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Synthesis of nb_3alga superconductor by induction heating technique at atmospheric pressure

A.Camacho[1,2]*, A.Rossi[1], V.Palmieri[1,2]

[1]INFN, Laboratori Nazionali di Legnaro, Legnaro (Padova)I-35020 – (ITALY)
[2]Università degli studi di Padova, Dipartimento di Fisica ed Astronomia, Padova I 35122 – (ITALY)
E-mail: Andrea.Camacho@lnl.infn.it

Abstract : It is well known that A15 superconductors are fabricated by many different methods that require highly specialized systems and/or high costs. A simple method is proposed to synthesize A15 compounds: Nb_3Ga, Nb_3AlandNb_3AlGa on metallic niobium samples at atmospheric to be adapted for a future application on Superconducting RF cavities (SRF). The technique is based on electromagnetic (EM) induction heating in anoble gas environment. To verify the technique, the samples annealed were characterized by determining their critical temperature, XRD pattern and SEM mapping of the superconducting layer. The results indicate that the ternary compound can be manufacturedusinga specific heat treatment that produces a direct transformation of A15 phase from high temperatures with a critical temperature of 18 K, demonstrating its potential application for Superconducting RF cavities.

INTRODUCTION

Superconducting A15 compounds were observed in 1931 and today they are of a great importance due to their high critical temperature in the vicinity of 20 K[1]. In 1984 Clemente[2] investigated properties of A15 compounds prepared by melt-spin quenchingtechnique obtaining the transition temperature for: $Nb_3Ga$of 20.0K, V_3Ga of 15.0K, and for Nb_3Al 18.4K which increased up to 18.7K and 20.0K with the addition of Si and Ge, respectively. More recently Takeuchi et al.[3] studied NbAl and its ternary A15 compound $Nb_3(Al,Ge)$ and $Nb_3(Al,Si)$ prepared by a continuous liquid quenching technique using a high-speed moving copper tape as a substrate, heated at a proper temperature. Furthermore,small contents of Si(Ge) showed a supersaturated bcc phase as quenched state for NbAl alloy. The increase in Si(Ge) content in the alloy led to the direct formation of an A15 phase from the molten state. Banno N. et al.[4] developed a new method designated as TRUQ (transformation-heat-based up-quenching) which improves the stoichiometry of the A15 Nb_3Al phase and enhances the high-field Jc performance in Nb_3Al superconductors, obtaining a Jc of 550 A mm^{-2} for the superconducting area at 23 T and 2 K. The most common method reported in the literature is the rapid heating, quenching and transformation (RHQT) for different types of A15 superconductors. However, Lee et al.[5] performed a comparison of Nb_3Al composites processed using both ordinary RHQT and TRUQ methods. D.C. Magnetization measurements at 12 K indicated a 1 T improvement in irreversibility field, H*, for the TRUQ strand compared with ordinary RHQT strands. Other techniques such as the arc-melting method, chemical vapor deposition (CVD), sputtering, etc. are used to synthesize A15 superconductors. According to such methods, some of them are limited by the low deposition rate, high specialization of the system, high costs and the superconductor materials are prepared at experimental level.

The present paper reports the development of induction technique for the preparation of Nb_3Ga, Nb_3Al and Nb_3AlGa samples, characterized by a rapid heating, high temperatures annealing (~2000 °C), vacuumless, self-heating of the sample, short time of treatment (seconds or few minutes), clean quartz chamber and economic system. The technique will be adaptedfor a future application on Superconducting RF cavities (SRF), based on self-heating of the cavity. Indeed, it is well known that A15 materials have not been successfully applied for cavities. Recently, only Nb_3Sn SRF cavities have given important results in the world.[6]

EXPERIMENTAL PROCEDURE

Equipment and instrumentation

The technique proposed is based on the induction heating power supply that converts AC line power to a higher frequency alternating current, delivers it to a work coil and creates an electromagnetic field within the coil. The samples (described in the section B) are placed in that field which induces eddy currents. The friction from these currents generates precise, clean, non-contact heat on samples. A water-cooling system is generally required to cool the work coil and induction system. The chamber is constitutedby a quartz tube sealed to aluminum flanges using a Viton O-ring as shown Figure 1. The sample is placed inside the quartz tube using a niobium wirethat hold it and centered in the work coil. On the bottom flange, an inert gas, either argon or helium, provides an inert environment. The power supply and the whole process are continuously monitored through parameters such as sample position, temperature, pressure and type of gas and its flow rate. A pyrometer,model IRtec P-200, reads the temperature of the samplein the range (250-3000) ºC. Theheat treatmentbased on RHTQ method, was controlled by changing the voltageofthe power supply. The sample is annealed at high temperatures

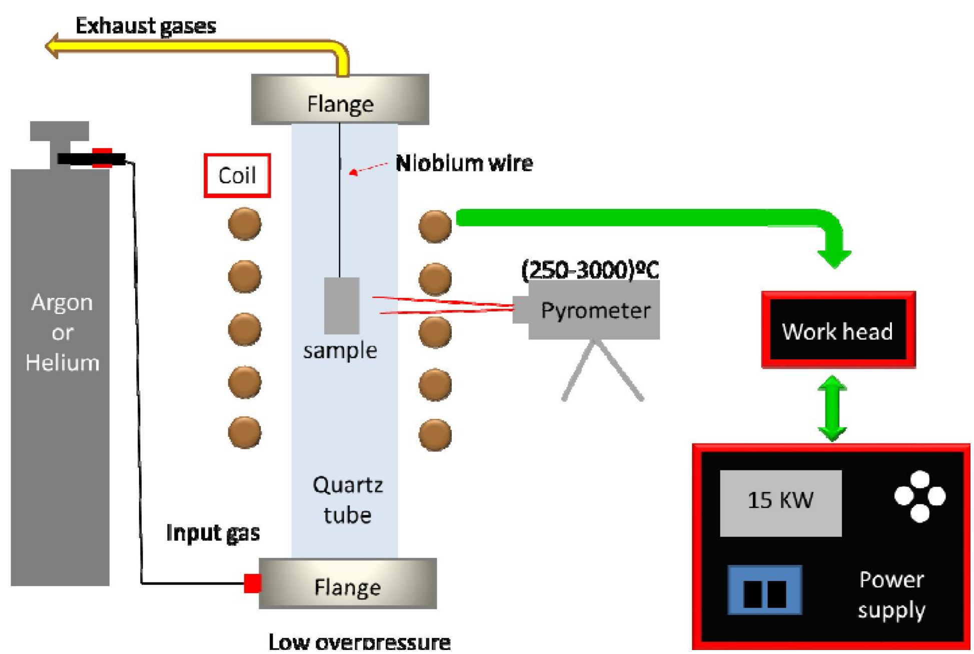

Figure 1 : Schematic induction heating system composed by a quartz chamber under an inert environment, work coil, work head, power supply and sample annealed

above 1400 °C for various periods of time, and then the sample is quenchedat high flow rate in argon or helium. The high temperature allows the diffusion of gallium and/or aluminum in the niobium surface to precipitate the desired A15 phase, while the quenching process avoids a phase change.

A15 sample preparation

Niobium metal samples of (20x10x5) mm wereused to synthesize A15 superconductors. Before annealing the samples, they were chemically treated using a BCP solution (Hydrofluoric acid 40%, Nitric acid 65% and Phosphoric Acid 85%) with a 1:1:2 ratio, in order to clean the surface and remove the possible contaminants that can interfere with the diffusion of gallium and/or aluminum onthe niobium surface. The samples to be annealed are prepared using liquid gallium (99.9% pure) or/and aluminum foil (thickness ~10 μm-99.9% pure). The mix of liquid gallium and aluminum foil is called "paste". In Nb-Al sample configuration, the aluminum foil was simply positioned on the top of niobium sample. The liquid gallium and the aluminum-gallium paste were spread on the top of niobium samples with plastic spatula. According to the phase diagram of the systems Nb-Ga[7], Nb-Al[8] and Nb-Al-Ga[9,10], the initial chemical compositions were selected by atomic percent to precipitate the A15 phase. For binary compounds, 20 at. % of Ga and 20 at. % of Al were selected,assuming300 μm of thickness forthe diffusion of gallium/aluminum into the niobium sample. For ternary compounds,the range of A15 phase in the phase diagram is wider than binary compounds, thus the chemical composition to be selected is varied. However, the atomic percent of niobium is considered between75 and 83 at. % to obtain a stoichiometry of 3:1.

Film characterization

The superconducting transition temperature (Tc), defined as the middle of the superconducting transition, was measured using an inductive measurement technique, performed in ahelium dewar. The inductive measurement consists in placing the annealed sample between two coils, whichthe primary coil, driven by an alternating current, generates anelectromagnetic field thatpenetrates the annealed sample in the normal state and generates a voltage in thesecondary pick-up coil. When the superconducting state is reached during the cooling process, the magnetic field is expelled from a superconductor (Meissner Effect) and the phase shift in the mutual inductance of the coils is recorded providing the Tc value. The crystal structure and lattice constants of the films were determined by X-ray diffraction (XRD) using a X-ray beam wavelength of 1.5405 Å (Cu Kα1) and an angular range from 2θ = 20 to 2θ = 120 in a $\theta - \theta$ configuration. The chemical composition and morphologies were determined by a Scanning Electron Microscope (SEM) Philips mod. XL-30.

Validation of the technique for the preparation of a15 superconductors

This study reportsthe most significant results obtained after annealing 61 samples by the electromagnetic induction technique; specifically, 10, 6 and 45 samples correspond to Nb-Ga, Nb-Al and Nb-Al-Ga systems. The variation of the superconducting transition temperature, Tc, observed from the A15 type compounds Nb_3Ga, Nb_3Al and Nb_3AlGa has been correlated with heat treatment andthe diffusion mechanisms.

Binary compounds

This section reports on samples annealed for 10 minutes, with temperatures from 1500 °C up to 1800 °C. The temperature is controlled by changing the voltage in the power supply. The inductive measurements illustrated in Figure 2, show avariation of the superconducting transition temperature, Tc,all near 12 K, an average of 3 K above of niobium transition (9 K). The difficulty in synthesizing thebinary A15 compoundsNb_3Ga and Nb_3Al is related to the competition from more stable phases, such as the σ phases (Nb_2Al and Nb_5Ga_3) and α-Nb phases (solid solution in bcc structure of niobium). Moreover, the fact that A15 phase is stable in a narrow region of Nb-Ga and Nb-Al phase diagrams (~20 % at.) means that the control of the temperature and time during theheat treatment have to beprecise to avoid the phase change. The critical temperature valuesare not satisfactory in comparison with critical temperature reported in literature, 20 K for Nb_3Ga and 18.8 K

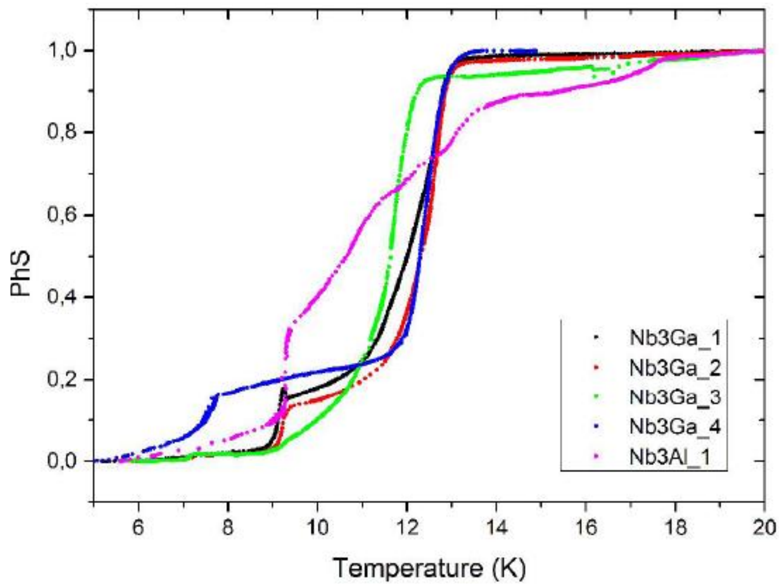

Figure 2 : Phase shift vs critical temperature obtained for binary compounds Nb-Ga and Nb-Al

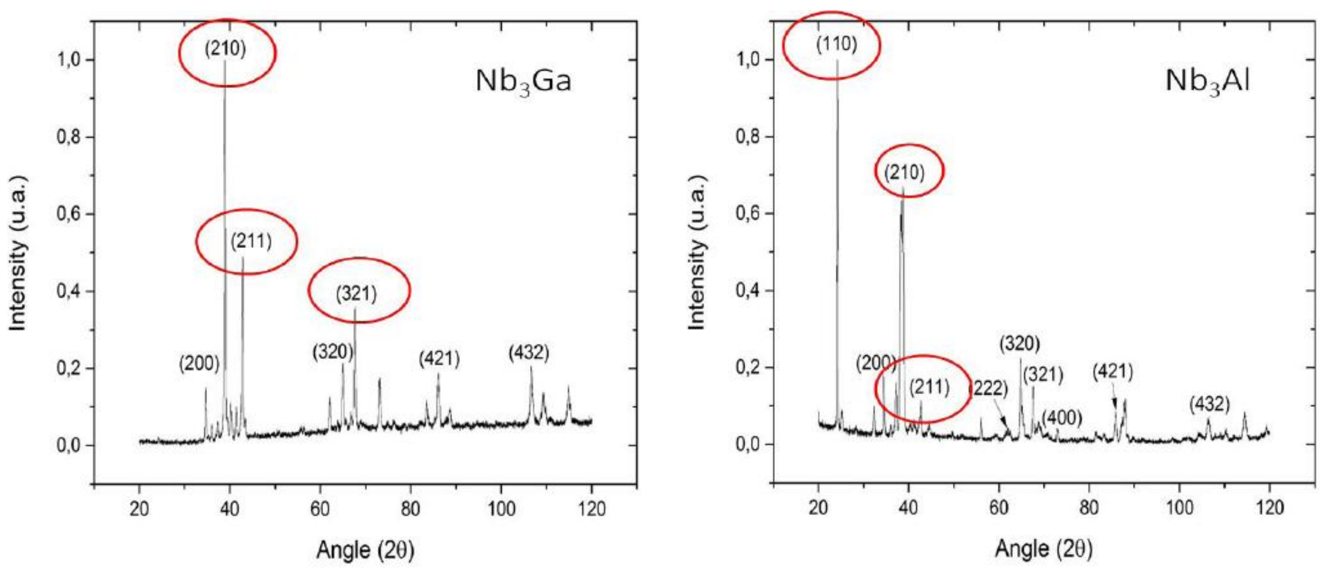

Figure 3 : XRD patterns for binary compounds Nb_3Ga and Nb_3Al

for Nb_3Al[8,11]. Analyzing the heat treatment performed, for the samples annealed that did not reach temperatures higher than 1500ºC, only Nb superconducting transitions were evidenced, i.e. at temperatures below 1500°C the energy for the segregation of the A15 phase is not enough. On the other hand,for the samples that reached temperatures in the range of 1600 and 1800°C, the superconducting A15 phase was evidentwith poor superconducting properties. A systematicexamination of thetime and temperature history suggests that the annealing process for 10 minutesat high temperatures degrades the superconducting phase initially formed. The configuration of samples(niobium-aluminum or gallium-niobium) used allowsa continuous diffusion of gallium or aluminum atoms in niobium, even if the stoichiometry desired, 3:1, was already formed. Thus, the Tc degradation indicates the formation of a Nb-rich plus poor Nb_3("B"= Al or Ga) phase.

Figure 3 shows the X-ray diffraction patternmatch with Nb_3Ga and Nb_3Al compounds. The main diffraction planes (210), (211) and (321) are clearly observed for Nb_3Ga compoundsand the lattice parameter for a representative Nb_3Ga sample annealed is 5.1809 Å, very close to the standard lattice parameter, 5.1800 Å. This result suggests that the Nb-

Ga sample is close to the stoichiometry 3:1 and the crystal structure is β-W type. Moreover, for Nb_3Al samples the main diffraction planes (210), (211) and (110) are observed,but the intensities of the X ray diffraction are differentin comparison with the standard X-ray diffraction pattern,I(210)>I(211) >I(110). The fact that thediffraction peak of Nb-Al annealed sampleis much higher in the plane (110) can suggesta distortion in the unit cell of the crystal structure. Indeed, the lattice parameter is5.2141 Å, much higher than the standard value, 5.1780 Å. The small difference in the lattice parameter for Nb_3Ga samples can explain the sharp transition width, while the big difference of the lattice parameter for Nb_3Al confirm the broad superconducting transition of Nb_3Al compounds.

Ternary compounds. TheNb-Al-Ga sampleswere annealed around 1 minute changing the temperature from 1420°C up to 2000 °C. The heating rate during the heat treatment performed on Nb-Al-Ga samples was ~ 90 C°/s, while the cooling rate determined by the argon flux was 50 C°/s. Figure 4 shows high and sharp superconducting transitions, between 17.5 and 18 K, with ΔTc ~0.35 K. These results suggest that the superconducting A15 phase precipitated directly from high temperatures after the quench process. The high cooling rate prevents the destruction of the superconducting phase since the time spent in the range of (800- 1100) ºC is lower when the A15 phase can be destroyed[12]. The ternary compound Nb-Al-Ga seems to stabilize the A15 phase in the range of temperatures between 1450 °C and 2000 °C. The principal effect of the Al-Ga-Nb system appears to be an increase in the volume fraction of A15 phase in the sample cross-section, since the A15 phase is stable in thewidest chemical composition in comparison with the binary compounds, which is reflected inΔTc.

A scanning electron microscopic examination showsthe pure niobium and A15 superconducting

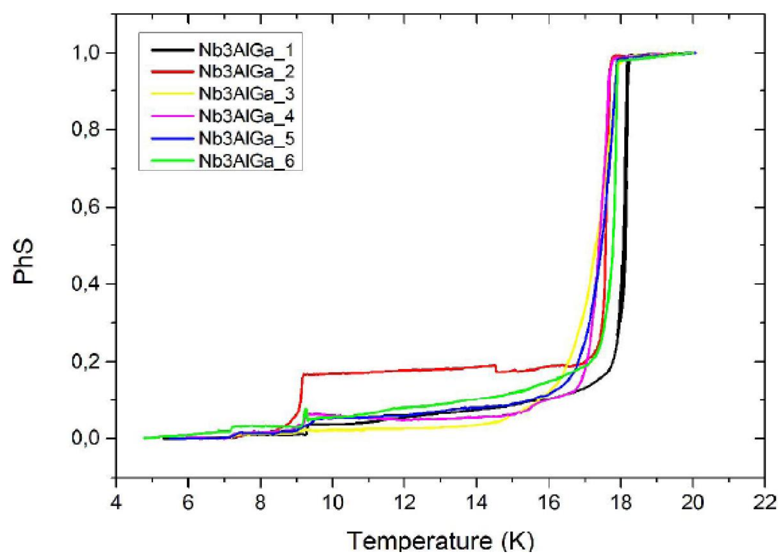

Figure 4 : Phase shift vs. critical temperature for ternary compounds Nb-Al-Ga

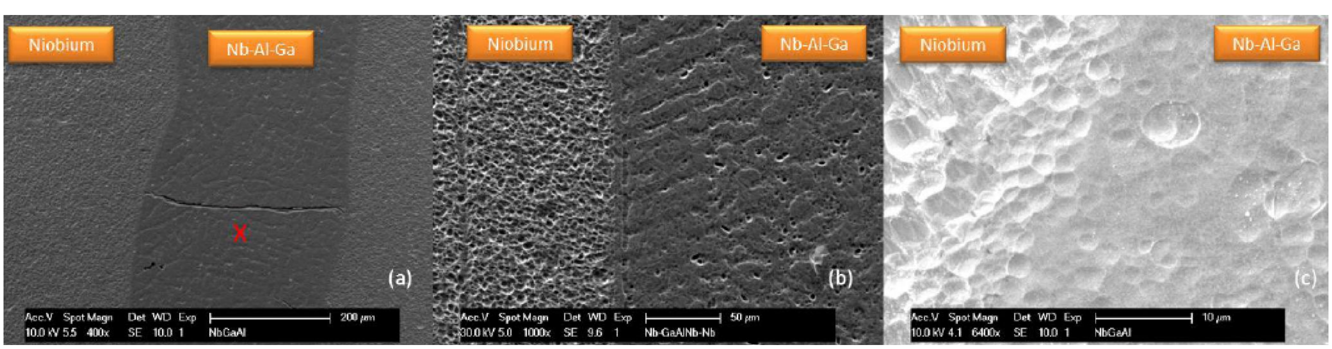

Figure 5 : Interfaces of pure Nb layer and Nb-Al-Ga layer: (a) at 400X. (b) at 1000X. (c) at 6400X

interface (see Figure 5). The”clear gray”zones correspond to niobium, while the”dark gray”zone corresponds to the superconducting layer. A mix of cleavages and acrack are observed, the source of which can be attributed to the residual stresses after the quenching process and the brittle behaviour of A15 compounds. Going deeper in themicrostructureof the niobium-superconducting interface, the microphotograph reveals a granular morphology which seems like a sponge, while the morphology of the superconducting layer looks flat. This can possibly bedue to the corrosive property ofgallium whichsmoothens the niobium sample when it diffuses. The chemical composition of the superconducting layer was measured randomly in 5 different points, and then, the values were averaged. The chemical compositionwithout taking into account the presence of oxygen was: 73% at. Nb, 13.3% at. Ga and 14.2% at. Al. which indicates, according to the phase diagram,the precipitation of A15 and A2 phases[9,10].

X-ray diffraction patterns of $Nb_3(Ga,Al)$ exhibit the main diffraction planesin common for both systems Nb_3Ga and Nb_3Al, (210) and (211). However, the planes (321) of Nb_3Ga and (110) of Nb_3Al were not observed, which suggest a new order in the crystal structure. In fact, the lattice parameter estimated for $Nb_3(Ga,Al)$ sampleis5.1904Å, between the lattice parametersobtained for Nb_3Ga and Nb_3Alsamples annealed (a-Nb_3Ga< a-$Nb_3(Al,Ga)$< a-Nb_3Al). The re-orderingin the crystal structure can be possible with an improvement of the aluminum diffusion on niobium samples, onlywhen galliumwas added. Map analysis in the interface of niobium and superconducting layer shows that gallium diffuses preferentially through the grain boundaries which is inherent in itscorrosive property. On the other hand, the aluminum diffuses uniformly through whole cross section (see Figure 6). One hypothesis about the improvement of the superconducting properties from binary to ternary compounds is that the gallium hinders the formation of aluminum oxide suggested from the map microphotograph O(K)-Nb(L) in which it seems that oxygen follows the path of gallium. Despite the fact that gallium diffuses preferentially

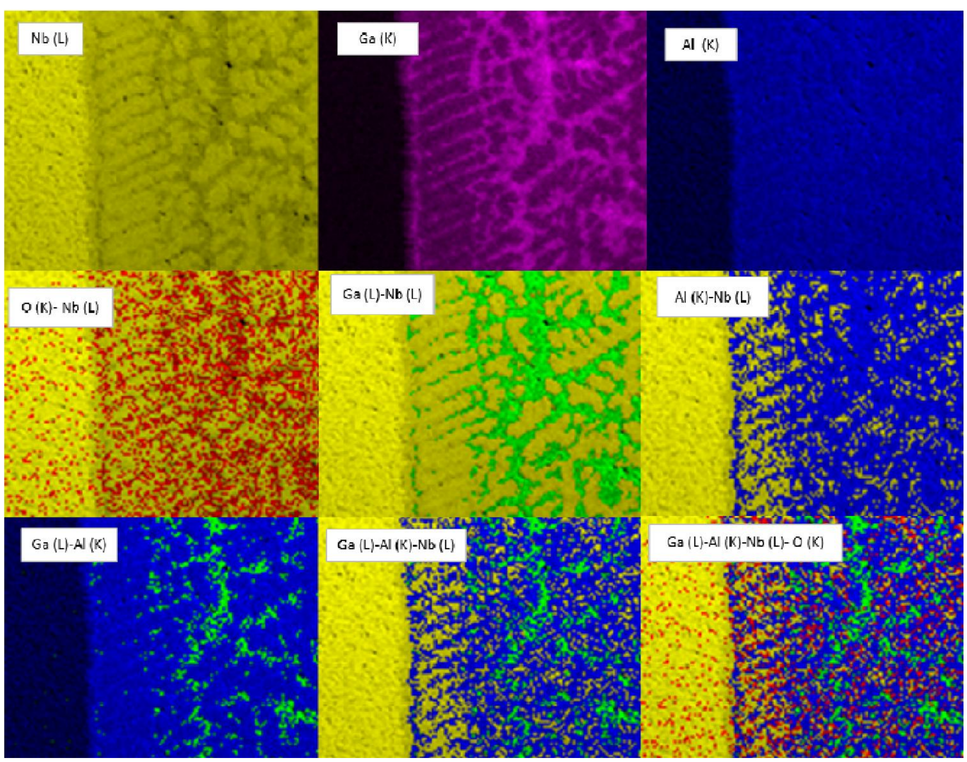

Figure 6 : Map analysis of the interface of niobium and A15 superconducting layer with the presence of the following elements:oxygen (K) in red with Smin: 11/Smax: 99, gallium (L) in green with Smin:17/Smax: 405, aluminum (K) in blue with Smin:19/ Smax: 296, niobium (L) with Smin:151/Smax:2805 and gallium (K) in purple with Smin: 21/ Smax: 366. Smin /Smax means the minimum and maximum X-ray counts which are related to the more opaque and brighter pixel respectively

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through the grain boundaries, the ternary or pseudo-binary compound Nb_3AlGa formed by Nb_3Al and Nb_3Ga have an optimum critical temperature, and these pseudo binary compounds are formed in the entiresuperconducting layer which means that the A15 superconducting phase is present in the whole cross section.

CONCLUSIONS

In In the present work, a simple, economic and useful methodology to obtain $Nb_3(AlGa)$ superconducting compounds by means of electromagnetic induction heating was implemented. The best critical temperature, (18 ±0.35) K, was obtained by annealing the niobium-gallium-aluminum sample around 1 minute at 1420 °C with a chemical composition of 73% at. Nb, 13.3% at. Ga and 14.2% at. Al for 300 μm of thickness. The heat treatment to precipitate the A15 phase required only around one minute, high temperatures (higher than 1420°C) and a fast cooling rate (~50°C/s). The ternary compounds suggest that Nb-Ga and Nb-Al systems are complementary because the aluminum improves the adherence of the gallium over niobium, while the gallium avoids the oxidation of aluminum, improving the diffusion of aluminum into niobium. Finally, the ternary or pseudo binary compound Nb_3AlGa formed by Nb_3Al and Nb_3Ga is formed in the entire cross section after performed a heat treatment within a rangeof temperatures (1450 - 2000)°C and wider chemical composition in comparison with binary compounds. The ternary compound stabilizes the A15 superconducting phase demonstrating its potential application for a future production of Nb_3AlGa Superconducting RF cavities.

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