



Oxide-dispersion driven phase and microstructural evolution with an analytical framework for critical current density in synergistically yttria-titania doped Nb₃Sn

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ABSTRACT

This study presents a heat treatment–doping effect of individual and synergic nano-oxide Y₂O₃ and TiO₂ dispersoids on Nb₃Sn towards the interrelation among phase, microstructure and properties. Synergic doping of Y₂O₃ and TiO₂ to Nb₃Sn resulted in T_c of 18 K after annealing at 400 °C for 9 h. A lower T_c of 16 K was observed for as-sintered pristine Nb₃Sn. Pristine samples were susceptible to heat treatment, indicated by the wide transition width of 2 K in T_c . A high overall J_c of 5.17×10^5 A/cm² (10 K, 2 T) was observed for Y₂O₃ and TiO₂ co-doped Nb₃Sn sample annealed at 400 °C for 9 h compared to the overall J_c of 2.3×10^5 A/cm² for as-sintered. Solutionized and quenched samples showed poor overall J_c performance, with the lowest J_c of 9.1×10^4 A/cm² for the pristine. A higher NbO phase fraction led to a degraded overall J_c performance in TiO₂ doped sample. A superior overall J_c performance for co-doped sample was due to the synergic presence of Y₂O₃ and TiO₂ at grain boundaries of Nb₃Sn which acted as blanket to restrict the NbO formation. An analytical model to predict the microstructurally governed overall J_c performance at different applied fields was developed.

1. Introduction

Nb₃Sn is among such traditional superconductors which carry a potential for critical applications like future colliders and particle accelerators. Nb₃Sn superconductors have been found to serve in many applications like superconducting magnets in NMR, MRI etc. [1]. A high critical current density, J_c is desirable for such applications and to cater the demand of future applications. The microstructural changes of Nb₃Sn have shown to channelize the J_c and upper critical field, B_{c2} via the magnetic flux pinning effects [2–5]. This is directly linked with the grain structure, especially with grains involving a higher grain boundary fraction in A15 structured superconductors [6], desirable for additional flux pinning support [2,7]. The aspect of doping Nb₃Sn is also utilized in engineering the microstructure, as also indicated in the literature [8,9]. Out of the several available dopants, hexagonally packed structured dopants were keenly observed for modifying the superconducting property of Nb₃Sn [9]. The choice of dopants, basis of their purity

specifically in elemental form adds up the cost for bulk or wire fabrication. Recently some studies highlighted the use of the dopants through internal oxidation process, using elemental additions with an active oxygen source as SnO₂ to form oxides of those additions. This process is used mainly in refining the Nb₃Sn microstructure [10–12]. The process of internal oxidation has led to appealing results in functional property enhancement i.e., J_c and upper critical field, B_{c2} when compared to the elemental doping itself [10]. The nano-oxides formed as a result of internal oxidation process serves as additional flux pinning centers (APCs), enhancing the J_c . This internal oxidation process, however, still requires dopant in their elemental form which adds up the cost. Whilst a direct influence of the oxide dopants could have an impact on the superconducting functionality of Nb₃Sn and also on the phase and microstructure evolution. Additionally, the oxide dopants are economical when compared to the cost of their elemental counterparts. However, the current literature still lacks a detailed and systematic study on the utilization of oxide dopants for Nb₃Sn bulk. Such studies are readily

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available for superconductors like MgB_2 and YBCO where the oxide dopants have been observed to play a crucial role in modifying J_c [13,14].

In one of our recent studies on the effect of doping Y and Ru to Nb_3Sn , we observed that the formation of yttria (Y_2O_3) phase out of residual yttrium (Y) due to its limited solubility in Nb_3Sn led to a positive variation in functional behaviour; particularly the J_c [9]. These secondary Y_2O_3 phase particles also helped enhancement of J_c in NbTi by acting as an additional artificial flux pinning center (APC) [15]. So, we are expecting a very high chance of creating APCs by using oxide dopants as dispersoids within the Nb_3Sn matrix. This can be directly linked to the deviations in microstructural features as we have observed in [2,4,9]. The correlation of microstructural changes with phase stability is not a well understood phenomenon for oxide-doped Nb_3Sn in the existing literature. From the available oxides of known elemental dopants to Nb_3Sn , Ti had been extensively researched for Nb_3Sn . The oxide form of Ti i.e., TiO_2 is very cheap and easily available compared to its elemental form Ti. An addition of TiO_2 to other superconductors i.e., Bi-2223 [16,17] and MgB_2 [18,19] stabilizes the superconducting phase and enhances the functional properties. A very limited study had been reported for TiO_2 addition to Nb_3Sn [20]. This study further utilized TiO_2 as an addition to Nb_3Sn .

Another challenge is the optimization of concentration of the oxide dispersoids to modify properties of Nb_3Sn . This study also highlights the method of optimizing the oxide dispersoid concentration in Nb_3Sn through mechanical alloying route. Further, we had also observed that sintering temperature would play a crucial role in determining the properties of mechanically alloyed Nb_3Sn bulk [21]. Effects of different heat treatment conditions on the functional behaviour of bulk Nb_3Sn are, however, yet to be understood. This was a crucial factor to understand the superconducting behaviour of Nb_3Sn isolating the effect induced by only the grain size. Therefore, this study also aims to address the role of different heat treatment conditions on the superconducting properties of oxide-doped Nb_3Sn bulk. A low temperature heat treatment of the range $200^\circ\text{C} - 400^\circ\text{C}$ is used in the current work, so that the alloy can also be used in conjunction with the bronze route. Combining the effects of phase equilibria and formation kinetics with the oxide dispersoids modification to Nb_3Sn , a microstructure – functional property link is established. Using this correlation method, the mechanism behind the functional changes were understood. Advanced characterization techniques like electron backscattered diffraction and automated crystal orientation mapping (ACOM) through transmission electron microscopy (TEM) was used to accurately define the microstructure.

Additionally, a link between the J_c and flux pinning behaviour through suitable pins was established using a developed analytical model. The model was validated using the experimental data for different samples. Further, this analytical model was able to precisely predict the J_c performance. This model quantitatively defines the J_c values based on the available microstructural features like effective and non-effective pinning phase fractions.

In our earlier study we found that the doping with Y_2O_3 and TiO_2 in a synergic way able to enhance both the T_c and J_c [20]. However, the role of different post sintering heat treatment conditions was not analysed. Further, this work focuses on understanding the mechanism for the enhancement of the abovementioned properties in a structure–property correlative approach. The emphasis was also given in designing a model to understand the microstructure evolution with synergic doping in this study.

2. Materials and methods

2.1. Alloy fabrication

Pure Nb_3Sn powder (Goodfellow, 99.99% pure, $250\ \mu\text{m}$), yttria powder (ACS materials, 99.9% pure, Y_2O_3) and rutile (Thermofisher scientific, 99.8% pure, TiO_2), was taken in a stainless steel (SS) jar

Table 1

Heat treatment conditions for different samples with their identification abbreviations.

Samples/ Heat treatment conditions	As-sintered	Annealed at 200 °C (9 hrs)	Annealed at 400 °C (9 hrs)	Solutionized + Quenched at 400 °C (9 hrs)
Pristine Nb_3Sn	AS _{Prt}	AN ^{200° C/9h} _{Prt}	AN ^{400° C/9h} _{Prt}	SQ ^{400° C/9h} _{Prt}
$\text{Nb}_3\text{Sn} + 2\ \text{wt}\%$ Y_2O_3	AS _{Y₂O₃}	AN ^{200° C/9h} _{Y₂O₃}	AN ^{400° C/9h} _{Y₂O₃}	SQ ^{400° C/9h} _{Y₂O₃}
$\text{Nb}_3\text{Sn} + 2\ \text{wt}\%$ TiO_2	AS _{TiO₂}	AN ^{200° C/9h} _{TiO₂}	AN ^{400° C/9h} _{TiO₂}	SQ ^{400° C/9h} _{TiO₂}
$\text{Nb}_3\text{Sn} + 1\ \text{wt}\%$ $\text{Y}_2\text{O}_3 +$ $1\ \text{wt}\%$ TiO_2	AS _(Y₂O₃+TiO₂)	AN ^{200° C/9h} _(Y₂O₃+TiO₂)	AN ^{400° C/9h} _(Y₂O₃+TiO₂)	SQ ^{400° C/9h} _(Y₂O₃+TiO₂)

(RETSCH, grade 1.4112) with SS balls of diameter, $\phi = 5\ \text{mm}$. The ball to powder weight ratio was maintained as 10:1. The setup was then placed in RETSCH PM100 planetary ball mill and milled at 300 rpm with 20 mins of cooling time after every 10 mins of milling to avoid excessive heat generation. The powder was initially milled at different speed i.e., 100 rpm, 200 rpm, 300 rpm and 400 rpm. The speed of 400 rpm shows extensive agglomeration between powder particles and the cold welding of powder particles with the balls even after 30 mins of milling. The milling was performed for different time periods, restricted up to a time interval of 2.5 h as beyond this time extensive agglomeration and cold welding between particles and milling media took place. A small amount of milled powders was removed after every desired timeframe for characterization purposes. The doping concentration was optimized using Nb_3Sn doped with Y_2O_3 . Y_2O_3 was chosen to have comparison of the parameters as per our earlier study, utilizing Y as a dopant to Nb_3Sn . Different Y_2O_3 concentrations i.e., 0.5 wt%, 2 wt% and 5 wt% were chosen to identify the optimized doping concentration. The choice of these concentrations was based on the idea that the concentrations in near vicinity may not affect the crystallite size or lattice variations much.

The resultant milled powder ($\sim 5\ \text{gms}$) was fabricated to pellet bulk by placing those in a graphite die placed in FCT system spark plasma sintering (SPS) furnace at an electrode pressure of 50 MPa, pulsed at 1200°C for 2 mins. These conditions of pressure and time were chosen to ensure maximum densification of the pellets. The diameter of the sintered disc was 20 mm and a thickness of 3 mm owing to the die constraints in SPS technique. The sintered disc was then cut using a Chennai metco-based low speed saw and heat treated under different conditions within the range $200^\circ\text{C} - 400^\circ\text{C}$ in a Tempsens HTF1200 made furnace fitted with Pfeiffer vacuum rotary and turbomolecular pump. The heat treatment conditions used in the current study along with the abbreviation terminology used in this study is presented in Table 1. The resultant samples were grinded and polished using SiC papers of suitable grades and mirror finished using $0.5\ \mu\text{m}$ particle sized colloidal silica for the characterization purpose.

2.2. Phase analysis

The phase analysis study was conducted using Rigaku Ultima IV X-ray diffractometer within the 2θ range of 25° to 75° at a step size of 0.02° and a scan rate of $2^\circ/\text{min}$. The phase match was done using international centre for diffraction data (ICDD) powder diffraction file (PDF) database cards. Apart from phase analysis, calculations on crystallite size, lattice strain and lattice parameter of phases were carried out using the Williamson-Hall formulation in Malvern Panalytical X'Pert Highscore plus software. The analysis was further confirmed through Rietveld refinement method using Full Prof software.

Table 2

Sample dimensions corresponding to the samples subjected to different heat treatment conditions.

Condition	a (mm)	b (mm)	c (mm)
AS _{Prt}	3.03	2.41	0.72
AS _{Y₂O₃}	3.07	2.37	1.49
AS _{TiO₂}	2.53	2.09	0.50
AS _(Y₂O₃+TiO₂)	2.51	1.80	0.54
AN _{Prt} ^{200° C/9h}	2.32	2.06	0.47
AN _{Y₂O₃} ^{200° C/9h}	2.38	2.28	0.54
AN _{TiO₂} ^{200° C/9h}	2.61	2.44	0.53
AN _(Y₂O₃+TiO₂) ^{200° C/9h}	2.29	2.24	0.51
AN _{Prt} ^{400° C/9h}	2.56	2.34	0.57
AN _{Y₂O₃} ^{400° C/9h}	2.35	2.14	0.48
AN _{TiO₂} ^{400° C/9h}	2.42	1.85	0.50
AN _(Y₂O₃+TiO₂) ^{400° C/9h}	2.62	2.37	0.52
SO _{Prt} ^{400° C/9h}	1.80	1.47	0.47
SO _{Y₂O₃} ^{400° C/9h}	2.26	1.34	0.44
SO _{TiO₂} ^{400° C/9h}	2.55	2.24	0.49
SO _(Y₂O₃+TiO₂) ^{400° C/9h}	1.96	1.91	0.48

2.3. Functional characterization

The superconducting measurements were carried out using Quantum Design magnetic property measurement systems (MPMS3) utilizing the vibrating sample magnetometer (VSM) mode. A cuboidal geometry sample with dimensions a , b and c were considered for the measurements such that the direction of $c \parallel$ applied field axis. The sample

dimensions corresponding to the heat treatment conditions shown in Table 1 is presented in Table 2. The sample centering was done at an applied field of 50 Oe (5 mT) after placing the sample in straw with one side of straw blocked using Kapton tape. A low field was used just to induce some magnetic effect to get optimal magnetic response in detecting sample's magnetic behaviour and to identify the sample position for measurement. The applied field was removed before cooling down procedure. The measurement step rate was 1 K/min with a step size of 1 K and within the range of 10–22 K.

Further, moment-applied field (m-H) loops were used for calculation of critical current density (J_c) at 10 K using Bean's critical model [2]. The 10 K temperature was chosen so as to allow the moment – applied field (m-H) loops to get closed. The loops did not close at the 4.2 K temperature even at the instrumental limit field of 7 T. This study reports a higher non superconducting phase fraction in certain cases which will be discussed in the later part of text, the terminology of J_c is changed to overall J_c i.e., $J_{c_{overall}}$ or J_{c_o} to indicate the correct behaviour. This J_{c_o} is defined as the critical current density calculated over the total sample cross-section which includes the effect of both superconducting and non-superconducting phase fractions. This J_{c_o} differs from the intrinsic J_c , which is defined only for the superconducting Nb₃Sn phase. Hence, a J_{c_o} terminology will be used for this study.

2.4. Microstructural analysis

The initial microstructural analysis was carried out using Jeol 7800F prime field emission scanning electron microscope (FESEM), equipped with Oxford Instruments energy dispersive x-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD) detectors. Subsequent analysis was carried out using a TESCAN Magna LMU made scanning transmission electron microscope equipped with an Ametek EDX

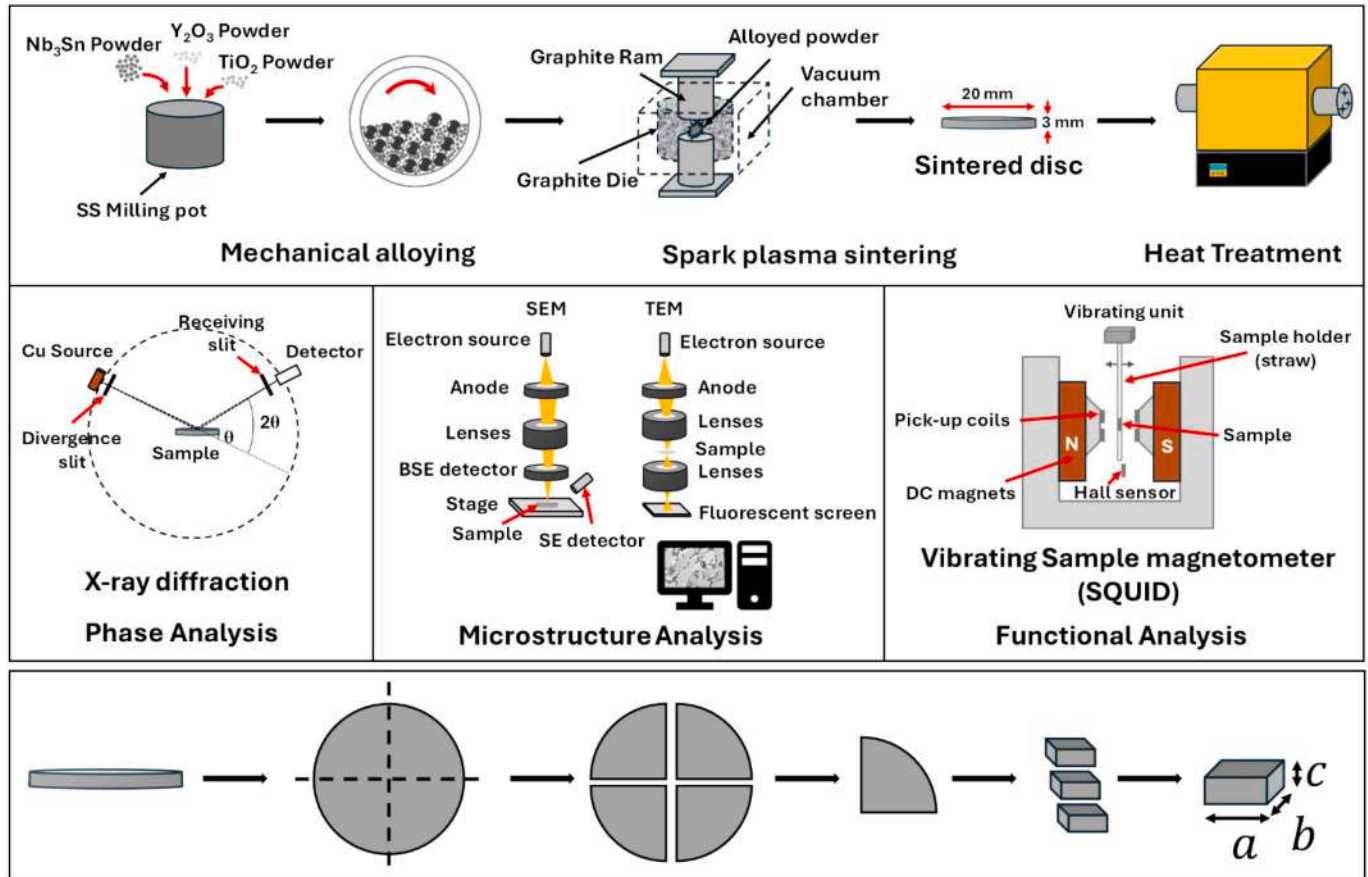


Fig. 1. Schematic diagram of experimentation carried out in this work.

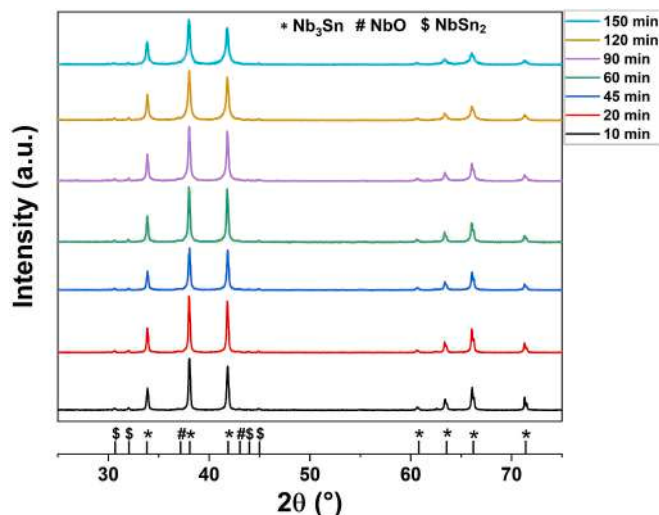


Fig. 2. X-ray diffractogram showing the phases formed at different milling time for pristine Nb_3Sn sample.

detector.

Electron backscattered diffraction (EBSD) was performed using a FEI™ Quanta 3D FEG scanning electron microscope operated at 20 kV, equipped with an EDAX Velocity Super™ camera. EDAX OIM Analysis 9 was used to analyse and index the orientation data. Kikuchi patterns were collected at a resolution of 120×120 pixels with a 4×4 binning. A Spherical harmonic-based EBSD indexing method (implemented in OIM Analysis 9™) was employed to index different phases for phase identification and orientation mapping.

The advanced microstructural characterization was carried out using a Jeol JEM 2800 transmission electron microscope (TEM) fitted with a Jeol EDX detector at an accelerating voltage of 200 kV. The TEM lamellae were prepared using Thermofisher Scios 2 focused ion beam SEM (FIB-SEM) by deposition of carbon at region of interest followed by milling using Si ions. The TEM based orientation imaging micrographs (TEM-OIM) were captured using Nano-megas precision electron diffraction (PED) technique attached to JEM 2800 under STEM mode. The step size is 30 nm within and a total point of 200 along x and y direction of a square grid. The imaging system is kept at 2 m relative to electron source.

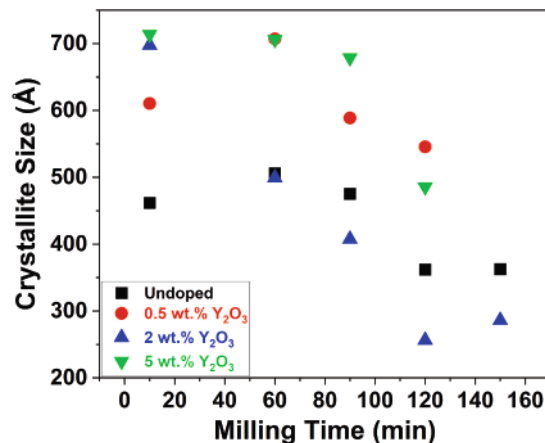
The experimental methodology is shown in Fig. 1.

3. Results and discussion

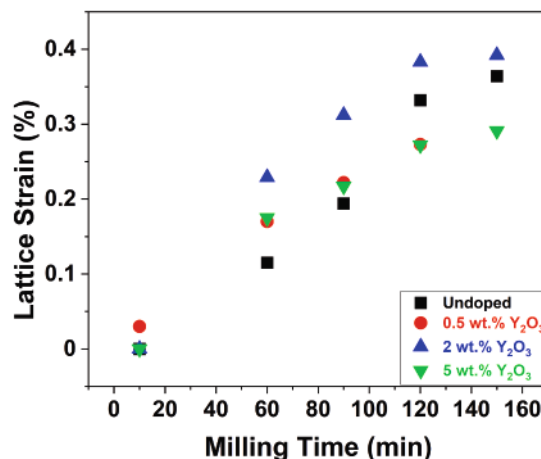
3.1. Optimization of dopant concentration for mechanically alloyed Nb_3Sn

The milling conditions play a crucial role in varying both microstructural and functional behaviour of Nb_3Sn . Over milling of powders can make the Nb_3Sn structure amorphous, while an under milling condition won't help achieving an optimal functional behaviour. The milling speed was decided based on the trial-and-error rule, where a high speed of 400 rpm resulted in cold welding between powder and milling media. The speed of 300 rpm was optimized for a ball to powder weight ratio of 10:1, to impart high energy to the powder for refinement of particles to nano-range [22]. A size of nano-range was desirable for better densification of powder particles during sintering phase.

Fig. 2 shows the indexed X-ray diffractograms for the powders milled at different time intervals. The identified phases were Nb_3Sn (ICDD: 01-073-2817), NbSn_2 (ICDD: 01-072-8778) and NbO (ICDD: 01-089-5297). Here ICDD indicates the reference code from International Center for Diffraction Data powder diffraction file (PDF) database. The possibility of formation of NbSn_2 is likely be due to the interactional reaction



(a)



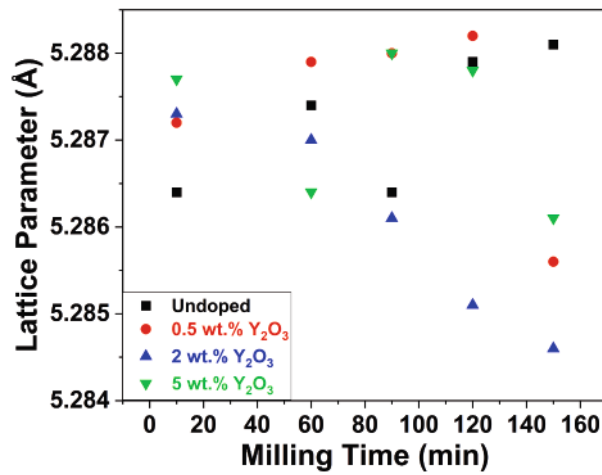
(b)

Fig. 3. (a) Crystallite size and (b) lattice strain as a function of milling time for different dopant concentration.

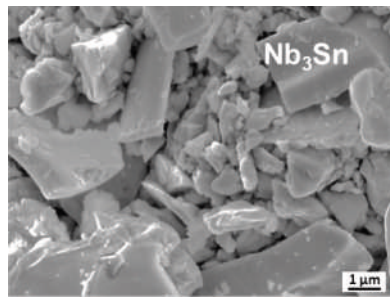
between the residual Sn and the dissociated Nb from the Nb_3Sn phase during high-energy milling process. Pure Sn was one of the constituents being present in the as-received powder [9]. This dissociated Nb was equally susceptible towards the oxygen from the environment to form the NbO phase. This intake of oxygen is not so uncommon for such milling processes [9]. Milling is known to create more reactive surfaces, which combined with high affinity of Nb for oxygen, can easily form the NbO phase despite maintaining stringent conditions of inert atmosphere [9,20].

The impact of mechanical alloying directly reflects over the effect induced on the crystallite size and lattice strain. The crystallite size and lattice strain directly impacts the functional properties like critical temperature and critical current density. These values of crystallite size and lattice strain was estimated from X-ray diffraction (XRD) technique. Although estimating the crystallite size through XRD technique does not give very accurate results but it gives an insight about the behavioural pattern to gauge the functional properties. This method is also helpful in determination of an optimized dopant concentration by understanding the effect of dopant on crystallite size and lattice strain. This study utilized Williamson-Hall (W-H) method, employing pseudo-Voigt peak fitting function, $pV(x)$ for the determination of crystallite size and lattice strain. The fit function is a sum of Lorentzian peak function, $L(x)$ and Gaussian peak function, $G(x)$ and the functions are weighted by a weighing parameter, η whose value ranges between 0 and 1.

$$pV(x) = \eta G(x) + (1 - \eta)L(x) \quad (1)$$

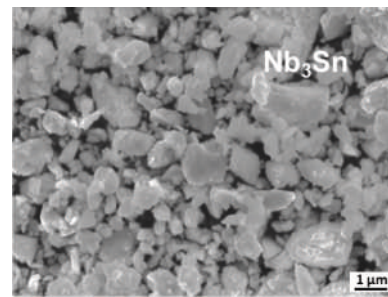


(a)



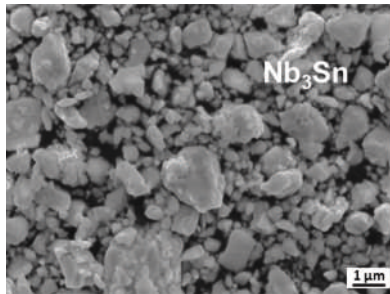
10 min

(b)



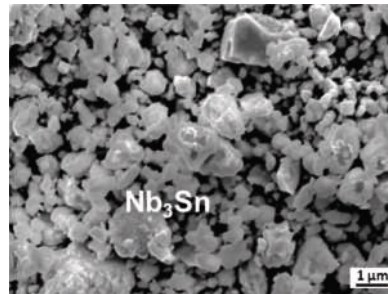
60 min

(c)



120 min

(d)



150 min

(e)

Fig. 4. (a) Lattice parameter calculation of Nb₃Sn phase for different dopant concentrations. Scanning electron micrograph for Y₂O₃ doped milled samples for milling period of (b) 10 min, (c) 60 mins, (d) 120 mins and (e) 150 mins showing Nb₃Sn powder particles.

The $G(x)$ and $L(x)$ function depends on the full width at half maxima (FWHM), peak height (intensity) and peak position (θ). The fitted parameters were used in the W-H equation to determine the crystallite size and lattice strain.

$$\beta \cos \theta = 4 \varepsilon \sin \theta + \frac{ka}{D} \quad (2)$$

here β is peak broadening, θ is diffraction angle in degrees, ε is lattice strain, k is a constant indicating shape factor with a value of 0.9 [23], a is X-ray source wavelength i.e., 1.54 Å for Cu K α and D is crystallite size. The calculated values were matched with the values calculated through Rietveld refinement procedure in the Full Prof software. For the process of Rietveld refinement, whole data profile within the selected 2θ range of 25° to 75° is fitted using a pseudo-Voigt function. A proper fitting was

ensured for the peaks with higher ' 2θ ' values to reduce the error in measurement. During fitting, the refinement of parameters like lattice constants, FWHM using Caglioti widths and atomic positions parameters were carried out.

Fig. 3 shows the variation of crystallite size and lattice strain of pristine Nb₃Sn and Y₂O₃ doped Nb₃Sn as a function of milling time. Y₂O₃ doping was considered to analyse these effect due to a limited solubility of Y in Nb or Sn such that an excess quantity of dopant can be avoided. Ti from TiO₂ on the other hand was observed to displace Nb, so it would be difficult to identify the optimal amount in case of Nb₃Sn doped with TiO₂. It is clear from Fig. 3a that 120 mins (2 h) of milling time stands as optimized and desirable as beyond this time, the crystallite size of undoped Nb₃Sn sample begins to increase. This increase in crystallite size could be a result of particles agglomeration because of repeated cold

welding. Further, the milling time was restricted to 2.5 h just at the verge of extensive cold welding of powder particles with the milling media. A lower crystallite size is also desirable for good densification post sintering. Fig. 3a also highlights the choice of different concentrations of Y_2O_3 doped in Nb_3Sn .

As observed, Nb_3Sn doped with 2 wt% Y_2O_3 possessed the relatively smallest crystallite size of 25.6 ± 2.2 nm. This observation states that doping with 2 wt% Y_2O_3 possesses a smaller crystallite size than the other chosen concentrations of Y_2O_3 i.e., 0.5 wt% Y_2O_3 and 5 wt% Y_2O_3 in this study. A smaller crystallite size is desirable to improve the sample densification and functional properties. Crystallite size gives an estimation about the grain boundary fraction. In A15 structured superconductor like Nb_3Sn , critical current density is mainly driven by the fraction of grain boundaries as these boundaries serve as flux pinning sites. Further a continuous decreasing value of crystallite size with increasing milling duration for 2 wt% Y_2O_3 doped sample is a result of severe plastic deformation (SPD). An increase in the crystallite value for 5 wt% doping suggests an agglomeration taking place as the doping limit has surpassed. This agglomeration could be in between the Nb_3Sn particles with Y_2O_3 and between Y_2O_3 residues. Also, from Fig. 3b, it was observed that the lattice strain was highest for the 2 wt% Y_2O_3 -doped sample.

As the milling proceeded, the SPD might result in generation of higher strain with a steady decline in crystallite size. This could be the reason why Nb_3Sn doped with Y_2O_3 was observed to be induced with increasing lattice strain when the milling period increases. The sample doped with 2 wt% Y_2O_3 showed highest lattice strain as a result of lowest crystallite size. The other inference from the Fig. 3 could be that the SPD process could bring in changes in the lattice strain because of the changes in lattice parameter shown by Fig. 3a. Also, with the increase of milling time, peak broadening could be seen due to induced strain by the milling media within the lattice. This induced strain resulted in the reduction of crystallite size, thereby causing peak broadening and hence, a decrease in the peak intensity of Nb_3Sn .

Fig. 4a shows the variation in lattice parameters of Nb_3Sn doped with different concentrations of Y_2O_3 as a function of different milling time periods. The Nb_3Sn sample doped with 2 wt% Y_2O_3 showed a continuous decreasing trend in the lattice parameter as a function of an increase in milling time. The presence of high strain in the crystal lattice may result in lattice contraction to relieve those strain [24]. The induced strain is of compressive nature due to generation of defects caused by SPD as mentioned earlier. This correlates with the observed decrease in lattice parameter in Fig. 4a with the increase in lattice strain shown in Fig. 3b. The contraction in lattice begins when the strain values reach a limiting value to nucleate defects or dislocations to relieve those strains. This strain field is also manifested in the form of the shift in XRD peak. The milling had also an effect on the size of powder particles. The refinement of the powder particles because of milling time could be observed from the secondary electron (SE) micrograph shown in Fig. 4b-e for the pristine Nb_3Sn sample. The average particle size was estimated from the SE micrograph by using linear intercept method. The estimated size of particles varies from $\sim 250 \pm 3.6 \mu m$ for a milling time of 10 min to a particle size range of $200 \text{ nm} \pm 20.37 \text{ nm}$ to $1 \pm 0.13 \mu m$ after milling for a time period of 2 h. A higher percentage of nano-sized particles ($> 80\%$) was present for a milling period of 2.5 h with some particle agglomeration. Post this period, extensive agglomeration of powder particles and cold welding with milling media was observed. The final estimated particle size at milling period of 2.5 h was estimated within the range of $80 \pm 7.1 \text{ nm}$ to $500 \pm 43.5 \text{ nm}$.

A similar doping concentration of 2 wt% TiO_2 was utilized for Nb_3Sn with same milling parameters. Also, an earlier study on other A15 superconductor i.e., Nb_3Al was reported to enhance its functional behaviour when a synergic doping of Sn and B was used [25]. The individual utilization of Sn [26] and B [27] was observed to enhance the functional property. However, when used in a combined manner, the functional property gets enhanced further. Hence, this study also utilized a synergic

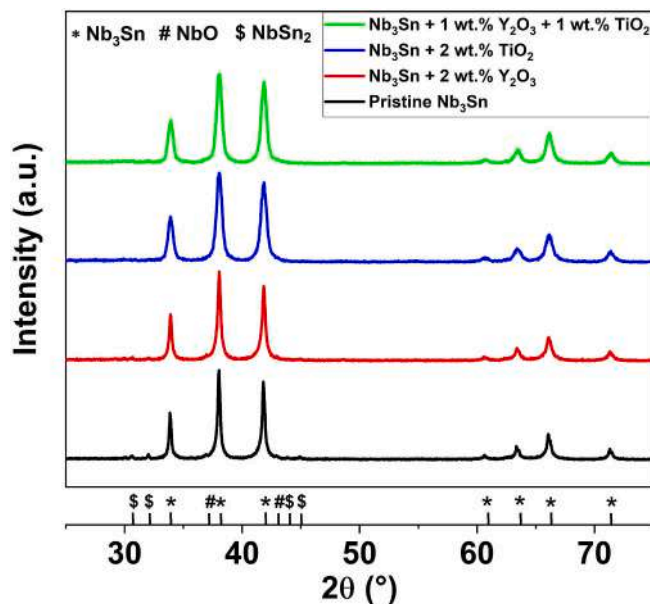


Fig. 5. X-ray diffractogram for undoped and doped samples, milled for 120 mins.

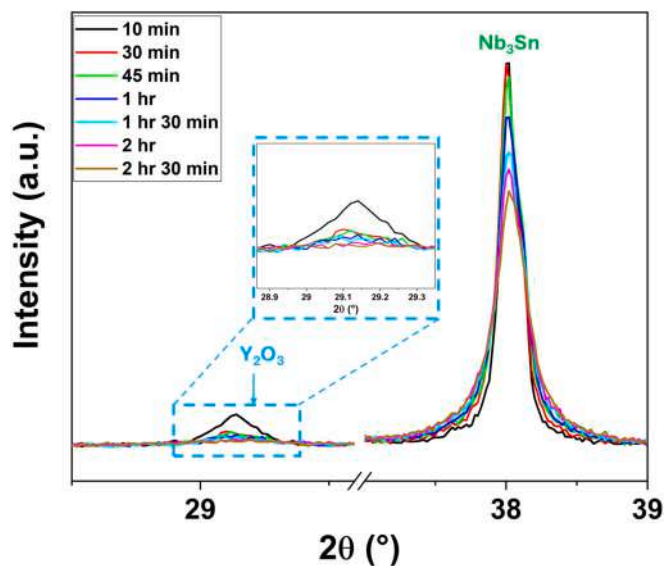


Fig. 6. X-ray diffractogram showing Y_2O_3 with progressing milling time for Nb_3Sn doped with 5 wt% Y_2O_3 .

doping of Y_2O_3 and TiO_2 to Nb_3Sn . The total dopant concentration was kept as 1 wt% each to avoid dopant excess to Nb_3Sn .

Since it was slightly difficult to identify the overall phases present in the milled powders using energy dispersive spectroscopy technique of SEM, the phase analysis was carried out using an XRD. An equal amount of powder was used to carry out the XRD measurements for undoped, Nb_3Sn doped with 2 wt% Y_2O_3 , 2 wt% TiO_2 and co-doped with 1 wt% Y_2O_3 and 1 wt% TiO_2 samples. The XRD analysis has been presented in the Fig. 5 for the considered doped and undoped samples. No distinct peaks for the dopants were visible in the diffracted patterns. This might be possible due to the lower concentration of the dopant used [28]. The peaks were, however, visible for the higher doping concentration i.e., 5 wt% Y_2O_3 in Nb_3Sn , as shown by Fig. 6. Fig. 6 shows a small peak around 2θ angle of 30° indicating the presence of Y_2O_3 which disappeared with the increase of milling time. The disappearance of Y_2O_3 peak could be due to the mixing of the signal with noise because of poor signal to noise

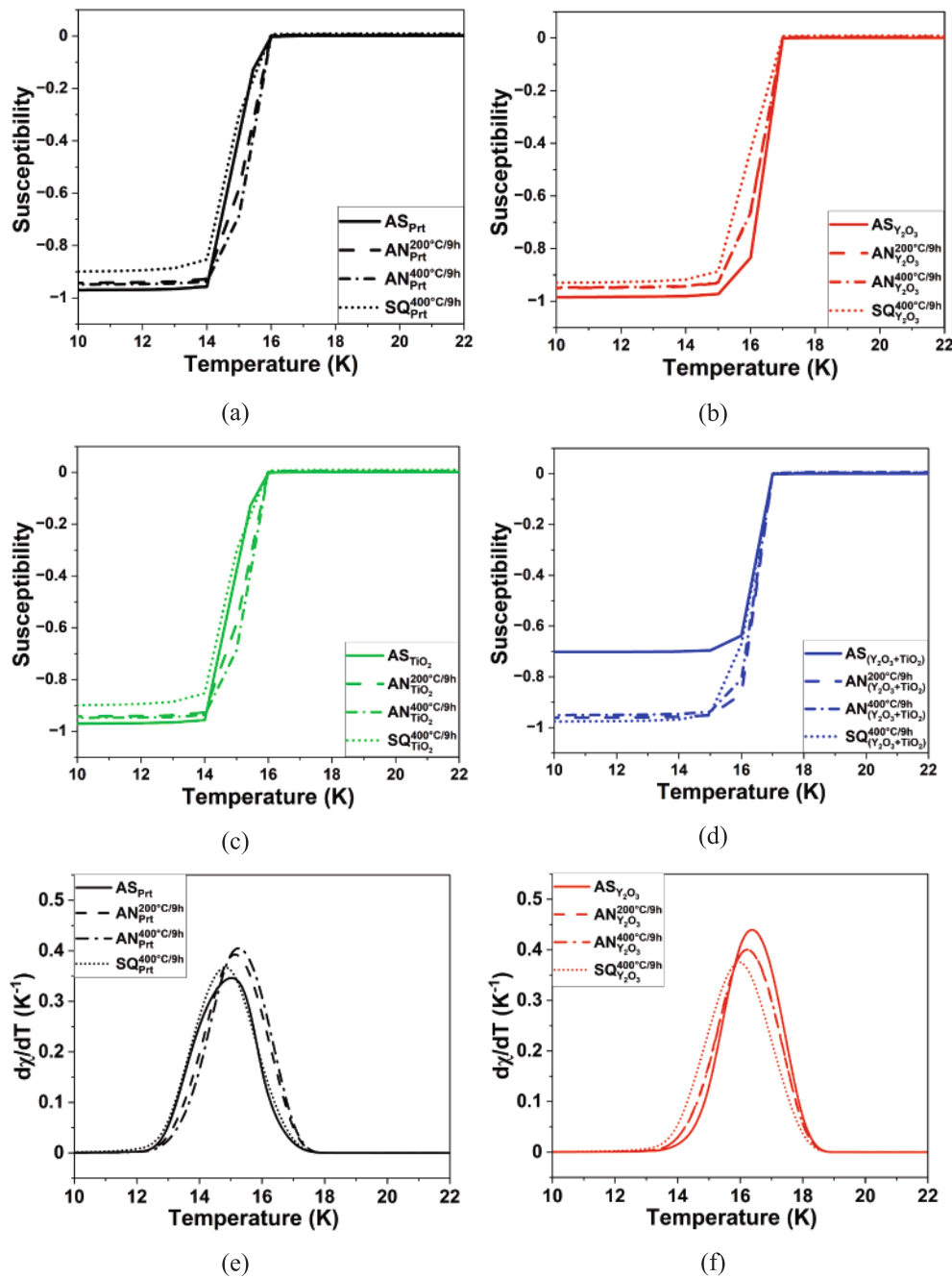


Fig. 7. (a-d) Susceptibility plot as a function of temperature measured at 5 mT applied field for the samples underwent different heat treatment conditions and (e-h) corresponding $\frac{d\chi}{dT}$ curves as a function of temperature for the samples.

ratio for very low intensity peaks. This observation of absence of dopant peak at low dopant concentration also matches with the results from one of our previous studies on doping of Y with Nb₃Sn [9]. The disappearance of Y₂O₃ peak could also be linked to the dissolution of Y₂O₃ in Nb₃Sn. The atomic radius of Y (1.80 Å) is larger than that of either Nb (1.43 Å) or Sn (1.45 Å); the increase in lattice parameter for the 5 wt% Y₂O₃ doped Nb₃Sn indicates dissolution after dissociation of Y₂O₃ in Nb₃Sn lattice. In 2 wt% Y₂O₃ doped Nb₃Sn, due to lattice contraction by relatively higher strain, the dissociation and dissolution of Y₂O₃ would be relatively less compared to 0.5 wt% and 5 wt% Y₂O₃ sample. The Y from Y₂O₃ dissolution may prefer one of the available sites i.e., either lattice site of Nb or Sn within the A15 structure. Due to a size mismatch between Y and Nb (~20.5 % higher for Y) and between Y and Sn (~19.4

% higher for Y), the resulting strain would induce a compressive stress. Due to this compressive stress, there would be a lattice expansion which results in an increase in lattice parameter values in Nb₃Sn doped with 5 wt% Y₂O₃. Further, the increase in lattice parameter for undoped and 0.5 wt% Y₂O₃ doped Nb₃Sn sample could be a result of occupation of interstitial site by either Nb or Sn atom as a result of SPD. In case of 2 wt % Y₂O₃ doped sample, there would be a trade-off between occupation of interstitial site by Nb/Sn and defect site by Y such that overall nature of strain becomes compressive. This compressive strain was the reason for lattice contraction. The agglomeration of Y₂O₃ nano-sized particles could be higher in case of 5 wt% Y₂O₃ doped Nb₃Sn sample than 0.5 wt% Y₂O₃ doped sample. This agglomeration results in less availability of free Y₂O₃ phase particles for dissociation. Hence, this also resulted in the

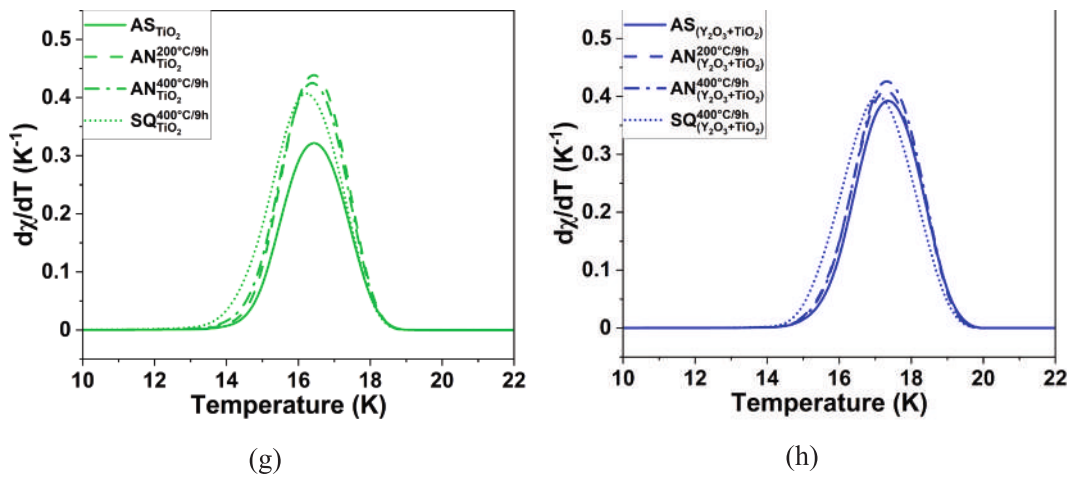


Fig. 7. (continued).

higher Y_2O_3 dissolution in the 0.5 wt% to Nb_3Sn than 5 wt% Y_2O_3 doped sample.

The example calculation for N for the AS_{Prt} sample is shown below by using the a , b and c data from Table 2:

$$N = \left[\frac{4 \times (3.03 \times 10^{-3}) \times (2.41 \times 10^{-3})}{4 \times (3.03 \times 10^{-3}) \times (2.41 \times 10^{-3}) + 3 \times (0.72 \times 10^{-3}) (3.03 \times 10^{-3} + 2.41 \times 10^{-3})} \right] = 0.71$$

3.2. Effect of heat treatment on superconducting performance of pristine and doped Nb_3Sn

The milled powder after the optimization of milling time and the dopant concentration was then sintered using spark plasma sintering technique at 1200 °C for 2 mins under a pressure of 50 MPa. This sintering condition was utilized based on the inferences carried out from another study on effect of sintering conditions on doped Nb_3Sn bulk formation [21]. Different sets of samples were diced from the sintered bulk and conditioned to various heat treatment conditions as detailed in Table 1. The low heat treatment temperatures were chosen based on the annealing temperature conditions used for Nb_3Sn wires during the drawing process [29]. This choice was also preferred to ensure that no significant grain growth of Nb_3Sn matrix phase would take place during the said heat treatment conditions. These different sets of samples were analysed for critical temperature, T_c of the Nb_3Sn phase.

Moment-temperature (m - T) curves were converted to susceptibility-temperature (χ - T) curves for the evaluation of critical temperature of the concerned phase (T_c) at an applied field ($B_{applied}$) of 50 Oe (5 mT) under zero field cooled (ZFC) condition. The magnetic susceptibility (χ) was calculated using the equations (3)–(5) given below [30].

$$\chi_{absolute} = \frac{moment \times 4\pi \times 10^{-7}}{Volume of sample \times B_{applied}} \quad (3)$$

$$\frac{1}{\chi} = \left(\frac{1}{\chi_{absolute}} - N \right) \quad (4)$$

$$N = \left[\frac{4ab}{4ab + 3c(a+b)} \right] \quad (5)$$

here moment is represented in Acm^2 . N is known as demagnetization factor and a , b and c are dimensions of cuboidal sample in mm with c || applied field ($B_{applied}$). $\chi_{absolute}$ is the absolute value of susceptibility without considering the demagnetization factor, as given by Eq. (3).

This value of N is then fed into Eq. (4) to calculate the magnetic susceptibility (χ).

The onset T_c was determined where the value of magnetic susceptibility reaches zero i.e., the sample behaves no longer as a superconductor. Fig. 7a-d show the susceptibility curves as a function of temperature for the samples undergone different heat treatment conditions for an applied magnetic field of 5 mT. The susceptibility values give a definitive result where a value of -1 indicates perfect diamagnetism due to Meissner effect. Also, the demagnetizing effect due to sample geometry is considered in the susceptibility values [31]. Fig. 7a shows that the transitions of T_c observed for the pristine samples. As observed, the pristine samples are sensitive to the heat treatment conditions, marked by the width in the transition region. Fig. 7b-d shows the transitions for individually doped with Y_2O_3 and TiO_2 and co-doped Nb_3Sn sample. The transition widths are relatively narrower, indicating the samples are relatively less sensitive to the heat treatment conditions compared with pristine samples. That was more clearly evident from the $\frac{d\chi}{dT}$ curves as a function of temperature, shown in Fig. 7e-h, where a wide transition was shown by the pristine samples compared to the doped ones by 1 K. This wide transition width was due to presence of non-superconducting NbO and $NbSn_2$ phases. Due to these inhomogeneities, there could be composition variations which resulted in partial Meissner effect and a broader transition width. While this transition width reduced to 1 K for the individual doing and co-doping. This indicates that the dopant helps in the homogenization of Nb_3Sn phase in the co-doped sample. Further, the annealed conditions i.e., 200 °C and 400 °C for 9 h was better for the pristine and doped samples. On comparing the effect of doping under the different heat treatment conditions, as shown in Fig. 8, the $AN_{(Y_2O_3+TiO_2)}^{400^\circ C/9h}$ sample performed better. This was an indication that the better homogeneity fraction in Nb_3Sn phase was achieved for the co-doped samples. The values of onset T_c were indicated in the Table 3. The corresponding onset T_c values were almost similar for the pristine samples, individually doped samples and co-doped samples. The difference lies at the transition regions, as

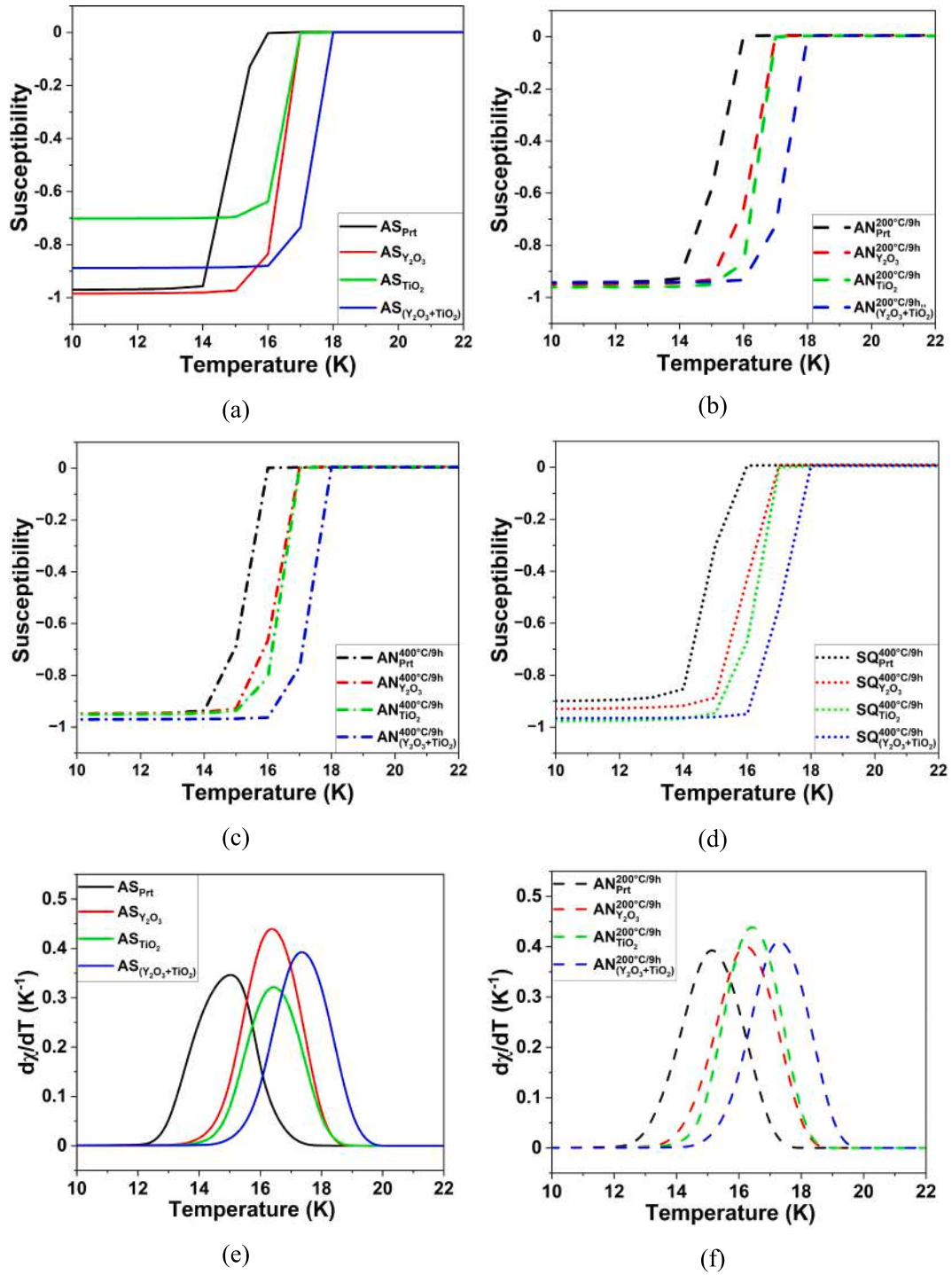


Fig. 8. (a-d) Susceptibility plot as a function of temperature measured at 5 mT applied field for the pristine and doped samples at different heat treatment conditions and (e-h) corresponding $\frac{d\chi}{dT}$ curves as a function of temperature for the samples.

mentioned earlier. Also, the relatively lower T_c values for SQ samples could be due to more inhomogeneity by NbO and NbSn₂ phase leading to the slight decrease in stoichiometric superconducting phase fraction. The T_c variation is linked to the Sn content in Nb₃Sn phase, defining the superconducting phase homogeneity, for which the lower Sn content deteriorates the T_c . For example, in the case of AN_{Y₂O₃+TiO₂}^{400°C/9h} sample, Sn content of 25.0 at.% Sn corresponds to a small ΔT value of 0.1 K, while for SQ_{Prt}^{400°C/9h} sample with Sn content range from 17.4 to 22.3 at.% Sn

composition for Nb₃Sn has a ΔT value of ~2 K. This also indicates that the AN_{Y₂O₃+TiO₂}^{400°C/9h} sample occupies the perfect stoichiometry for the A15 Nb₃Sn phase.

To analyse the effect of these heat treatment conditions on overall critical current density, J_{c0} , we calculated the J_{c0} using Bean's critical

model
$$\left(J_{c0} = \frac{2 \times \Delta M}{b \left(1 - \frac{b}{3a} \right)} \right)$$
 from the M-H loops measured at 10 K, as

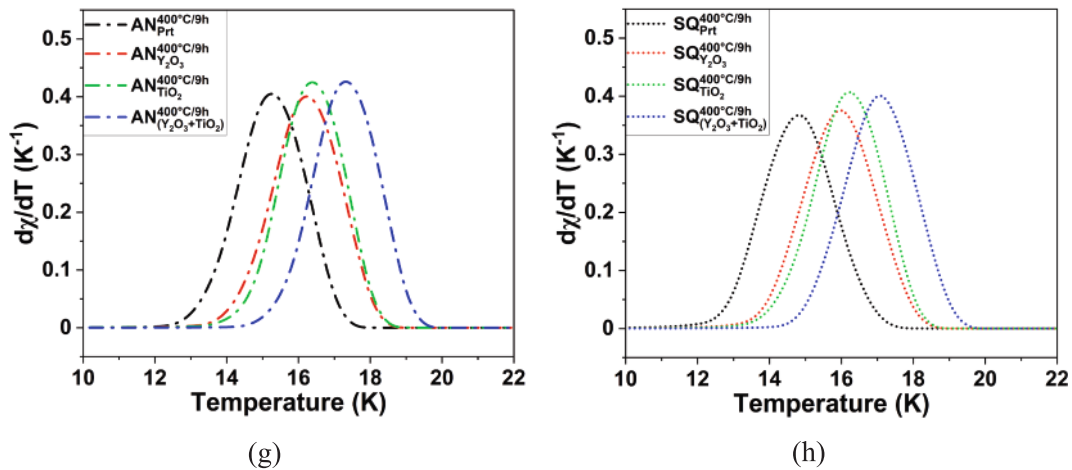


Fig. 8. (continued).

Table 3

Onset T_c values for the samples under different heat treatment conditions.

Sample	Onset T_c (K)	Sample	Onset T_c (K)
AS _{Prt}	16.0004	AN _{Prt} ^{400° C/9h}	16.00109
AS _{Y₂O₃}	17.0006	AN _{Y₂O₃} ^{400° C/9h}	17.0042
AS _{TiO₂}	17.0005	AN _{TiO₂} ^{400° C/9h}	17.0042
AS _(Y₂O₃+TiO₂)	18.0018	AN _(Y₂O₃+TiO₂) ^{400° C/9h}	18.0084
AN _{Prt} ^{200° C/9h}	16.00165	SQ _{Prt} ^{400° C/9h}	16.00189
AN _{Y₂O₃} ^{200° C/9h}	17.005	SQ _{Y₂O₃} ^{400° C/9h}	17.00332
AN _{TiO₂} ^{200° C/9h}	17.0042	SQ _{TiO₂} ^{400° C/9h}	17.00262
AN _(Y₂O₃+TiO₂) ^{200° C/9h}	18.0042	SQ _(Y₂O₃+TiO₂) ^{400° C/9h}	18.002

shown in Fig. 9a-d. The temperature of 10 K was chosen to obtain a closed M–H loop due to limitations in the applied magnetic field of up to ± 7 T. The ΔM represents the width of m-H loop normalized by sample volume ($\Delta M = \frac{\Delta m}{\text{Volume of sample}}$). Now, Fig. 9e-h presents the J_c curves for the samples undergone different heat treatment conditions as mentioned in Table 1. The calculated J_c values at 2 T, 10 K is presented in Table 4. The pristine, Y₂O₃ doped and TiO₂ doped Nb₃Sn samples were observed to have highest J_c of 2.28×10^5 A/cm², 3.95×10^5 A/cm² and 2.14×10^5 A/cm² at 2 T, 10 K respectively under the as-sintered condition when compared with the same sample undergone different heat treatment conditions mentioned in Table 1. While co-doped sample possessed highest J_c of 5.17×10^5 A/cm² at 2 T, 10 K under annealed condition of 400 °C for 9 h when compared within the same set of heat treatment conditions as shown in Fig. 9. The probable reason behind this observation could be that the as-sintered sample might contain small vortices (possibly nuclei sites in the nano-range) for flux pinning. Upon the heat treatment, nucleation of Y₂O₃ and TiO₂ occurred on these sites, causing the nucleation susceptible sites to disappear and/or leading to some extent of grain growth of Nb₃Sn phase. The grain growth of Nb₃Sn phase could result in relative lesser boundary fraction, reducing the pinning sites of Y₂O₃ and TiO₂ phase available at the grain boundaries. In the case of Y₂O₃ doped sample, the difference was significant between the as-sintered and heat-treated samples, $\sim 59\%$ higher for the as-sintered sample than that of annealed at 400 °C for 9 h. Presence of Y₂O₃ as additional pinning centers may explain this behaviour, the effect of which got trade-off with the amount of grain growth with the treatment conditions. This was also true for TiO₂ doped sample, but since the TiO₂ had more oxidising tendency, an evolution of non-superconducting phase i.e., NbO might have degraded the J_c . This mechanism had been

explained in the later part of the text. There was also an optimal trade-off between the grain growth of Nb₃Sn phase, additional flux pinning by Y₂O₃ and TiO₂ phase and the phase evolution for the co-doped sample which underwent heat treatment conditions. For the case of pristine samples, the AS_{Prt} sample had a J_c of 2.3×10^5 A/cm² at 2 T, 10 K, while the lowest J_c of 9.03×10^3 A/cm² at 2 T, 10 K was recorded for SQ_{Prt}^{400° C/9h} sample. The recorded J_c values for all the samples at 2 T, 10 K was presented in the Table 4. The SQ samples in all the cases were reported to have lowest J_c . As observed from the case of T_c , the possible explanation for the low J_c for SQ samples could be absence of good superconducting phase fraction. Further on comparing the J_c data for the dopants under different heat treatment conditions, as shown by Fig. 10a-d, it was found that the co-doped samples had highest J_c . Of all these presented data, this co-doped sample in annealed condition, AN_(Y₂O₃+TiO₂)^{400° C/9h} possessed a highest J_c value of 5.17×10^5 A/cm² at 2 T, 10 K. From the J_c data presented in Fig. 10, the samples annealed at 400 °C for 9 h had the higher J_c than the samples annealed at 200 °C for 9 h. The co-doped samples showed the higher J_c values under each mentioned heat treatment conditions. Further, the TiO₂ doped Nb₃Sn samples showed lower J_c at the lower fields under the said heat treatment conditions. The best J_c performer i.e., AN_(Y₂O₃+TiO₂)^{400° C/9h} samples were plotted with worst performer i.e., SQ_{Prt}^{400° C/9h} samples for the flux pinning forces. This was done to understand the flux pinning mechanisms and the generalized idea can thus be utilized for the other samples.

Fig. 11a shows the flux pinning force, F_p as a function of applied field, B , calculated using Lorentz criterion, $F_p = J_c \times B$. The maximum pinning force value of 1.04×10^5 AT/cm² was achieved for AN_(Y₂O₃+TiO₂)^{400° C/9h} sample at an applied field of 1.79 T. The lowest value of 1.82×10^4 AT/cm² was achieved for SQ_{Prt}^{400° C/9h} sample at an applied field of 1.77 T. The maximum point of flux pinning force for the considered samples falls below 2 T region. This observation indicated that the maximum flux pinning took place at the lower field. To identify the flux pinning mechanism, Dew Hughes model was utilized [32,33]. A normalized flux pinning force, f_p was plotted as a function of reduced field, b . The f_p was calculated using the relation, $f_p = \frac{F_p}{F_{pmax}}$, while the reduced field was calculated using $b = \frac{B}{B_{irr}}$. The B_{irr} , also known as irreversibility field was calculated by extrapolating J_c - B curve to the point where value of J_c approaches zero [20]. The value is presented in Table 5 for the AN_(Y₂O₃+TiO₂)^{400° C/9h} sample. The B_{irr} is observed to not changing any significantly for the TiO₂ doped sample while for the co-doped sample, it got increased.

A fitting relation, $f_p \propto b^p(1-b)^q$ was used for fitting the curves to identify the type of pinning centers as per the Dew Hughes model [32].

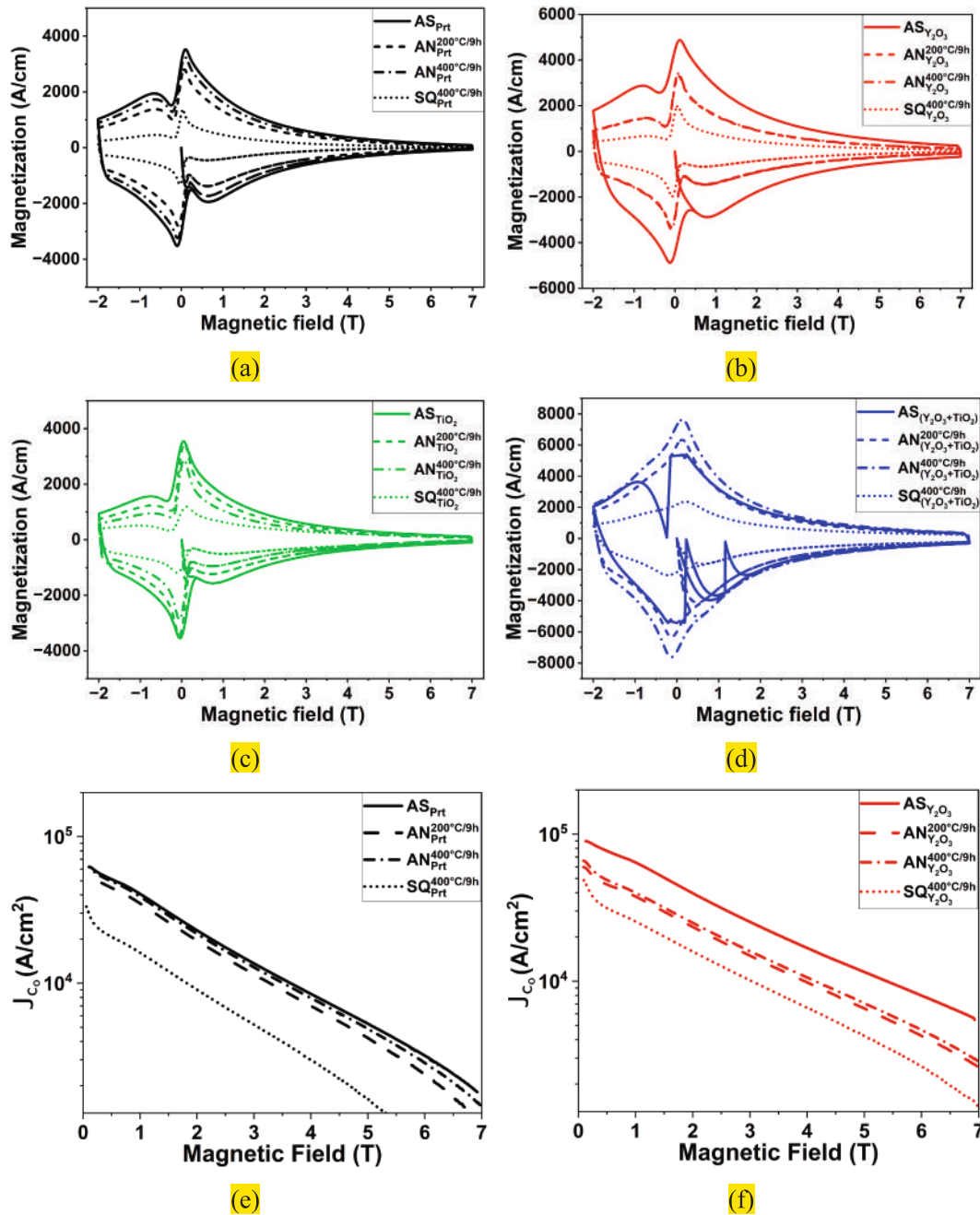


Fig. 9. (a-d) Magnetization – applied field loops and (e-h) overall critical current density, J_c , as a function of applied field for the samples subjected to different heat treatment conditions, measured at 10 K.

The surface normal (also known as grain boundary normal) pins follow the relation, $f_p \propto b^{\frac{1}{2}}(1-b)^2$ and point normal pins follow as $f_p \propto b(1-b)^2$. The peak position, b_{peak} for surface pins as per the model was 0.2. As can be observed from Fig. 11b, the $AN_{Prt}^{400^\circ C/9h}$ samples had major contribution from the pinning centers occurring at the grain boundaries. Further the b_{peak} value for $AN_{(Y_2O_3+TiO_2)}^{400^\circ C/9h}$ occur around 0.17, which confirms an additional flux pinning action via volume $\Delta\kappa$ pins. A shift in peak positions of f_p curves towards higher b values for the $SQ_{Prt}^{400^\circ C/9h}$ samples indicate the contribution towards flux pinning was fulfilled by the combination of surface and point pinning centers. A b_{peak} value of 0.33 corresponds to the contribution caused by the point pins centers. The peaks of f_p for the $SQ_{Prt}^{400^\circ C/9h}$ samples range between the b values of

0.24 to 0.26. This shift corresponds to the pinning action arising from the non-superconducting phase regions i.e., NbO within the Nb₃Sn matrix, whose dimensions may be smaller than the flux line spacing [34]. Now since in the A15 structured alloys like Nb₃Sn, effective pinning was provided by the surface pinning centers [35], this result highlights that the $AN_{(Y_2O_3+TiO_2)}^{400^\circ C/9h}$ samples were the better performer. Now, to understand how these surface pins effectively enhance the superconducting behaviour, further experimentation was carried out.

3.3. Effect of dopants and heat treatment conditions on microstructure of sintered Nb₃Sn

A detailed examination of the microstructure hence becomes essen-

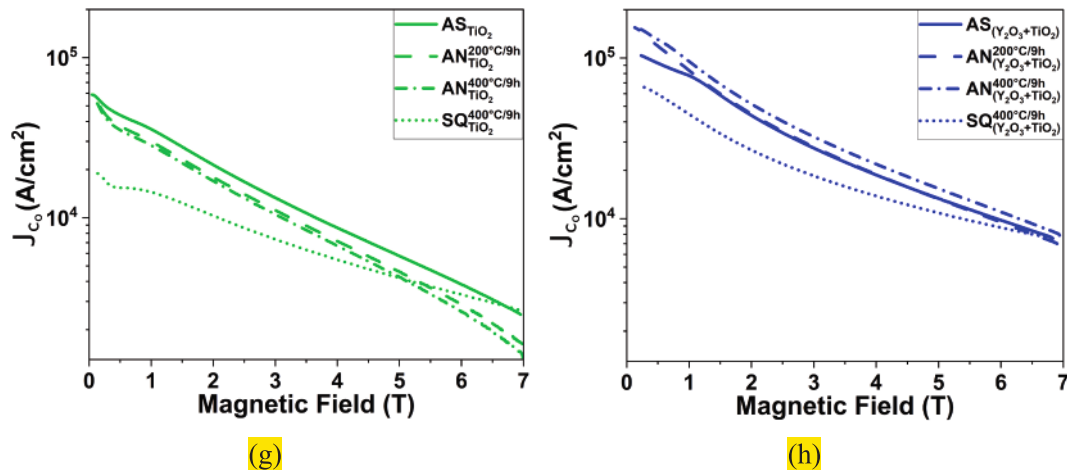


Fig. 9. (continued).

Table 4

J_{c0} Values for the samples under different heat treatment conditions, measured at 10 K.

Sample	J_{c0} at 2 T, 10 K (A/cm ²)	Sample	J_{c0} at 2 T, 10 K (A/cm ²)
AS _{Prt}	2.28×10^5	AN _{Prt} ^{400°C/9h}	2.17×10^5
AS _{Y2O3}	3.95×10^5	AN _{Y2O3} ^{400°C/9h}	2.49×10^5
AS _{TiO2}	2.14×10^5	AN _{TiO2} ^{400°C/9h}	1.69×10^5
AS _(Y2O3+TiO2)	4.39×10^5	AN _(Y2O3+TiO2) ^{400°C/9h}	5.17×10^5
AN _{Prt} ^{200°C/9h}	1.95×10^5	SQ _{Prt} ^{400°C/9h}	0.91×10^5
AN _{Y2O3} ^{200°C/9h}	2.34×10^5	SQ _{Y2O3} ^{400°C/9h}	1.59×10^5
AN _{Y2O3} ^{200°C/9h}	2.34×10^5	SQ _{Y2O3} ^{400°C/9h}	1.59×10^5
AN _{TiO2} ^{200°C/9h}	1.79×10^5	SQ _{TiO2} ^{400°C/9h}	1.03×10^5
AN _(Y2O3+TiO2) ^{200°C/9h}	4.49×10^5	SQ _(Y2O3+TiO2) ^{400°C/9h}	2.67×10^5

tial to further identify the estimated behaviour of flux pinning of various heat-treated samples. To examine the presence of different phases within the microstructure, compositional analysis using a scanning electron microscopy (SEM) tool was performed. The initial microstructural variation with doping effect for the AN^{400°C/9h} samples was presented in Fig. 12. This condition was chosen to correlate the J_{c0} with microstructure as the co-doped sample exhibited the best J_{c0} performance under this annealing treatment. From the Fig. 12, the dark grey region majorly comprises of NbSn₂ and NbO phases embedded within the Nb₃Sn matrix (bright features). The observation of these phases was in-line with the XRD data for the bulk samples [20]. For the doped samples, the Y₂O₃ and TiO₂ phases are segregated with the NbSn₂ and NbO phase mixture as highlighted by the arrows in Fig. 12. The elemental composition maps are presented in Fig. 13. It was somewhat clear from the maps that the greyish region was deficient in Sn and richer towards O. Since, from the results of SEM-EDX, it could not be clearly confirmed about the phases getting segregated and the grain characteristics of Nb₃Sn. This information was very crucial to understand as these might play a key role in defining the functional aspects of the bulk alloy.

To confirm these variations, we performed an electron backscatter diffraction (EBSD) analysis for all the samples. The conventional EBSD indexing using the Hough transform approach however was not useful due to overlapping of NbO and Nb₃Sn reflectors, as detailed later in the text and excessive noise in the captured data. So, a relatively newer technique, known as dictionary indexing (DI) or spherical indexing (SI), was used to overcome these limitations—these work by comparing the experimental patterns to a set of simulated patterns. DI uses a library of simulated patterns for a specific crystal structure [36,37]. This

technique, although robust, has high data usage and gives poor angular resolution in its preliminary form. To counter this limitation, simulated theoretical EBSD patterns were correlated with spherical harmonic functions and for individual EBSD patterns. This technique is much faster and more accurate and can resolve fine differences in patterns using intensity correlations [37].

In the current work, NbO and Nb₃Sn phases have very similar space groups. 225: Fm $\bar{3}$ m and 223: Pm $\bar{3}$ n, respectively. As shown in Table 6, four out of five reflectors were common, which posed a great difficulty in indexing them using the Hough transform. Given the very different structure factors (F_{hkl}) for these reflectors, there was possibility of this to reflect on the intensities of the Kikuchi bands. This difference in intensities was then used to index these phases using Spherical Indexing. The Master patterns for these phases were generated using OIM Analysis 9™ software. These essentially were simulated patterns fitted to a spherical harmonic function. The experimental patterns were then back-projected to a sphere and compared with the simulated master pattern. Due to the intensity correlation, this technique could unambiguously index these two phases. Hence, the biggest advantage of this spherical indexing technique is that even with similar space groups, the phase indexing can be done on the basis of non-similar reflectors like structure factor. A very weak Kikuchi band i.e., with a low signal to noise ratio can be accurately indexed using the simulated master pattern. Fig. 14 shows the phase maps for all the samples annealed at 400 °C for 9 h. Finer NbO grains represented by green colour can be observed to be embedded in the relatively coarser grained Nb₃Sn matrix represented by red colour. A significantly higher fraction of NbO phases was evident for samples doped with TiO₂, ~17.2% higher than the reference pristine Nb₃Sn sample. We suspected that these NbO phase particles can be a reason for the variation in J_{c0} . A higher NbO fraction (~57%) in AN_{TiO2}^{400°C/9h} sample deteriorated its J_{c0} as indicated in Fig. 10. This higher NbO fraction reduced the overall Nb₃Sn phase fraction. While in the case of AN_{Y2O3}^{400°C/9h} sample, absence of strong oxidising agent i.e., TiO₂, a higher Nb₃Sn phase fraction (~58%) was formed. Combining this with additional Y₂O₃ phase as pinning center resulted in a higher J_{c0} . This J_{c0} performance was also dependent on boundary fraction [2–5,7,38] and type [5,7,39] which plays an important role in providing sites for flux pinning centers. β -(Nb, Zr) and β -Nb(Ti) secondary phase particles in case of Zr and Ti alloyed Nb₃Sn respectively serving as flux pins were located at the boundaries for J_{c0} enhancement [2,5,7]. Based on the misorientation angles between adjacent grains, the grain boundaries are classified as the low angle grain boundary (LAGB) and high angle grain boundary (HAGB) fraction.

Fig. 15 shows the LAGB and HAGB fraction in the band contrast or image quality maps. The LAGBs were calculated for misorientations

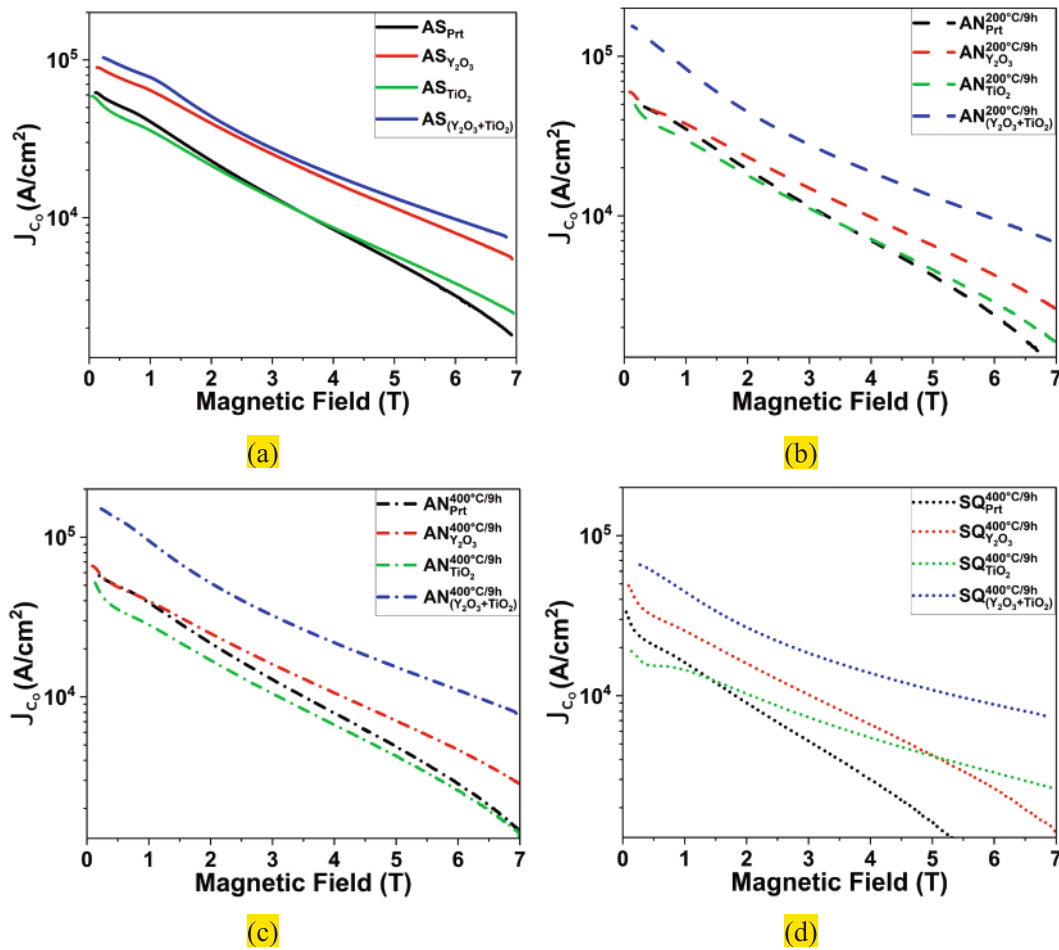


Fig. 10. (a-d) Overall critical current density, J_{c0} as a function of applied field for the pristine and doped samples at different heat treatment conditions, measured at 10 K.

ranging between 5° – 15° and HAGBs were calculated for the misorientations greater than 15° . From the Fig. 15, it was clear that the HAGBs were much higher in fraction than LAGBs. As reported by Togano and Tachikawa, HAGBs generally offer stronger flux pinning force for the Nb_3Sn superconducting phase and hence a high J_{c0} [40]. In our case, the fraction of HAGBs observed to lie within the range of 0.92 to 0.95. The higher fraction of HAGBs were found for the undoped Nb_3Sn i.e., 0.95 though this sample showed poorest performance at higher fields. So, HAGBs were not the pinning sites in our case. Nakamura et. al showed that the flux pinning for Bi-2223 occurs across LAGBs while HAGBs showed no such pinning effect [41]. In the case of undoped Nb_3Sn sample, we suspect the pinning action was therefore, only driven by LAGBs. Also, as per the observation for the doped samples, the J_{c0} performance was being driven by more than one mechanism in various samples. The dopants themselves might have played a critical role in enhancing J_{c0} , similar to the case of elemental doping. From the results of Fig. 14 and Fig. 15, however, it was not fully evident about the role of the dopants. We further extended our analysis to transmission electron microscopy (TEM). We had selected the reference $\text{AN}_{\text{Prt}}^{400^\circ\text{C}/9\text{h}}$ and $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample with highest J_{c0} for the analysis to identify the microstructural metrics aiding J_{c0} . The idea behind the choice is to consider the extremities, as this will also give the idea about the property variation of Y_2O_3 and TiO_2 doped samples. In the case of $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample, it showed highest J_{c0} even when the NbO fraction was $\sim 56\%$. Considering the poorer J_{c0} performance of $\text{AN}_{\text{TiO}_2}^{400^\circ\text{C}/9\text{h}}$ with higher NbO phase fraction, the $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample was expected to

behave the same way. This deviation in the result indicates some additional mechanisms were also playing the role in enhancing the J_{c0} performance of $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample. Hence, the understanding of J_{c0} variation requires additional analysis. Since the dopants were difficult to locate using the SEM-EBSD technique, the phase analysis was performed using orientation imaging microscopy (OIM) in TEM, as mentioned in the later part of the text.

Fig. 16 shows the bright field micrograph with corresponding selected area diffraction pattern (SADP) for the pristine and co-doped Nb_3Sn samples. As inferred from the SEM-EDX data and EBSD phase maps, a large portion was covered by Nb_3Sn matrix phase and NbO second phase. Different locations were analysed to determine the different phases. Since the phase proportions were uniformly distributed in the matrix, multiple phases were visible to merge at any possible location. Hence, a relatively smaller aperture (aperture size: 200 nm) was used to accurately identify the corresponding diffraction spots. Due to minute presence of dopants segregation, it is very difficult to trace down their locations of segregation across the whole sample. Therefore, a scanning transmission electron microscopy (STEM)-EDX analysis was further carried out as shown in Fig. 17. The data presented for pristine Nb_3Sn sample and co-doped Nb_3Sn sample matches with the data from SEM-EDX presented in Fig. 13. Segregation of different phases was evident from the elemental maps. Fig. 17a shows the composition map for $\text{AN}_{\text{Prt}}^{400^\circ\text{C}/9\text{h}}$ sample. The composition maps for $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample shown in Fig. 17b, shows the elemental segregation of Ti and Y across the same location, indicating an overlapping spectrum of Ti and Y soft X-rays. Also, due to an inaccuracy in identification of different elements

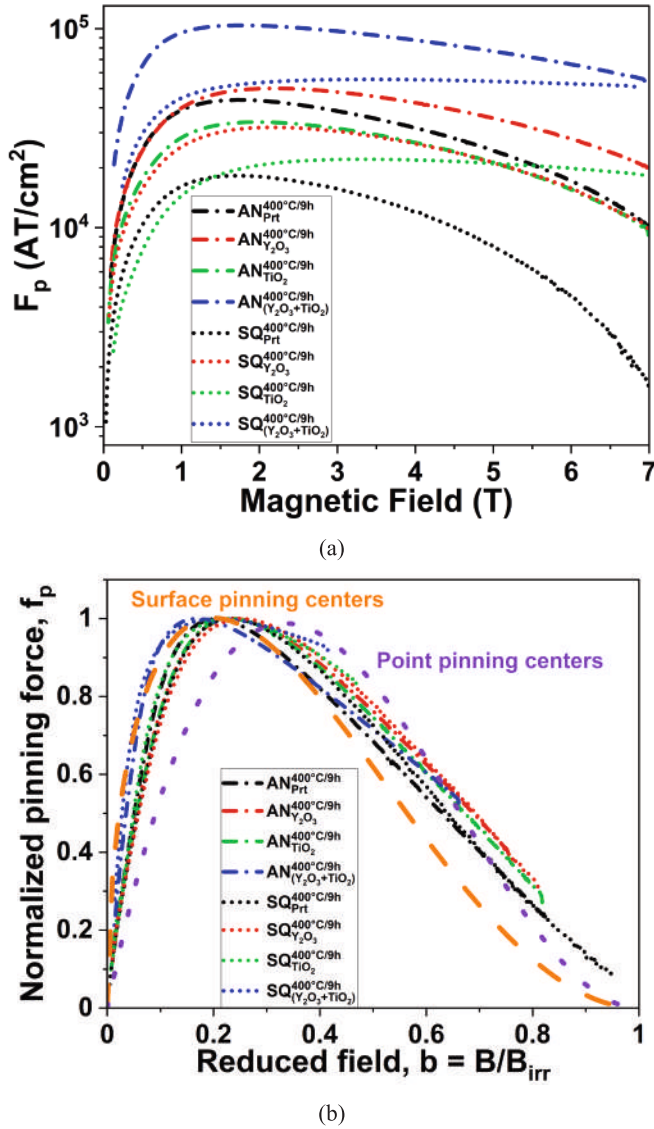


Fig. 11. (a) Flux pinning force, F_p as a function of applied field for the $AN^{400^\circ C/9h}$ and $SQ^{400^\circ C/9h}$ samples and (b) normalized flux pinning force, f_p as a function of reduced field, b .

Table 5
Extrapolated B_{irr} for the $AN^{400^\circ C/9h}$ sample conditions.

Sample	B_{irr} (T)
$AN^{400^\circ C/9h}_{Pt}$	8.47
$AN^{400^\circ C/9h}_{Y_2O_3}$	9.25
$AN^{400^\circ C/9h}_{TiO_2}$	8.54
$AN^{400^\circ C/9h}_{(Y_2O_3+TiO_2)}$	10.50

the data based on STEM-EDX is not very reliable in understanding the different phases which might get formed. Hence, a TEM-based OIM study was carried out in STEM mode, also known as automated crystal orientation mapping (ACOM). The measurement was performed using ASTAR, Nanomegas. The combination of precision electron diffraction (PED) with ASTAR helps to resolve the features down to 1 nm in most cases [42].

Fig. 18a-b presents the STEM micrographs for $AN^{400^\circ C/9h}_{Pt}$ and

$AN^{400^\circ C/9h}_{(Y_2O_3+TiO_2)}$ samples respectively. The dark region corresponds to the Nb_3Sn phase. Further, the Fig. 18c-d shows the phase map evaluated using STEM-ACOM for $AN^{400^\circ C/9h}_{Pt}$ and $AN^{400^\circ C/9h}_{(Y_2O_3+TiO_2)}$ samples across the region shown in Fig. 18a-b. The segregation of different phases along with the dopants were clear from these phase maps. An overview about the phase formation kinetics for the different phase can be understood from these phase maps. The formation of the NbO and Nb_3Sn phases had been shown using the schematic in Fig. 19.

3.4. Mechanism of phase evolution in best and worst J_{c0} performers and establishment of microstructure-property link

Fig. 19 presents the proposed mechanism of phase evolution during the sintering phase of the milled powder and as per the observations from Fig. 18c-d. In Fig. 19a, the active oxygen source, which may have been available from the milling process and from the dopants, combine with the available Nb to form the NbO phase. As mentioned earlier, the residual Sn particles combined with Nb to form $NbSn_2$ phase within the Nb_3Sn matrix. Following the sintering process and further annealing treatments, helped the growth of NbO and $NbSn_2$ phase within the Nb_3Sn matrix and the resultant phase map is evident in Fig. 18c. On the other hand, due to the co-doping of Y_2O_3 and TiO_2 in the Nb_3Sn phase, the Y_2O_3 and TiO_2 phase particles have segregated at the grain boundaries of Nb_3Sn grains, as shown in Fig. 19b. These segregations appear to form a blanket across the Nb_3Sn phase and hence limit the diffusion of Nb further to react with incoming oxygen source to form the NbO phase. So, an imposed hinderance results in relatively lower NbO phase fraction within the Nb_3Sn matrix in the co-doped sample as shown in Fig. 18d. This quantitative coverage of Y_2O_3 and TiO_2 phases across the boundaries is shown by the calculations below for the co-doped sample.

Total grain boundary length of all the phases (Fig. 18d) = 463 μ .

Boundary length for Y_2O_3 phase = 17.88 μ .

Boundary length for TiO_2 phase = 40.32 μ .

Phase grain boundary fraction = $\frac{\sum \text{boundary length of the given phase}}{\text{Total boundary length of all phases}}$

Phase grain boundary fraction for Y_2O_3 = $\frac{17.88}{463}$ = 0.04.

Phase grain boundary fraction for TiO_2 = $\frac{40.32}{463}$ = 0.09.

So, the Y_2O_3 phase covers 4 % and TiO_2 phase covers 9 % of the total grain boundaries. In total this 13 % coverage by the dopants were able to effectively reduce the percentage of NbO phase formation. The free energy of formation ($\Delta_f G^\circ$) for Y_2O_3 , TiO_2 and NbO phases are -1816.61 kJ/mol, -959.91 kJ/mol and -387.85 kJ/mol respectively [43–45]. This indicates that the Y_2O_3 and TiO_2 phases being stable oxides compared to NbO , cannot act as an active O source for the formation of NbO in the Nb_3Sn doped/co-doped samples. Despite having the least free energy of formation of NbO compared to Y_2O_3 and TiO_2 , these phases, as observed from Fig. 19b, can hinder the NbO phase growth by forming a blanket across the Nb_3Sn phase. The phase segregations within the microstructure hence had an impact on the critical current density, J_{c0} . Also, Y_2O_3 being a very stable oxide compared to TiO_2 , a higher fraction of phase segregation of TiO_2 was visible relative to Y_2O_3 within the Nb_3Sn matrix.

Now referring to Fig. 10 to explain the observed J_{c0} variation for the $AN^{400^\circ C/9h}_{(Y_2O_3+TiO_2)}$ sample, a flux pinning model was used to determine the pinning mechanism. The model presented by Dew Hughes [32] and Higuchi et al. [46] confirms that an additional volume pinning by Δk pins was responsible for relatively highest J_{c0} for the $AN^{400^\circ C/9h}_{(Y_2O_3+TiO_2)}$ sample. Since the presence of Y_2O_3 were additionally pinning down the flux for $AN^{400^\circ C/9h}_{Y_2O_3}$ sample, an additional contribution could be followed by the TiO_2 phase particles for $AN^{400^\circ C/9h}_{(Y_2O_3+TiO_2)}$ sample. From the phase segregation mechanism, we knew that the dopants arranged themselves across the boundaries, a higher visible TiO_2 phase particles across the boundaries can help in pinning the flux. Now in this case the flux pinning

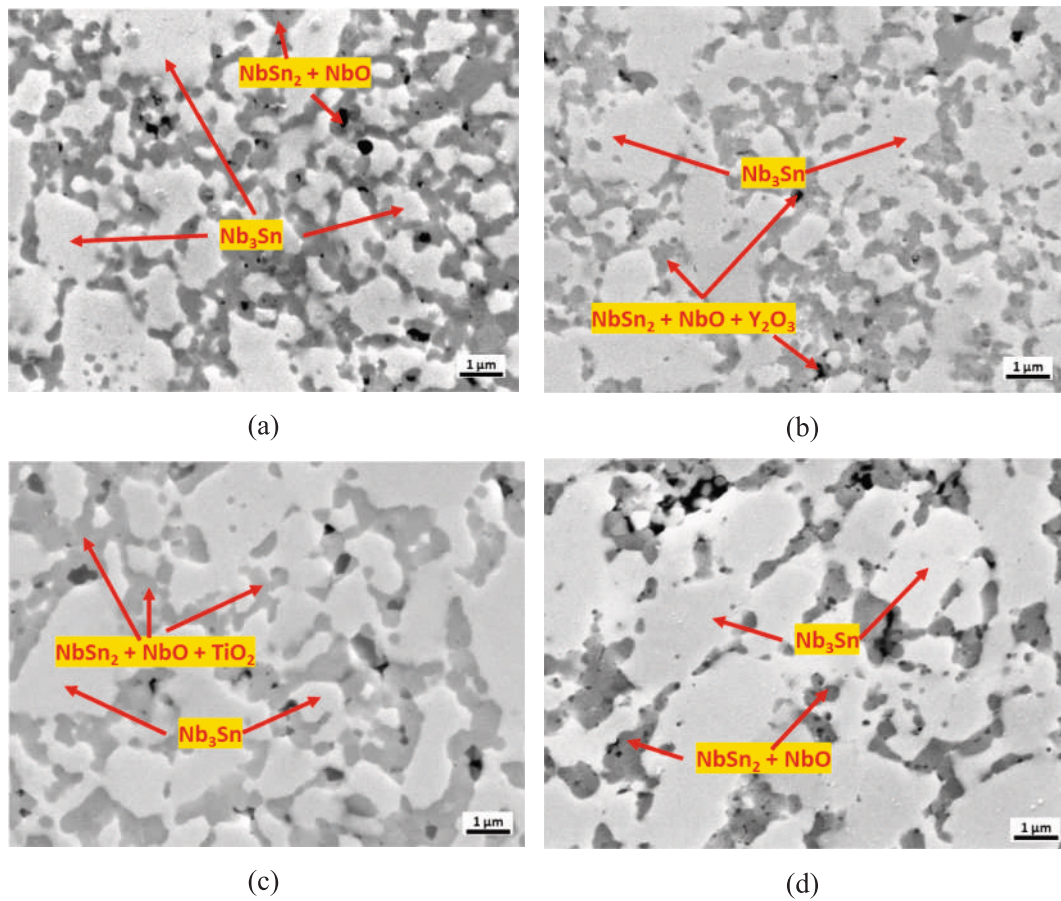


Fig. 12. Secondary electron micrograph for (a) Undoped, doped with (b) 2 wt% Y_2O_3 , (c) 2 wt% TiO_2 and (d) 1 wt% Y_2O_3 + 1 wt% TiO_2 samples annealed at 400 °C for 9 hrs.

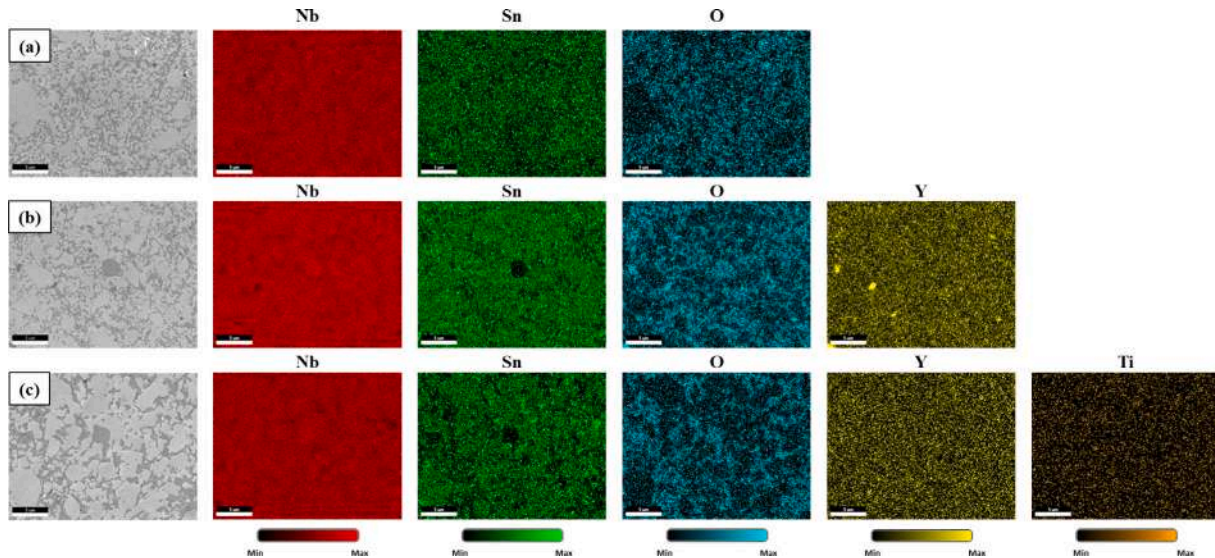


Fig. 13. SEM – EDX composition maps for (a) Undoped, doped with (b) 2 wt% Y_2O_3 and (c) 1 wt% Y_2O_3 + 1 wt% TiO_2 for samples annealed at 400 °C for 9 hrs.

action was stronger relative to $\text{AN}_{\text{Y}_2\text{O}_3}^{400^\circ\text{C}/9\text{h}}$ and $\text{AN}_{\text{TiO}_2}^{400^\circ\text{C}/9\text{h}}$ alone. This may indicate that due to the proximity effect of the superconducting phase, the TiO_2 phase particles may also behave as volume $\Delta\kappa$ pins. This proximity effect could only be possible when the non-superconducting phase was present in excess, which was possible in the case of $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample, where largely TiO_2 was visible across grain

boundaries of Nb_3Sn . Therefore, a possible reason for why the $\text{AN}_{(\text{Y}_2\text{O}_3+\text{TiO}_2)}^{400^\circ\text{C}/9\text{h}}$ sample possess a higher J_c , among the considered sample was clear using the structure – property correlative approach.

Lastly, the individually doped and co-doped Nb_3Sn , the change in the J_c values for these samples can also be related to the compositional variation, which affected T_c . The co-doped sample was expected to have

Table 6

Standard reflectors (hkl) used for Hough indexing with corresponding structure factors (F_{hkl}) for NbO and Nb₃Sn.

NbO		Nb ₃ Sn	
Reflector (hkl)	F_{hkl}	Reflector (hkl)	F_{hkl}
002	23.02	002	22.95
012	19.88	022	16.18
112	19.45	111	14.75
044	14.51	024	8.921
123	12.72	224	7.7794

wide homogeneity range than the individual doped and pristine one and hence achieved a higher J_{c0} . Also, another important aspect i.e., differences in J_{c0} values between the annealed co-doped and sintered co-doped sample is addressed here. Sintered co-doped sample might have accumulated some residual stress due to the rapid thermal cycle during

sintering stage. This residual stress may generate the stress gradient leading to internal stresses between the crystallites [47]. This internal stress creates weak link at the grain boundaries, affecting J_{c0} . The annealing process could have relieved those stresses and hence the measured J_{c0} was higher than those of the sintered samples.

4. Analytical model

To the best of our knowledge, no unified mathematical framework correlating the J_{c0} and the relationship has been derived for the microstructure-dependent overall critical current density, J_{c0} considering any of the microstructural metric parameters has yet been developed. Therefore, we tried establishing an analytical model to predict J_{c0} and checked with the resultant experimentally determined behaviour of J_{c0} of this study. The model takes into consideration the fraction of effective and non-effective pins to predict the behaviour of J_{c0} . The

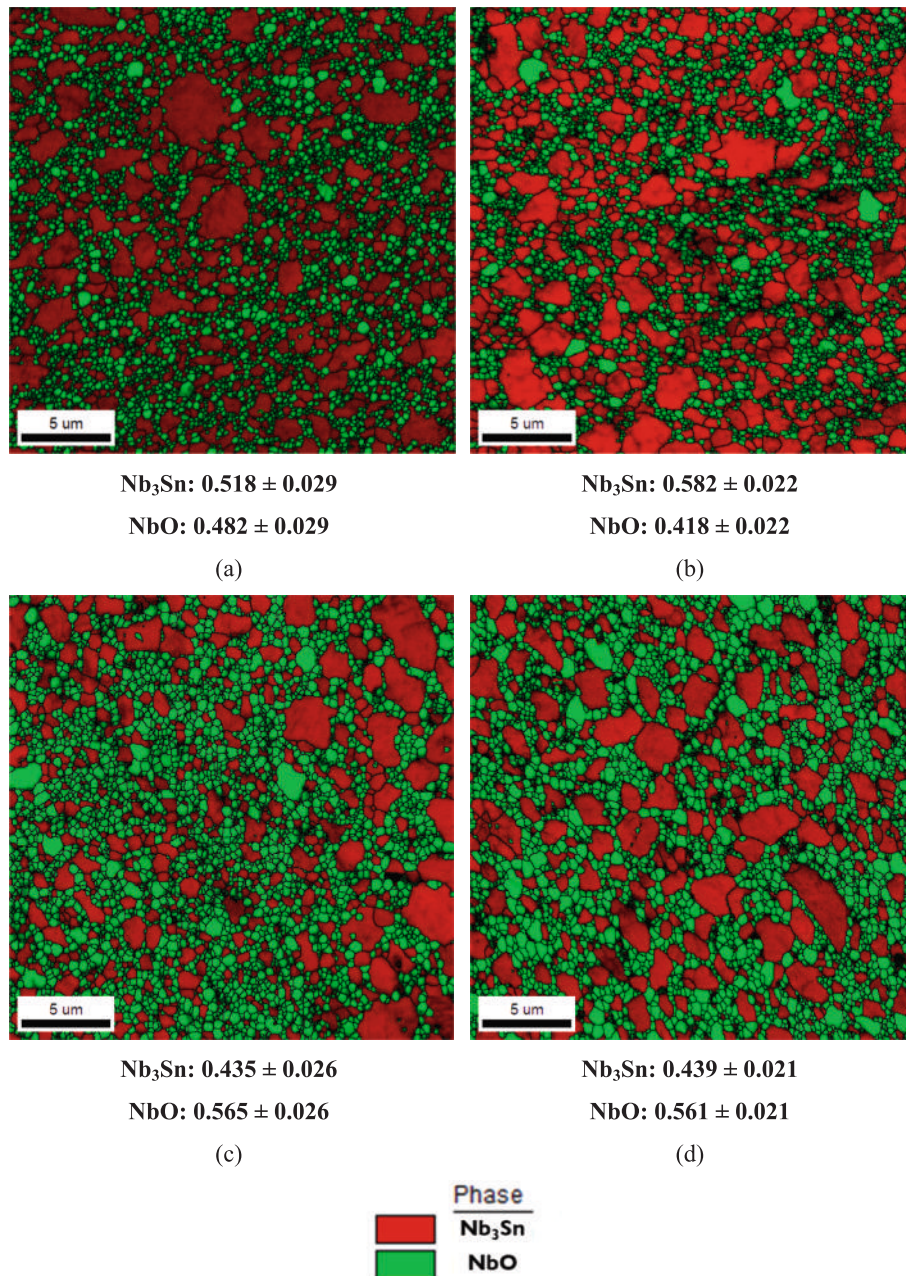


Fig. 14. EBSD phase maps for (a) Undoped, doped with (b) 2 wt% Y₂O₃, (c) 2 wt% TiO₂ and (d) 1 wt% Y₂O₃ + 1 wt% TiO₂ for samples annealed at 400 °C for 9 hrs.

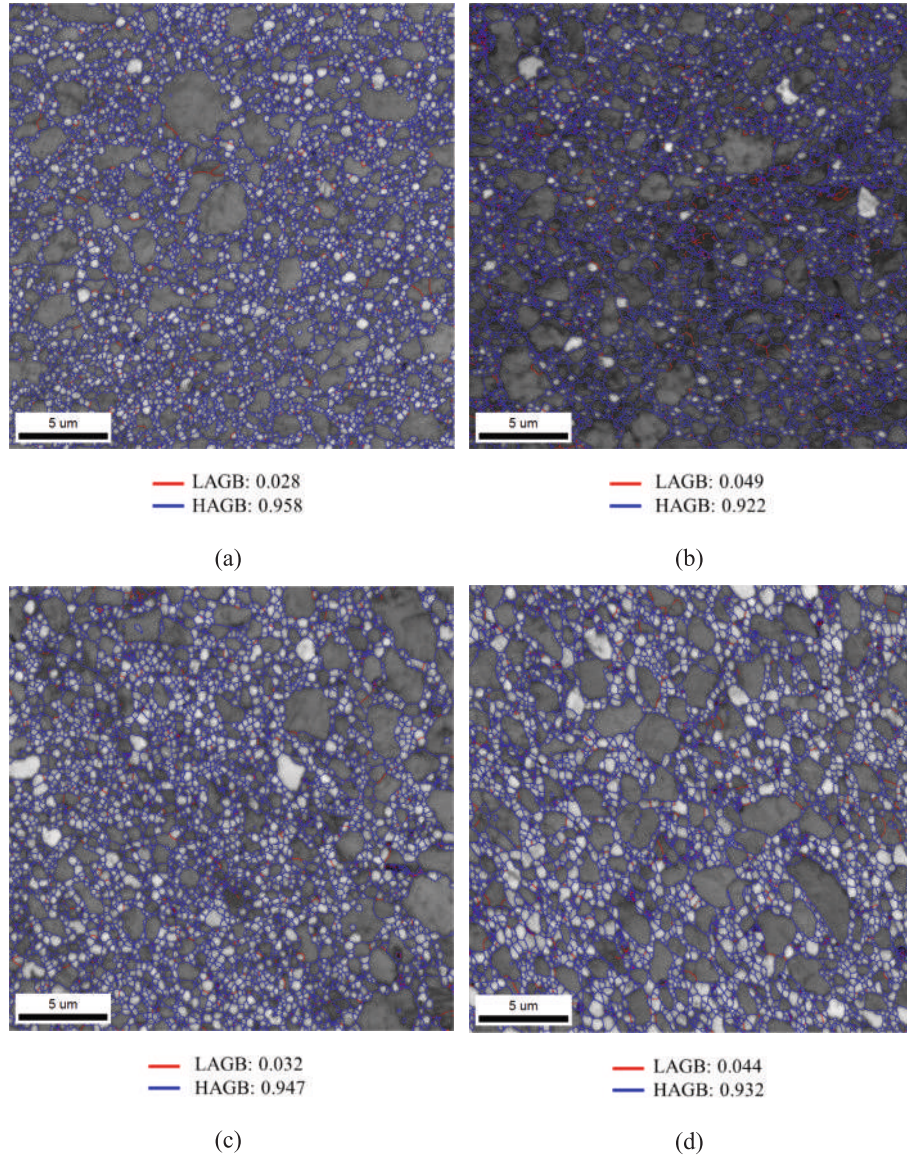


Fig. 15. Image quality maps with low angle grain boundary (LAGB) and high angle grain boundary (HAGB) for (a) Undoped, doped with (b) 2 wt% Y₂O₃, (c) 2 wt% TiO₂ and (d) 1 wt% Y₂O₃ + 1 wt% TiO₂ for samples annealed at 400 °C for 9 hrs along with corresponding boundary fractions.

model had been developed considering various relationships as derived by Brandt [48] and Campbell [49].

The empirical relation between the flux pinning force density and flux quantum, ϕ_o with a value $2.068 \times 10^{-15} \text{ T} \cdot \text{m}^2$ and overall critical current density, J_{c0} ($\text{A} \cdot \text{m}^{-2}$) can be derived from the similar concept of force experienced by a curved dislocation present in a deformed material.

$$f_L = J_{c0} \cdot \phi_o \quad (6)$$

where f_L is pinning force per unit length of Nb₃Sn phase. The flux remains pinned as long as $f_L \leq f_{p,eff}$ with $f_{p,eff}$ is the effective pinning force per unit length of superconductor. In the limiting condition,

$$f_L = \Omega \cdot f_{p,eff}, \Omega < 1 \quad (7)$$

$$K \cdot f_{p,eff} = J_{c0} \cdot \phi_o \quad (8)$$

Ω is the proportionality constant and K is a constant for inequality between f_L and $f_{p,eff}$.

Now, for the magnetic field penetration from the surface to an

interaction depth d , the flux quantum is denoted by $\phi_o = B \cdot d$. Additionally, the surface provides a barrier to the flux motion which is defined by Bean's model as $\delta = (\mu_o B J_{c0} d)^{\frac{1}{2}}$.

$$\phi_o = B \cdot d = \frac{\delta^2}{\mu_o J_{c0}} \quad (9)$$

here B is applied magnetic field (T), d is the interaction length (m) between the flux lines and the pin and δ is the surface barrier to the flux and μ_o is the vacuum permeability, $\mu_o = 10^{-7} \text{ Tm/A}$.

$$J_{c0} \phi_o = \frac{\delta^2}{\mu_o} = \frac{2\epsilon_L}{L} \quad (10)$$

Also, $F_L = J_{c0} \cdot \phi_o = \frac{\text{energy}}{\text{length}} = \frac{\text{vortex line tension}(\epsilon_L)}{R}$, where vortex line tension is analogous to dislocation line tension and R is the radius of the loop or the vortex formed. At the moment of loop formation, the bowed segment is approximated as semicircle whose chord length is L . Therefore, $R = \frac{L}{2}$.

From Eq. (10),

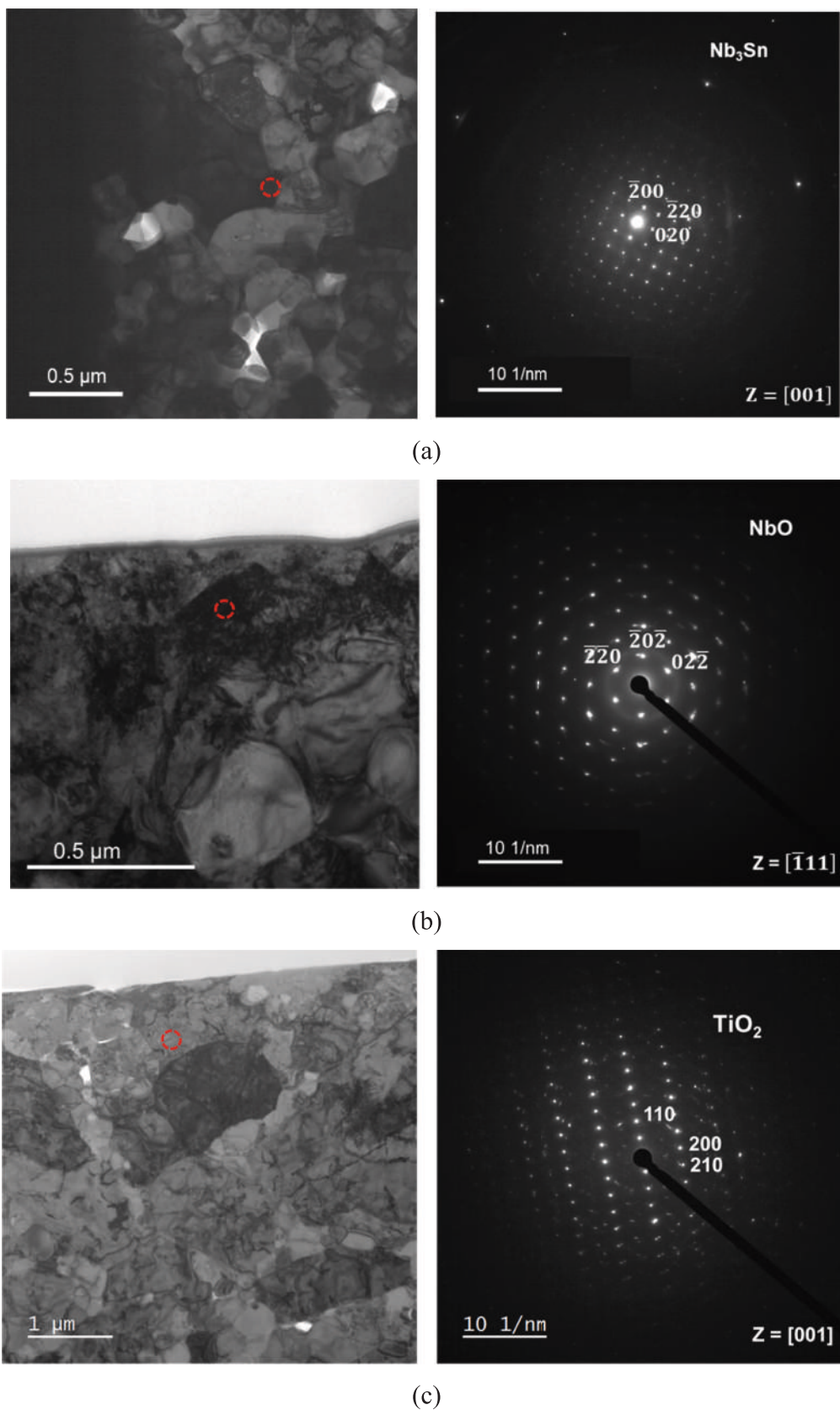
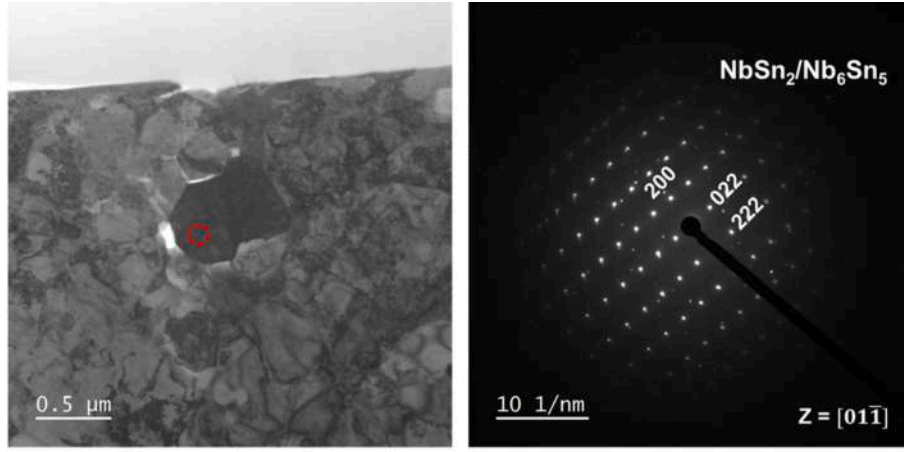


Fig. 16. Transmission electron micrograph along with selected area diffraction pattern for (a-b) Pristine Nb₃Sn and (c-d) Nb₃Sn doped with Y₂O₃ and TiO₂ annealed at 400 °C showing different phases formed. The red rings show the location of diffraction spot.



(d)

Fig. 16. (continued).

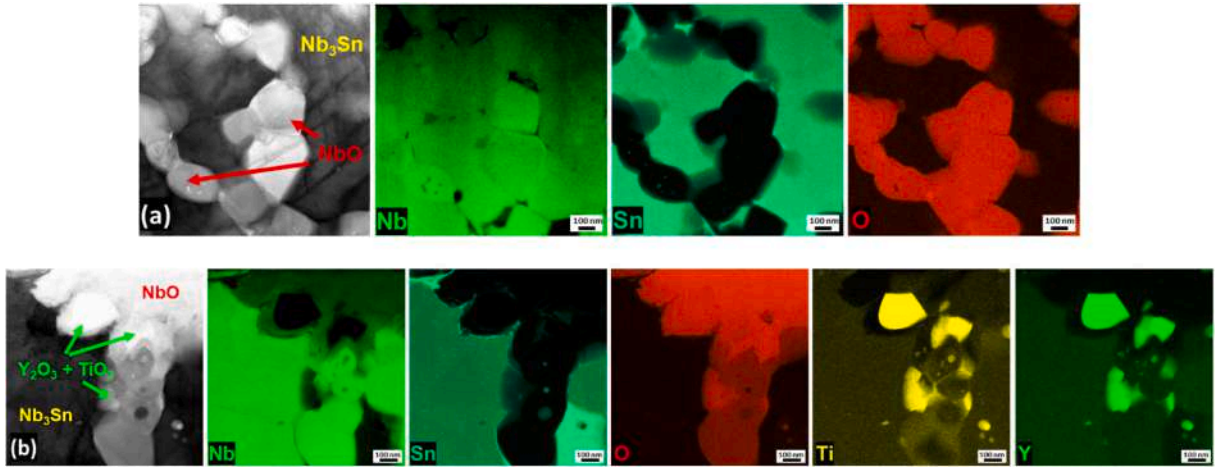


Fig. 17. Scanning transmission electron micrograph with corresponding elemental maps for (a) Pristine Nb₃Sn and (b) Nb₃Sn doped with Y₂O₃ and TiO₂ samples annealed at 400 °C for 9 hrs.

$$J_c = \frac{2\varepsilon_L}{L\phi_o} \quad (11)$$

$$\varepsilon_L = \frac{1}{2\mu_o} \int_{r_{core}}^{r_{max}} B^2(r) \bullet 2\pi r dr \quad (12)$$

$B(r)$ is the microscopic field for a single flux line in cylindrical shape of radius r with core radius same as coherence length, ξ and maximum radius equivalent to penetration depth, λ . Here the $B(r)$ function is approximated by J.R. Clem [50] and is given by,

$$B(r) = \frac{\phi_o}{2\pi\lambda^2} K_o\left(\frac{r}{\lambda}\right) \quad (13)$$

Substituting the value of Eq. (13) in Eq. (12), we get

$$\varepsilon_L = \frac{1}{2\mu_o} \int_{\xi}^{\lambda} \frac{\phi_o^2}{4\pi^2\lambda^4} \left[K_o^2\left(\frac{r}{\lambda}\right) \right] \bullet 2\pi r dr \quad (14)$$

$$\varepsilon_L = \frac{\phi_o^2}{4\pi\mu_o\lambda^4} \int_{\xi}^{\lambda} r \bullet K_o^2\left(\frac{r}{\lambda}\right) dr \quad (15)$$

where $K_o(\alpha)$ is the modified Bessel function for an argument α .

Substituting in Eq. (15), $x = \frac{r}{\lambda}$. Therefore, $x_{min} = \frac{r_{min}}{\lambda} = \frac{\xi}{\lambda}$ and $x_{max} = \frac{r_{max}}{\lambda} = 1$ as $r_{max} = \lambda$.

Also, $r = x\lambda \Rightarrow dr = \lambda dx$

$$\varepsilon_L = \frac{\phi_o^2}{4\pi\mu_o\lambda^4} \bullet \lambda^2 \int_{x_{min}}^{x_{max}} x \bullet K_o^2(x) dx \quad (16)$$

$$\varepsilon_L = \frac{\phi_o^2}{4\pi\mu_o\lambda^2} \int_{x_{min}}^{x_{max}} x \bullet K_o^2(x) dx \quad (17)$$

$$\varepsilon_L = \frac{\phi_o^2}{4\pi\mu_o\lambda^2} \left(\int_{x_{min}}^{x_k} x \bullet K_o^2(x) dx + \int_{x_k}^{x_{max}} x \bullet K_o^2(x) dx \right) \quad (18)$$

For $x < x_k$ (x_k is the point in between the coherence length (core), ξ and penetration depth (maximum radius), λ) i.e., $x_k \ll 1$, $K_o(x) \approx \frac{1}{x}$ [48] and for $x > x_k$, $\varepsilon_L \approx$ constant due to tension at the surface.

Therefore,

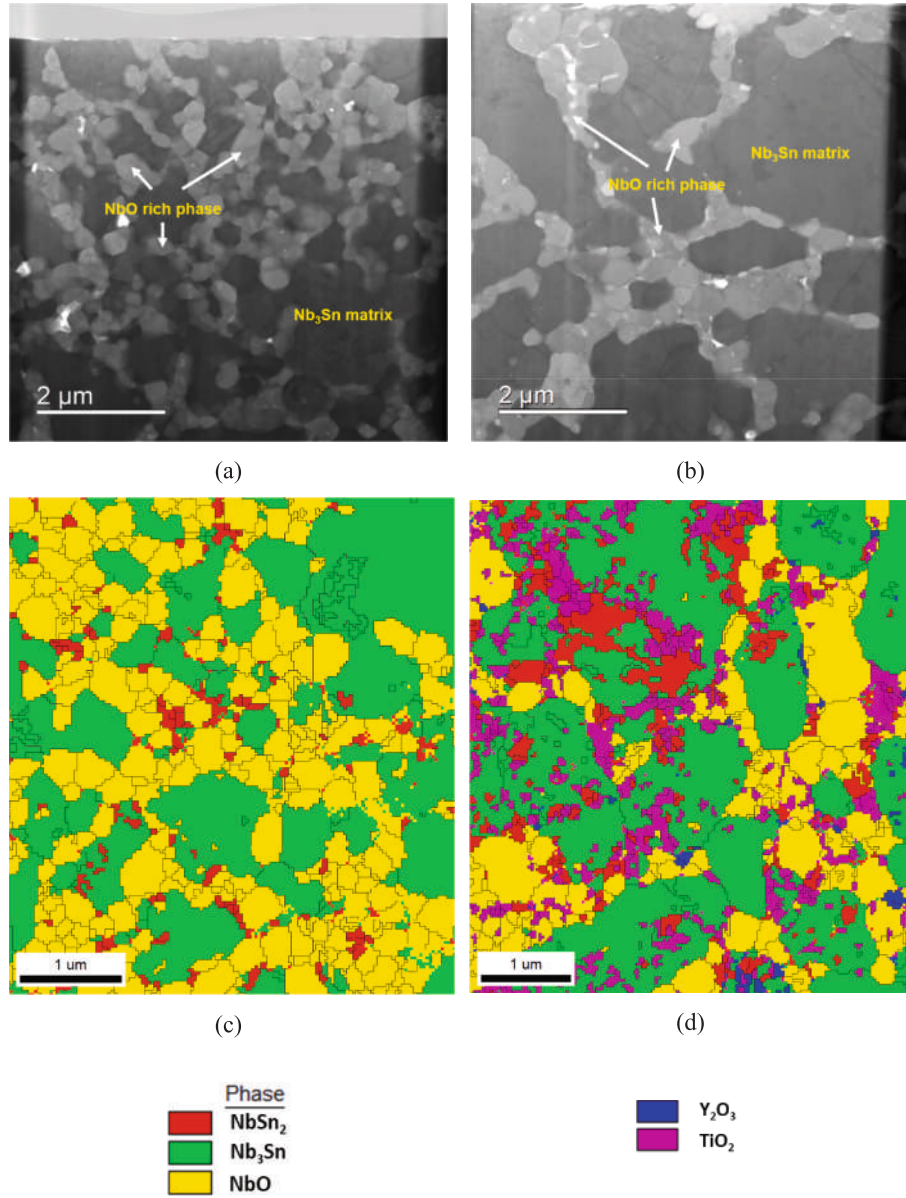


Fig. 18. Scanning transmission electron micrograph (STEM) showing grain size distribution for (a) Pristine Nb₃Sn and (b) Nb₃Sn doped with Y₂O₃ and TiO₂ samples annealed at 400 °C for 9 hrs. Further phase map based on orientation imaging micrograph (OIM) captured in transmission electron microscope using precision electron diffraction for (c) Pristine Nb₃Sn and (d) Nb₃Sn doped with Y₂O₃ and TiO₂ samples annealed at 400 °C for 9 hrs.

$$\varepsilon_L = \frac{\phi_o^2}{4\pi\mu_o\lambda^2} \ln\left(\frac{a'}{\xi}\right) \quad (19)$$

Substituting the value of ε_L from Eq. (14) to Eq. (6) we get,

$$J_{c_o} = \frac{2}{L\phi_o} \left[\frac{\phi_o^2}{4\pi\mu_o\lambda^2} \ln\left(\frac{a'}{\xi}\right) \right] \quad (20)$$

At x_k , where k is the Ginzburg-Landau parameter, $a' \approx \Gamma a_o$, where Γ is a phenomenological constant and a_o is inter-vortex spacing. The vortices arrange themselves in a periodic fashion to minimize repulsive interaction and energy, usually in the form of hexagonal (triangular) lattice [51]. The intervortex spacing (a_o) for this triangular lattice is given by $a_o = \sqrt{\frac{2\phi_o}{\sqrt{3}B}}$ [52] and hence, J_{c_o} is defined by

$$J_c = \frac{2}{L\phi_o} \left[\frac{\phi_o^2}{4\pi\mu_o\lambda^2} \ln\left(\frac{\Gamma \bullet \sqrt{\frac{2\phi_o}{\sqrt{3}B}}}{\xi}\right) \right] \quad (21)$$

Considering the effect of pins and the temperature dependence of penetration depth, λ and coherence length, ξ , the Eq. (21) can be generalized by Eq. (22).

$$J_{c_o} = \psi \times \eta \times \frac{(f_{eff\ pins})^4}{(f_{non-eff\ pins})^2} \times \frac{1}{r_{pins}} \times \frac{1}{\phi_o} \left[\frac{\phi_o^2}{4\pi\mu_o\lambda_T^2} \ln\left(\frac{\Gamma \bullet \sqrt{\frac{2\phi_o}{\sqrt{3}B}}}{\xi_T}\right) \right] \quad (22)$$

The temperature dependence is defined as, $\lambda_T = \frac{\lambda_o}{\sqrt{1 - \left(\frac{T_{test}}{T_c}\right)^4}}$ and

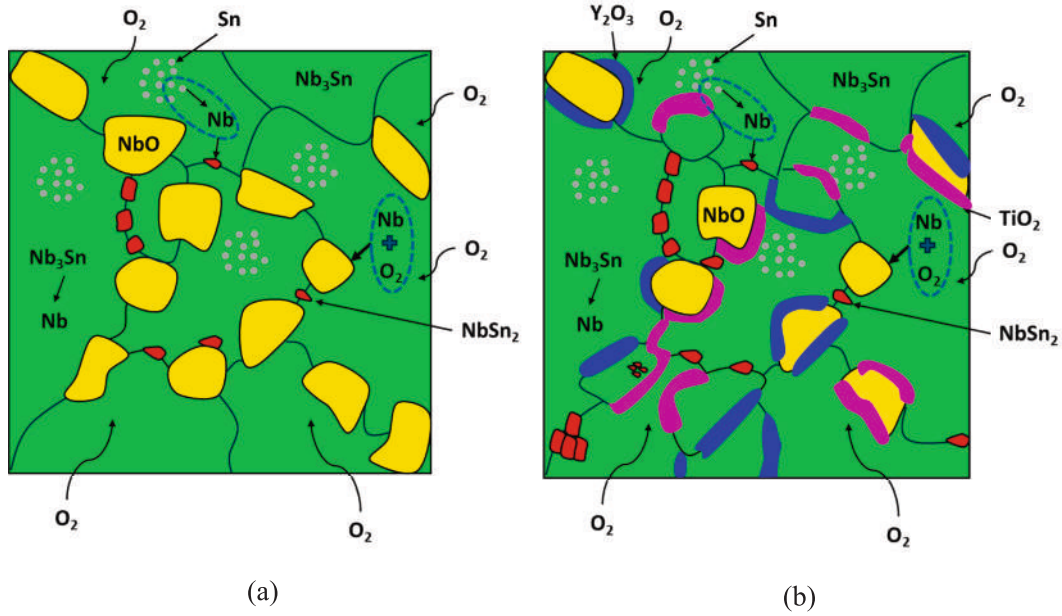


Fig. 19. OIM schematic showing the proposed mechanism of phase growth for (a) Pristine Nb₃Sn and (b) Nb₃Sn doped with Y₂O₃ and TiO₂ samples annealed at 400 °C for 9 hrs.

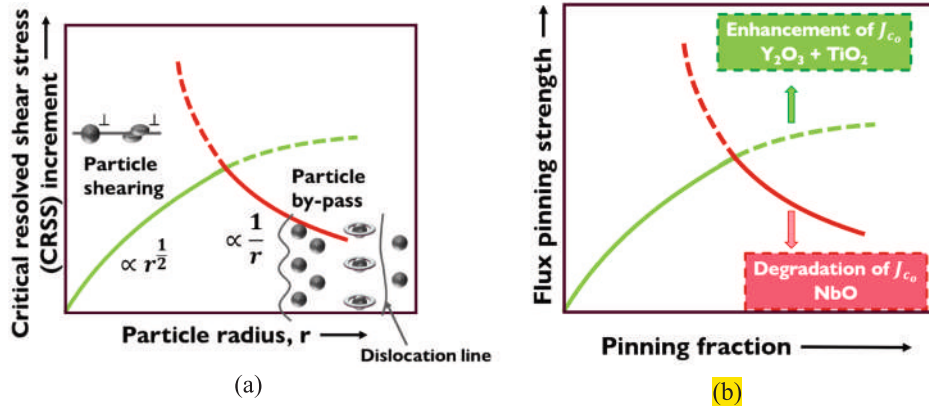


Fig. 20. Schematic relating the (a) dislocation-particle interaction model with the (b) flux lines interaction with effective and non-effective pins.

$\xi_T = \frac{\xi_0}{\sqrt{1 - T_{est}/T_c}}$ [53] with $\lambda_0 = 40$ nm [48] and $\xi_0 = 3.5$ nm [48] for Nb₃Sn.

The temperature dependence of J_{c0} arises from these temperature dependent quantities. ψ is a constant with value range of 20–25, η is a factor depending on the nature pin types with a value range of 0.5–1, where ‘0.5’ represents the domination by point pins and ‘1’ represents surface pins, $f_{eff,pins}$ and $f_{non-eff,pins}$ are fraction of effective and non-effective pins present in the sample and r_{pins} is the average radius of effective and non-effective pins. Based on the experimental J_{c0} data shown by Fig. 10 and the J_{c0} correlation with Fig. 18c-d, the additional parameters i.e., effective and non-effective pin fractions were observed to play a key role towards the J_{c0} . The ratio and the power for the effective and non-effective pin fraction was determined by correlating the behaviour of pinning with dislocation-particle interaction mechanism. Such correlation was hypothesized considering the flux lines interact with the nano-dispersoids in a similar way. A schematic shown by Fig. 20 helps to understand this behaviour. Below a critical radius the dislocation pass through the particle by shearing it while beyond the critical radius, dislocation loops around the particle and by-pass it. While the magnetic flux lines are imaginary, the correlations follow as; a fraction of non-effective pins degrades the J_{c0} performance, whereas a

fraction of effective pins, pin down the magnetic flux, enhances the J_{c0} performance. Since the shear mechanism is dominated by nano-sized particles equivalent to the nano-dispersoids, directly correlated with J_{c0} . Similarly, the bigger particles cause the dislocation to loop around and bypass, tend to degrade the strength or J_{c0} performance, inversely related to J_{c0} . Considering this factor the average radius is introduced in the Eq. (22) to highlight the actual effect on J_{c0} . An average radius is used because the size range of the effective and non-effective lie within the same order. The additional parameters used i.e., η as pin domination parameter is used to account for contribution of pinning domination by surface or point pinning. The constant ψ is used as a seed value for the curve fit.

The experimentally calculated data of J_{c0} shown in Fig. 10c was utilised as reference to validate the model. For the pristine Nb₃Sn sample, as mentioned earlier in section 3.3, the low angle grain boundaries (LAGBs) served as the effective flux pinning sites and NbO phase as the non-effective pins. The experimentally evaluated data for the pristine sample i.e., 1.30×10^4 A/cm² (10 K, 4 T) nearly matches with the predicted J_{c0} data of 1.05×10^4 A/cm² (10 K, 4 T) from Eq. (22). The LAGB fraction (f_{LAGB}) was ~ 0.04 and f_{NbO} 0.48. Similarly, for the co-doped sample, the Y₂O₃ and TiO₂ nano-sized phase particles served as

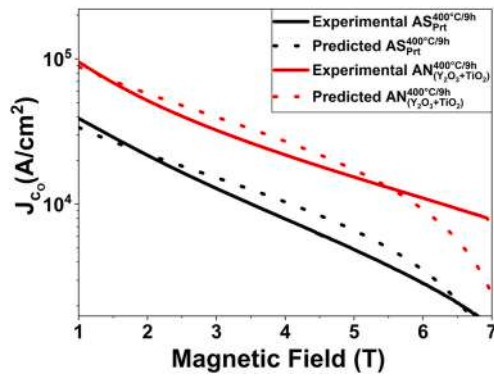


Fig. 21. Superimposed J_{c0} for the experimentally determined and calculated from Eq. (22) for the pristine and co-doped sample, annealed at 400 °C for 9 h.

the effective pins ($f_{eff,pins} = f_{Y_2O_3} \cdot f_{TiO_2}$) with $f_{Y_2O_3}$ 0.02 and f_{TiO_2} 0.14 and NbO served as non-effective pinning center (f_{NbO} 0.56). The experimentally determined data of 2.17×10^4 A/cm² (10 K, 4 T) closely matches with the calculated data of 2.53×10^4 A/cm² (10 K, 4 T) from the model in Eq. (22). This data matching for two different samples validates our model. So, using the above equation, a superimposed J_{c0} curves had been plotted for both the measured and calculated data for the co-doped sample, shown in Fig. 21. The predicted data nearly matches with the experimentally determined data with an R^2 value of 97.8 % while a slight deviation was observed at higher fields. This deviation could be due to the overpowered pinning effect of non-effective pins over the effective ones due to their higher fraction. This model is also effective to give the insights on the J_{c0} quantification when the microstructural features like phase fraction and pinning radius is present. With these features available, the real time J_{c0} values can be evaluated at different step size for the applied field ranges. The good agreement between the analytical predictions and experimental observations further suggests that the reported J_{c0} values realistically represent the true superconducting response of the microstructure. The influence of non-superconducting phases such as NbO and NbSn₂ would have got already intrinsically embedded in the measured magnetization signal.

5. Conclusion

This study highlights the effect of heat treatment on phase formation and microstructural evolution and superconducting properties in the absence and presence of Y₂O₃-TiO₂ nano dispersoids. These phases had an effect on T_c data with more uniform Nb₃Sn phase being available in co-doped condition. A high T_c of 18 K was observed for AN^{400 °C/9h}_(Y₂O₃+TiO₂) sample while the lower T_c of 16 observed for AS_{Prt} sample. The spherically indexed EBSD data reveals that the NbO fraction being impediment to J_{c0} performance in pristine and TiO₂ doped sample. The presence of co-doping of Y₂O₃ and TiO₂ provide a barrier to the evolution of this NbO fraction by segregation of the oxides at the grain boundaries of Nb₃Sn. This crucial insight was presented by TEM-ACOM study, and it helped in understanding of the phase formation mechanism. Additionally, these nano dispersoids served as effective flux pinning centers and overpowered the non-effective NbO pins, resulting in enhancing the J_{c0} performance. A high J_{c0} of 5.17×10^5 A/cm² at an applied field of 2 T was observed for AN^{400 °C/9h}_(Y₂O₃+TiO₂) compared to the lowest J_{c0} of 9.1×10^4 A/cm² for the SQ_{Prt}^{400 °C/9h} condition. Our developed model could accurately predict the role of each pin in quantifying the J_{c0} values and the predicted results of 1.05×10^4 A/cm² (10 K, 4 T) and 2.53×10^4 A/cm² (10 K, 4 T) closely match with the experimental data of 1.30×10^4 A/cm² (10 K, 4 T) and 2.17×10^4 A/cm² (10 K, 4 T) for the AN^{400 °C/9h}_(Y₂O₃+TiO₂) samples respectively.

cm² (10 K, 4 T) and 2.17×10^4 A/cm² (10 K, 4 T) for the AN^{400 °C/9h}_(Y₂O₃+TiO₂) samples respectively.

CRedit authorship contribution statement

Nitin Srivastava: Writing – original draft, Methodology, Formal analysis, Data curation. **Bhargav R. Sudhalkar:** Writing – original draft, Software, Methodology. **Souptik Pal:** Resources, Methodology. **Alok Singh:** Software, Methodology, Formal analysis. **Nobuya Banno:** Writing – review & editing, Visualization, Software, Resources, Formal analysis, Data curation. **Sangeeta Santra:** Writing – review & editing, Visualization, Supervision, Resources, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

References

- [1] N. Banno, Low-temperature superconductors: Nb₃Sn, Nb₃Al, and NbTi, Superconductivity 6 (2023) 100047, <https://doi.org/10.1016/j.supcon.2023.100047>.
- [2] N. Srivastava, S. Santra, Effect of independent alloying of zirconium with bronze and niobium on superconducting properties of Nb₃Sn in a Cu(Sn)/Nb system, Scr. Mater. 231 (2023) 115466, <https://doi.org/10.1016/j.scriptamat.2023.115466>.
- [3] S. Santra, A. Paul, Role of Zr on growth kinetics and microstructural evolution of the superconductor V₃Ga by the bronze technique, Philos. Mag. Lett. 97 (2) (2017) 58–65, <https://doi.org/10.1080/09500839.2016.1274834>.
- [4] S. Santra, S.K. Makineni, S. Suwas, K. Chattopadhyay, A. Paul, Role of Ti on growth, morphology and microtexture evolution of A15-based V₃Ga superconductor by bronze technique, Mater. Des. 110 (2016) 404–413, <https://doi.org/10.1016/j.matdes.2016.07.143>.
- [5] D. Sharma, D. Kalyan, S.K. Makineni, S. Santra, Effect of Zr on growth kinetics, microstructure and microtexture of Nb₃Sn by bronze technique, J. Alloy. Compd. 935 (2023) 168140, <https://doi.org/10.1016/j.jallcom.2022.168140>.
- [6] R.M. Scanlan, W.A. Fietz, E.F. Koch, Flux pinning centers in superconducting Nb₃Sn, J. Appl. Phys. 46 (5) (1975) 2244–2249, <https://doi.org/10.1063/1.321816>.
- [7] S. Santra, S.K. Makineni, G. Shankar, S. Suwas, K. Chattopadhyay, S.V. Divinski, A. Paul, Insight into the effect of Ti-addition on diffusion-controlled growth and texture of Nb₃Sn intermetallic superconductor phase, Materialia 6 (2019) 100276, <https://doi.org/10.1016/j.mtl.2019.100276>.
- [8] N. Banno, T. Morita, Z. Yu, T. Yagai, K. Tachikawa, Effect of Zn addition and Ti doping position on the diffusion reaction of internal tin Nb₃Sn conductors, Supercond. Sci. Technol. 32 (11) (2019) 115017, <https://doi.org/10.1088/1361-6668/ab4632>.
- [9] N. Srivastava, G.A.B. Matthews, J. Liu, S.C. Speller, C.R.M. Grovenor, S. Santra, Effect of dopant solubility and excess doping on the superconducting properties of doped Nb₃Sn prepared by field assisted sintering technique, J. Alloy. Compd. 1002 (2024) 175526, <https://doi.org/10.1016/j.jallcom.2024.175526>.
- [10] X. Xu, X. Peng, M. Sumption, E.W. Collings, Recent progress in application of internal oxidation technique in Nb₃Sn strands, IEEE Trans. Appl. Supercond. 27 (4) (2017) 1–5, <https://doi.org/10.1109/TASC.2016.2625780>.

- [11] F. Buta, M. Bonura, D. Matera, G. Bovone, A. Ballarino, S.C. Hopkins, B. Bordini, X. Chaud, C. Senatore, Very high upper critical fields and enhanced critical current densities in Nb₃Sn superconductors based on Nb-Ta-Zr alloys and internal oxidation, *J. Phys. Mater.* 4 (2) (2021) 025003, <https://doi.org/10.1088/2515-7639/abe662>.
- [12] L.R. Motowidlo, P.J. Lee, C. Tarantini, S. Balachandran, A.K. Ghosh, D. C. Larbalestier, An intermetallic powder-in-tube approach to increased flux-pinning in Nb₃Sn by internal oxidation of Zr, *Supercond. Sci. Technol.* 31 (1) (2017) 014002, <https://doi.org/10.1088/1361-6668/aa980f>.
- [13] X.F. Pan, C.H. Cheng, Y. Zhao, Effect of rare-earth oxides doping on the superconductivity and flux pinning of MgB₂ superconductor, *J. Supercond. Nov. Magn.* 24 (5) (2011) 1611–1616, <https://doi.org/10.1007/s10948-010-1066-4>.
- [14] G. Simon, M. Miryala, Impact of doping on MgB₂ superconductors: a comprehensive review, *J. Alloys Comp. Commun.* 3 (2024) 100023, <https://doi.org/10.1016/j.jacomc.2024.100023>.
- [15] T. Mousavi, P.S. Grant, S.C. Speller, C. Grovenor, New nanoscale artificial pinning centres for NbTi superconductors, *Mater. Des.* 198 (2021) 109285, <https://doi.org/10.1016/j.matdes.2020.109285>.
- [16] H. Fallah-Arani, A. Sedghi, S. Baghshahi, F. Shahbaz tehrani, R.S. Moakhar, N. Riahi-Noori, N.J. Nodoushan, Bi-2223 superconductor ceramics added with cubic-shaped TiO₂ nanoparticles: Structural, microstructural, magnetic, and vortex pinning studies, *J. Alloys Comp.* 900 (2022) 163201, <https://doi.org/10.1016/j.jallcom.2021.163201>.
- [17] J.-C. Grivel, A. Jeremie, R. Flukiger, The influence of TiO₂ additions on the formation and the superconducting properties of the (Bi,Pb)2Sr₂Ca₂Cu₃O_{10-y} phase, *Supercond. Sci. Technol.* 8 (1) (1995) 41, <https://doi.org/10.1088/0953-2048/8/1/007>.
- [18] H. Kishan, V.P.S. Awana, T.M. de Oliveira, S. Alam, M. Saito, O.F. de Lima, Superconductivity of nano-TiO₂-added MgB₂, *Physica C* 458 (1) (2007) 1–5, <https://doi.org/10.1016/j.physc.2007.02.014>.
- [19] V.G. Prokhorov, V.L. Svetchnikov, J.S. Park, G.H. Kim, Y.P. Lee, J.-H. Kang, V. A. Khokhlov, P. Mikheenko, Flux pinning and the paramagnetic Meissner effect in MgB₂ with TiO₂ inclusions, *Supercond. Sci. Technol.* 22 (4) (2009) 045027, <https://doi.org/10.1088/0953-2048/22/4/045027>.
- [20] N. Srivastava, S. Pal, S. Santra, Oxide-dispersion-driven enhancement of superconducting performance of mechanically alloyed Nb₃Sn bulk via co-doping with Y₂O₃ and TiO₂, *Adv. Eng. Mater.* 27 (2025) 2500201, <https://doi.org/10.1002/adem.202500201>.
- [21] N. Srivastava, G.A.B. Matthews, S. Speller, C. Grovenor, S. Santra, Effect of sintering temperature on the superconducting properties of mechanically alloyed Ru- and Y-doped Nb₃Sn, *Mater. Charact.* 229 (2025) 115549, <https://doi.org/10.1016/j.matchar.2025.115549>.
- [22] W. Sun, J. Cheng, S. Chen, Preparation and superconducting properties of Nb₃Sn by mechanical alloying, *J. Low Temp. Phys.* 205 (3) (2021) 100–111, <https://doi.org/10.1007/s10909-021-02608-5>.
- [23] V. Uvarov, I. Popov, Metrological characterization of X-ray diffraction methods at different acquisition geometries for determination of crystallite size in nano-scale materials, *Mater. Charact.* 85 (2013) 111–123, <https://doi.org/10.1016/j.matchar.2013.09.002>.
- [24] A.B. Andrade, N.S. Ferreira, M.E.G. Valerio, Particle size effects on structural and optical properties of BaF₂ nanoparticles, *RSC Adv.* 7 (43) (2017) 26839–26848, <https://doi.org/10.1039/C7RA01582H>.
- [25] Y. He, X. Li, Z. Qian, Z. Yan, G. Shi, X. Sun, Z. Ma, Improvement of critical current density in Nb₃Al superconductors co-doped by Sn-B, *J. Alloy. Compd.* 1021 (2025) 179715, <https://doi.org/10.1016/j.jallcom.2025.179715>.
- [26] X. Li, F. Lan, X. Wen, H. Zhao, Q. Ma, Z. Qian, L. Ma, Z. Ma, Y. Liu, Enhanced critical current density in the low-temperature sintered Nb₃Al superconductor with Sn doping, *Intermetallics* 119 (2020) 106708, <https://doi.org/10.1016/j.intermet.2020.106708>.
- [27] X. Li, Y. He, J. Tan, L. Zhao, Z. Du, S. Chen, Z. Ma, Enhancement of critical current density of Nb₃Al superconductors by B doping, *Physica Status Solidi (a)* 221 (2) (2024) 2300577, <https://doi.org/10.1002/pssa.202300577>.
- [28] Z. Gao, S. Santra, C.R.M. Grovenor, S.C. Speller, Effect of cubic and hexagonal boron nitride additions on the microstructure and properties of bulk MgB₂ superconductors, *Supercond. Sci. Technol.* 35 (8) (2022) 084002, <https://doi.org/10.1088/1361-6668/ac7616>.
- [29] H. Krauth, “Fabrication and application of NbTi and Nb₃Sn superconductors,” niobium.tech. [Online]. Available: <https://niobium.tech/-/media/niobiumtech/attachments-biblioteca-tecnica/nt-fabrication-and-application-of-nbti-and-nb3sn-superconductors.pdf>.
- [30] N. Srivastava, S. Santra, A novel bulk (Nb,Zr,Pt)67Ti33 high-entropy alloy superconductor: synthesis and structure–property relationship, *J. Mater. Chem. C* 12 (26) (2024) 9773–9783, <https://doi.org/10.1039/D4TC01500B>.
- [31] S. Mugiraneza, A.M. Hallas, Tutorial: a beginner's guide to interpreting magnetic susceptibility data with the Curie-Weiss law, *Commun. Phys.* 5 (1) (2022) 95, <https://doi.org/10.1038/s42005-022-00853-y>.
- [32] D. Dew-Hughes, Flux pinning mechanisms in type II superconductors, *Philosoph. Mag.: J. Theor. Experiment. Appl. Phys.* 30 (2) (1974) 293–305, <https://doi.org/10.1080/14786439808206556>.
- [33] S. Santra, T. Davies, G. Matthews, J. Liu, C.R.M. Grovenor, S.C. Speller, The effect of the size of NbTi filaments on interfacial reactions and the properties of InSn-based superconducting solder joints, *Mater. Des.* 176 (2019) 107836, <https://doi.org/10.1016/j.matdes.2019.107836>.
- [34] G.A.B. Matthews, S. Santra, R. Ma, C.R.M. Grovenor, P.S. Grant, S.C. Speller, Effect of the sintering temperature on the microstructure and superconducting properties of MgB₂ bulks manufactured by the field assisted sintering technique, *Supercond. Sci. Technol.* 33 (5) (2020) 054003, <https://doi.org/10.1088/1361-6668/ab7c53>.
- [35] D.P. Hampshire, H. Jones, Flux flow in high-temperature type II superconductors governed by the activation of Frank-Read sources and the resultant motion of core dislocations, *J. Phys. C Solid State Phys.* 21 (2) (1988) 419, <https://doi.org/10.1088/0022-3719/21/2/024>.
- [36] F. Ram, M. De Graef, Phase differentiation by electron backscatter diffraction using the dictionary indexing approach, *Acta Mater.* 144 (2018) 352–364, <https://doi.org/10.1016/j.actamat.2017.10.069>.
- [37] W.C. Lenthe, S. Singh, M.D. Graef, A spherical harmonic transform approach to the indexing of electron back-scattered diffraction patterns, *Ultramicroscopy* 207 (2019) 112841, <https://doi.org/10.1016/j.ultramic.2019.112841>.
- [38] S. Santra, S. Suwas, A. Paul, Effect of Nb orientation and deformation on the growth of Nb₃Sn intermetallic superconductor by bronze technique, *Philos. Mag. Lett.* 95 (10) (2015) 504–510, <https://doi.org/10.1080/09500839.2015.1112045>.
- [39] S. Santra, A. Paul, Effect of Ga content in Cu(Ga) on the growth of V₃Ga following bronze technique, *Intermetallics* 70 (2016) 1–6, <https://doi.org/10.1016/j.intermet.2015.11.004>.
- [40] K. Togano, K. Tachikawa, Textures in diffusion-processed superconducting Nb₃Sn and V₃Ga layers, *J. Appl. Phys.* 50 (5) (1979) 3495–3499, <https://doi.org/10.1063/1.326345>.
- [41] N. Nakamura, G.D. Gu, K. Takamuku, M. Muarkami, N. Koshizuka, Magneto-optical observation of flux pinning at the grain boundary in a Bi₂Sr₂CaCu₂O_x superconductor, *Appl. Phys. Lett.* 61 (25) (1992) 3044–3046, <https://doi.org/10.1063/1.108004>.
- [42] N. Banno, T. Moronaga, T. Hara, K. Asai, T. Yagai, In-depth S/TEM observation of Ti-Hf and Ta-Hf-doped Nb₃Sn layers, *Supercond. Sci. Technol.* 37 (3) (2024) 035019, <https://doi.org/10.1088/1361-6668/ad2982>.
- [43] S. Ignatowicz, M.W. Davies, The free energy of formation of NbO and Ta₂O₅, *J. Less Common Metals* 15 (1) (1968) 100–102, [https://doi.org/10.1016/0022-5088\(68\)90011-8](https://doi.org/10.1016/0022-5088(68)90011-8).
- [44] R. A. Robie, B. S. Hemingway, and J. R. Fisher, “Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures,” U.S. Geological Survey ; For sale by the Supt. of Docs., U. S. G.P.O., 1452, 1978. doi: 10.3133/b1452.
- [45] S.S. Zumdahl, *Chemical Principles*, Houghton Mifflin, 2005.
- [46] T. Higuchi, S.I. Yoo, M. Murakami, Comparative study of critical current densities and flux pinning among a flux-grown NdBa₂Cu₃O_y single crystal, melt-textured Nd-Ba-Cu-O, and Y-Ba-Cu-O bulks, *Phys. Rev. B* 59 (2) (1999) 1514–1527, <https://doi.org/10.1103/PhysRevB.59.1514>.
- [47] E.C.L. Chesneau, B.A. Glowacki, I. MacDougall, Residual stress and the critical current in superconducting tapes, *Cryogenics* 37 (10) (1997) 615–618, [https://doi.org/10.1016/S0011-2275\(97\)00046-5](https://doi.org/10.1016/S0011-2275(97)00046-5).
- [48] E.H. Brandt, The flux-line lattice in superconductors, *Rep. Prog. Phys.* 58 (11) (1995) 1465, <https://doi.org/10.1088/0034-4885/58/11/003>.
- [49] A.M. Campbell, The interaction distance between flux lines and pinning centres, *J. Phys. C Solid State Phys.* 4 (18) (1971) 3186, <https://doi.org/10.1088/0022-3719/4/18/023>.
- [50] J.R. Clem, Simple model for the vortex core in a type II superconductor, *J. Low Temp. Phys.* 18 (5) (1975) 427–434, <https://doi.org/10.1007/BF00116134>.
- [51] D.Y. Vodolazov, F.M. Peeters, Rearrangement of the vortex lattice due to instabilities of vortex flow, *Phys. Rev. B* 76 (1) (2007) 014521, <https://doi.org/10.1103/PhysRevB.76.014521>.
- [52] A.V. Pan, P. Esquinazi, Decoupling transition of two coherent vortex arrays within the surface superconductivity state, *Phys. Rev. B* 70 (18) (2004) 184510, <https://doi.org/10.1103/PhysRevB.70.184510>.
- [53] M. Hosseinzadeh, S.R. Ghorbani, H. Arabi, On the determination of pinning mechanisms and regimes in type-II superconductors with weak thermal fluctuations, *J. Supercond. Nov. Magn.* 33 (4) (2020) 971–980, <https://doi.org/10.1007/s10948-019-05356-6>.