

# The nano-lead advantage: synergizing phase stability and high- $T_c$ performance in Hg-1223 superconductors

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## ABSTRACT

High-temperature superconducting samples of the nominal composition  $\text{HgBa}_2\text{Ca}_2\text{Cu}_{3-x}\text{Nano-Pb}_x\text{O}_{8+\delta}$  (with  $x = 0.00, 0.05, 0.10$ , and  $0.15$ ) were synthesized via the solid-state reaction technique to investigate the impact of Nano-lead substitution on phase stability and superconducting properties. X-ray diffraction (XRD) analysis confirmed that all samples crystallized in the tetragonal Hg-1223 phase, identifying a monotonic expansion of the unit cell volume driven by the ionic radius mismatch between the host and dopant cations. Quantitative phase analysis demonstrated a remarkable enhancement in phase purity, with the volume fraction of the high- $T_c$  Hg-1223 phase increasing from 57.10% in the undoped sample to 79.40% at  $x = 0.15$ . Additionally, the Size-Strain Plot (SSP) method proved statistically superior to the Scherrer method for crystallite size estimation by effectively decoupling lattice strain. Morphological characterization using Field Emission Scanning Electron Microscopy (FESEM) revealed that Nano-Pb doping significantly promoted microstructural densification and grain connectivity, thereby reducing porosity. Electrical resistivity measurements indicated a non-monotonic behavior in the critical transition temperature ( $T_c$ ); an initial suppression at  $x = 0.05$  was attributed to electronic disorder and carrier concentration shifts, while higher doping levels restored and enhanced superconductivity. Consequently, the sample with  $x = 0.15$  achieved a maximum  $T_c$  of 130.48 K, a result ascribed to the synergistic effects of optimized phase purity and improved inter-grain connectivity.

**Keywords:** Hg-1223 Superconductor, Nano-lead Substitution, Critical Temperature, Phase Stability, Microstructure.

## 1. INTRODUCTION

When a material reaches its critical temperature ( $T_c$ ), a radical transformation occurs in its physical state, entering the superconducting state. This state is characterized by two unique properties: the complete disappearance of electrical resistance and the emergence of perfect diamagnetism (the Meissner effect). Mechanically, this transformation depends on the formation of Cooper pairs, where electrons bond together to form bosons with integer spin, enabling them to flow through the crystal lattice without any energy loss, thus explaining the absence of resistance [1]. This diamagnetic phenomenon manifests as the Meissner effect, where the material expels external magnetic fields, leaving its interior magnetically shielded [1], [2]. Historically, this phenomenon was first observed by Heike Kamerlingh Onnes in 1911 during his experiments with mercury. As research progressed, these materials were classified into two types (types I and II), noting that type II does not fully exhibit the Meissner effect [2], [3]. The year 1986 witnessed a significant breakthrough with the discovery of high-temperature superconductors (HTS), specifically in cuprate compounds (copper oxides). These materials exceeded the expectations of classical BCS theory, demonstrating the ability to operate at temperatures sometimes exceeding the boiling point of liquid nitrogen

(77 K) [4]. This remarkable advancement paved the way for the application of superconductors in vital and complex applications, ranging from high-resolution medical imaging devices to quantum computing technologies [5].

This breakthrough has led to the creation of ceramic materials, in 1986, which have critical temperatures above 90 K, and therefore, marked the beginning of the high temperature superconductors. This was an important breakthrough in the sense that it allowed the utilization of liquid nitrogen, which is affordable and readily available in the ambient temperature, 77 K, as a cryogenic coolant [6]. The discovery of these materials has in turn led to an abundance of experimental studies and usage, and research efforts continue to identify compounds with even higher critical temperatures, to enable superconducting technologies to become more widely deployable. The high-temperature superconducting ceramic compounds can be characterized by the availability of a copper-oxide ( $\text{CuO}_2$ ) layer or layers in the crystalline structure [7].

Studies of the crystal structure and superconducting behavior of the Hg-based cuprate system, namely the highest form of Hg-1223 have evolved significantly into the basic characterization of the material and advanced chemical substitution strategies. The basic knowledge of the

superconductivity, crystal structure, and resistivity profile on the Hg-1223 compound was established by Huang *et al.* (1993) [8], who reported a top critical temperature ( $T_c$ ) of about 133.2 K. A few years later, Tokiwa-yamamoto *et al.* (1994), [9] reported synthesis procedures of these HgBaCaCuO compounds with distinctly defined superconducting transitions that reached transition temperatures up to 135 K. Bertinotti *et al.* [10] in 1995 utilized the X-ray single crystal method to clarify the influence of oxygen stoichiometry with a  $T_c$  of about 133 K confirmed in optimally doped single crystals. Furthermore, Shao *et al.* (1995) [11] discussed the implications of chemically substituting mercury with Nano-lead to increase phase stability, reporting critical transition temperatures ( $T_c$ ) up to 129 K in the Nano-Pb doped system. Based on this, Giri *et al.* (2007) [12] studied the co-incorporation of antimony (Sb) and Nano-lead (Nano-Pb), and stated that the (Hg, Sb, Nano-Pb)1223 showed a transport critical temperature ( $T_c$ ) of 77 K. In the last ten years, researchers have focused much attention on maximizing these compounds; a recent study by Jasim (2012) [13] about the Hg<sub>0.8</sub>Cu<sub>0.15</sub>Sb<sub>0.05</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+x</sub> studied the Hg<sub>0.8</sub>Cu<sub>0.15</sub>Sb<sub>0.05</sub>Baskota-Cu-Sb-Ba-Cu-O 8 compound and improved sintering conditions to enhance the percentage of the superconductive phase. Jasim and Al-Khafaji [14] further extended this to thallium (Tl) replacement in the Hg<sub>0.6</sub>Tl<sub>0.4</sub>Ba<sub>2</sub>C<sub>2</sub>(Cu<sub>1-x</sub>Ag<sub>x</sub>) to obtain  $T_c$  values of approximately 130 K and with better kinetics of formation. Lastly, Jasim and Mohammed (2018) [15] compared the impact of a partial replacement of copper with nickel oxide and established an optimal offset  $T_c$  of 137 K of the Ni-doped sample. More recently, Baqi *et al.* (2022) [16] reported that substituting calcium with zinc oxide in the Hg<sub>0.9</sub>Ag<sub>0.1</sub>Ba<sub>2</sub>Ca<sub>2-x</sub>Zn<sub>x</sub>Cu<sub>3</sub>O<sub>8+d</sub> system resulted in a maximum  $T_c$  of 132 K at a zinc concentration of  $y = 0.05$ . Most recently, Jasim *et al.* (2024) [17] revisited Nano-lead substitution in the Hg<sub>1-x</sub>Nano-Pb<sub>x</sub>Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+d</sub> system, observing a maximum critical temperature  $T_c$  (offset) of 125.4 K for the composition with  $x = 0.15$ .

The primary motivation of this work stems from the inherent limitations of Hg-1223 superconductors, specifically phase impurity and weak intergrain connectivity, which severely restrict their practical efficiency. To address these challenges, this study aims to optimize the performance and phase stability of the Hg-based cuprate system by systematically investigating the explicit effects of nano-lead (nano-Pb) substitution in the nominal composition of HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>(nano-Pb)<sub>x</sub>O<sub>8+δ</sub> synthesized via a solid-state reaction pathway. Our hypothesis is that incorporating nano-Pb into the crystal lattice acts as a critical stabilizing agent, lowering thermodynamic reaction barriers and reducing lattice strain to enhance both structural integrity and superconducting transport. The novelty of this research lies in decoupling the microstrain and crystallite size effects using the Size-Strain Plot (SSP) method—demonstrating its statistical superiority over the traditional Scherrer approach—and establishing a direct correlation between nano-Pb-induced microstructural densification and the non-monotonic behavior of the critical transition temperature ( $T_c$ ). Ultimately, this work reveals that an optimum substitution level ( $x = 0.15$ ) not only increases the

high  $T_c$  phase volume fraction to 79.40% and densifies the microstructure, but also synergistically maximizes the critical transition temperature to 130.48 K, thereby providing a viable roadmap for developing chemically stable, high-performance superconducting ceramics.

## 2. MATERIALS AND METHODS

This study employed a rigorous experimental approach to prepare a series of Hg-based superconductor samples with the composition (HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>Nano-Pb<sub>x</sub>O<sub>8+δ</sub>), utilizing varying Nano-lead substitution ratios (high-purity nanoparticles (average size < 100 nm) to ensure higher reactivity and better integration into the crystal lattice). The preparation methodology relied on a two-stage solid-state reaction technique using a precursor method to ensure high homogeneity and control over the resulting phase. In the first stage, the precursor mixture was prepared by weighing precise stoichiometric amounts of barium, calcium, Nano-lead, and copper oxides. This mixture was then subjected to wet mechanical grinding using 2-propanol (or isopropanol) as a medium in a garnet mortar for approximately one hour to ensure complete mixing and the formation of a homogeneous suspension. Following drying, the mixture underwent thermal calcination at 800°C for three hours under a controlled heating and cooling cycle, resulting in the formation of the primary precursor (HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>Nano-Pb<sub>x</sub>O<sub>8+δ</sub>).

The second step was to determine the ultimate structure of the superconductor. In this regard, the previously prepared precursor was mixed with mercuric oxide (HgO) and in accordance to the weight ratios. The resulting nanopowder was subsequently compacted under hydraulic pressure of 7 ton/cm<sup>2</sup> to yield pellets of 1.3 cm diameter that were highly dense. The pellets were then subjected to an intense, multi-step sintering procedure. The first sintering was performed in ambient air at a temperature of approximately 900 °C, and the samples were allowed to cool and ground followed by re-pressing to facilitate the interparticle contact. This grinding step is an intermediate step which increases the reaction rate by having the reaction step 1212 actively participate in the transformation, preventing the process of making the pure, high-quality Hg-1223 phase too long. A long sintering process was then carried out under flowing oxygen conditions (28 h) and long annealing of the sample at 500°C was performed to attain the required oxygen saturation level to ensure superconductivity. It is important to acknowledge that the inclusion of lead (Pb) introduces toxicity concerns. However, the use of nano-Pb in this controlled solid-state synthesis minimizes potential environmental exposure during preparation. Furthermore, the incorporation of Pb into the highly stable ceramic matrix of the final Hg-1223 structure significantly mitigates leaching risks, ensuring that the enhanced superconducting properties can be investigated safely.

To do physical characterization and determine the critical temperature ( $T_c$ ), the synthesized samples were subjected to the electrical resistivity versus temperature measurements in the range of (77-300 K) in a traditional four-probe configuration to eliminate the influence of the Nano-lead resistance. The specimen was placed in a vacuum

cryostat, thus provided with thermal insulation, and platinum-based micro-thermal sensors were attached to it. To ensure the correctness of the electrical data, the low current direct-current supply (10 mA) was utilized to operate the sample, and the potential difference was measured with high accuracy by measuring it with a sensitive nanovoltmeter. This allowed the calculation of resistivity with the sample geometry and standard equation with a high degree of precision and accuracy [18, 19]:

$$\rho = Vwt/IL \quad (1)$$

where the applied current would be ( $I$ ), and the potential difference would be ( $V$ ), with the internal probes being different. As a measure to ensure that the results obtained during calculation were accurate the geometric sizes of the specimen were measured accurately using a digital vernier caliper. The measured dimensions were the width ( $w$ ), thickness ( $t$ ), and effective length ( $L$ ) of the specimen and the latter was the distance between the possible measurement electrodes.

To verify the structural properties and phase identification of the synthesized samples, X-ray diffraction (XRD) was performed using a Philips spectrometer. The measurements were conducted using copper (Cu-K $\alpha$ ) radiation as the source at a wavelength of 1.5405 Å, with operating conditions set at an acceleration voltage of 40 kV and a current of 20 mA. This technique was systematically employed to track and study the phase transitions of the various synthesized compounds, allowing for a precise understanding of their crystallization and internal structure. In addition to qualitative characterization, quantitative analysis was performed to estimate the volumetric ratio of each phase ( $V_{\text{phase}}$ ) within the sample by analyzing the intensity of the resulting spectral peaks and applying the mathematical relationship described in reference [20].

$$V_{ph} = \frac{\Sigma I_o}{(\Sigma I_o + \Sigma I_1 + \Sigma I_2 + \Sigma I_n)} \times 100 \quad (2)$$

In this relationship, the value ( $I_a$ ) indicates the intensity of the diffraction peak belonging to the specific phase under study, while the values ( $I_1, I_2, \dots, I_n$ ) represent the integrated intensities of the diffraction peaks belonging to all phases comprising the X-ray spectrum.

To calculate the crystallite size, the modified Scherrer method was used to include the data of all the diffraction peaks, which minimized the errors that were usually involved in estimating the size through one high-intensity reflection. This approach follows by restating the standard Scherrer equation into a linear equation as shown below [21]:

$$\cos\theta = K\lambda/D\beta \quad (3)$$

where  $\lambda$  represents the wavelength of the X-ray source (e.g., 1.5406 Å),  $\theta$  is the Bragg diffraction angle,  $\beta$  is the full width at half maximum (FWHM) of the peaks in radians,  $K$  is the shape factor (typically 0.9), and  $D$  denotes the crystallite

size. To perform the calculation, a graph is plotted with  $\cos\theta$  on the vertical axis (y-axis) and  $1/\beta$  on the horizontal axis (x-axis) for the available diffraction peaks. The data points are then fitted with a straight line, and the slope of this line is determined. The average crystallite size ( $D$ ) is subsequently calculated from the value of this slope, as the slope equates to  $K\lambda/D$ .

A more accurate analysis was obtained by the Size-Strain Plot (SSP) method where the crystallite size and lattice strain was concurrently measured using low-angle reflections as they have higher weight in the analysis and the intrinsic data is more precise. In this model, the crystallite size distribution will be considered to follow a Lorentzian profile and the strain distribution will be modeled as a Gaussian. The linear regression equation that governs this approach is [22]:

$$(d_{hkl} \beta_{hkl} \cos\theta)^2 = K\lambda/D (d_{hkl}^2 \beta_{hkl} \cos\theta) + (\epsilon/2)^2 d_{hkl}^4 \quad (4)$$

where  $d_{hkl}$  is the interplanar spacing between the lattice planes,  $\beta_{hkl}$  is the FWHM in radians,  $\theta$  is the Bragg angle,  $K$  is the shape constant,  $\lambda$  is the X-ray wavelength,  $D$  is the average crystallite size, and  $\epsilon$  represents the lattice strain. The calculation is performed by plotting  $(d_{hkl} \beta_{hkl} \cos\theta)^2$  on the y-axis against  $(d_{hkl}^2 \beta_{hkl} \cos\theta)$  on the x-axis. From the linear fit of these points, the crystallite size ( $D$ ) is obtained from the slope of the line, while the lattice strain ( $\epsilon$ ) is derived from the root of the y-intercept.

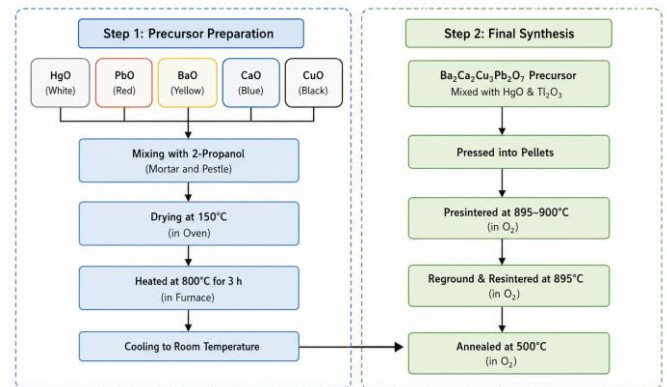


**Figure 1.** Three-dimensional schematic illustration of the two-step solid-state synthesis and electrical transport characterization of HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>Nano-Pb<sub>x</sub>O<sub>8+δ</sub> ( $x = 0.0, 0.05, 0.10$  and  $0.15$ ) high-temperature superconductors.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structural Study

Based on the X-ray diffraction patterns presented in Figure 2, the primary observation is that the synthesized samples have successfully crystallized in the tetragonal Hg-1223 phase structure, as the main diffraction peaks can be indexed to the standard JCPDS 42-0051 card with Miller indices such as (102), (103), (104), and (113) clearly visible. The sustained appearance of the characteristic spectral peaks across all doping levels (from  $x = 0.00$  to  $x = 0.15$ ) provides conclusive evidence for the preservation of the tetragonal symmetry of the HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>Nano-

$\text{Pb}_x\text{O}_{8+\delta}$  crystal lattice, despite the Nano-lead substitution process. This observation is of paramount importance, as it demonstrates that the doping process did not induce a destructive phase shift, but rather resulted in a structural modification within the superconducting matrix. This is clearly reflected in the increasing intensity and variability of the reflections with increasing Nano-lead content.

Turning to the quantitative analysis of the lattice dimensions, shown in Table 1, a clear and physically significant expansion in the unit cell size is observed, increasing in a regular, progressive manner from  $223.0 \text{ \AA}^3$  in the undoped sample to  $228.0 \text{ \AA}^3$  at  $x = 0.15$ . This volumetric expansion is primarily attributed to the significant elongation of the c-axis coefficient, which increased from  $15.25 \text{ \AA}$  to a peak of  $15.53 \text{ \AA}$  at  $x = 0.10$ . The precise scientific explanation for this phenomenon lies in the substantial difference between the ionic radii of the host and dopant cations. Specifically, the Nano-lead ion (particularly in its Nano- $\text{Pb}^{+2}$  oxidation state with a radius of approximately  $1.19 \text{ \AA}$ ) has a considerably larger ionic radius than the copper ion (around  $0.73 \text{ \AA}$ ) or the mercury cation that it may replace or structurally interact with. As documented in superconductor ionic substitution studies, the insertion of a larger atomic-sized ion into the crystal lattice induces expansion in the oxygen coordination polyhedra to accommodate this additional space, necessarily increasing the lattice constants and thus the overall expansion of the unit cell volume [23].

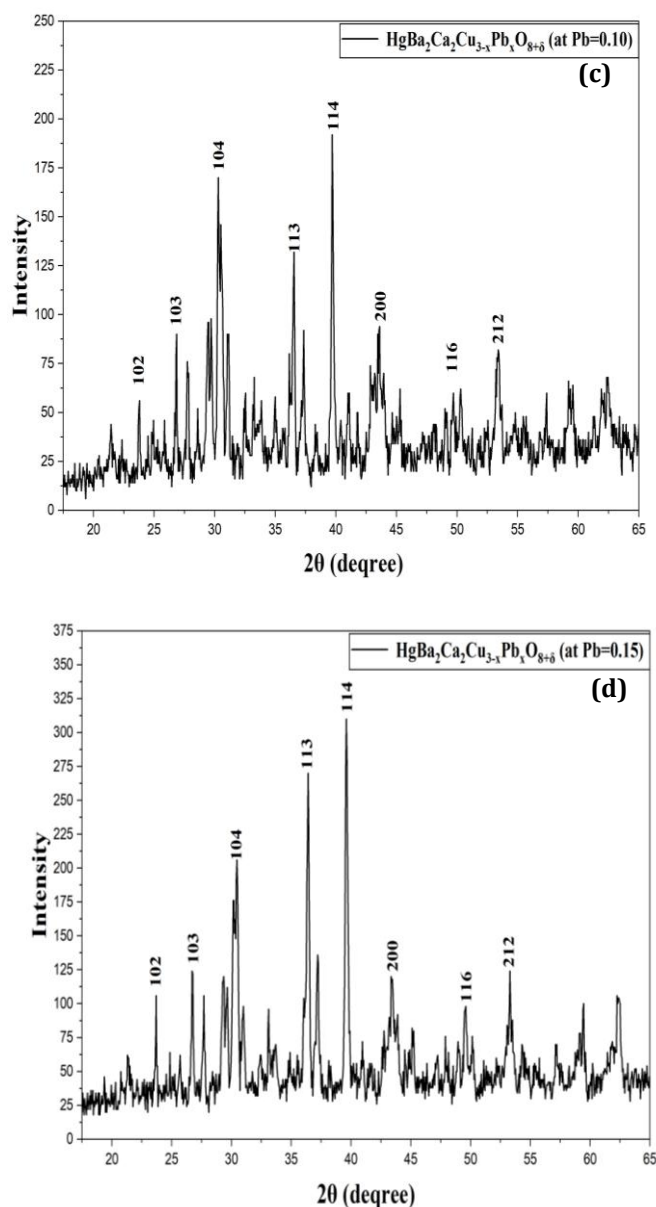
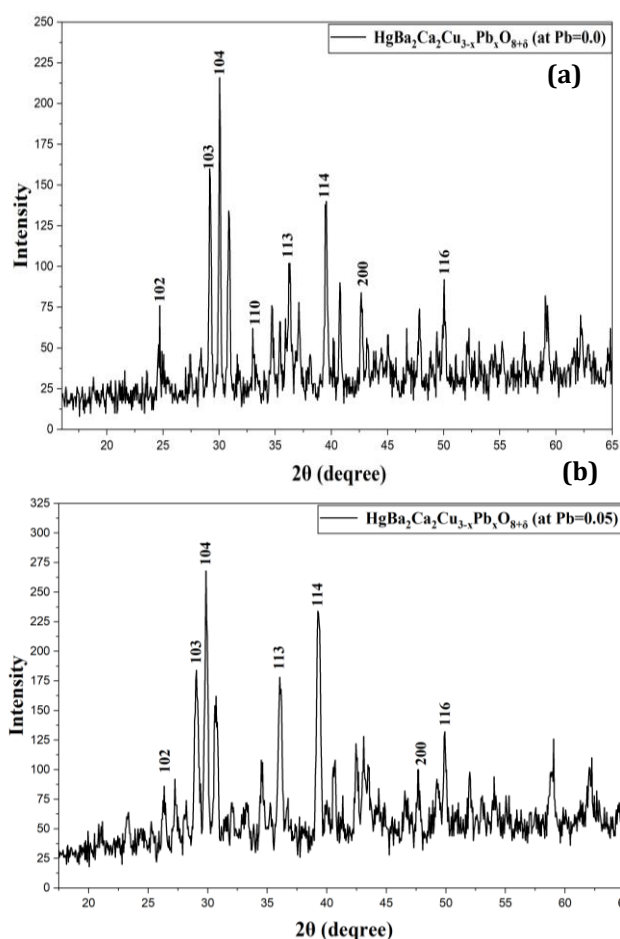


**Figure 2.** X-ray diffraction patterns of the  $\text{HgBa}_2\text{Ca}_2\text{Cu}_{3-x}\text{Nano-Pb}_x\text{O}_{8+\delta}$  superconductor samples with varying doping concentrations: (a)  $x = 0.00$ , (b)  $x = 0.05$ , (c)  $x = 0.10$ , and (d)  $x = 0.15$ . The main peaks are indexed to the tetragonal Hg-1223 phase standard (JCPDS 42-0051).

Furthermore, the quantitative phase analysis in Table 1 reveals a remarkable improvement in the phase purity of the synthesized samples, with the volume fraction of the main Hg-1223 phase (Vph) rising sharply from 57.10% in the undoped sample to 79.40% in the  $x = 0.15$  sample. Simultaneously, the secondary impurity phases decrease from 42.90% to 20.60%, which indicates that Nano-lead acts as a crucial stabilizing agent during the synthesis process. Scientific literature confirms that Nano-lead doping lowers the thermodynamic reaction barrier and stabilizes the stacking of the copper-oxide and mercury layers, thereby promoting the formation of the desired high- $T_c$  phase and suppressing the intergrowth of lower-order phases like Hg-1212 [24].

**Table 1.** Lattice parameters and phase volume fractions of the nano-Pb-substituted  $\text{HgBa}_2\text{Ca}_2\text{Cu}_{3-x}\text{Nano-Pb}_x\text{O}_{8+\delta}$  system.

| Sample (nano-Pb content) | Lattice Parameter a (Å) | Lattice Parameter c (Å) | c/a Ratio | Unit Cell Volume (V) | Main Phase (Vph) (Hg-1223) | Secondary/Impurity Phase | d(200) (Interatomic Dist.) |
|--------------------------|-------------------------|-------------------------|-----------|----------------------|----------------------------|--------------------------|----------------------------|
| x=0.00                   | 3.824                   | 15.25                   | 3.99      | 223.0Å <sup>3</sup>  | 57.10%                     | 42.90%                   | 1.912Å                     |
| x=0.05                   | 3.818                   | 15.43                   | 4.04      | 224.9Å <sup>3</sup>  | 63.90%                     | 36.10%                   | 1.909Å                     |
| x=0.10                   | 3.828                   | 15.53                   | 4.06      | 227.6Å <sup>3</sup>  | 72.00%                     | 28.00%                   | 1.914Å                     |
| x=0.15                   | 3.836                   | 15.49                   | 4.04      | 228.0Å <sup>3</sup>  | 79.40%                     | 20.60%                   | 1.918Å                     |

When the Scherrer method (Figure 3) is applied to the diffraction data, a relatively low correlation between crystallite size and peak broadening is obtained as indicated by the low values of coefficient of determination ( $R^2$ ) of between 0.013 and 0.179 among all the samples.

This approach is based on the assumption that it is only the finite size of crystallites that Nano-leads to the broadening of the peaks, omitting the effects of microstrain that are caused by lattice defects and ionic substitutions. The assumption is an insufficient one in the case of the  $\text{Hg}(\text{Ba}, \text{Nano-Pb})$ -1223 system, where Hg cations are replaced by Nano-Pb cations, Nano-leading to substantial lattice distortion because of the mismatch in the ionic radius of the two ions. The resulting dispersion of the linear plots indicates that the calculated crystallite size derived using the Scherrer equation with a range of 225 nm to 420 nm is possibly overestimated or inaccurate since they do not separate the strain broadening factor.

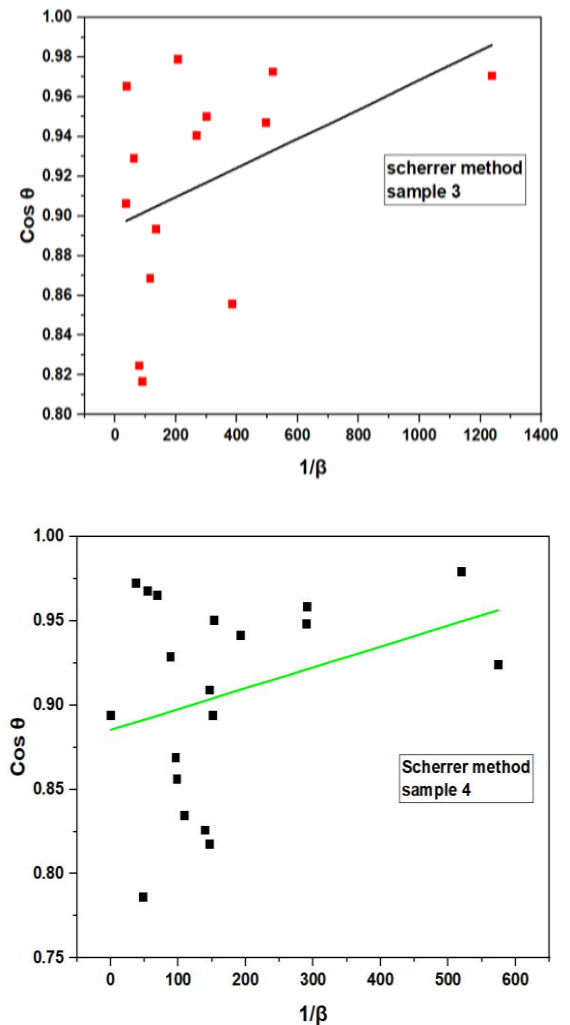
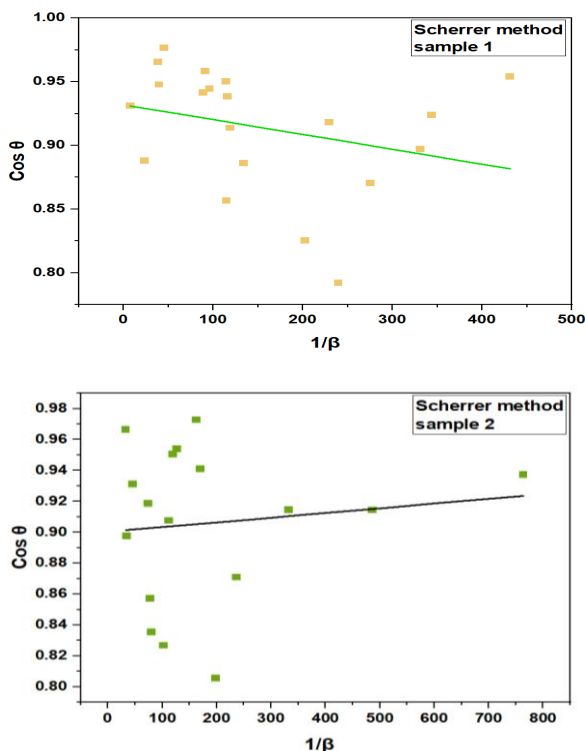


**Figure 3.** The Scherrer method for all samples.

In contrast, the Size-Strain Plot (SSP) method (Figure 4) demonstrates a superior fit to the experimental data, validating its suitability for strain-affected ceramic superconductors. The SSP plots of  $(d\beta\cos\theta)^2$  versus  $(d^2\beta\cos\theta)$  exhibit a high degree of linearity, with  $R^2$  values improving dramatically to between 0.79 and 0.95. The statistical analysis confirms that is in line with the statement that the maximum broadening in the specimens

considered is regulated by the joint effect of crystallite size and lattice strain and so a modelling structure and the assumptions are that a convolution between Gaussian and Lorentzian profiles takes place. In line with this thinking, crystallite sizes obtained through SSP method that are found to be around 154 nm to 273 nm are a more physically stringent estimate of the coherent scattering domains. The observation that sizes calculated by SSP are always smaller than those calculated by Scherrer analysis is consistent with the standard crystallographic theory because the removal of the strain term naturally lowers the domain size calculation. The observation that sizes calculated by SSP are always smaller than those calculated by Scherrer analysis is consistent with the standard crystallographic theory because the removal of the strain term naturally lowers the domain size calculation.

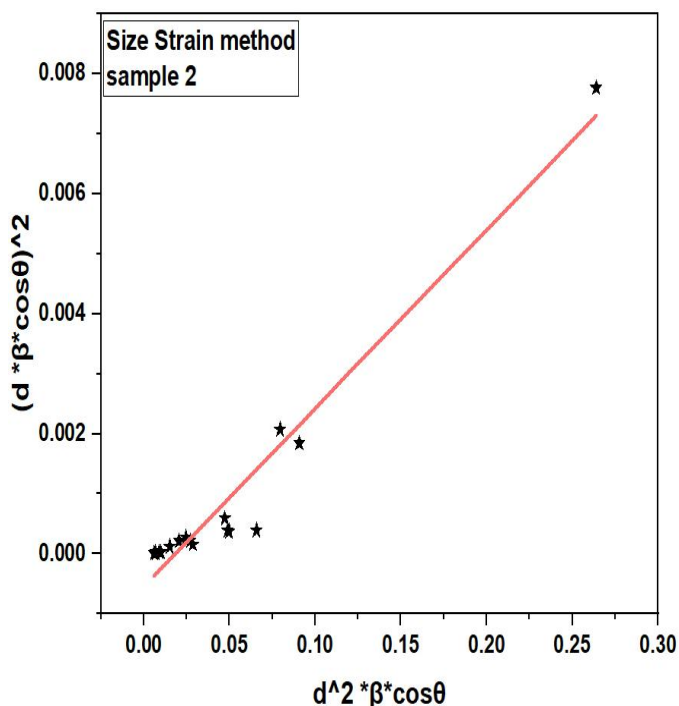
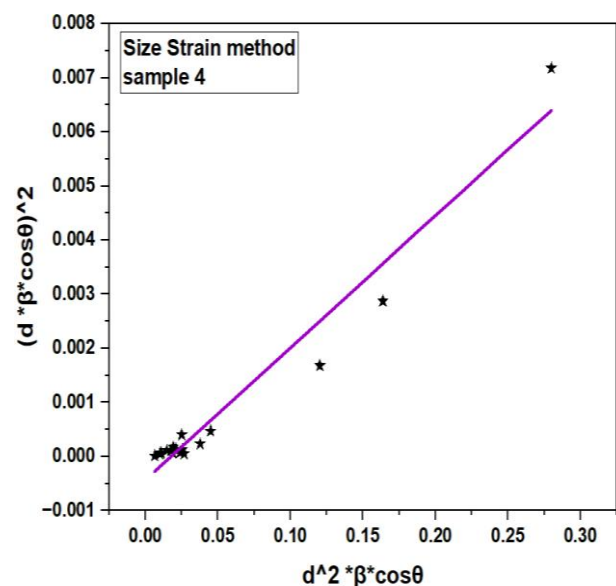
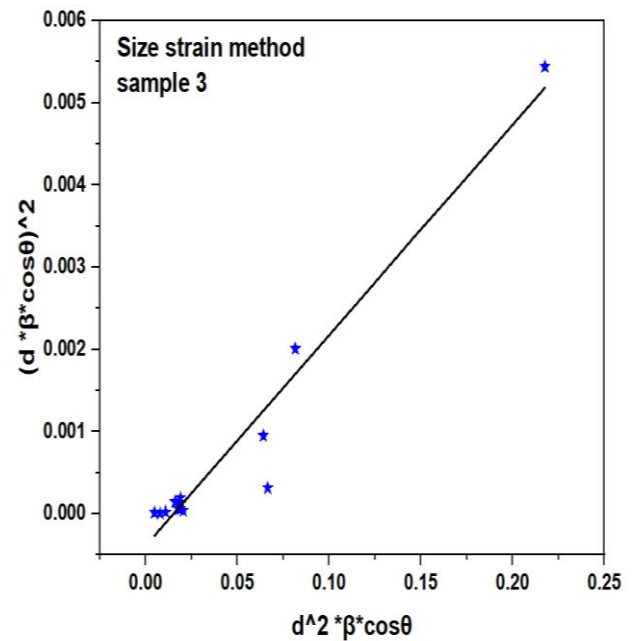
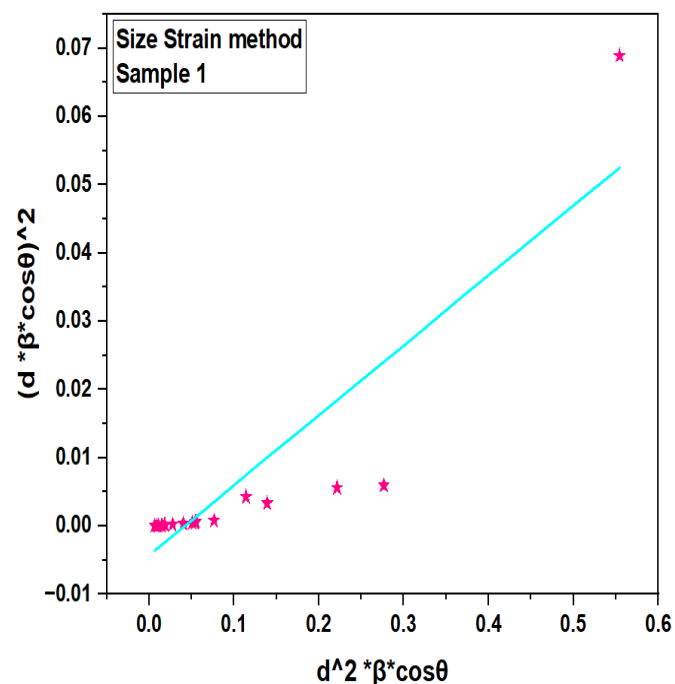


Figure 4. Size-strain method for all samples.

Furthermore, the influence of Nano-Pb doping on the crystallinity and grain growth of the Hg-1223 phase is evident from the quantitative data. The undoped sample ( $x=0.00$ ) exhibits a crystallinity of 55.68%, which increases markedly to 75.28% and 77.67% with Nano-Pb doping levels of  $x = 0.05$  and  $x = 0.15$ , respectively. This tendency implies that Nano-Pb replacement increases the kinetics of phase formation and stabilizes the crystal structure, likely reducing the volatility of Hg and promoting grain connectivity. The development in the crystal size is, however, non-monotonic; it rises to 154 nm in the pure sample, then reaches its highest point of 272 nm at  $x = 0.10$ , then becomes smaller to 165 nm at  $x = 0.15$ . This interaction suggests that there is a promotion of grain growth that is caused by favorable reaction thermodynamics and, thereafter, inhibition at a higher level of doping. Decrease in size at  $x = 0.15$  can be explained by the Zener pinning effect, whereby the surplus dopants or secondary phases form at the grain boundaries, preventing further movement of the grain boundaries.

**Table 2.** XRD analysis and crystallite size estimation (Scherrer vs. Size-Strain Plot method) for Hg-1223 with varying nano-Pb concentrations.

| NO. OF Sample                        | Sample 1                                                           | Sample 2                                                                                      | Sample 3                                                                                    | Sample 4                                                                                      |
|--------------------------------------|--------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|
| Compound                             | HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>3</sub> O <sub>8+δ</sub> | HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>2.95</sub> nano-Pb <sub>0.05</sub> O <sub>8+δ</sub> | HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>2.9</sub> nano-Pb <sub>0.1</sub> O <sub>8+δ</sub> | HgBa <sub>2</sub> Ca <sub>2</sub> Cu <sub>2.85</sub> nano-Pb <sub>0.15</sub> O <sub>8+δ</sub> |
| Area of Crystalline Peaks            | 394.3745                                                           | 728.0625                                                                                      | 322.287                                                                                     | 795.791                                                                                       |
| Area of all Peaks                    | 708.2712                                                           | 967.13145                                                                                     | 669.124                                                                                     | 1024.51335                                                                                    |
| Crystallinity                        | 55.681 %                                                           | 75.280 %                                                                                      | 48.165 %                                                                                    | 77.675 %                                                                                      |
| Average FWHM (Rad.)                  |                                                                    |                                                                                               |                                                                                             |                                                                                               |
| or                                   | 0.017448886 rad                                                    | 0.010755704 rad                                                                               | 0.009121876 rad                                                                             | 0.097469409 rad                                                                               |
| Average β (Rad.)                     |                                                                    |                                                                                               |                                                                                             |                                                                                               |
| Average d-spacing                    | 2.041483395                                                        | 2.025411644                                                                                   | 2.264618794                                                                                 | 2.141614592                                                                                   |
| Crystallite Size (D)                 |                                                                    |                                                                                               |                                                                                             |                                                                                               |
| By Scherrer Method                   | 225.958 nm                                                         | 283.033 nm                                                                                    | 420.121 nm                                                                                  | 255.201 nm                                                                                    |
| R-Square (COD) by Scherrer Method    | 0.08149                                                            | 0.01304                                                                                       | 0.17959                                                                                     | 0.10189                                                                                       |
| Intercept in Scherrer Method         | 0.93197 ± 0.01782                                                  | 0.90031 ± 0.01783                                                                             | 0.89465 ± 0.01907                                                                           | 0.88535 ± 0.02008                                                                             |
| Crystallite Size (D)                 |                                                                    |                                                                                               |                                                                                             |                                                                                               |
| By Size Strain Method                | 154.005 nm                                                         | 183.716 nm                                                                                    | 272.700 nm                                                                                  | 165.651 nm                                                                                    |
| R-Square (COD) by Size Strain Method | 0.79371                                                            | 0.95161                                                                                       | 0.94962                                                                                     | 0.95727                                                                                       |
| Intercept in Size Strain Method      | -0.00424*10 <sup>-4</sup> ± 0.00191*10 <sup>-4</sup>               | -5.44648*10 <sup>-4</sup> ± 1.31822*10 <sup>-4</sup>                                          | -3.89592*10 <sup>-4</sup> ± 1.16308*10 <sup>-4</sup>                                        | -4.33764*10 <sup>-4</sup> ± 1.15411*10 <sup>-4</sup>                                          |

### 3.2. Morphological Study

The Field Emission Scanning Electron Microscopy (FESEM) micrographs presented in Figure 5 (a–d) reveal a distinct evolution in the surface morphology and microstructure of the HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>Nano-Pb<sub>x</sub>O<sub>8+δ</sub> compound as the Nano-lead (Nano-Pb) concentration increases. The micrographs clearly indicate that a substitution of mercury with Nano-lead is one of the key elements to alter the granular structure and density of superconducting matrix. In the undoped sample with x = 0.00 (Figure 5a), morphology is that of rather porous structure with loosely packed grains and prominent voids. This is consistent with the structural

data that this sample has the lowest crystallinity of 55.68 % and large share of impurity phases, which typically hinder grain coalescence and Nano-lead to a less connected microstructure. With further increment in Nano-Pb doping level to x = 0.05 and x = 0.10 (Figures 5b and 5c), a gradual increase in the microstructure densification is recorded. The cavities are reduced, and the grains start to be more connected. According to this trend, the sintering process is made easier by the introduction of Nano-lead, probably through the reduction of the thermodynamic reaction barrier and as a flux which facilitates the fusion of the grains. This morphological enhancement is related to the X-ray diffraction analysis, which indicated that there was a

substantial increase in the crystallite size with a peak of about 272 nm at the  $x = 0.10$  doping percentage. It is essential that the porosity of these intermediate samples is reduced to increase the transport properties of the material, since it reduces the scattering centers, which normally increase the resistance to electron flow.

The most favorable morphology is observed in the sample with  $x = 0.15$  (Figure 5d), which exhibits a highly compacted surface with fused grains and minimal porosity. This dense microstructure corresponds to the highest recorded crystallinity of 77.67% and the highest volume fraction of the superconducting Hg-1223 phase at 79.40%. The strong granular bonding observed in these samples plays a crucial role in strengthening the weak links at grain boundaries, a key factor in sustaining superconductivity at high temperatures. This structural robustness perfectly matches and explains the electrical results, with this particular structure registering a high critical temperature ( $T_c$ ) of 130.48 K. Notably, although FESEM images of the sample at  $x = 0.15$  showed a very dense and cohesive structure, the crystal size calculated from the diffraction data actually decreased to about 165 nm compared to the sample at  $x = 0.10$ . The identified physical behavior can be explained by the Zener pinning phenomenon, in which a higher concentration of impurities or secondary phase constituents along grain-boundaries acts as a barrier and therefore inhibits excessive grain-boundary migration and produces a very compact microstructure with smaller, more uniformly distributed grains. This special combination of a high density and grain-size control is the essential part of increasing the phase stability and the material efficiency in terms of superconductivity functioning.

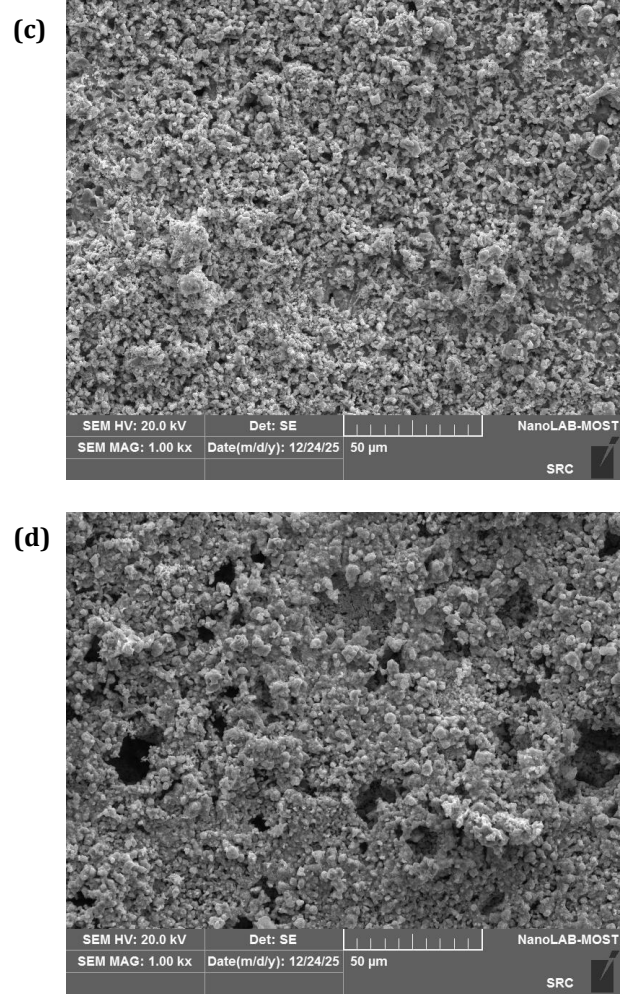
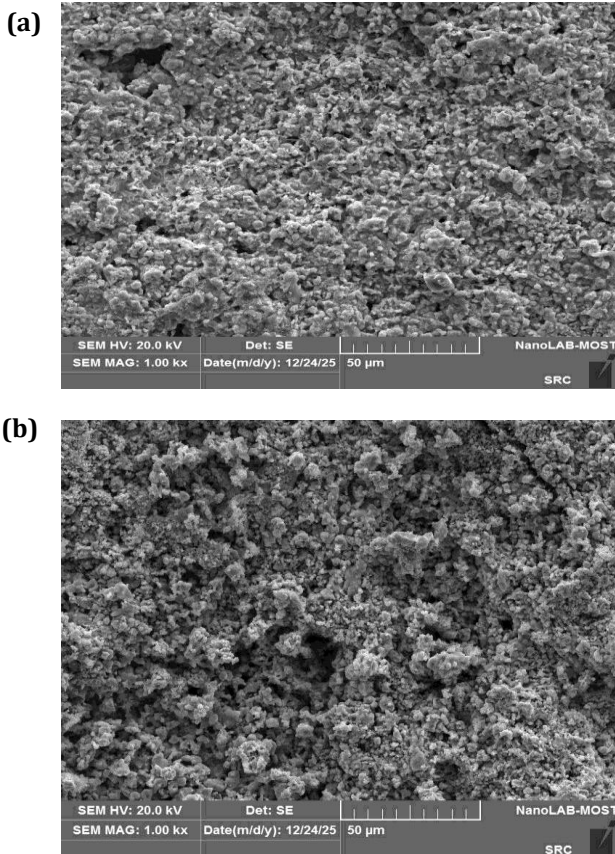


**Figure 5.** FESEM micrographs of HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3-x</sub>Nano-Pb<sub>x</sub>O<sub>8+δ</sub> HTSC samples at : a) at  $x = 0.00$ , b) 0.05, c) 0.10 and d) 0.15.

### 3.3. Electrical Transport Studies

The electrical resistivity measurements shown in Figure 6 exhibit non-monotonic behavior of the critical temperature ( $T_c$ ) with increasing Nano-lead doping concentrations. While the undoped sample ( $x = 0.00$ ) recorded a relatively high  $T_c$  value of 125.42 K, a significant decrease in this value was observed at the beginning of Nano-lead substitution in the sample ( $x = 0.05$ ), reaching 117 K. Interestingly, this temperature decrease occurred despite X-ray diffraction data confirming an increase in the volume proportion of the desired superconducting phase (Hg-1223) from 57.10% to 63.90%. This observation is consistent with what has been reported in the scientific literature, which suggests that although Nano-lead plays a role in stabilizing the Hg-1223 phase, it may complicate the transition to superconductivity during the initial substitution stages [20]. Following this initial drop, the critical temperature ( $T_c$ ) systematically rose to 122.5 K at  $x = 0.10$ , reaching a maximum of 130.48 K at  $x = 0.15$ . To explain the unusual decline in  $T_c$  at  $x = 0.05$ , when the critical temperature dropped in spite of a general enhancement in the phase purity, the complicated balance between the stability of crystallography and the concentration of charge carriers should be considered. The density of charge carrying holes ( $p$ ) in the conductive CuO<sub>2</sub> planes is indisputably the main determinant of  $T_c$  in cuprate superconductors. This

dependence is in the face of a parabolic relationship, and there is an actual optimal doping level in which the  $T_c$  would be maximum [25, 26].

The original addition of Nano-lead at  $x = 0.05$  would probably interfere with the electronic balance of the substance. The Nano-lead, although it serves as a stabilizer of the crystal lattice enhancing the crystal Hg-1223 phase formation at the expense of the impurity phases, also changes the valence and oxygen stoichiometry ( $\delta$ ) of the charge reservoir layers [27, 28]. It is scientifically likely that in this particular low concentration the substitution moved the hole carrier density out of the optimum of that of the undoped sample. This electronic disorder briefly dominates the advantages of the higher structural phase purity Nano-leading to the measured decrease to 117 K. But with the Nano-lead content increasing even higher to  $x = 0.10$  and  $x = 0.15$  the system breaks through this electronic barrier. The volume percentage of the superconducting phase would be at its highest point at  $x = 0.15$  at 79.40% and the microstructure would be very dense and connected as observed in the FESEM results. At this increased doping regime, the system probably restores a positive oxygen stoichiometry, returning the carrier concentration to the optimal regime. The highest  $T_c$  of 130.48 K is therefore the combination of a synergistic effect, the high purity of the superconducting phase and the better inter-grain connectivity that enables supercurrent flow [29] and an optimized electronic state.

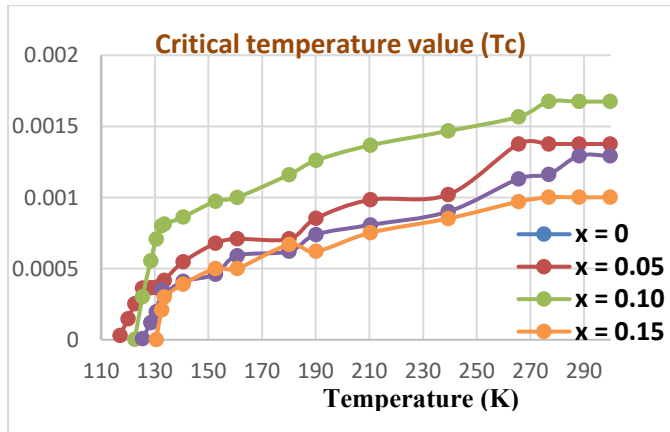


**Figure 6** Temperature dependence of electrical resistivity for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_{3-x}\text{Nano-Pb}_x\text{O}_{8+\delta}$  HTSC samples at : a) at  $x = 0.00$ , (b)  $x = 0.05$ , (c)  $x = 0.10$ , and (d)  $x = 0.15$ .

Compared to recent literature on Hg-based high-temperature superconductors, the synergistic enhancement observed at  $x = 0.15$  confirms that optimizing the hole carrier concentration through nano-Pb substitution directly mitigates electronic disorder. While previous studies highlighted structural stabilization, our findings demonstrate that the densified microstructure, driven by optimized nano-Pb content, minimizes grain-boundary weak links. This dual mechanism intragrain electronic balance and intergrain microstructural connectivity explains the significant recovery and enhancement of the transition temperature ( $T_c$ ).

## CONCLUSION

This study successfully synthesized high-temperature superconducting samples of the nominal composition  $\text{HgBa}_2\text{Ca}_2\text{Cu}_{3-x}\text{Nano-Pb}_x\text{O}_{8+\delta}$  via the solid-state reaction technique to investigate the impact of Nano-lead substitution on phase stability and superconducting properties. X-ray diffraction (XRD) analysis confirmed that all samples crystallized in the tetragonal Hg-1223 phase, identifying a monotonic expansion of the unit cell volume driven by the ionic radius mismatch between the host and dopant cations. Quantitative phase analysis demonstrated a remarkable enhancement in phase purity, with the volume fraction of the high- $T_c$  Hg-1223 phase increasing from 57.10% in the undoped sample to 79.40% at  $x = 0.15$ . Additionally, the Size-Strain Plot (SSP) method proved statistically superior to the Scherrer method for crystallite size estimation by effectively decoupling lattice strain. Morphological characterization using Field Emission Scanning Electron Microscopy (FESEM) revealed that Nano-Pb doping significantly promoted microstructural densification and grain connectivity, thereby reducing porosity. The evaluation of electrical resistivity showed a non-monotonic behavior in the critical transition temperature ( $T_c$ ). The initial suppression at  $x = 0.05$  was due to electronic disorder and modifications of carrier concentration, and greater doping concentrations recovered and enhanced superconductivity. Based on this, the specimen with  $x = 0.15$  reached a peak  $T_c$  of 130.48 K, and the result was attributed to the combined effect of maximized phase purity and increased inter-grain connectivity. Despite the significant improvements achieved, this study has certain limitations. The primary challenge remains the toxicity and handling requirements of the precursor materials (Hg and Pb), which necessitate strict, enclosed environments for synthesis. Future research should focus on investigating the long-term environmental stability of the nano-Pb doped samples and their superconducting response under varying external magnetic fields.

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