The Synthesis of Pb2Sr2Sm1-xCaxCu3O8 AND Characterization of its Structural and Superconducting Properties.

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ABSTRACT

THE SYNTHESIS OF Pb₂Sr₂Sm₁₋ₓCaₓCu₃O₈ AND CHARACTERIZATION OF ITS STRUCTURAL AND SUPERCONDUCTING PROPERTIES

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Northern Illinois University 2020
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Superconducting lead-based cuprate materials of the 2213 structural type, Pb₂Sr₂MCu₃O₈ (M=Sm₁₋ₓCaₓ, Y₁₋ₓCaₓ, Er₁₋ₓCaₓ and Yb₁₋ₓCaₓ), were synthesized and characterized using x-ray powder diffraction and the Rietveld structural refinements method. Pb₂Sr₂Sm₁₋ₓCaₓCu₃O₈ single crystals were grown by an optimized flux method using various combinations of PbO/PbF₂ solvents. Samples with different Sm/Ca ratios were investigated for their superconducting properties. Magnetic measurements reveal the presence of a transition at 120K. Preliminary x-ray diffuse scattering experiment at the Advanced Photon Source of Argonne National Laboratory demonstrates the high quality of one of our crystals and the presence of rod-like diffuse scattering connecting the Bragg peaks in the direction of the reciprocal c-axis.
THE SYNTHESIS OF Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$ AND CHARACTERIZATION OF ITS STRUCTURAL AND SUPERCONDUCTING PROPERTIES

BY

DEBLINA DAS
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A THESIS SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE MASTER OF SCIENCE

DEPARTMENT OF PHYSICS

Thesis Director:
Dr. Omar Chmaissem.
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DEDICATION

My parents and husband, Kallol, who kept me stronger
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CHAPTER 1
INTRODUCTION

1.1 Superconductivity

Superconductivity is a phenomenon that certain systems display below a characteristic critical transition temperature, $T_C$, with the materials losing their electrical resistance and expelling any magnetic fields they might be subjected to. Superconductivity was first observed in 1911 by Kamerlingh-Onnes and his graduate student when they noticed the vanishing resistivity of mercury when cooled below the boiling point of helium (4.2K). Dismissing this observation at first as erroneous, Kamerlingh-Onnes repeated the experiment multiple times until he became convinced that the state of zero resistance is a real intrinsic property of mercury and that he has just discovered a previously unknown electrical phase which he termed superconductivity [1]. In 1913, Kamerlingh-Onnes received the Nobel Prize in Physics for his discovery [1,2].
1.2 Theoretical Developments of Superconductivity

Several theoretical models were proposed to explain the unusual properties of superconductors. Below, I will summarize some key concepts of the theory of superconductivity.

1.2.1 Meissner effect

At temperatures above $T_C$, magnetic fields can penetrate through the superconducting material as they do with any normal metal, but not when the material is cooled to below $T_C$. In 1933, Meissner and Ochsenfeld [3] proposed that magnetic fields are expelled from the interior of a superconductor
because of the existence of surface electric currents shielding its interior. Meissner and Ochsenfeld concluded that the magnetic field lines pass around the superconductor’s surface instead of through it. This phenomenon has become known as the Meissner effect.

![Figure 1.2: Arrows in the figure represent magnetic field lines penetrating through (left) or expelled from the inside of a generic superconductor at temperatures above and below $T_C$, respectively [4].](image)

Depending on how and when superconductivity breaks down under the application of external magnetic fields, superconductors are classified into two categories, type I and type II. Type I superconductors refer to materials in which superconductivity is abruptly suppressed above a critical magnetic field $H_c$. Type II superconductors, on the other hand, exhibit two different critical magnetic fields, namely $H_{c1}$ and $H_{c2}$. In a type-II superconductor, once the field exceeds the first critical value $H_{c1}$ the magnetic flux starts to creep through the material. If the magnetic field is further increased, the penetrating magnetic flux density gradually increases with the material remaining superconducting until reaching $H_{c2}$ above which superconductivity is destroyed. Type-I superconductors are mostly simple elements such as lead (Pb), Zinc (Zn), Tin (Sn), etc., while Type-II superconductors consist of zero resistance alloys and compounds with complex magnetic characters. [3,5-8]
1.2.2 BCS Theory

The premise of the theory of superconductivity starts with net attractive interactions between the electrons at the Fermi surface. Cooper showed that in the presence of Fermi sphere with additional electrons the exclusion principle alters the two-electron problem which results in the possible existence of bound states despite their weak attraction [9]. Electron pairs, acting like bosonic particles, that form through this mechanism are known as Cooper pairs. The bound electrons would remain paired if their binding energy is stronger than the lattice thermal vibration energy required to break them apart. As a result, currently known superconductors operate at low temperatures where the lattice thermal vibrations are small enough to allow the formation and persistence of the Cooper pairs [10].

Later in 1957, a pioneering team, Bardeen, Cooper and Schrieffer, from the University of Illinois, successfully conceived a theoretical model (famously known as the BCS theory) which describes the microscopic mechanics of superconductivity. Superconductors that can be explained by this theory are classified as conventional superconductors which can be either Type I or Type II. The BCS theory describes how phonons mediate the formation of Cooper pairs with the two coupled electrons having opposite spins and momenta. Cooper pairs condensate into a coherent macroscopic ground state where they can move with zero resistance through the superconducting crystal without any significant loss of momentum or energy [10,11].

Many experimental observations gave support to the BCS theory. A Fermi surface band gap was demonstrated to change, in agreement with the theory, in the vicinity of critical temperatures and critical magnetic fields along with an exponential decay of the heat capacity below $T_c$. The Fermi surface band gap in conventional superconductors is in clear contrast with
the gapless Fermi surface of regular metals. The BCS theory predicts the band gap width in Type I superconductors as $E_g \sim \frac{7}{2} kT_C$ where $T_C$ is the critical temperature and $k$ is the Boltzmann’s constant [12-13].

Another key result of the BCS theory relates to nuclear mass variations and the isotope effects. By studying the superconducting properties of materials synthesized using different isotopes of the same element, $T_C$ was determined to be inversely proportional to the square root of the nuclear mass with a phonon frequency $\sqrt{\frac{k}{M}}$. These studies led to cementing the role of phonons as a key ingredient in the formation of Cooper pairs [14-15].

With the success of the BCS theory in explaining superconductivity and placing an upper $T_C$ limit of about 30 K, the problem of superconductivity was thought of as a low temperature physics phenomenon. The $T_C$ cap dampened enthusiasm and all research efforts for the next couple of decades until the discovery, in early 1980’s, of high temperature superconductivity (High-$T_C$) in a novel family of copper-based superconducting oxides (known as Cuprates). High-$T_C$ Cuprates are unconventional superconductors with a complex multigap Fermi surface that the BCS theory fail to explain.
1.3 Development of Unconventional Superconductors

Time evolution of superconductors is shown in Figure 1.2. Despite all efforts, the critical temperature of superconductors remained lower than 20 K for a long time. Niobium-Germanium (Nb$_3$Ge), discovered in 1973, retained the next $T_C$ record of 23.2 K for about 13 years until 1986.

![Figure 1.3: Materials with record superconducting transition temperatures as a function of time, showing BCS superconductors, high-temperature Cuprate superconductors and Iron-based superconductors. Image credit: B Glowacki, Taming high-temperature superconductivity (CERN courier 11 August 2017).](image-url)
In April 1986, Bednorz and Müller [16-17] reported superconductivity below 35 K in a new perovskite copper-based ceramic oxide, namely La$_{2-x}$Ba$_x$CuO$_4$. It was the first member of a novel class of unconventional high-$T_C$ superconductors with the next two decades witnessing the discovery of many derivative compounds leading to a record $T_C = 133$ K for HgBa$_2$Ca$_2$Cu$_3$O$_{6+\delta}$ [18] at ambient pressure and 164 K under high pressure [19].

In 1987, two teams led by Wu of the University of Alabama and Chu of the University of Houston joined forces and discovered superconductivity in YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) with a critical temperature of 93K. It was the first superconductor with a transition temperature above the boiling temperature of liquid nitrogen (77 K), which was an extraordinary accomplishment [20]. Liquid nitrogen, being easily accessible and much cheaper than liquid helium, made the exploration of new superconducting materials easier for scientists worldwide.

Attempts to explore the YBCO system quickly led to the development of other superconducting and non-superconducting derivative materials. Alibadi et al. [21], for example, were able to isolate a new phase, namely Y$_3$Ba$_5$Cu$_8$O$_{18}$ (Y-358), with a maximum $T_C$ of 102K. Unlike YBCO, the structure of this phase contains five CuO$_2$ planes and two CuO chain layers. Derivative Y-358 materials were also fabricated with Y replaced by rare earth elements like Sm and Nd, for example [22], with superconducting transition temperatures of 97.5 K, 97 K and 95 K for RE$_3$Ba$_5$Cu$_8$O$_{18}$ samples where RE=Y, Sm and Nd, respectively.

Cuprate superconductors ruled for the next two decades following their discovery, and it was not until 2006 that a novel family of superconductors based on iron was discovered. Iron-pnictide superconductors are layer structures of either FeAs or FeP. Iron-based superconductors started their journey with the observation of superconductivity at 4 K in LaOFeP [23]. Great
interest has been drawn to this superconducting system with the report of $T_c$ as high as 26 K in LaFeAsO$_{1-x}$F$_x$ by Kamihara et al. [24]. It was not long until Takahashi et al. [25] proved the effectiveness of a 4 GPa pressure to raise the transition temperature of this material to 43K. Soon after, Chen et al. [26] reported the discovery of bulk superconductivity in a similar material with La replaced by Sm, SmFeAsO$_{1-x}$F$_x$, with a similar high transition temperature of 43K. Soon after, $T_c$ as high as 55 K was reported for SmFeAsO$_{1-x}$F$_x$ at ambient pressure [27-28]. In a related development, Rotter et al. [29] reported the discovery of superconductivity up to 38 K in (Ba$_{1-x}$K$_x$)Fe$_2$As$_2$ (122 structure) where superconductivity depends on the potassium doping level. Later, Rotter’s group worked with charge neutrally doped BaFe$_2$(As$_{1-x}$P$_x$)$_2$ achieving critical temperatures up to 30 K [30]. Another superconducting iron arsenide system, LiFeAs (111), has been reported by Wang et al. [31] with a $T_c$ up to 18 K. In the iron chalcogenides, on the other hand, FeSe (11 family) exhibits a $T_C$ of 8 K as reported by Hsu et al. [32]. Since then, many more complex derivative superconducting families have been discovered as in the 17K superconducting (Fe$_2$P$_2$)(Sr$_4$Sc$_2$O$_6$) system which consists of alternating stacks of anti-fluorite Fe$_2$P$_2$ and perovskite-based Sr$_4$Sc$_2$O$_6$ oxide layers [33]. Superconductivity with a high transition temperature of 37.2 K has been achieved in (Sr$_4$V$_2$O$_6$)(Fe$_2$As$_2$) system [34]. Another new layered iron arsenide oxide (Fe$_2$As$_2$)(Ca$_4$(Mg,Ti)$_3$O$_y$) has been discovered by Ogino et al. [35] with a $T_C$ of 43K.

The quest of reaching room temperature superconductivity remains a hot topic. The application of high pressures is perhaps one of very few effective methods proven to enhance superconductivity. For example, subjecting a sample of sulfur hydride to a 90 GPa pressure induces a sharp drop in resistivity with a superconducting transition temperature of 203K [36]. The higher $T_C$ might have resulted from the decomposition and transformation of H$_2$S to H$_3$S under high pressure which is corroborated by further calculations [37-38]. While we’re still far from
achieving our ultimate goal of room temperature superconductivity at ambient pressures, recent reports of superconductivity in LaH$_{10}$ at 250 K under geological pressures (170 GPa) give us hope that one day, hopefully soon, the right composition may be found capable of supporting superconductivity at even higher temperatures all the way to 300 K and beyond [39]. Tremendous progress has been made in a field that was once thought of as dead.

1.4 Superconductivity in PSYCCO

Superconductivity in the Pb$_2$Sr$_2$(Y$_{1-x}$Ca$_x$)Cu$_3$O$_{8+y}$ system (PSYCCO) was first discovered by Cava et al. in 1988 [40]. When the trivalent Y cations are replaced by divalent Ca cations, PSYCCO becomes superconductive. In this PSYCCO structure, oxygen deficient CuO$_6$ chain layers are sandwiched between two pyramidal PbO bilayers and produce anisotropic physical properties. Compared to other superconducting structures like YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO), PSYCCO exhibits a somewhat lower superconducting transition temperature peaking at ~80 K but it exhibits a great chemical flexibility which makes it suitable for in-depth investigations of the relationship between its crystalline structure and superconducting mechanism and properties [41].

In 1989, Capponi et al. [42] produced several Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_{8+\delta}$ samples with various oxygen contents and investigated the oxidization properties of the materials by isothermal thermogravimetric analysis measurements. Further characterizations by x-ray and electron diffraction demonstrated that for the x=0 sample, the upper limit for $\delta$ is about 1.9 oxygen atom per unit formula. When oxidization is performed at low temperature, the single-phase material
appears to be orthorhombic but when the process is repeated at higher temperature of 450°C and above, the x-ray patterns were indexed on a tetragonal unit cell basis. Electron diffraction analysis later confirmed that the compound remains orthorhombic. Several samples with $\delta$ ranging between 0 and 1.8 were prepared and analyzed. A miscibility gap was found in samples within the $\delta=0$ to 1 oxygen content range with the observation of two PSYCCO phases distinguished only by a slight change in their unit cell c-parameters ($c=15.835\,\text{Å}$ and $15.725\,\text{Å}$). It is also reported that the elongated $a_p$ parameter correlates with the Cu$^{2+}$O square chain formation as previously seen in YBa$_2$Cu$_3$O$_{7-\delta}$. In Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_{8+\delta}$, the oxidation process involves the partial conversion of Pb$^{2+}$ into Pb$^{4+}$ which makes the process more complicated.

On the other hand, a comparative study, performed by Marezio et al. [43], of the structure and properties of PSYCCO and YBCO demonstrated that the oxygen uptake in PSYCCO is detrimental to superconductivity while it is an essential ingredient for achieving superconductivity in YBCO. In an as-made Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_{8+\delta}$ sample with a transition temperature $T_C$ of 78K, superconductivity was fully suppressed after oxygenation. Interatomic bond-lengths analysis suggests that the pyramidal Pb$^{2+}$ and the monovalent Cu$^{1+}$ ions in the oxygen depleted parent material become octahedrally (partially) and squarely coordinated, respectively, with copper converting fully to divalent Cu$^{2+}$ while the Pb$^{2+}$ cations partially convert to Pb$^{4+}$ as they oxidize. The authors reported that the data strongly suggest a highly distorted PbO layers in which two polyhedral coordination coexist, one is suitable for the lone pair Pb$^{2+}$ and another for Pb$^{4+}$. The study explains that oxidization is accompanied by charge localization in the Pb sublattice which in turns reduces the mobility of the electron holes, preventing them from moving towards the
superconducting CuO\textsubscript{2} layers. This process suppresses the superconductivity. Charge localization is supported by electron diffraction data as well.

In a similar manner, Chaillout et al. [44,45] described the structure of Pb\textsubscript{2}Sr\textsubscript{2}YC\textsubscript{u}O\textsubscript{8} as a sequence of layers in which Y and Cu\textsuperscript{1+} (chain layer sandwiched between two PbO layers) are both oxygen depleted. Due to the low oxidation state of Cu, the oxygen depleted parent material does not superconduct. After oxidization, extra positive charge carriers are introduced but they become localized and trapped by the Pb sublattice. On the other hand, doping with divalent Ca\textsuperscript{2+} at the trivalent Y\textsuperscript{3+} site in the oxygen depleted material induces superconductivity below 80K by increasing the average oxidation state of Cu in the pyramidal CuO\textsubscript{2} layers. The extra carriers oxidize Cu\textsuperscript{2+} to Cu\textsuperscript{3+} in the CuO\textsubscript{2} planes instead of converting Pb\textsuperscript{2+} to Pb\textsuperscript{4+}. Chaillout and coworkers explained this process as the result of a proximity effect due to (Y,Ca) being located between two adjacent CuO\textsubscript{2} layers. Heating an oxygenated non-superconducting Pb\textsubscript{2}Sr\textsubscript{2}Y\textsubscript{1-x}Ca\textsubscript{x}Cu\textsubscript{3}O\textsubscript{8+δ} material to 450°C in N\textsubscript{2} re-induce superconductivity. Chaillout and coworkers conclude that Cu\textsuperscript{1+} and Pb\textsuperscript{2+} cations are partially oxidized in oxygenated Pb\textsubscript{2}Sr\textsubscript{2}Y\textsubscript{0.5}Ca\textsubscript{0.5}Cu\textsubscript{3}O\textsubscript{8+δ} to Cu\textsuperscript{2+} and Pb\textsuperscript{4+}, respectively. Due to this unfavorable oxidation, extra charges are required to complete the oxidation of Pb and Cu chains which get pulled from the superconducting CuO\textsubscript{2} layers to the (PbO)(Cu)(PbO) reservoir block. As a result, superconductivity is suppressed by this charge transfer.

Neutron, x-ray and electron diffraction measurements were carried out by Marezio et al. [46] to study the relationship between superconductivity and structure for several Pb\textsubscript{2}Sr\textsubscript{2}Y\textsubscript{1-x}Ca\textsubscript{x}Cu\textsubscript{3}O\textsubscript{8+δ} samples. As in the famous YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-δ} analogs, oxygen was observed to occupy the same empty sites in the Cu chain layer. The oxidation of some Pb\textsuperscript{2+} cations to 4+ was
found to lead to cationic ordering of Pb$^{2+}$ and Pb$^{4+}$ which impedes the charge transfer to the conducting (CuO$_2$) planes, consequently, no superconductivity is induced in the oxidized samples.

J.S Xue et al. [47] reported the successful growth of high quality Pb$_2$Sr$_2$(R/Ca)Cu$_3$O$_{8+y}$ single crystals using seed crystals in PbO-NaCl flux. The authors reported that controlled oxygen partial pressure is key to achieving good crystals with the desired compositions. NaCl flux was observed to lower the eutectic temperature of the PbO-PSYCCO system and to encapsulate the melt during growth; thus, providing a barrier between the melt and the surrounding atmosphere. As a result, NaCl appears to relax the stringent atmospheric conditions that are otherwise needed for crystal growth in the absence of NaCl.

Single crystals of Pb$_2$Sr$_2$(Y$_{1-x}$Ca$_x$)Cu$_3$O$_{8+δ}$ have been synthesized from PbO-NaCl and PbO-KCl flux by Kriebel et al. [48]. To find optimal growth conditions, different temperatures were tested. It was shown that large size crystals are produced when a temperature gradient of 5K is applied carefully using oxygen partial pressure of 3% balanced with nitrogen for a duration of at least 3-4 weeks of single crystal growth. Low mosaicity and well-defined lattice constants were confirmed by neutron diffraction experiments. Very good cationic homogeneity with a lateral resolution of 15 nm to 1 μm was observed by high resolution energy dispersive x-ray (EDX) measurements. In order to achieve high transition temperatures, several Y/Ca ratios were attempted with Pb$_2$Sr$_2$(Y$_{0.67}$Ca$_{0.33}$)Cu$_3$O$_z$ providing the best results.

Magnetization measurements of a Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_8$ single-crystal were carried out by Reedyk et al. [49] in magnetic fields up to 1.5 T and a temperature range between 5 and 250 K. The authors observe sharply defined diamagnetic transitions at $T_c$ with the field oriented perpendicular to the c-axis. Broader transition onsets were observed with the magnetic field
applied parallel to the c-axis with diamagnetism fluctuations persisting to temperatures above \( T_c \). To extract the temperature dependence of the in-plane upper critical field, magnetization in the vicinity of \( T_c \) for various field strengths were analyzed, \( H_{c2} \) near \( T_c \).

To summarize, superconducting PSYCCO single crystals exhibit higher critical temperatures when grown in PbO-NaCl flux. The oxygen incorporation induces positive charges to oxidize the Cu\(^{1+}\) cations to 2\(^+\) and some of the Pb\(^{2+}\) cations to 4\(^+\). The formation of Cu\(^{2+}\) and Pb\(^{4+}\) hampers the charge transfer from the reservoir block to the conducting CuO\(_2\) planes, consequently, no superconductivity is induced in the oxidized samples.

1.5 Motivation

While studying the literature for \( \text{Pb}_2\text{Sr}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8 \) (PSRCCO where \( R = \text{Y or rare earth elements} \)), I noticed that most of the work was dedicated to PSYCCO (R=Y). Very limited studies reported the synthesis of this system with other rare earth elements. This is particularly true when searching for \( \text{Pb}_2\text{Sr}_2\text{Sm}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8 \) (R = Sm). Our interest in samarium stems from its proven success in boosting superconductivity in the pnictide superconductors. Therefore, the goal of this thesis was to synthesize PSRCCO samples (R = rare earth) in powder form and to grow single crystal of PSSCCO (R = Sm). Magnetic and structural properties of the synthesized samples were investigated. X-ray scattering data have shown structural properties not seen in the literature, to the best of our knowledge. The grown crystals are planned for advanced diffuse scattering measurements at the Advanced Photon Source at Argonne National Laboratory. Preliminary
measurements show great promise of unusual structural properties that necessitate further investigations beyond the scope of this thesis.

1.6 Outline of Thesis

Crystal structure properties of Pb$_2$Sr$_2$R$_{1-X}$Ca$_X$Cu$_3$O$_8$ and the charge transfer mechanisms will be presented in Chapter 2. Material preparation, measurement techniques and special consideration of reactants and their behavior is presented in Chapter 3. Experimental results, analysis and discussions will be presented in Chapter 4. In Chapter 5, conclusions are drawn together with suggested future work building on my findings.
CHAPTER 2
BACKGROUND

2.1 Structure of Pb$_2$Sr$_2$R$_{1-x}$Ca$_x$Cu$_3$O$_8$ and Charge Transfer Mechanism

![3D representation of Pb$_2$Sr$_2$R$_{1-x}$Ca$_x$Cu$_3$O$_8$ structure using VESTA software](image)

<table>
<thead>
<tr>
<th>Site</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td></td>
</tr>
<tr>
<td>R (Y or Sm)</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.1: Pb$_2$Sr$_2$R$_{1-x}$Ca$_x$Cu$_3$O$_8$ structure in 3D representation using VESTA software [49].
The Pb$_2$Sr$_2$RCu$_3$O$_8$ (where R represents Y or any lanthanoid or a mixture of Y/lanthanoid with Ca) family of superconductors is promising because of its flexible structural framework allowing a wide range of cation solid solutions together with a tunable oxygen stoichiometry [40,44-47,51]. This family of materials forms for all the lanthanoid elements and crystallizes in a common structure [52]. Using x-ray and neutron diffraction data, the parent structure of this family has been determined as being orthorhombic with the symmetry of Cmmm space group. Electron microscopy measurements performed by Zandbergen et al. [53] confirmed the structure of Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_8$ in agreement with the neutron and x-ray results proposed by Cava et al. [54].

The structure of Pb$_2$Sr$_2$R$_{1-x}$Ca$_x$Cu$_3$O$_8$ can be described as a sequence of layers where the lanthanoid ions are sandwiched between two CuO$_2$ layer. The crystal structure consists of sheets stacked along the c-axis in the following sequence: (CuO$_2$)$_c$ (R)$_o$ (CuO$_2$)$_c$ (SrO)$_o$ (PbO)$_c$ (Cu)$_c$ (PbO)$_o$ (SrO)$_o$ (CuO$_2$)$_c$ (R)$_o$ (CuO$_2$)$_c$ where the subscripts o and c show whether the cation on each slice is situated on the origin or the center of the sheet. In this structure, the Y and Cu layers are oxygen depleted. A common characteristic of these superconductors is that Cu in the (CuO$_2$) (SrO) blocks form corner sharing CuO$_5$ pyramids. The Sr cations are surrounded by 9 oxygen atoms whereas the Y cations are coordinated with 8 oxygen atoms existing in the CuO$_2$ layers above and below. The Pb cations are surrounded by 5 oxygen atoms in a pyramidal configuration. Due to the lone pair Pb$^{2+}$ electrons, Pb-O distances order over a long range and give rise to the observed orthorhombic distortion [44-47,51,53].

The undoped Pb$_2$Sr$_2$YCu$_3$O$_8$ compound is non-superconducting. As mentioned in Chapter 1, the addition of extra positive charges by oxidizing the Cu chain layer does not induce superconductivity because the extra positive charges transferred from the (CuO$_6$) layers to the (PbO) layers do not reach the conduction layers (CuO$_2$). The distortion of the structure, as well as
charge localization on the (PbO) layers reduce the mobility of electron holes preventing them from reaching the conduction (CuO\(_2\)) layers and hence the compound remains non superconducting [44-47,51,53].

On the other hand, Pb\(_2\)Sr\(_2\)YCu\(_3\)O\(_8\) can be made superconducting by the partial replacement of trivalent Y with divalent Ca cations. The process suggests that electron holes formed on the (Y/Ca) layer are transported to the CuO\(_2\) conduction neighboring layers. Doping of the lanthanoid site with Ca oxidizes some Cu\(^{2+}\) ions into Cu\(^{3+}\) or to Cu\(^{2+}\) instead of oxidizing Pb\(^{2+}\) to Pb\(^{4+}\). As such the average oxidation state of Cu becomes larger than 2+ and the material becomes superconducting [44-47,51,53].

Crystal structure of a material is studied using the x-ray diffraction method. Diffraction data provide invaluable information the analysis of which can help us understand the crystal structure and its relationship with the magnetic and superconducting properties of the material. Here, a basic overview of x-ray diffraction is introduced to understand the experiments and analysis performed in this thesis.

2.2 X-ray Diffraction Mechanism

An electromagnetic radiation is diffracted when the spacing in a grating is on the same order of magnitude as the incident wavelength. The interatomic spacings in a crystal are comparable to common in-house x-ray’s wavelengthwhichmakesitsuitablefor diffraction and investigations of the crystal structure. X-ray diffraction can be simply described as an elastic scattering of the x-
ray photons by a periodic array of atoms in a crystal. Bragg’s law states that constructive interference occurs when x-rays reflect from parallel lattice planes separated by distance spacing \( d \) with a path length difference \( 2d \sin\theta \) (where \( \theta \) is the angle of incidence) equivalent to integer multiple of the x-ray’s wavelength [10].

\[
n\lambda = 2d\sin\theta \quad \ldots \ldots (1)
\]

This relation was first formulated in 1913 by physicists Sir W.H. Bragg and his son Sir W.L. Bragg and is known as Bragg’s law. The amplitude of a scattered electromagnetic wave is-

\[
F = \int dV n(r) e^{i(\Delta k \cdot r)} \quad \ldots \ldots (2)
\]

where \( \Delta k = k - k' \) is the difference between the incident and scattered \( k \) and \( k' \) wavevectors, \( e^{i(k-k').r} \) is the difference in phase factor and the amplitude of the wave scattered from a volume element is proportional to the local electron concentration \( n(r) \).

When the Fourier component \( n(r) = \sum_G n_G e^{iG \cdot r} \) is placed in equation (2) then we end up with the expression of scattering amplitude as

\[
F = \sum_G \int dV n_G e^{i(G - \Delta k) \cdot r} \quad \ldots \ldots (3)
\]

where the summation is over reciprocal lattice points \( G \), the integral is over the sample volume, \( n_G \) is the electron density at a specific \( G \), \( \Delta k = k - k' \) is the difference between the wave vector of incident and scattered radiation and \( r \) is a point in real space. The reciprocal lattice vector \( G = h b_1 + k b_2 + l b_3 \) which defines a point \((hkl)\) on the reciprocal lattice with \( b_1, b_2, \) and \( b_3 \) being unit vectors along the reciprocal lattice axes. In the case of elastic scattering condition, \( |k| = |k'| \) and the Bragg scattering from a periodic lattice is \( \Delta k = G \) which lead us to the equation of the form
This equation serves as the diffraction condition and it is satisfied when for a given \( G \) there is only one \( k \) for which constructive interference occurs. When the orientation of a large number of crystals is randomly distributed as in the case of a polycrystalline sample, the diffraction condition for a given reciprocal lattice vector with a magnitude \( |G|/2 \) will satisfy the equation (4) and constructive interference must occur giving rise to a diffraction peak [10].

The scattering of x-rays from periodically arranged atoms gives rise to a diffraction pattern which contains information that can be used to understand the material’s periodicity or its structure. Different softwares are used to analyze the data and extract the relevant results, fit the profile, calculate the lattice parameters etc. In this thesis, powder x-ray diffraction is carried out for all the samples synthesized in the laboratory. To analyze the collected x-ray powder diffraction (XRD) data, EXPGUI interface [55] to the General Structural Analysis System (GSAS) [56] was used.
CHAPTER 3
MATERIALS SYNTHESIS

3.1 Special Considerations

To avoid contaminations, experimental equipment such as mortars and pestles, were thoroughly cleaned in a 50% HCl solution before each synthesis step. After drying, the equipment was wiped with acetone to remove any remaining dust or oil residue. It is important to repeat the same procedure before each experiment.

3.2 Powder Synthesis: Solid State Reaction

At first, Pb₂Sr₂M₁₋₅CaₓCu₃O₈ (M=Y) powder samples were prepared from an appropriate mixture of high purity powders of PbO (99.9%), SrCO₃ (99.99%), Y₂O₃ (99.99%), Ca₂CO₃ (99.99%) and CuO (99.99%). The powders were thoroughly mixed and homogenized then placed in an alumina boat (Al₂O₃) for heat treatment in a Lindberg furnace and a flowing gas of high purity nitrogen. The furnace was ramped to 850°C in about 12 hours and the M=Y powders were annealed at this temperature for an additional 12 hours period before cooling slowly to room temperature. X-ray diffraction was performed immediately after synthesis.
The same procedure was followed to prepare additional mixtures of Pb$_2$Sr$_2$M$_{1-x}$Ca$_x$Cu$_3$O$_8$ with M = Er, Yb and Sm. High purity Er$_2$O$_3$ (99.99%), Yb$_2$O$_3$ (99.99%) and Sm$_2$O$_3$ (99.99%) precursor materials were used. While samples with M= Y, Yb and Er formed easily at 850°C, we found that the M=Sm sample melts at this temperature. Several temperatures were then tested until determining that 725°C produce the desired Sm-based 2213 structures. Repeated annealing was necessary to produce black powders with the best properties. The annealed precursors were ground and homogenized before each annealing. Samples were checked with x-rays after each annealing to verify phase formation and purity. Data were collected in the angular range from 5 to 100 degrees using a Rigaku Dmax diffractometer. The collected data were analyzed using GSAS and EXPGUI software suite [55, 56].

3.3 Single Crystal Growth: Flux Method

A second goal of my research work focuses on the growth of high-quality single crystals using the flux method. The synthesized Pb$_2$Sr$_2$M$_{1-x}$Ca$_x$Cu$_3$O$_8$ (M = Sm) materials were mixed with PbO and PbF$_2$ in different ratios. In our first attempt, we used the same conditions, see Table 3.1, reported by Chaillout at el. [44,45] for the growth of Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_8$ single crystals at temperatures of about 980°C. While this method appears to work fine with the M=Y version of this family, our M=Sm batch boiled violently with most of the materials spilling out into an alumina tray holding the crucible. Nonetheless, this attempt provided some valuable information regarding the temperature and flux requirements for Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$. 
Table 3.1

Experimental Condition

<table>
<thead>
<tr>
<th>Crystal Growth Attempt</th>
<th>Sm/Ca ratio</th>
<th>PbO:PbF&lt;sub&gt;2&lt;/sub&gt; ratio</th>
<th>Temperature (°C)</th>
<th>Cooling time in °/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.5/0.5</td>
<td>2:0.5</td>
<td>980</td>
<td>3</td>
</tr>
</tbody>
</table>

After the first unsuccessful outcome, the flux ratio and temperature profile were systematically changed to find the optimal experimental conditions. Select attempted experimental conditions are shown in Table 3.2.

Table 3.2

Experimental Conditions

<table>
<thead>
<tr>
<th>Crystal Growth Attempt</th>
<th>Sm/Ca ratio</th>
<th>PbO:PbF&lt;sub&gt;2&lt;/sub&gt; ratio</th>
<th>Temperature (°C)</th>
<th>Cooling time in °/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>0.5/0.5</td>
<td>1:0.25</td>
<td>900</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>0.5/0.5</td>
<td>2:0.5</td>
<td>900</td>
<td>2</td>
</tr>
<tr>
<td>IV</td>
<td>0.5/0.5</td>
<td>3:0.5</td>
<td>900</td>
<td>2</td>
</tr>
<tr>
<td>V</td>
<td>0.5/0.5</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
</tr>
<tr>
<td>VI</td>
<td>0.6/0.4</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
</tr>
<tr>
<td>VII</td>
<td>0.7/0.3</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
</tr>
<tr>
<td>VIII</td>
<td>0.8/0.2</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
</tr>
</tbody>
</table>
3.4 MPMS

To determine the critical superconducting transition temperatures of our samples, measurements were performed using a quantum design magnetic properties measurement system (MPMS). Powder samples and single crystals were measured in a weak magnetic field of 200 Oe at temperatures between 4K and 150 K.
CHAPTER 4
RESULTS AND DISCUSSIONS

4.1: Structural Characterization using X-Ray Diffraction

Phase formation and phase purity of our synthesized powder samples have been determined using x-ray diffraction at room temperature. Systematic analyses of the data were performed using Rietveld structural refinement techniques as implemented in the General Structure and Analysis Suite program (GSAS) [56]. Fig. 4.1 displays a best-fit Rietveld refinement of the parent Pb$_2$Sr$_2$Y$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ (PSYCCO) material. As shown in the figure, a relatively phase pure sample was successfully produced with the structure refined using the orthorhombic space group Cmmm [54]. An orthorhombic structure is expected for samples prepared under reducing conditions, like ours, indicative of an overall oxygen content of 8.0 atoms per unit formula. Orthorhombic PSYCCO samples are superconducting [40] while those annealed in oxygen are tetragonal and non-superconducting [46] with an oxygen content exceeding 9.0 atoms per unit formula.
Figure 4.1: Rietveld refinement pattern for Pb$_2$Sr$_2$Y$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$. Collected intensities are represented by the plus sign (+) while the solid blue line represents a calculated pattern using an orthorhombic space group Cmmm structural model.

With the data in figure 4.1 serving as a reference pattern, a direct comparison of all x-ray patterns collected for Pb$_2$Sr$_2$Y$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$, Pb$_2$Sr$_2$Yb$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$, Pb$_2$Sr$_2$Er$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ and Pb$_2$Sr$_2$Sm$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ demonstrates the successful formation of the desired (2213) phase in all the samples, Figure 4.2. The quality of the samples is similar to those reported in the literature for similar 2213 phases although the patterns also show trace amounts of extra intensities (more significant for the M = Yb sample) that the main phase fail to index. Table 4.1 lists the refined unit cell parameters and unit cell volume for the various samples. Lattice parameters obtained in this work agree with those published in the literature [47,58].
Figure 4.2: XRD patterns of powder samples containing different rare earth elements (a) Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_8$, (b) Pb$_2$Sr$_2$Yb$_{1-x}$Ca$_x$Cu$_3$O$_8$, (c) Pb$_2$Sr$_2$Er$_{1-x}$Ca$_x$Cu$_3$O$_8$, (d) Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$. 
Table 4.1 Refined unit cell lattice parameters and unit cell volume for Pb$_2$Sr$_2$M$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ (where M = Yb, Er, Y and Sm). The average ionic radius refers to that of the M/Ca-site. Ionic radii used in this study are taken from R.D Shannon [57].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Ionic Radius (Å)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Volume(Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$<em>2$Sr$<em>2$Yb$</em>{0.5}$Ca$</em>{0.5}$Cu$_3$O$_8$</td>
<td>1.0525</td>
<td>5.373(2)</td>
<td>5.413(2)</td>
<td>15.753(4)</td>
<td>458.1(4)</td>
</tr>
<tr>
<td>Pb$<em>2$Sr$<em>2$Er$</em>{0.5}$Ca$</em>{0.5}$Cu$_3$O$_8$</td>
<td>1.062</td>
<td>5.3670(1)</td>
<td>5.410(1)</td>
<td>15.740(1)</td>
<td>457.0(1)</td>
</tr>
<tr>
<td>Pb$<em>2$Sr$<em>2$Y$</em>{0.5}$Ca$</em>{0.5}$Cu$_3$O$_8$</td>
<td>1.0695</td>
<td>5.376(1)</td>
<td>5.414(1)</td>
<td>15.739(2)</td>
<td>458.1(1)</td>
</tr>
<tr>
<td>Pb$<em>2$Sr$<em>2$Sm$</em>{0.5}$Ca$</em>{0.5}$Cu$_3$O$_8$</td>
<td>1.0995</td>
<td>5.413(1)</td>
<td>5.452(2)</td>
<td>15.734(3)</td>
<td>464.3(2)</td>
</tr>
</tbody>
</table>

Figure 4.3 Dependence of the lattice parameters $a$, $b$ and $c$ on the ionic radius, $<r_{M/Ca}>$, of Pb$_2$Sr$_2$M$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ where M = Yb, Er, Y and Sm.
Plotting the lattice parameters as a function of the average $\mathbf{M/Ca}$ ionic radius $<r_{M/Ca}>$, Figure 4.3, reveals linear trends with the $a$ and $b$ parameters increasing slightly while the $c$-axis decreases upon increasing $<r_{M/Ca}>$ in agreement with similar results reported by Xue et al. [47]. Figure 4.4 shows the unit cell volume expanding up to 1.6% upon increasing $<r_{M/Ca}>$ because of the oppositely changing $a$ and $b$ (increasing) and $c$ (decreasing) lattice parameters.

![Graph showing evolution of unit cell volume of Pb$_2$Sr$_2$M$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ with respect to average ionic radius $<r_{M/Ca}>$.](image)

Figure 4.4 Evolution of the unit cell volume of Pb$_2$Sr$_2$M$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ where M = Yb, Er, Y and Sm with respect to the average ionic radius $<r_{M/Ca}>$.

Noticing the relative high purity of Sm and Er-based samples, we now focus our attention on the synthesis of a series of Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$ (PSSCCO) powder samples with varying Sm/Ca content ($0.2 \leq x \leq 0.5$). The choice of this under-investigated Sm-based system was made because of the rich chemistry of Sm having variable oxidation states and low
temperature magnetic properties. Unlike Y which can only be trivalent and non-magnetic, Sm\(^{2+}\), Sm\(^{3+}\) and Sm\(^{4+}\) with different magnetic properties could be stabilized, thus, providing us with an additional tuning knob that can be explored to manipulate the charge transfer mechanism in PSSCCO and its impact on the competing superconducting and magnetic properties of the targeted compositions. Synthesis of the samples with different Ca ratios required significant adjustment of the temperature between 550\(^\circ\)C and 800\(^\circ\)C. Repeated grinding and annealing were helpful, but no additional efforts were made to ensure higher purity of all the samples because they will be used as precursors and melted to grow single crystals.

Once again, the orthorhombic space group Cmmm has proven successful in describing the structure of all the samples in this series. With x-rays being insensitive to oxygen especially in the presence of heavy elements like Pb and Sm, no attempts were made to extract meaningful bond-lengths or bond-angles. However, the refinements were used to establish the successful incorporation of Ca in increasing amounts at the Sm site. Refined unit cell lattice parameters and unit cell volume are listed in Table 4.2 and plotted in Figures 4.6-4.7.
Figure 4.5: X-ray diffraction patterns of powder samples containing different amounts of Sm and Ca: (a) Pb$_2$Sr$_2$Sm$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$, (b) Pb$_2$Sr$_2$Sm$_{0.6}$Ca$_{0.4}$Cu$_3$O$_8$, (c) Pb$_2$Sr$_2$Sm$_{0.7}$Ca$_{0.3}$Cu$_3$O$_8$, and (d) Pb$_2$Sr$_2$Sm$_{0.8}$Ca$_{0.2}$Cu$_3$O$_8$. 
Table 4.2 Refined unit cell lattice parameters and unit cell volume for Pb$_2$Sr$_2$ACu$_3$O$_8$ (where A = Sm$_{0.5}$Ca$_{0.5}$, Sm$_{0.6}$Ca$_{0.4}$, Sm$_{0.7}$Ca$_{0.3}$ and Sm$_{0.8}$Ca$_{0.2}$). Ionic radii used in this study are taken from R.D Shannon [57].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Ionic Radius (Å)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>Volume(Å$^3$)</th>
</tr>
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<td>5.464(2)</td>
<td>15.760(6)</td>
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</tr>
<tr>
<td>Pb$<em>2$Sr$<em>2$Sm$</em>{0.7}$Ca$</em>{0.3}$Cu$_3$O$_8$</td>
<td>1.0913</td>
<td>5.421(2)</td>
<td>5.461(2)</td>
<td>15.756(5)</td>
<td>466.4(4)</td>
</tr>
<tr>
<td>Pb$<em>2$Sr$<em>2$Sm$</em>{0.6}$Ca$</em>{0.4}$Cu$_3$O$_8$</td>
<td>1.0954</td>
<td>5.422(3)</td>
<td>5.463(4)</td>
<td>15.750(9)</td>
<td>466.6(7)</td>
</tr>
<tr>
<td>Pb$<em>2$Sr$<em>2$Sm$</em>{0.5}$Ca$</em>{0.5}$Cu$_3$O$_8$</td>
<td>1.0995</td>
<td>5.413(1)</td>
<td>5.452(2)</td>
<td>15.734(3)</td>
<td>464.3(2)</td>
</tr>
</tbody>
</table>

Figure 4.6: Dependence of the lattice parameters a, b and c on the average ionic radius $r_{A/Ca}$ for Pb$_2$Sr$_2$(A/Ca)Cu$_3$O$_8$ where A/Ca = Sm$_{0.5}$Ca$_{0.5}$, Sm$_{0.6}$Ca$_{0.4}$, Sm$_{0.7}$Ca$_{0.3}$ and Sm$_{0.8}$Ca$_{0.2}$. 
Figure 4.7: Evolution of the unit cell volume as a function of increasing the average ionic radius $r_{A/Ca}$ for Pb$_2$Sr$_2$(A/Ca)Cu$_3$O$_8$ where A/Ca = Sm$_{0.5}$Ca$_{0.5}$, Sm$_{0.6}$Ca$_{0.4}$, Sm$_{0.7}$Ca$_{0.3}$ and Sm$_{0.8}$Ca$_{0.2}$.

The graph in figure 4.6 shows that the lattice parameters a and b are nearly constant (slightly decreasing) while c is decreasing with increasing the average ionic radius of the M-site in Pb$_2$Sr$_2$ACu$_3$O$_8$. This observation is opposite the behavior observed by Koike et al. [58] for their Ca-substituted Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_8$ series. Curiously, the unit cell volume of our Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$ series decreases upon increasing the average ionic size of the A/Ca (Sm$_{1-x}$Ca$_x$) site, Fig. 4.7. This counterintuitive observation can be explained as follows:

1. The increasing substitution of divalent Ca$^{2+}$ at the samarium site results in a linear shrinking of the unit cell volume. Assuming that the oxidation state of Sm is 2+, only steric effects
would be expected by the isovalent substitution of larger Ca\textsuperscript{2+} at the Sm\textsuperscript{2+} sites. Thus, one would expect an expanding rather than shrinking unit cell volume.

2. Since the unit cell is shrinking, we conclude that additional charges are added to the structure by the Ca substitution and that these charges are oxidizing the nearby Cu\textsuperscript{2+} pyramids into smaller Cu\textsuperscript{3+} which in turn can shrink the lattice. As such, the oxidation of copper compensates for and overweights the competing lattice expansion, expected from Ca doping, with the overall result being a smaller unit cell.

Introduction of additional charges in our system can be accomplished if the oxidation state of Sm is 3+ or 4+. Sm\textsuperscript{4+} can be ruled out because a simple charge balancing of the equation demonstrates that the oxygen content would have to be more than 8.0 per formula unit if the material were to be superconducting, as observed. For example, the charge balance for Pb\textsubscript{2}Sr\textsubscript{2}Sm\textsubscript{0.5}Ca\textsubscript{0.5}Cu\textsubscript{3}O\textsubscript{8} would be (2 x 2+) + (2 x 2+) + (0.5 x 4+) + (0.5 x 2+) + (1 x 1+) + (2 x v(Cu)) = 16; where v(Cu) is the oxidation state of Cu in the CuO\textsubscript{2} layers. This equation indicates that v(Cu) = 2+ and the material would not superconduct, in disagreement with the magnetic measurements made on single crystals of the same composition. In this exercise, we assumed the oxidation states of pyramidal Pb, Sm and Cu in the chain layer (in a linear dumbbell configuration with copper bonded with two oxygen atoms) to be 2+, 4+ and 1+, respectively. We also assumed that the oxygen content is 8.0 in agreement with the orthorhombic structure of the materials. Any additional oxygen would randomly oxidize part of the pyramidal Pb\textsuperscript{2+} ions into Pb\textsuperscript{4+}; thus, suppressing the lone pairs of Pb\textsuperscript{2+} and converting the corresponding pyramids into smaller octahedra. Therefore, PSSCCO materials with oxygen contents larger than 8.0 would be tetragonal and not superconducting which is not what we observe.
3. Finally, we can conclude that Sm is trivalent (Sm\(^{3+}\)) in this structure similar to the oxidation state of Y in Pb\(_2\)Sr\(_2\)Y\(_{1-x}\)Ca\(_x\)Cu\(_3\)O\(_8\). Charge transfer mechanism would be similar, and the extra charges added by Ca\(^{2+}\) substitution at the Sm\(^{3+}\) site would increase the average oxidation state of Cu in the CuO\(_2\) layers to above 2+; thus, making it superconducting. A simple recalculation of the charge balance equation \((2 \times 2+) + (2 \times 2+) + (0.5 \times 3+) + (0.5 \times 2+) + (1 \times 1+) + (2\times v(Cu)) = 16\) using Sm\(^{3+}\) instead of Sm\(^{4+}\) results in an average \(v(Cu) = 2.25^+\). Sm\(^{3+}\) is known to exhibit magnetic properties in structures with similar oxygen coordination. A strong competition would then be expected between the magnetic and superconducting order parameters on the adjacent Sm and Cu sublattices.

4.2: Single Crystal Growth of Pb\(_2\)Sr\(_2\)Sm\(_{1-x}\)Ca\(_x\)Cu\(_3\)O\(_8\)

Single crystal growth was performed using the flux method. Appropriate amounts of the pre-made PSSCCO powders were added to mixtures of PbO and PbF\(_2\) powders serving as flux. On our first attempt, using conditions successfully employed for Y-based 2213 (PSYCCO), the sample boiled violently and reacted with the surrounding quartz tube of the furnace which resulted in breaking it. All reactions were carried out in a fume hood. This experiment indicated that the melting point of Sm-based 2213 (PSSCCO) must be significantly lower than that of the Y-based analogs. Changes were made accordingly to the PbO:PbF\(_2\) flux ratio and to the maximum growth temperature. Several attempts were made as detailed in Table 4.3 with the best crystals obtained at a relatively low temperature of \(\sim 900^\circ\)C along with slow cooling rates. Crystals were successfully grown with PSSCCO precursors containing no less than 30\% Ca at the Sm site. Most
of the crystals were squarish or rectangular thin platelets as shown in Figure 4.9. Crystals as large as ~1mm x 1mm x 0.2 mm were grown with the short dimension being the crystal’s c-axis. Crystals suitable for x-ray single crystal diffraction of about 0.3 mm to 0.6 mm each side were abundant. The Sm/Ca ratio of 0.8/0.2 batch yielded very small crystals of poor visual quality.

Table 4.3

<table>
<thead>
<tr>
<th>Run</th>
<th>Sm/Ca ratio</th>
<th>PbO:PbF₂ ratio</th>
<th>Temperature (°C)</th>
<th>Cooling time in °/hr</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.5/0.5</td>
<td>2:0.5</td>
<td>980</td>
<td>3</td>
<td>No crystal growth</td>
</tr>
<tr>
<td>II</td>
<td>0.5/0.5</td>
<td>1:0.25</td>
<td>900</td>
<td>2</td>
<td>No crystal growth</td>
</tr>
<tr>
<td>III</td>
<td>0.5/0.5</td>
<td>2:0.5</td>
<td>900</td>
<td>2</td>
<td>No crystal growth</td>
</tr>
<tr>
<td>IV</td>
<td>0.5/0.5</td>
<td>3:0.5</td>
<td>900</td>
<td>2</td>
<td>Few crystal growth</td>
</tr>
<tr>
<td>V</td>
<td>0.5/0.5</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
<td>Good crystal growth</td>
</tr>
<tr>
<td>VI</td>
<td>0.6/0.4</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
<td>Good crystal growth</td>
</tr>
<tr>
<td>VII</td>
<td>0.7/0.3</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
<td>Good crystal growth</td>
</tr>
<tr>
<td>VIII</td>
<td>0.8/0.2</td>
<td>3:0.5</td>
<td>900</td>
<td>1.5</td>
<td>Poor quality of crystal growth</td>
</tr>
</tbody>
</table>
Figure 4.8: Images of various Pb$_2$Sr$_2$Sm$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ single crystals with dimension (a) 1.3 mm*1.3 mm, (b) 0.65 mm*0.43 mm, (c) 0.8 mm*1.2 mm, (d) 0.93 mm*1.3 mm

Figure 4.9: (a) and (b) Images of Pb$_2$Sr$_2$Sm$_{0.6}$Ca$_{0.4}$Cu$_3$O$_8$ single crystals having the dimension as 0.27 mm*0.33 mm, (c) and (d) Images of Pb$_2$Sr$_2$Sm$_{0.7}$Ca$_{0.3}$Cu$_3$O$_8$ single crystals having the dimension as 0.41 mm*0.46 mm and 0.39 mm*0.44 mm
4.3 Magnetic Measurements

Using a quantum design magnetic properties measurement system (MPMS), the superconducting properties and critical transition temperatures of some representative crystals were measured. The magnetic properties of a few crystals are presented in this section.

![Figure 4.10: MPMS result of single crystal of Pb$_2$Sr$_2$Sm$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$.](image)

The diamagnetic properties of two different crystals from the same batch Pb$_2$Sr$_2$Sm$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$ were tested. The crystals were selected such that one is much larger than the other in order to probe for possible sample inhomogeneity. As shown in Fig. 4.10 (raw non-normalized data), both crystals are superconducting with a $T_C$ of ~ 50K. Indeed, the superconducting transitions are wide indicative of some sample inhomogeneity with the larger
crystal exhibiting a pronounced second transition at about 30K. Additional measurements were made on various crystals from the different batches as shown in Figs. 4.11 and 4.12.

Figure 4.11: MPMS result of single crystal of Pb$_2$Sr$_2$Sm$_{0.6}$Ca$_{0.4}$Cu$_3$O$_8$.

Figure 4.12: MPMS result of single crystal of Pb$_2$Sr$_2$Sm$_{0.7}$Ca$_{0.3}$Cu$_3$O$_8$. 
Figures 4.11 and 4.12 show the magnetic properties for two crystals extracted from the Pb$_2$Sr$_2$Sm$_{0.6}$Ca$_{0.4}$Cu$_3$O$_8$ and Pb$_2$Sr$_2$Sm$_{0.7}$Ca$_{0.3}$Cu$_3$O$_8$ batch. In addition to the superconducting transition expected below ~80 K (here ~50 K), we observed a weak magnetic signal below about 12 K which can be attributed to the magnetic ordering of the Sm sublattice. Intriguingly, we also observe a superconducting-like transition at ~ 120 K for both crystals. We note, however, that the magnetic signal is very small, and that this result could be due to secondary filamentary inclusions in the crystal. More investigative work is needed to optimize the growth conditions of single crystals in this compositional range. I hope that the results I obtained and presented in my thesis would serve as the backbone for future work by other students in Dr. Chmaissem’s group.
CHAPTER 5
CONCLUSIONS AND FUTURE WORK

5.1: Conclusions

Through this research, I investigated the various synthesis conditions that lead to the successful formation of one of the most complex stoichiometries in the field of materials science and solid-state physics and chemistry. The synthesis of materials consisting of 6 elements as in our Pb₂Sr₂Sm₁₋ₓCaₓCu₃O₈ system, for example, necessitates the use of stringent conditions in order to avoid the more stable and simpler to form binary compositions and perovskite-based by-products (e.g., SrPbO₃, SrCuO₂ₓ+ₓ, etc). Samarium has proven challenging because it wouldn’t form with high enough quality unless the synthesis temperature is significantly lowered. As shown in this work, I successfully fabricated several compositions using different rare earth elements and investigated the effects of ionic size on their properties using x-ray diffraction and the Rietveld structural refinements method. Of these materials, Er and Sm-based materials were identified as very promising candidates for further investigations. Several single crystal batches were attempted using various Sm/Ca ratios and flux compositions until best growth conditions were achieved. Rectangular or squarish single crystal platelets were produced with the two long crystal edges measuring about 0.3 - 1 mm. The short crystal’s axis, typically about 0.1 0.2 mm, is in the direction of the c-axis. It’s worth noting that the size of these crystals is ideal for x-ray scattering measurements at the Advanced Photon Source at Argonne National Laboratory.
While the superconducting properties of our crystals generally agree with those observed with similar materials (e.g., PSYCCO with R = Y or other rare earth elements), we obtained crystals that exhibit peculiar superconducting-like transitions at ~120 K. Unfortunately, the weak signal of these crystals does not allow us to make a firm conclusion regarding the exact nature of this high transition temperature and whether the crystals are truly superconducting or not. Further investigations are needed with crystals grown in large enough sizes to optimize the superconductivity signal and render the samples suitable for resistivity and specific heat measurements and neutron diffraction.

5.2 Future Work

To better understand the relationship between superconductivity, magnetism and structure, the growth of large crystals of the highest quality is a must. Bigger crystals would enable the collection of quality neutron data from which one can separate the magnetic reflections from the nuclear ones and better understand the influence of Sm on the local structure and the mechanism of the competing magnetic and superconducting order parameters within the same material.

Our Pb$_2$Sr$_3$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$ crystals were primarily grown using flux compositions consisting of PbO, PbF$_2$, CuO, NaCl, or a mixture of those. Although successful, we believe that other flux combinations or growth techniques must be attempted to achieve the ultimate goal of large neutron
size crystals of the highest structural and superconducting qualities. For example, the literature demonstrates that the use of seed crystals in conjunction with PbO/NaCl flux composition produce significantly bigger Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_8$ crystals [47]. The same method was repeated for Pb$_2$Sr$_2$Er$_{1-x}$Ca$_x$Cu$_3$O$_8$ by the same researchers resulting in crystals twice as large. In that study, seed crystals were dropped into the crucible at a temperature below the melting point. The authors demonstrate that the seed method does not affect the quality of the superconducting properties. I would like to think that the large number of small crystals I produced in this study can be used as seeds in Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$ system. Along with the change in flux, ramping and cooling rates should also be tested to pinpoint their effects on the shape and size of the crystals as we have observed in our attempts using various PbO-PbF$_2$ concentrations and cooling rates. Magnetization measurements can be used to determine the effect of various Sm/Ca ratios on the superconducting behavior of Pb$_2$Sr$_2$Sm$_{1-x}$Ca$_x$Cu$_3$O$_8$. In our study the superconducting transition was not sharp. It will be beneficial for future studies if a system can be developed for the mechanical extraction of the crystals without breaking them.

Finally, a proof of principle experiment was conducted at beamline 6-ID-D at the Advanced Photon Source in which the full reciprocal space of one of our crystals was measured at room temperature, wavelength=0.142475 Å, sample-to-detector distance = 644 mm. Description of the experimental setup and analysis of the data is beyond the scope of this thesis but the scans shown in Figures 5.1 demonstrate the perfect ordering of a single crystal observed along the 001 direction, Figure 5.1(a). Room temperature lattice parameters indexed based on an average tetragonal lattice are $a = b = 5.4$ (Å) and $c = 15.8$ (Å). A close-up examination of the same $hk$ plane with $\ell = 0$ shows the expected twins that arise from the actual orthorhombic symmetry of the crystal structure, Figure 5.1(b). However, more surprising was the observation of the same
pattern, although weaker or more diffuse, for \( \ell \) = half-integer values (e.g. \( \ell = 0.5, 1.5, 2.5, \) etc), see Figure 5.1(c) for example. The presence of such peaks usually indicates the doubling along the direction in which it is observed (here the c-axis) with such a doubling arising from the ordering of atoms, charge, spins or any other elementary building block units (e.g., PbO_5/PbO_6 or CuO_2/CuO_4 ordering, etc). Further examination of the data along the \( \ell \) direction shows the presence of rod-like diffuse scattering connecting all the Bragg peaks along the 001 direction, Figure 5.1(d). Diffuse scattering of this nature are more complex to model and are usually connected with order/disorder modulations that could arise due to various parts of the crystal structure (e.g., short range ordering of oxygen interstitials and vacancies, short range ordering of Pb^{2+}/Pb^{4+} clusters, etc). Although not attempted here, it is my hope that a future student would be successful at growing better crystals and be up to the challenge of collecting and analyzing diffuse scattering data.
Figure 5.1: Reciprocal space of PSYCCO crystal measured at room temperature, at the Advanced Photon Source beamline 6-ID-D, Argonne National Lab.
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