: The only cavity made with paste 2. The other 6 cavities were coated with gallium.

As seen in the table 21 and figure 66, the results obtained were not the desired as the cavities were melted or normal conductor. This is due to the heating and cooling process in cavities is completely different from the samples i.e. to cool the cavity takes at least 3 times more than on samples. Obviously, the mass is a problem because it is more difficult to dissipate the heat on cavities than samples. Therefore, set the time and voltage in order to obtain a superconducting layer was complicated and completely different to the determined on samples.

Since the cavities were melted in many cases, it was taken a piece of the equator zone and measurement if there is a superconducting transition but only niobium transition was evidence or can be considered a very short phase shift on cavity_1 at 12,94 K and Δ Tc 0,89 K.



Fig.67. Phase shift vs. temperature for cavities 1, 2 and 3.

The parameters recorded and the temperature - time profile are shown below.

Cavities	Stage	Time	Voltage	
#		[s]	[V]	
	R1	1,5	91-450	
	A1	30	450	
	D1	-	-	
	B1	-	-	
	R2	1,5	450-670	
6 and 7	A2	5	670	
	D2	0,5	670-500	
	B2	3	500	
	R3	0,5	500-650	
	A3	3	650	
	D3	0	650-0	

Table 22. Voltage and time parameter for cavities 6 and 7.



Fig.68. Temperature and time profiles for cavities.

Further study is required for superconducting cavities for Nb-Al-Ga system but our research work is necessary to change the cooling system to avoid melt the cavities.

CHAPTER 4. CONCLUSIONS

On the present work was implemented a methodology to obtain Nb₃AlGa compound for samples by means of induction heating, but unfortunately further studies are necessary to obtain Nb₃AlGa coating on 6GHz cavities.

The Nb-Ga and Nb-Al system are complementary because the aluminum improves the wettability of the gallium over niobium, while the gallium corrodes the surface of niobium, improving the diffusion of aluminum.

The gallium acts as polish solution according to microphotographs obtained by SEM measurements making flatter the superconducting layer in comparison with bulk niobium sample.

The temperature measurement is very sensitive to changes in time (milliseconds) and voltage. Also, errors on temperature are reported due to the metallization chamber walls and sensibility of the pyrometer.

Reproducibility problems by induction heating system are present as at the same parameters on voltage and time different critical temperatures were found.

Enclose the volume of the paste 2 is the key of the treatment to decrease the amount of gallium and aluminum evaporated as force the diffusion of the elements within niobium. Also, short times for annealing by induction are necessary to precipitate the superconducting A15 phase. That means we need a closed configuration indeed the best samples were those performed in a niobium sandwich configuration.

Samples with a heat treatment below to 1500°C do not present a superconducting transition and if it is obtained the critical temperature is around 12 and 13 K. While, when the temperature of annealing was between 1500 and 1900 °C the phase shift was obtained between 14 and 18 K.

Finally, despite it was posed a methodology, it can be improved by the recommendations outlined below.

CHAPTER 5. RECOMMENDATIONS

For future experiments by means of induction heating it is necessary to consider a better cooling system for cavities in order to enhance the control on the cooling system.

Better control of the niobium-aluminum-gallium stoichiometry.

Fix all the possible parameters such as: sample position into the chamber, sample mass, flux, gas purity and contaminations to obtain reproducible results.

Perform the post-annealing on samples for long time, more than 2 weeks, in vacuum system to improve the long range ordering.

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ANNEXES



A1. Temperature vs. time for NbGaAl samples.



A2. Temperature vs. time for NbGaAl_P samples.



A3. Temperature vs. time for NbAlGa_C samples.



A4. Temperature vs. time for NbAlGa_CS samples.



A5. Temperature vs. time for NbAlGa_CS samples.

Sample	Stage	Time	Voltage
#		[s]	[V]
	R1	500 [ms]	0-600
	A1	1,5	600
	D1	500 [ms]	600-0
NbGaAl_4	B1	3	0
	R2	500 [ms]	0-600
	A2	1,3	600
	D2	Time Vo $[s]$ [$500 [ms]$ $0 1,5$ 6 $500 [ms]$ 60 3 $0 1,5$ 60 $500 [ms]$ $0 1,3$ 60 $500 [ms]$ $0 1,3$ 60 $500 [ms]$ $0 1$ 5 $500 [ms]$ 56 4 2 $500 [ms]$ 56 4 2 $500 [ms]$ 56 4 2 $500 [ms]$ 60 4 2 $500 [ms]$ 60 $500 [ms]$ 60 <td< td=""><td>600-0</td></td<>	600-0
	R 1	500 [ms]	0-560
	A1	1	560
	D1	500 [ms]	560-0
	B1	4	0
	R2	500 [ms]	0-560
NbGaAl_5	A2	1	560
	D2	500 [ms]	560-0
	B2	4	0
	R3	500 [ms]	0-560
	A3	1	560
	D3	500 [ms]	560-0
	R1	500 [ms]	120-250
	A1	4	250
	D1	500 [ms]	250-0
	B1	4	0
	R2	500 [ms]	0-600
NbGaAl_6	A2	800 [ms]	600
	D2	500 [ms]	600-0
	B2	4	0
	R3	500 [ms]	0-600
	A3	800 [ms]	600
	D3	500 [ms]	600-0

Table A1. Voltage and time set on power supply.

*Continuation of the table A1.

	R1	500 [ms]	120-250		R1	2	84-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
	R2	500 [ms]	0-600		R2	500 [ms]	0-520
NbGaAl_7	A2	1	600	Nb-Al-Ga- D1	A2	1	520
	D2	500 [ms]	600-0		D2	500 [ms]	520-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-600		R3	500 [ms]	0-520
	A3	1,2	600		A3	1,5	520
	D3	500 [ms]	600-0		D3	500 [ms]	520-0
	R1	500 [ms]	84-250		R1	4	84-250
	A1	4	250		A1	5	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
	R2	500 [ms]	0-550	Nb-Al-Ga-	R2	500 [ms]	0-520
NbGaAl_8	A2	1	550		A2	1	520
	D2	500 [ms]	550-0	12	D2	500 [ms]	520-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-550		R3	500 [ms]	0-520
	A3	1,5	550		A3	1,5	520
	D3	500 [ms]	550-0		D3	500 [ms]	520-0
	R1	500 [ms]	120-250		R1	1,5	84-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
NIL	R2	500 [ms]	0-600		R2	500 [ms]	0-550
IND- Gawire	A2	1	600	ND-AI-Ga-	A2	1	550
Gawne	D2	500 [ms]	600-0	13	D2	500 [ms]	550-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-600		R3	500 [ms]	0-550
	A3	1,5	600		A3	1,5	550
	D3	500 [ms]	600-0	1	D3	500 [ms]	550-0

*Continuation of the table A1.

	R1	1,5	84-250		R1	1,5	84-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
	R2	500 [ms]	0-550		R2	500 [ms]	0-550
ND-AI-Ga- C1	A2	800 [ms]	550	ND-AI-Ga- C4	A2	800 [ms]	550
Nb-Al-Ga- C1	D2	500 [ms]	550-0	C I	D2	500 [ms]	550-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-550		R3	500 [ms]	0-550
	A3	750 [ms]	550		A3	800 [ms]	550
	D3	500 [ms]	550-0		R1 1,5 A1 4 D1 500 [ms] B1 4 R2 500 [ms] A2 800 [ms] D2 500 [ms] B2 4 R3 500 [ms] B2 4 R3 500 [ms] D3 500 [ms] B1 3,5 R1 1,5 A1 4 D1 500 [ms] B1 3,5 R2 500 [ms] B1 3,5 R2 500 [ms] D2 500 [ms] B2 4 R3 500 [ms] B2 4 R3 500 [ms] B2 4 R3 500 [ms] B1 4 D1 500 [ms] B1 4 B1 4 B2 3,5 B1 4	550-0	
	R1	1,5	84-250		R1	1,5	84-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0	Nb-Al-Ga-	B1	3,5	0
NIE AL Co	R2	500 [ms]	0-550		R2	500 [ms]	0-550
ND-AI-Ga- C2	A2	1	550		A2	900 [ms]	550
C2	D2	500 [ms]	550-0	03	D2	500 [ms]	550-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-550		R3	500 [ms]	0-550
	A3	1	550		A3	850 [ms]	550
	D3	500 [ms]	550-0		D3	1 $500 [ms]$ 142 $500 [ms]$ 2 $800 [ms]$ 2 $500 [ms]$ 2 4 3 $500 [ms]$ 3 $800 [ms]$ 3 $800 [ms]$ 3 $500 [ms]$ 1 $1,5$ 1 4 1 $500 [ms]$ 1 $3,5$ 2 $500 [ms]$ 1 $3,5$ 2 $500 [ms]$ 2 $900 [ms]$ 2 $500 [ms]$ 3 $500 [ms]$ 3 $500 [ms]$ 3 $500 [ms]$ 1 $1,5$ 1 4 2 $500 [ms]$ 2 $3,5$ 3 $500 [ms]$	550-0
	R1	1,5	84-250		R1	1,5	84-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B 1	4	0
Nb A1 Co	R2	500 [ms]	0-550	NID AL Co	R2	500 [ms]	0-550
ND-AI-Ga-	A2	900 [ms]	550	ND-AI-Ga- C6	A2	900 [ms]	550
0.5	D2	500 [ms]	550-0	0	D2	500 [ms]	550-0
	B2	4	0		B2	3,5	0
	R3	500 [ms]	0-550		R3	500 [ms]	0-580
	A3	850 [ms]	550		A3	500 [ms]	580
	D3	500 [ms]	550-0		D3	900 [ms]	580-0
	R1	1,5	84-250		R1	1,5	84-250
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	A1	4	250		A1	5	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	3,5	0
Nh Al Ca	R2	500 [ms]	0-550		R2	500 [ms]	0-500
NU-AI-Ga- C7N	A2	900 [ms]	550	ND-AI-Ga-	A2	1,2	500
C/N	D2	500 [ms]	550-0	0.10	D2	500 [ms]	500-0
	B2	3,5	0		B2	3,5	0
	R3	500 [ms]	0-580		R3	500 [ms]	0-500
	A3	500 [ms]	580		A3	1,2	500
	D3	900 [ms]	580-0		D3	500 [ms]	500-0
	R1	1,5	84-250		R 1	1,5	84-250
	A1	4	250		A1	1,5	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0	Nb-Al-Ga- C11	B1	3,5	0
Nh Al Co	R2	500 [ms]	0-550		R2	500 [ms]	0-500
NU-AI-Ga-	A2	900 [ms]	550		A2	1,2	500
Co	D2	500 [ms]	550-0		D2	500 [ms]	500-0
	B2	3,5	0		B2	3,5	0
	R3	500 [ms]	0-600		R3	500 [ms]	0-500
	A3	800 [ms]	600		A3	1,2	500
	D3	900 [ms]	600-0		D3	500 [ms]	500-0
	R 1	1,5	84-250	Nb-Al-Ga- C12	R1	1,5	84-200
	A1	5	250		A1	1,5	200
	D1	500 [ms]	250-0		D1	1,5	200-0
	B1	3,5	0		B1	4	0
Nb-Al-Ga- C9	R2	500 [ms]	0-550		R2	500 [ms]	0-500
	A2	1,2	550		A2	1,3	500
	D2	500 [ms]	550-0		D2	250 [ms]	500-0
	B2	3,5	0				
	R3	500 [ms]	0-500				
	A3	1,2	500				
	D3	900 [ms]	500-0				

	R1	15	84-180		R 1	500 [ms]	120-250
		1,5	180		Δ1	<u> </u>	250
Nb-Al-Ga- C13		4	180.0		D1	500 [me]	250.0
	DI DI	1,5	180-0		DI DI	<u> </u>	230-0
		500 [ms]	0 500	-		4 500 [ms]	0 520
	K2	300 [IIIS]	<u>0-300</u>		K2	<u> </u>	<u> </u>
	A2 D2	1,3	500 0	CS_2	A2 D2	1,3	520
	D2	250 [ms]	500-0	-	D2	500 [ms]	520-0
Nb-Al-Ga-	KI	800 [ms]	84-500	-	B2	4	0
C14	Al	1,3	500	-	R3	500 [ms]	0-570
	D1	0	500-0	-	A3	1,3	570
Nb-Al-Ga-	R1	800 [ms]	84-570		D3	500 [ms]	570-0
C15	A1	1,3	570		R1	500 [ms]	120-250
	D1	0	570-0	-	A1	4	250
	R1	500 [ms]	120-250	-	D1	500 [ms]	250-0
	A1	4	250		B1	4	0
	D1	500 [ms]	250-0	CS_3	R2	500 [ms]	0-520
	B1	4	0		A2	1,45	520
	R2	500 [ms]	0-545		D2	500 [ms]	520-0
ND-AI-Ga-	A2	2	545		B2	4	0
C10	D2	500 [ms]	545-0		R3	500 [ms]	0-570
	B2	4	0		A3	1,3	570
	R3	500 [ms]	0-580		D3	500 [ms]	570-0
	A3	2	580		R1	500 [ms]	120-250
	D3	500 [ms]	580-0		A1	4	250
	R1	500 [ms]	120-250		D1	500 [ms]	250-0
	A1	4	250		B1	4	0
	D1	500 [ms]	250-0		R2	500 [ms]	0-520
	B1	4	0	CS_4	A2	1,3	520
	R2	500 [ms]	0-520		D2	500 [ms]	520-0
CS_1	A2	1	520		B2	4	0
	D2	500 [ms]	520-0		R3	500 [ms]	0-570
	B2	4	0		A3	1,3	570
	R3	500 [ms]	0-570		D3	500 [ms]	570-0
	A3	1,2	570				
	D3	500 [ms]	570-0	1			

	R1	500 [ms]	120-250	-	R1	500 [ms]	120-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
	R2	500 [ms]	0-520		R2	500 [ms]	0-550
CS_5	A2	1,3	520	CS_8	A2	2	550
	D2	500 [ms]	520-0		D2	500 [ms]	550-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-570		R3	500 [ms]	0-580
	A3	1,3	570		A3	2	580
	D3	500 [ms]	570-0		D3	500 [ms]	580-0
	R1	500 [ms]	120-250	CS_9	R1	500 [ms]	120-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
	R2	500 [ms]	0-520		R2	500 [ms]	0-545
CS_6	A2	1,3	520		A2	2	545
	D2	500 [ms]	520-0		D2	500 [ms]	545-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-580		R3	500 [ms]	0-580
	A3	1,3	580		A3	2	580
	D3	500 [ms]	580-0		D3	500 [ms]	580-0
CS_7	R1	500 [ms]	120-250	CS_10	R1	500 [ms]	120-250
	A1	4	250		A1	4	250
	D1	500 [ms]	250-0		D1	500 [ms]	250-0
	B1	4	0		B1	4	0
	R2	500 [ms]	0-520		R2	500 [ms]	0-541
	A2	2	520		A2	2	541
	D2	500 [ms]	520-0		D2	500 [ms]	541-0
	B2	4	0		B2	4	0
	R3	500 [ms]	0-580		R3	500 [ms]	0-586
	A3	1,3	580	-	A3	1,2	586
	D3	500 [ms]	580-0		D3	500 [ms]	586-0

	R1	500 [ms]	120-250	CS_14	R1	500 [ms]	120-255
	A1	4	250		A1	6	225
	D1	500 [ms]	250-0		D1	500 [ms]	225-0
	B1	4	0		B1	3	0
	R2	500 [ms]	0-541		R2	500 [ms]	0-450
CS_11	A2	2	541		A2	6,5	450
	D2	500 [ms]	541-0		D2	500 [ms]	450-0
	B2	4	0		B2	5	0
	R3	500 [ms]	0-586		R3	500 [ms]	0-588
	A3	1,2	586		A3	1,1	588
	D3	500 [ms]	586-0		D3	500 [ms]	588-0
	R1	500 [ms]	120-250		R1	500 [ms]	120-180
	A1	4	250		A1	6	180
	D1	500 [ms]	250-0		D1	500 [ms]	180-0
	B1	4	0	CS_15	B1	3	0
	R2	500 [ms]	0-560		R2	500 [ms]	0-350
CS_12	A2	1,3	560		A2	5,5	350
	D2	500 [ms]	560-0		D2	500 [ms]	350-0
	B2	4	0		B2	5	0
	R3	500 [ms]	0-588		R3	500 [ms]	0-550
	A3	1,2	588		A3	1	550
	D3	500 [ms]	588-0		D3	500 [ms]	550-0
	R1	500 [ms]	120-300	CS_16	R1	500 [ms]	120-180
	A1	4	300		A1	6	180
	D1	500 [ms]	300-0		D1	500 [ms]	180-0
CS_13	B1	4	0		B1	3	0
	R2	500 [ms]	0-565		R2	500 [ms]	0-310
	A2	5	565		A2	7	310
	D2	500 [ms]	565-0		D2	500 [ms]	370-0
	B2	5	0		B2	5	0
	R3	500 [ms]	0-588		R3	500 [ms]	0-550
	A3	1,1	588		A3	1	550
	D3	500 [ms]	588-0		D3	500 [ms]	550-0

	R1	500 [ms]	120-180
	A1	6	180
	D1	500 [ms]	180-0
	B1	3	0
	R2	500 [ms]	0-350
CS_17	A2	6	350
	D2	500 [ms]	350-0
	B2	5	0
	R3	500 [ms]	0-550
	A3	1	550
	D3	500 [ms]	550-0
	R1	500 [ms]	120-180
	A1	6	180
	D1	500 [ms]	180-0
	B1	3	0
	R2	500 [ms]	0-350
CS_18	A2	5,5	350
	D2	500 [ms]	350-0
	B2	5	0
	R3	500 [ms]	0-550
	A3	1	550
	D3	500 [ms]	550-0

• Note: On samples with red color, the profile was repeated due to the overcharge of the power supply.