SYNTHESIS AND CHARACTERIZATION OF SOME LEAD CONTAINING AND RELATED SULFIDES

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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In this study complete substitution of O by S in Pb-Sr-Ca-Cu-O superconducting system that has the general formula $Pb_2Sr_2ACu_3O_{8+\delta}$, had been attempted. Instead of Y and Ca, only Ca was used in A site as it has comparable ionic radius to the rare-earth elements. The obtained sample, $Pb_2Sr_2CaCu_{3-y}S_x$, was then characterized by XRD, IR, SEM, EDX and four-probe conductivity technique. It was investigated to find out whether the conducting properties were retained.

X-Ray powder diffraction pattern of $Pb_2Sr_2CaCu_{3-y}S_x$ was found to be very similar to PbS diffraction pattern reported in JCPDS Card No.5-592 which has the rock salt structure with a=5.946A°. $Pb_2Sr_2CaCu_{3-y}S_x$ was indexed in monoclinic system with a=5.947, b=5.941, c=11.98A° and β=90.19°. Since c unit cell dimension is almost twice of a and b, it is concluded that a superstructure formation had resulted which is common for complex sulfides.

Formation of $Cu_{2-x}S$ crystals was detected by XRD and SEM indicating the multiphase formation at complete substitution as reported in the literature. However, contrast to some studies given in the literature, sulfur really enters into the lattice positions as well as forming another phase. This can be deduced from the enlargement of unit cell dimensions in sulfur doped material compared with corresponding oxide. This is expected as S^{2-} has larger ionic radius than O^{2-}.

The absence of oxygen bands in IR and EDX spectra is taken to be the proof of the complete substitution of O by S by using the solid gas reaction.

This $Pb_2Sr_2CaCu_{3-y}S_x$ was found to be metallic when measured by four-probe conductivity technique designed in our laboratory working in liquid N_2 temperature-room temperature range.

In order to understand the true structure of $Pb_2Sr_2CaCu_{3-y}S_x$, various stoichiometries of Pb-Sr-Ca-Cu system had been synthesized. All the products had XRD pattern similar to PbS even when the sample contains no lead ($Sr_2CaCu_3S_x$). This proves the assumption that all the atoms present in the system contribute to the crystal structure and not PbS forms alone.

Synthesis and characterization of related quaternary, ternary and binary sulfides were also done by using the specially designed sulfidizing system.

Keywords: $Pb_2Sr_2CaCu_{3-y}S_x$, sulfide compounds, sulfur substitution, sulfidizing reactions.

ÖZ

BAZI KURŞUN İÇEREN VE İLGİLİ SÜLFÜRLERİN SENTEZİ VE KARAKTERİZASYONU

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Bu çalışmada genel formülü $Pb_2Sr_2ACu_3O_{8+\delta}$ olan Pb-Sr-Ca-Cu-O üstüniletken bileşiğinde O'nin S'le tamamen yer değiştirmesi denendi. A yerinde Y ve Ca yerine, sadece Ca kullanıldı. Kalsiyumun, nadir toprak elementlerine yakın iyonik yarıçapa sahip olmasi nedeniyle bu değişim yapıldı. Elde edilen madde, $Pb_2Sr_2CaCu_{3-y}S_x$, daha sonra X-ışınları toz difraksiyonu, IR, SEM, EDX ve dört-nokta iletkenlik ölçme teknikleriyle karakterize edildi. İletken özelliklerinin korunup korunmadığı incelendi.

Bu bileşiğin X-ışınları toz difraksiyonu deseninin, birim hücre boyutu a=5.946A^o olan kaya tuzu yapısındaki JCPDS Kart No.5-592, PbS'in difraksiyon desenine benzediği görüldü. $Pb_2Sr_2CaCu_{3-y}S_x$ monoklinik sistemde birim hücre boyutları a=5.947, b=5.941, c=11.98A^o ve β=90.19^o olarak indekslendi.'c' birim hücre boyutunun a ve b'nin yaklaşık iki katı olması nedeni ile kompleks sülfürlerde yaygın olan bir süperyapı elde edildiği görüldü.

X-ışınları ve SEM verilerinden, literatürde rapor edilen tamamen yer değiştirmede, çok faz oluşumunu gösteren $Cu_{2-x}S$ kristallerinin oluşumu gözlendi. Literatürde verilen bazı çalışmaların aksine, S aslında kısmen örgü yapısına girmekte fakat aynı zamanda başka bir faz oluşturmaktadır. Bu gerçek, oksit bileşiklerine kıyasla sülfürlü bileşiklerde, S^{2-} nin iyonik yarıçapının O^{2-} den daha büyük olması nedeniyle, birim hücre boyutlarında izlenen büyümeden çıkarılabilir.

Katı-gaz reaksiyonu kullanılarak, O'nin S'le tamamen yer değiştirdiği IR ve EDX spektrumlarında O'nin görülmemesiyle ispat edildi.

Laboratuvarımızda bulunan, sıvı azot-oda sıcaklık aralığında çalışan dört-nokta direnç ölçme tekniğiyle $Pb_2Sr_2CaCu_{3-y}S_x$'ın metalik olduğu bulundu.

$Pb_2Sr_2CaCu_{3-y}S_x$'ın gerçek yapısını anlamak için, Pb-Sr-Ca-Cu sistemi çeşitli metal iyonları oranlarında sentezlendi. Bütün bu sistemlerde XRD desenlerinin PbS yapısına uygun olduğu görüldü. Diğer kurşun içermeyen sistemlerde bile

($Sr_2CaCu_3S_x$) aynı yapı gözlendi. Bu gözlem de kristal yapısının sadece PbSden kaynaklanmadığını ve bütün atomların yapıya katkıda bulunduğu savını doğrulamaktadır.

Bu çalışmada laboratuvarda kendi olanaklarımızla gerçekleştirilmiş sülfürleyici ve indirgeyici bir sistem ile elde edilen metalik bileşiklere ilave olarak diğer bazı dörtlü, üçlü ve ikili sülfürlerin sentezi ve karakterizasyonu da yapıldı.

Anahtar Kelimeler: $Pb_2Sr_2CaCu_{3-y}S_x$, sülfür bileşikleri, sülfürle yer değiştirme, sülfürleme reaksiyonları.

To My Parents

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INTRODUCTION

1.1. Sulfide Compounds

All metal sulfides are solid at ordinary temperatures. These compounds may be divided into three groups: the sulfides of the more electropositive elements of the I, II, and IIIA groups; the sulfides of the transition metals (including Cu^{II}) and the sulfides of the elements of the II, III, IV, and VB groups [1].

The synthesis and characterization of new transition metal sulfides have gained a great deal of interest. This attention is partly due to the important technological applications of these materials and partly because of their remarkable diversity in structure and properties. As there is an increased demand for sophisticated structural tools and solutions, various complicated compounds are tried to be synthesized and characterized.

Layered transition metal chalcogenides have also attracted much attention because they have many useful properties that are a direct consequence of their low dimensional structures. Specifically, these materials consist of covalently bonded layers of metal atoms bridged by sulfur atoms, and have only weak van der Waals interactions between these layers. Although there are a wide variety of applications for these materials, such as uses in batteries, and as catalysts, only a limited number of phases and structure types (which are almost exclusively binary phases) are known [2].

There is a noticeable difference in the structure and bonding of most binary metal sulfide compounds compared to those of metal oxides. Sulfur is less electronegative and softer than oxygen, therefore it has a broader span of oxidation states and a stronger affinity for the softer metals. Similarities may be observed for most electropositive metals [3]. If compared for their structures, both binary alkali monoxides and monosulfides have the antiflourite structure. Also, rock salt structure is adopted by binary monosulfides and monoxides of the alkaline earth metals. However, as indicated by Shriver et al.[4], in contrast to the monoxides, most of the monosulfides have the nickel-arsenide structure. The different structures are consistent with the hard-soft acid base property. The rock salt structure of monoxides being favored by the ionic (harder) cation- anion combinations whereas the nickel-arsenide structure is favored by more covalent (softer) combinations and correspondingly shorter M-M separations.

Although there are similarities as mentioned above, sulfides tend to form covalent, layered type structures unlike to oxides which prefer ionic, three dimensional type structures. The layered sulfides are often two dimensional with weak S....S van der Waals interaction within the layers. The greater covalency of the metal-sulfur interactions reduces the relative charge on the metal ion thus enhancing metal orbital diffuseness. This softer metal center favors metal-metal bond formation and greatly influences the electronic structures and properties of the compounds. For the solid state sulfides, the reduced relative charge on the transition metal results in small electrostatic energy U, giving rise to smaller transfer energy required for the formation of metallic electrons [5]. Thus metallic and semimetallic sulfides are more common than oxides [6].

The disulfides of the d-metals fall into two broad classes that consist of layered compounds with the CdI_2 or MoS_2 structure and of compounds containing discrete S_2^{2-} groups. The layered disulfides are built from sandwiches consisting of a sulfide layer, a metal layer, and then another sulfide layer. These sandwiches stack together in the crystal with sulfide layers in one, adjacent to a sulfide layer in the next [4].

The lower electronegativity of the sulfur relative to oxygen leaves the valance 3s and 3p sulfur bands much closer in energy to the transition metal d-orbital manifold. In many compounds, such as the copper sulfides, formal oxidation states become ambiguous and oxidation-reduction chemistry may involve the sulfide bands more than the transition metal d-orbitals. In fact, the oxidation states of the late transition metals in ternary metal sulfide complexes are still a subject of controversy.

Spectroscopic [7] studies often indicate metal valencies which are lower than the expected values based on the assumption of a simple ionic formula.

Another property of the ternary transition metal sulfides is the relatively large number of incommensurate crystal structures [8]. The incommensurate compounds have two different sublattices that are structurally 'uncoupled' with unregistered periodicities. This sublattice mismatch can occur in layered compounds (e.g. the $AS.MS_2$ ' misfit layer compounds') or in 1D chain compounds (e.g. the $Ba_{1+x}Fe_2S_4$ phases).

The physical properties of the ternary transition metal sulfides are as diverse as their structural chemistry. The properties include superconductivity, ferro- and antiferromagnetism, fast ion conductivity and catalytic activity.

The synthesis of ternary metal sulfides (A-M-S) are done mainly by three methods [9].

1) Direct reaction of the elements or binaries at elevated temperatures (solid state method);

2) Sulfidization of oxide precursors (solid gas reactions);

3) Intercalation and exchange of A site ions.

Examples of some of the sulfide systems cited in the literature include binary sulfides [10-14], ternary sulfides [15-22] and quaternary sulfides [23-25].

In our laboratory, synthesis and characterization of both binary and ternary sulfides were extensively studied either by conventional solid state method or by using the specially designed sulfidizing gas system [26-31].

The synthesis of binary metal sulfides of groups IB, IIB and IVB has been the focus of much attention. These materials have an extensive array of commercial applications from semiconductors and pigments to luminescence devices. Binary metal sulfides can be obtained by the direct reaction of the elements at high temperatures for prolonged time periods, through the treatment of the element oxides with H_2S, or by precipitation of the metal cation from aqueous solution by a source of S^{2-}. Binary metal sulfides such as MoS_2 and WS_2 have been synthesized by using a solid-state metathesis reaction of anhydrous metal halide and sodium sulfide, the reaction being spontaneous on mixing reactive components. Molecular precursor routes to metal sulfides have been developed for bulk materials and for coatings. Henshaw et al. [13], report the convenient one step room temperature preparation of crystalline metal sulfides via elemental reactions in liquid ammonia, such as ES where E represents Pb, Ag, Zn and Cd.

Although alkaline earth chalcogenides such as CaS and SrS, have been of interest to phosphor researchers for over hundred years, a new interest aroused due to their possible potential application, not only in standard phosphor usage but also as the active component of devices for use in dosimetry and electroluminescence [32].

Considerable interest has focused on the exploration of reduced ternary group IV and V chalcogenides with novel metal-metal bond frameworks. This has led to discovery of many new compounds, such as $Ta_2Ni_3S_5$ and MXQ phases (M = Zr, Hf; X = Si, Ge, As, Sb; Q = S, Se, Te), [22].

There is a continuous effort to explore the synthesis and properties of new complex chalcogenides. The increased study on quaternary sulfides is a result of this growing attraction. Alkali metal intercalates of chalcopyrite ($ACuFeS_2$; A = K, Rb, or Cs) have attracted growing interest in recent years due to the potential applications of these materials in important technologies such as cathodes in electrochemical cells. Oledzka et al. [23] worked on physical properties of this system and found that all the samples showed semiconducting properties in contrast to metallic behavior predicted by theoretical calculations.

1.1.1. Sulfides of Copper

The Cu-S system is remarkably complex, and the structures of CuS and Cu_2S are not consistent with their formulation as cupric and cuprous sulfides. Cu^+ in particular have a very large affinity for S which may still be enhanced by lowering the symmetry of the cation environment. Copper has a preferance for monovalent state in sulfides rather than divalent state. It may be expected that Cu^{+1} with a d^{10} configuration to prefer a tetrahedral coordination by sulfur. Cu is indeed situated in tetrahedral holes of a close-packed sulfur lattice. In Table 1.1 several copper sulfide phases are reported.

Table 1.1. The sulfides of copper [1]

CuS (covallite) - stable below 500°C
$Cu_{1.75}S$ (anilite)
$Cu_{1.8}S$ (digenite)
    metastable low temperature form $\rightarrow$ cubic
    high temperature form $\rightarrow$ twinned rhombohedra
$Cu_{1.96}S$ (djurleite)
    low temperature form $\rightarrow$ complex (128 S/cell)
    high temperature form $\rightarrow$ metastable tetragonal (100°C)
Cu_2S (chalcocite)
    low temperature form $\rightarrow$ monoclinic (104°C)
    high temperature form $\rightarrow$ hexagonal (470°C)

1.1.2. Structure of Lead Sulfide

Lead sulfide which is also known as galena has the undistorted rock salt structure. NaCl (rock salt) structure could be described as interpenetrating face centered cubic (fcc) arrays of anions and cations of equal charge. The coordination number for both anions and cations are six. The centers of these six nearest neighbors trace out a regular octahedron. Therefore the structure can be considered as consisting of an fcc array of Cl^- (or Na^+) with a Na^+ (or Cl^-) ion in all octahedral "holes" (interstices) in the array [33].

1.1.3. Sodium Chloride Superstructures

These are structures in which A and/or X atoms of more than one kind are arranged in a regular way in the Na and Cl structure. There are four possible (distorted) NaCl superstructures:

a) tetragonal; b) rhombohedral; c) cubic and d) monoclinic.

Apart from cubic structure, complex sulfides and oxides provide many examples for NaCl (rock salt) superstructures [1].

1.1.4. Electrical Properties of Sulfides

(i) Sulfides of main-group elements

The bonding in non-molecular sulfides is probably described in the simplest way by means of a band picture. If the cation has a ns^2np^6 or $ns^2np^6(n-1)d^{10}$ configuration, the (n+1)s and (n+1)p orbitals of the cation will overlap the 3p and 3s orbitals of the sulfide ion. As a result a (bonding) valance band and an (antibonding) conduction band will occur (Fig 1.1.). Since sulfur is the more electronegative element in the compounds under discussion, the valance band is mainly due to the 3s and 3p orbitals of sulfur, the conduction band to the (n+1)s and (n+1)p orbitals of the metal.

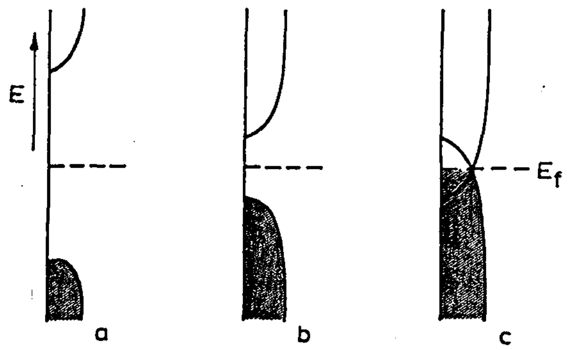

Fig. 1.1. Simplified band model of compounds of main-group vs. density of states; (a) an insulator; (b) an (intrinsic) semiconductor; (c) a metal.

(ii) Sulfides of transition metals

The metallic and semiconducting properties of sulfides arise from, the (n+1)s and (n+1)p orbitals of the transition metal interacting with the 3s and 3p orbitals of sulfur. The consequence of this interaction is the formation of a valance band (mainly due to sulfur) and a conduction band (mainly due to metal). These bands are as broad as approximately of the order of 10 eV, and the energy gap between valance and conduction band is one to a few eV in most transition metal sulfides. Not only the (n+1)s and (n+1)p orbitals of metal will interact with sulfur orbital but 3d does so as well. However this interaction is not significant compared to others. As a result of this minor interaction narrow bands will occur, but in many cases nd orbitals can be treated as essentially localized on the metal. If this energy lies within the energy gap between the top of the valance band and the bottom of the conduction band, the compound will be semiconducting. If, however, the energy of the oxidized state also lies below the top of the valance band, the cation will be (partly) reduced, holes will be created in the valance band and the compound will be broad-band metallic conductor [34].

1.2. Solid gas reactions

When the metal oxide, MO, is heated in the flow of carbondisulfide, CS_2, carbonyl sulfide, COS, or with the mixture of carbon monoxide, CO and sulfur, S_2, the following reactions will occur:

$2MO + CS_2 \rightarrow 2MS + CO_2$

$MO + COS \rightarrow MS + CO_2$

$2MO + 2CO + S_2 \rightarrow 2MS + 2CO_2$

This sulfidizing gas mixture of COS, CS_2, CO and small amounts of CO_2 and S_2 vapor has a reducing property also and was obtained by Owen et al.[35]. Welch, [36] stated that metal oxides or metals could be sulfidized under the stream of this reducing gas mixture. This sulfidizing and reducing gas mixture could be simply obtained by passing sulfur dioxide through activated charcoal at 1000, 1200 and 1400K.

The reactions happening in this process are as follow: [26, 29-31]

$SO_2 + 2C \leftrightarrow COS + CO$

$2COS \leftrightarrow CS_2 + CO_2$

$2COS \leftrightarrow 2CO + S_2$

$C + S_2 \leftrightarrow CS_2$

1.3. Pb-Sr-Ca-Cu-O Materials

Since the first observation of high transition temperature superconductivity in La-Ba-Cu-O, in 1986, progress in the understanding of this remarkable phenomenon has been coupled to the discovery of new materials. Three main families of copper-oxide- based high-Tc superconductors have been identified. These are$(La,M)_2CuO_4$, $LnBa_2Cu_3O_7$ and $(Tl,Bi)_m(Ba, Sr)_2Ca_{n+1}Cu_nO_{m+2n+2}$, where M represents a metal cation that may substitute some La sites, and Ln represents a lanthanide [37]. Cava et al. [38] and Subramanian et al. [39] discovered a new family of planar copper oxide superconductors with general formula $Pb_2Sr_2ACu_3O_{8+\delta}$ (Fig1.2) where A is a lanthanide or a mixture of Ln + Sr or Ca.

They could not yet prepare good bulk superconductors of single phase polycrystalline $Pb_2Sr_2LnCu_3O_8$. The reason for non-bulk superconductivity may be due to inhomogeneities in either oxygen content or Sr/Ln distribution.

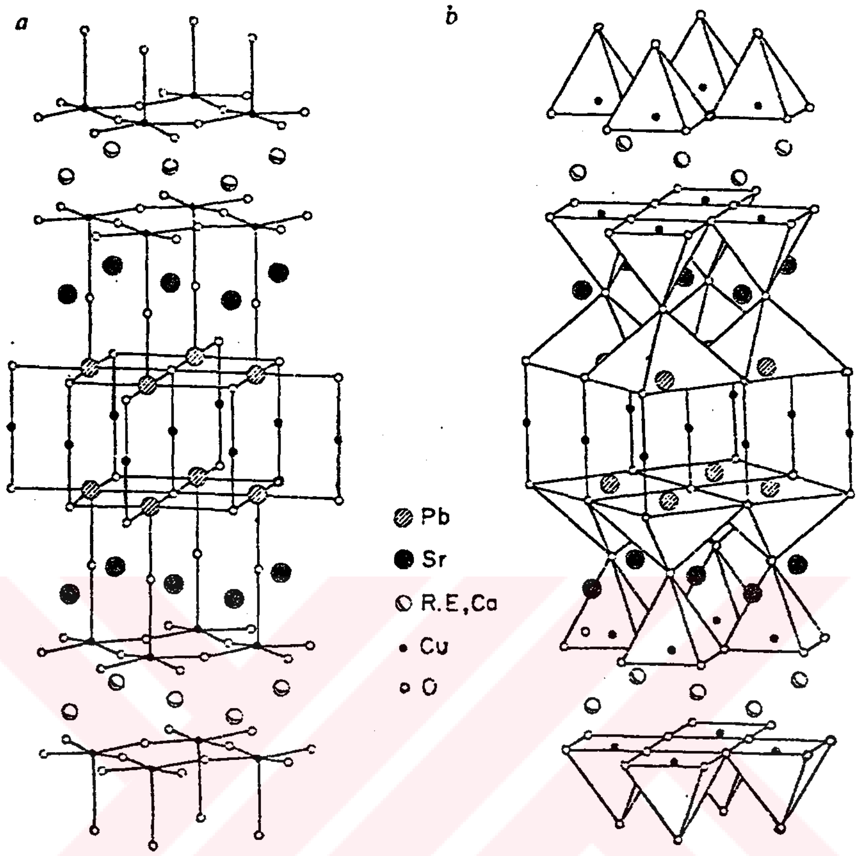

Fig.1.2. Two representations of the crystal structure for $Pb_2Sr_2ACu_3O_{8+\delta}$

The new phases have an orthorhombic unit cell which is based on a many layer perovskite structure.

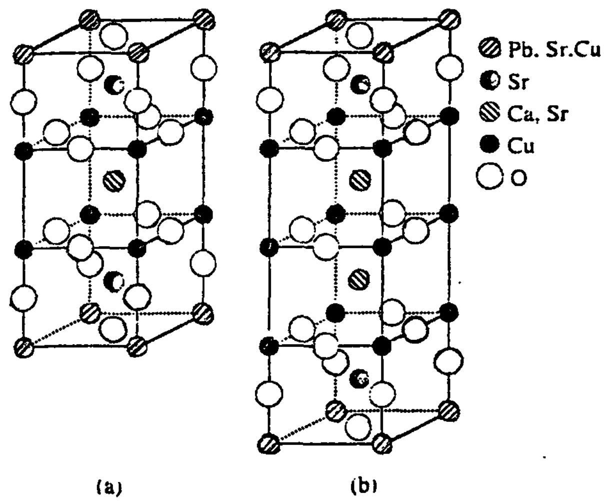

Fig.1.3. Schematic structures for (a) Pb-1212 and (b) Pb-1223 phases.

Tamura et al. [40] successfully obtained Pb-12(n-1)n superconductors, where n represents the number CuO_2 sheets between two adjacent 'charge reservoir' blocks in the crystal structure. This new homologous series consisting of Pb-based layered cuprates has a superconductivity at 115 K. This Pb- based superconductors are mainly two groups; "Pb"-1212 and "Pb"-1223 phases (Fig 1.3.). Later Wu et al.[41] found the basic structure that is constructed by a rock salt block which is formed by a sheet of Pb-O sandwiched by two sheets of Sr-O and (n-1) so called 'infinite layer' blocks, which are formed by alternative stack of n layers of Cu-O_2 and (n-1) layers of Ca. The existence of superstructure has been reported, on the other hand. Wu et al.[41,42] performed TEM, EDX and Rietveld analysis to both of the samples and suggested that the actual chemical formula for "Pb"-1223 phase can be written as $(Pb_{0.5}Sr_{0.25}Cu_{0.25})$-$Sr_2(Ca_{0.87}Sr_{0.13})_2Cu_3O_9$ and it has tetragonal symmetry (Fig. 1.4.)

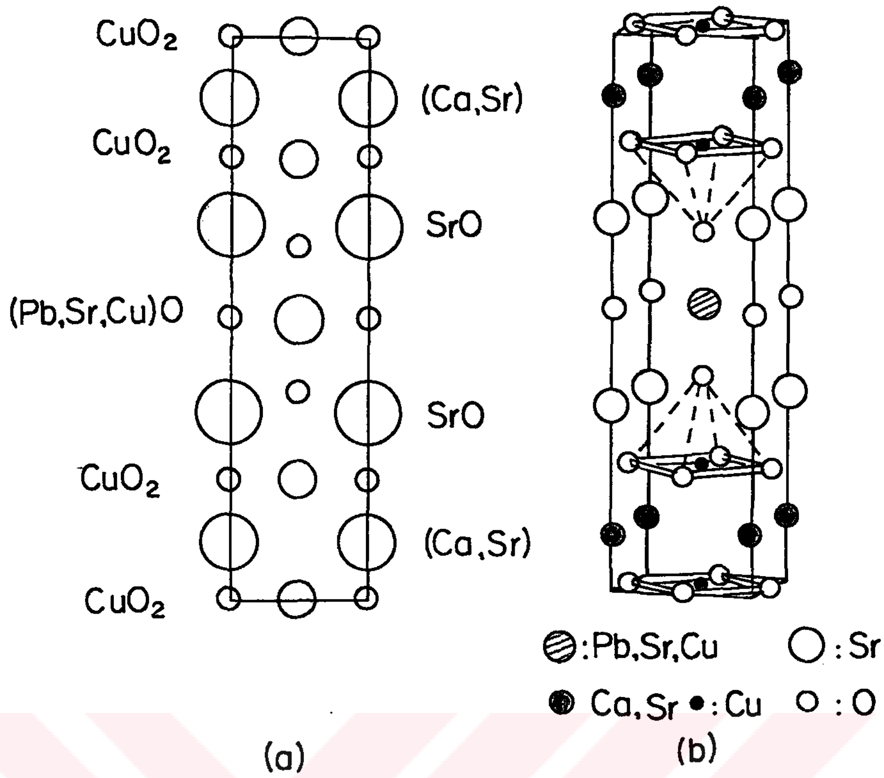

Fig.1.4. Structure of Pb-1223 phase (a) Structural projection along [100] and (b) a three dimensional view of the "Pb"-1223 phase.

"Pb"-1212 on the other hand can be expressed as $(Pb_{0.5}Cu_{0.3}Sr_{0.2})Sr_2(Ca_{0.6}Sr_{0.4})Cu_2O_y$ with an orthorhombic structure.

1.4. Sulfur Doped Oxide Superconductors

Since the discovery of high Tc superconductivity, it became very important to optimize the superconducting properties. One of the informative methods is the substitution of elements in the known high temperature superconducting oxides. By this way the superconducting mechanism can be extensively studied and besides new superconducting materials can be synthesized.

In an effort to increase T_c, various substitutions at both the cationic and anionic sites have been attempted.

The effects of substituting metallic elements by transition metals [43-45], rare earth metals [46-49] and alkaline earth metals [50-53] are thoroughly investigated. On the other hand replacement of oxygen by fluorine and chlorine [54] has also been carried out. It is of great interest to introduce other chalcogenide atoms into the known superconducting oxides. Therefore, sulfur and selenium atoms are used as substituents for oxygen. Slebarski et.al. [55] found that substitution of oxygen by selenium in YBCO drastically decreases Tc and changes the structure from orthorhombic to tetragonal.

Sulfur is the mainly studied element for anionic substitution. Substitution of oxygen by sulfur should effectively lead to a change in the orbital overlapping with Cu 3d state and modify the electronic distribution nearby. The overlap of sulfur 3p and copper 3d is larger than that of oxygen. Sulfur atoms replaced for oxygen may also change the crystal structure due to its larger ionic radius compared to oxygen.

Bhattacharya et al. [56] reported that, the substitution is expected to lead to a higher hybridization effect, as covalency increases from oxygen to sulfur, which could change superconducting properties of compounds. As a result this substitution is expected to improve both the electronic and magnetic properties.

The works on sulfur substitution by Taylor [57] and others [58-59] showed that complete substitution of oxygen by sulfur significantly reduces the superconducting properties. Both 50% and 100% substitution of CuS for CuO resulted in semiconducting materials with room temperature resistance in excess of $10^6\ \Omega$. A Ph. D study [28] have been carried in our laboratory also investigated complete substitution of oxygen by sulfur in YBCO ceramics. The result was that a, b cell parameters were close to the corresponding oxide but c was almost tripled, together with the loss of superconductivity. Actually, the sample showed a semiconducting property. Hence, the partial substitution is preferred and studied.

There is a contradiction among the studies regarding the effect of sulfur in the superconducting materials. The main question is whether sulfur is indeed incorporated in crystal lattice or causes the presence of multiphase like CuS and $BaSO_4$. While some claim that sulfur is in the crystal lattice, the others reported that sulfur does not actually sit in the lattice sites but instead forms other phases.

Based on their studies, some researchers [28, 56-57, 60-69], found out that sulfur atom sits in the superconducting crystal lattice. Existence of other phases claimed by others could not be detected by these authors. According to them one of the ways to understand (if sulfur atoms are actually homogeneously introduced into the system) is to compare the lattice parameters of doped and undoped samples. If there is an increase in the lattice parameters of doped sample this proves the existence of sulfur in the superconducting system.

The ones supporting the idea of sulfur in crystal lattice mainly worked on two systems. Nishikawa et al., Kozuka et al. and Fujihara et al. [67-69] had studied S doping of La-Sr-Cu-O superconductors to obtain $La_{2-x}Sr_xCuO_{4-y}S_y$. As it is expected the substitution of O by S may change electronic structure in vicinity of Cu and may affect the electrical and magnetic properties. La-Sr-Cu-O is an ideal system for studying the mechanism of high temperature superconductivity because of its simple structure and ability to form single phase without difficulty and a wide range of solid solution.

Nishikawa et al. [67] studied S substitution in $La_{2-y}M_yCuO_4$ where M= Sr, Ba. The randomness introduced by S doping does not seem to supress T_c. If randomness is introduced into atomic sites in CuO_2 planes then superconductivity will be destroyed. Thus S should be in LaO planes or outside CuO_2 planes. As S^{2-} has larger atomic radius even in LaO planes it induces a distortion. Kozuka et al. [68] also studied sulfur doping in La-Sr-Cu-O. It is found out that for $y > 0.2$ for $La_{2-x}Sr_xCuO_{4-y}S_y$, a new phase was formed. Also with the increase in S doping there was a change of crystal structure from tetragonal to orthorhombic at room temperature. The lattice parameters a, b showed an increase whereas c decreased. All of these changes resulted in the destruction of superconductivity. The appearance of semiconducting behavior in S doped materials may be caused by the reduction in the overlap of bands due to elongation in lattice plane.

As sulfur doping increases, two dimensional structure formation is less which corresponds to less distorted CuO_6 octahedra. That is axial oxygen comes closer to CuO_2 plane increasing electronic interaction between the axial oxygen and copper. Also since Cu-S bond is more covalent, the electron density of copper in the region along Cu-S bond is higher than that of Cu-O bond. Thus formal charge of Cu in doped sample may be less than Cu^{2+}.

Another important property of these doped compounds is that if they are subjected to a thermal cycle there will be a degradation of superconductivity indicating the thermal unstability.

All cited references are in agreement with each other that a and b lattice parameters increase with increasing sulfur content whereas there is a decrease in c parameter. This decrease of c is not only accompanied with a decrease in superconducting transition temperature but a transition from superconducting to metallic and even to semiconducting behavior.

As a result, it can be deduced that small amount of sulfur doping to La-Sr-Cu-O superconductors does not affect superconductivity and the sample appears to be single phase.

Apart from La-Sr-Cu-O system, sulfur doping is studied in YBCO type superconductors [56-57, 60-66] and it is observed that sulfur is introduced in crystal lattice. Ref. [61-64] observed that $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6S$ had similar superconducting properties with larger unit cell and larger Meissner effect than YBCO and yet the same Tc. Taylor et al. [57] have shown that 10% replacement of CuO by CuS in YBCO gave rise to a superconducting transition at 108K.

Taylor et al. [57] studied various proportions of sulfur doping in $YBa_2Cu_3O_7$. It was seen that at high amount of sulfur doping the superconducting properties are destroyed. Thus, further studies are only carried for samples with small sulfur doping. $YBa_2Cu_3O_6S$ showed similar Tc with $YBa_2Cu_3O_7$, however the disadvantage of this doped material is that upon repeated cycling of resistivity measurements, there is a degradation in the superconductivity. Bhattacharya et al. [56] and Felner et al. [61] also confirmed Taylor et al. study [57], and Felner et al. [61] suggested that there may be a formation of superstructure. Moreover by ESCA measurement, Bhattacharya et al. [56] showed that due to the increase in binding energy of Ba, S should be bonded to Ba more than to Cu. Palhan et al. [63] showed that sulfur doped samples are unstable and in time decompose to give $BaSO_4$ for YBCO type superconductors. In samples aged for six months, formation of several phase is seen whereas in fresh, newly prepared samples only a single phase is visible. Nakajima [66] also worked on very small sulfur substitution. Both Onyszkiewiez et al. and Kozuka et al.[65,68] found a decrease in c and increase in a and b parameters. If sulfur is incorporated in the crystal lattice we expect an increase in lattice parameters as the ionic radius of O is 0.132 nm whereas S has ionic radius of 0.184 nm. This decrease in c can be attributed to the fact that either ;

i) the anion sublattice lacks a certain amount of S^{2-}, which does not affect the cation sublattice as T_c is still high, or

ii) S^{2-} may occur at a different oxidation state, which involve a decrease in the ionic radius, [65].

All these indicate that to be able to obtain a pure phase sulfur doped superconductor, the preparation conditions such as reaction temperature, partial pressure of oxygen and ratios of cooling should be optimized.

All above mentioned authors claimed that sulfur doping does not cause the formation of other phases but rather single phase materials with sulfur incorporated in the crystal lattice. As a result of this T_c remains same for these samples.

Some authors [70-75], discovered that sulfur substitution for oxygen in YBCO ceramics causes the formation of multiphase rather than pure phase superconductors. Although, very small portions of doped sulfur enter into superconducting oxide phase, it is discussed that sulfur mainly forms sulfide layers at the surface of the superconducting grains. Thus while the sample appears to be superconducting at the center, it is not superconducting at the surface. Therefore considering the results of

EDX and SEM taken only at the surface will not be a sufficient proof since sulfur will seem to be incorporated into the parent oxide when it is actually not.

Cloots et al. [73], showed that sulfur is not uniformly distributed in samples by SEM and HROPM (High Resolution Optically Polarized Microscopy) observations taken at the core and the surface of the same pellet. Furthermore, it is suggested that there is a sulfide layer formation upon every YBCO grain. This maybe due to some aerodynamical effect in the synthesis, and to the difficulty of sulfur to migrate through the polycrystalline ceramics. That is due to thermal conditions sulfur diffuses out easily and reacts only at surface before the desired reaction takes place.

Cloots et al. [70] performed several studies on sulfur substitution for oxygen in $YBa_2Cu_3O_7$ ceramics. In all these studies, they always observed that sulfur atom does not significantly enter into lattice sites but rather forms multiphase. However, if thermal parameters are controlled, the formation of such phases could be eliminated. Electron diffraction microscopy of the sulfur doped samples is one of the way to see that sulfur is not uniformly distributed in the sample. Also the detection of an increase in sulfur content from the inner to the outer part of the pellet by EDX, shows the existence of different compositional regions probably related to the chemically different phases in different points of the pellet surface. The important outcome of this study is that the formation of hexagonal CuS grains at the surface could be seen. These grains appear within or more probably as a layer upon the surface of every YBCO grain.

The studies of Yarmoshenko [74] presented that X-Ray spectra revealed the entry of sulfur into the YBCO lattice and substitute oxygen atoms. At further increase of sulfur doping CuS phase formation on the surface of grains and sulfate groups are observed which may not be detected by X-Ray diffraction.

All studies on sulfur doping are consistent regarding the fact that at increased sulfur doping T_c decreases, and may be a transition from superconducting to metallic or even further to semiconducting behavior accompanied with change of crystal structure taking place.

Kurmaev [76] studied the compound $BiPb_{0.4}Sr_{1.6}Ca_2Cu_3O_{6.6}S_{0.7}$ and found out that the sulfate phase is being formed. Also for this case sulfur atoms do not enter to parent crystal lattice.

The authors, who argue that sulfur is not really in lattice positions, include Matsubara et al. [71] who studied sulfur substitution by using two different preparation methods. If CuS or Cu_2S are used, sulfate formation is observed. Whereas if $YBa_2Cu_3O_7$ is annealed in H_2S gas, sulfur is partially incorporated into crystal lattice in disordered form. The other important feature is that like one of the Cloots studies [73] the doped sample is superconducting at the center and semiconducting at the surface.

Felner and Barbara [60-61] and Gagnon et al. [72] all studied sulfur substitution in $RBa_2Cu_3O_7$ where R= Nd, Eu, Gd, Er. Although in refs [60-61] the formation of pure superconducting phase has been reported, Gagnon et al. [72] discussed that actually sulfur causes multiphase and does not enter into crystal lattice significantly. Yi et al. [54] also stated that single phase does not form, and there is a phase transition from orthorhombic to tetragonal which destroys superconductivity. This is due to the fact that as number of oxygen atoms per formula unit becomes smaller than about 6.5, the superconductivity is destroyed.

As briefly summerized, it is seen that there are basically four methods for preparation of sulfur doped materials.

1) Solid State Method (Example Ref. 65-68).

2) Direct reaction with elemental sulfur (Example Ref.73-75)

3) Reaction in flowing gas stream of H_2S (Example Ref.71)

4) Solid gas reaction using sulfidizing gas mixture (Example Ref.28)

1.5. Purpose of the Work

Cava et al. [38] and Subramanian et al. [39] prepared a new family of high temperature superconductors with the general formula $Pb_2Sr_2ACu_3O_{8+\delta}$ where A = Y and Ca. These new compounds have the characteristics CuO_5 square pyramid planes, however they belong to a distinct structural series with a wide scope for elemental substitution. With the discovery of these type of superconductors various substitution for A site was tried. Y free superconducting samples of Pb-Sr-Ca-Cu-O system was first studied by Wu and Tamura et al. [40-42], however the stoichiometry was somewhat different.

In this work, we first tried to synthesize Ln-free Pb-based materials like the studies of Wu and Tamura et al. [40-42]. Apart from this, our study was mainly devoted to complete substitution of oxygen by sulfur instead of partial substitution in $Pb_2Sr_2ACu_3O_8$ compounds. Calcium was selected as a dopant on Ln site since it has the ionic size similar to intermediate rare-earth element.

In the literature, generally, the partial substitution of O by S have been studied and reported that at higher sulfur content superconductivity was destroyed [57-59]. The substitution was carried out mainly in easy to work and well known superconductors like $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$. In this work, our aim is to synthesize a new compound $Pb_2Sr_2CaCu_3S_x$ and investigate whether superconducting properties are retained. For the synthesis a different experimental technique than given in most of the papers is used. Preparation of sulfides is carried out by solid gas reactions, using a reducing and a sulfidizing gas in the reaction furnace. The products obtained with this procedure are characterized by IR, X-Ray Powder Diffraction, SEM, EDX and conductivity measurments and elemental sulfur analysis. To identify the presence of multiphase initial compounds CaO, PbO, $Sr(NO_3)_2$ and CuO, are also sulfidized and the X-Ray powder diffraction results are compared with the JCPDS data of these compounds. Furthermore, some related ternary and quaternary sulfides are synthesized with the same purpose.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1. Chemical Substances

PbO: Riedel De Haen

$Sr(NO_3)_2$: Riedel De Haen

CaO: Merck

CuO: Merck

Potassium bromide used for IR pellets was of spectroscopic grade and was dried at 180° for two hours before it was used.

Nitrogen, N_2, sulfur dioxide, SO_2, gases and activated charcoal were obtained from local distributors. Calcium chloride, $CaCl_2$, was used for the removal of water.

All the reactions have been carried out in nitrogen atmosphere to avoid oxidation.

2.2. Instrumentation

1. X-Ray Powder Diffraction Equipment: Huber-Guiner G600 powder diffractometer which is computer controlled-automatic was used for taking X-Ray diffraction of the powders with CuK_{α} (λ=1.54051A^{o}) radiation and its software was used for calculation and refinement of unit cell dimensions. 30-40kV voltage and 12-20 mA current were appropriate for producing X-Rays. Philips diffractometer with PW 1050/25 goniometer was also used in which CoK_{α} (λ=1.79026A^{o}) radiation was produced by 30-40 kV voltage and 12-20 mA current.

2. Infrared Spectrometer: Nicolet 510 Fourier Transform Infrared Spectrometer was used for IR measurements in the region of 400-4000 cm^{-1}.

3. Scanning Electron Microscope: Microscopic measurements were done by Scanning Electron Microscope (SEM), (Jeol-scanning-electron microscope(JSM-6400)). Energy dispersive X-Ray Spectroscopy (EDX).

4. Four Probe Resistivity System: Resistivity measurements were carried out with the four probe technique using mechanical wire spring contact, on samples cut from bulk. Low resistance electrical contacts were made with silver paint. Temperature was controlled by a cryostat. The measuring system was constructed in our laboratory.

2.2.1. Conductivity Measuring System

Keithly equipment were purchased from Keithley company. The system composed of the following equipment.

I.) Model 197A Autoranging Microvolt DMM

II.) Model 580 Micro-Ohmmeter

III.) Capital Equipment Corp. IEEE-488 Interface Card and its special software program.

An IBM compatible 8086 personal computer was added to the system. As a thermocouple copper-constantan was used. A DC motor with an optimum rate per minute (rpm) to control sample movement into the Dewar cup was purchased and designed. All other mechanical parts were also designed in our laboratory.

To measure temperature, Model 197A Autoranging Microvolt DMM with copper-constantan thermocouple was used. The resistivity change was measured with Model 580 Micro-Ohmmeter using four probe techniques.

These two instruments were connected to the IBM compatible 8086 computer with IEEE-488 interface card. Turbo-Pascal program was used with turbopas and ieeepas.tpu files from the software system. The program was written in Turbo-Pascal language in our laboratory. It controls the system automatically and reads the resistance and voltage values of the setted samples. The data were used to draw graphics {R (ohm) vs. Temp. (K)} and changed to normalized values. The voltage measured were converted to Kelvin by using reference tables.

The program also controls the Model 197A Autoranging Microvolt DMM and Model 580 Micro-Ohmmeter automatically at the same time. Program opens a file and the data are saved into this file. Each measurement was done five times in order to take the average value for each measuring step. When the measuring process is finished, the zero value is entered and the program automatically stops the measurement process and closes the data file. The data obtained were used to draw graphics by using Windows Excel pocket program.

2.2.2. Device for Solid-Gas Reactions

A horizontal tubular furnace with a silica tube of 4 cm diameter and 60 cm length which was designed in our laboratory was used as a reaction chamber.

A tube filled with activated charcoal is inserted vertically into the furnace which is used for reduction chamber.

The temperature control was made with Cr-Ni thermocouple using temcometer type of heat control system.

Polyethylene tubes with glass connections and glass valves were used to construct the system. In order to prevent gas leakage, silicone type of adhesive materials were employed at the connections of the system. The residual gases were discarded outside through the tube from the window.

A gas mask was used for safety purposes, because sulfur dioxide and the reducing gases are dangerous for human health.

The solid-gas system is given in Fig.2.1.

2.3. Experimental Procedure

All samples were sulfidized at 800°C for five hours which were found to be the optimum conditions. For each set of experiments the reactants were weighed according to the stoichiometry of the desired reaction. The powders were very well ground in an agate mortar. The homogeneous mixture obtained were put in a porcelain boat, reweighed and placed in the furnace for solid gas reaction. During cooling to avoid oxidation nitrogen gas was flown through the reaction chamber until the desired temperature was reached and. The samples synthesized were investigated by X-Ray diffraction, Infrared Spectroscopy, SEM, EDX, conductivity measurements and elemental analysis for some of the products.

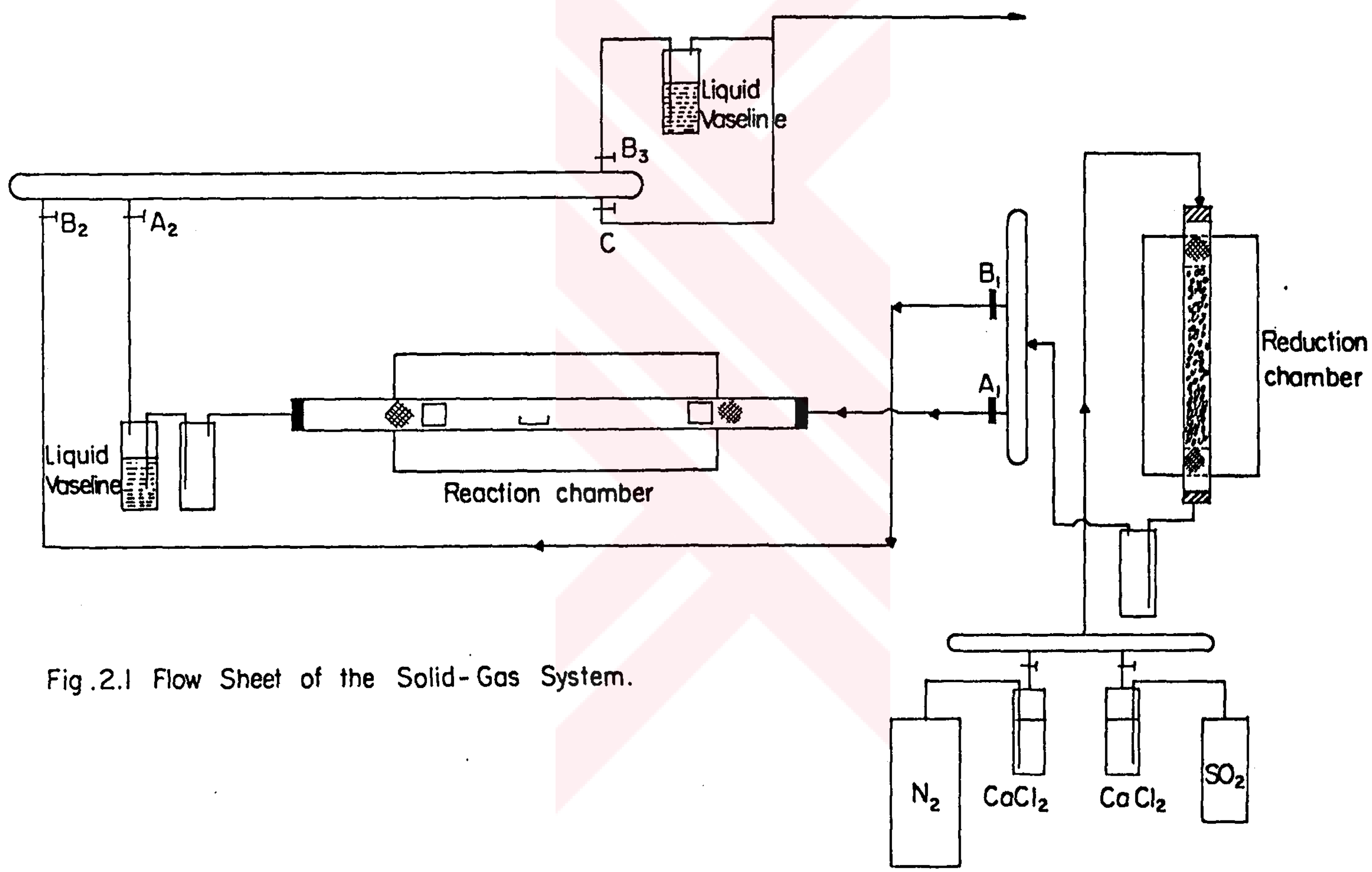

Fig.2.1 Flow Sheet of the Solid-Gas System.

2.3.1. Preparation of $Pb_2Sr_2CaCu_{3-y}S_x$ Material

Appropriate amounts of PbO, $Sr(NO_3)_2$, CaO and CuO were weighed according to atomic ratio Pb:Sr:Ca:Cu, 2:2:1:3 and well crushed in agate mortar. The mixture obtained were transferred into a porcelain boat and placed in the reaction chamber and sulfidized. The resulting product was predicted to be $Pb_2Sr_2CaCu_{3-y}S_x$ (Sample No 3D) and weak lines of $Cu_{2-x}S$ was observed in the X-Ray powder diffraction pattern. Therefore the ideal reaction could be written as:

$$2PbO\ (s) + 2Sr(NO_3)_2\ (s) + CaO\ (s) + 3CuO\ (s) + 2CS_2\ (g) + COS\ (g) + 5CO\ (g) + S_2\ (g) \rightarrow Pb_2Sr_2CaCu_{1.5}S_6\ (s) + Cu_{1.5}S\ (s) + 4NO_2\ (g) + 8CO_2\ (g)$$

All the reactions were repeated according to the same procedure. Therefore the experimental procedure for all the samples are summerized in Tables 2.1- 2.3

Table 2.1. Sulfidization of PbO + $Sr(NO_3)_2$ + CaO + CuO

PbO:Sr(NO₃)₂:CaO:CuO	Sample No
1:2:1:3	3A
0.5:2:1:3	3B
2:2:1:3	3D
2:1:1:3	4H
2:3:1:3	4F
2:4:1:3	4G

Table 2.2. Sulfidization of PbO + $Sr(NO_3)_2$ +CuO and PbO + CaO + CuO to give quaternary sulfides

Reactants	Atomic Ratio	Sample No
PbO:$Sr(NO_3)_2$:CuO	2:2:3	5C
PbO:CaO:CuO	2:1:3	5D

Table 2.3. Sulfidization of $Sr(NO_3)_2$+CaO; $Sr(NO_3)_2$ + CuO; CaO + CuO; PbO + Sr(NO3)2; PbO + CaO to give ternary sulfides

Reactants	Atomic Ratio	Sample No
$Sr(NO_3)_2$:CaO	2:1	4A
$Sr(NO_3)_2$:CuO	2:3	4B
CaO:CuO	1:3	4C
PbO:$Sr(NO_3)_2$	2:2	4K
PbO:CaO	2:1	4L

2.3.2. Sulfidization reactions of initial reactants (binary sulfides):

The initial reactants were separately sulfidized under the same experimental conditions as stated above and the proposed reactions are as follows:

$$4PbO\ (s) + COS\ (g) + CS_2\ (g) + CO\ (g) + 1/2S_2\ (g) \rightarrow 4PbS\ (s) + 3CO_2\ (g)$$

$$4Sr(NO_3)_2\ (s) + COS\ (g) + CS_2\ (g) + 5CO\ (g) + 1/2S_2(g) \rightarrow 4SrS\ (s) + 8NO_2\ (g) + 7CO_2\ (g)$$

$$CaO\ (s) + COS\ (g) + CS_2\ (g) + CO\ (g) + 1/2S_2\ (g) \rightarrow 4CaS\ (s) + 3CO_2\ (g)$$

$$7.2CuO\ (s) + COS\ (g) + CS_2\ (g) + 4CO\ (g) + 1/2S_2\ (g) \rightarrow Cu_{7.2}S_4\ (s) + 6CO_2\ (g)$$

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Preparation of Pb-Sr-Ca-Cu Sulfide Compounds

The synthesis of a new compound, $Pb_2Sr_2CaCu_3S_x$ was attempted first with the method given in experimental section. In this case Ca cation was located in A site and oxygen was totally replaced by sulfur in $Pb_2Sr_2ACu_3O_{8+\delta}$. The X-Ray powder diffraction data of the product (Fig.3.1.) was almost the same as PbS (galena) reported in JCPDS Card No. 5-0592 which has rock salt structure with the space group Fm3m and the unit cell dimension is 5.9362 A° [1,77]. Also, α-K_2UF_6 (JCPDS Card No: 12-42, cubic with a = 5.946 A°) has the same X-Ray diffraction pattern but with different intensities. In our case there were some splittings in the d-spacings showing that there is a distortion to monoclinic symmetry. Besides, there were some extra peaks, the strongest one at d= 1.96A° which belongs to $Cu_{2-x}S$ (JCPDS Card No.33-489), in the same diffraction pattern.

The powder pattern for $Pb_2Sr_2CaCu_3S_x$ was given in Table 3.1. It was indexed in the monoclinic system using the cell parameters similar to those of PbS. Some of the

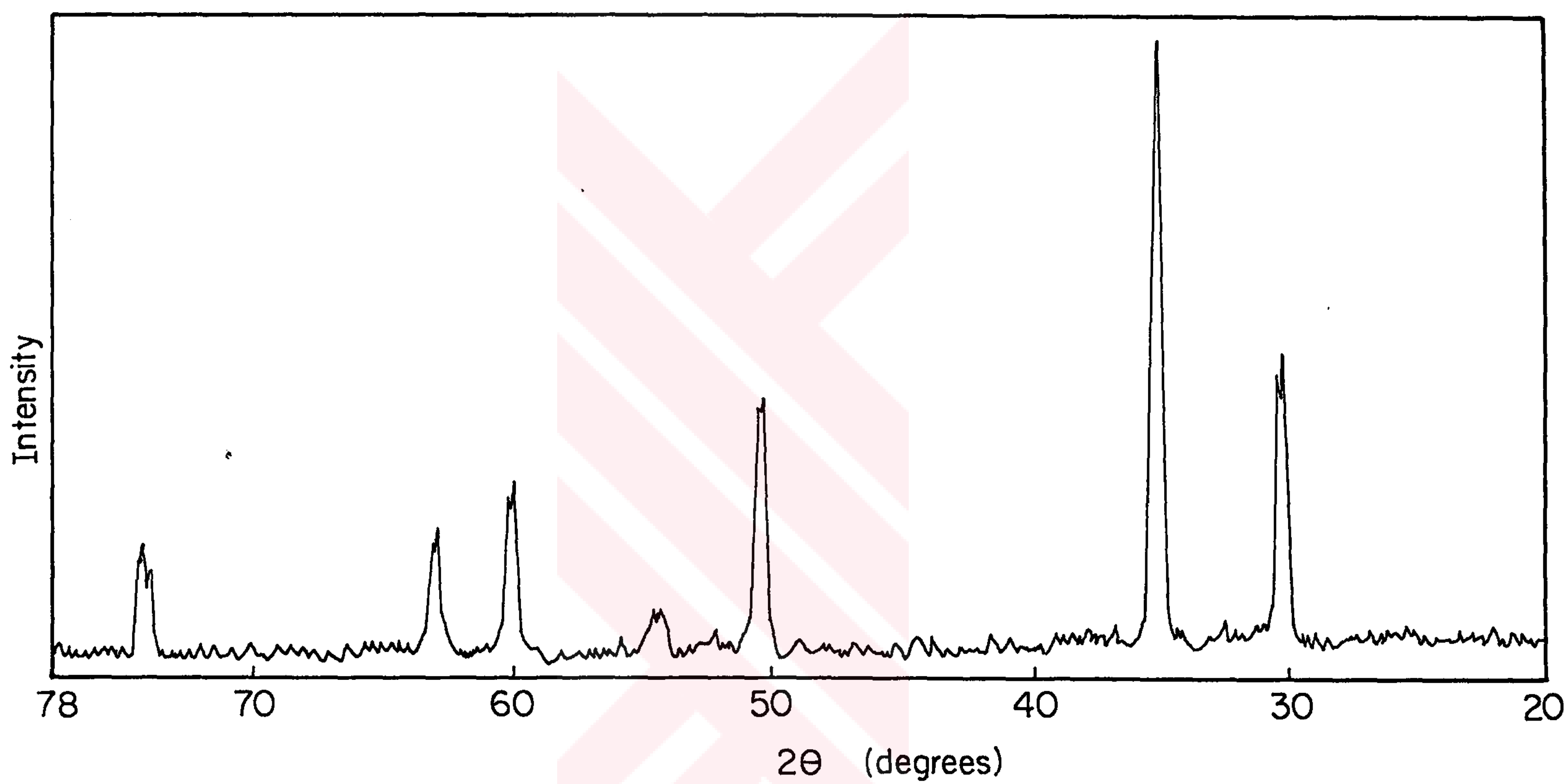

Fig. 3.1. X-Ray Powder Diffraction Pattern of $Pb_2Sr_2CaCu_{3-y}S_x$ (Sample No.3D)

Table 3.1.

X-Ray Powder Diffraction Data of $Pb_2Sr_2CaCu_{3-y}S_x$

Monoclinic (a=5.9477, b=5.9412, c=11.98A° β=90.19°)

Rad CoKα

Sample No: 3D $Pb_2Sr_2CaCu_{3-y}S_x$			**PbS (JCPDS Card No: 5-592)**		
d_{obs}	**I/I_o**	**hkl**	**d_{obs}**	**I/I_o**	**hkl**
3.43	45	11-2	3.43	84	111
3.42	50	112			
2.973	100	200	2.969	100	200
2.106	40	024			
2.104	38	220	2.099	57	220
1.794	30	13-2			
1.790	25	132	1.790	35	311
1.715	28	224			
1.713	22	007	1.714	16	222
1.487	18	400	1.484	10	400
1.485	20	040			
1.483	20	31-5			

weak lines including d = 1.96 A° were found to be impossible to index in this system. The unit cell dimensions were found to be as a= 5.947(8)A°, b=5.941(3)A°, c=11.98(1)A° and β= 90.19°(9). By looking at the cell dimensions, it is seen that the c length is almost twice of a and b unit cell dimensions. This enlargement indicates the formation of superstructure which is expected for these type of materials that contain many atoms. On the other hand, it is known that sulfur doping causes the formation of multiphase like CuS (covallite) [70]. In this work, since sulfidizing and reducing gas mixture was used in the synthesis of sulfide compounds, the formation of $Cu_{2-x}S$ was reasonable since part of the Cu^{2+} was reduced to Cu^{1+}. In the case of complete substitution the formula should be $Pb_2Sr_2CaCu_3S_x$ where x < 8 depending on the concentration of Cu^{+1}. On the other hand since $Cu_{2-x}S$ is present in the system as a different phase (JCPDS Card No 33-489), the final formula should be then $Pb_2Sr_2CaCu_{3-y}S_x$. In order to get a better understanding of the structure of this material EDX (Fig. 3.2.) and SEM (Fig. 3.3.) were done.

Suprisingly, both SEM and EDX analysis of the sample proved the presence of $Cu_{2-x}S$ crystals as a secondary phase at the surface of the pellet. The calculated formula was Cu_9S_6. In EDX again we detected that S was not homogeneously distributed in the sample but form multiphase. A small portion of sulfur may be in the actual conducting phase. Unfortunately, we could not do SEM analysis in the core of the same pellet. Hopefully, it would show different picture than the one taken at the surface. That is homogeneous distribution of sulfur in the sample would be

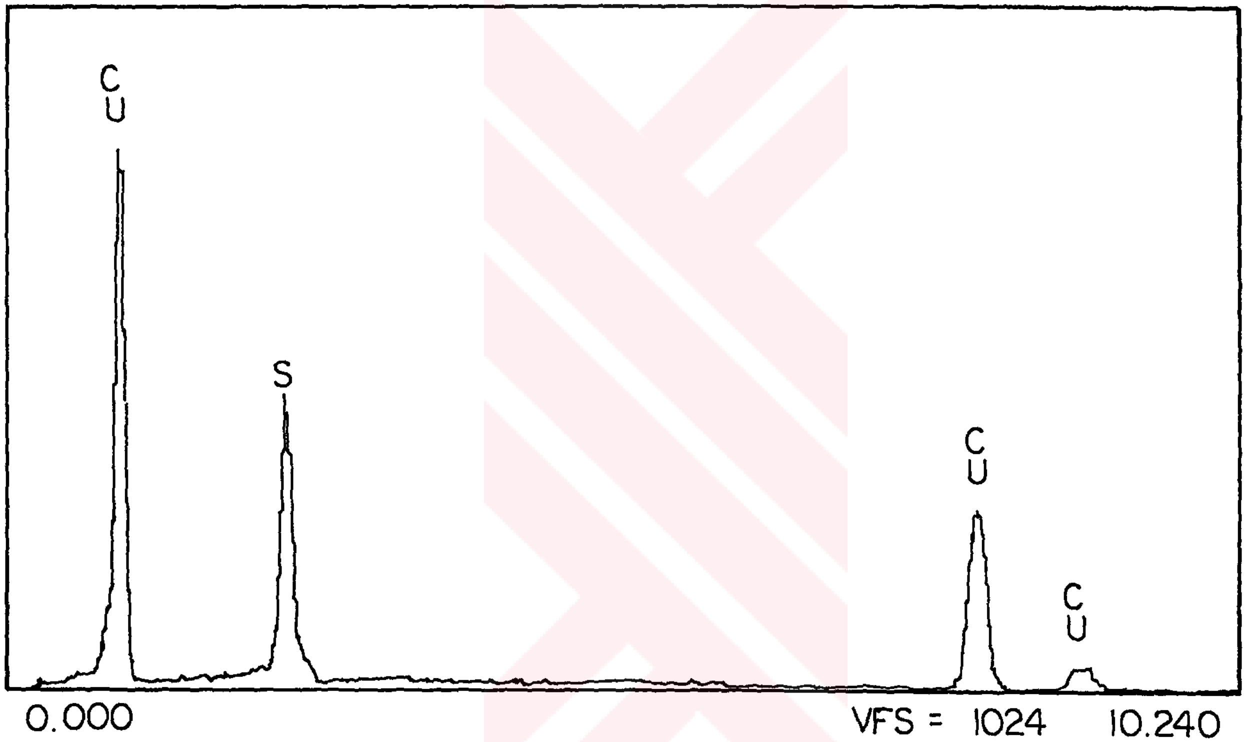

Fig. 3.2. EDX Spectrum of $Cu_{2-x}S$ in $Pb_2Sr_2CaCu_3S_x$ (Sample No 3D)

Fig.3.3. SEM Micrographs of $Pb_2Sr_2CaCu_{3-y}S_x$ (Sample No. 3D)

visible and this sulfur should be in the crystal lattice as there is an enlargement in the cell dimensions compared to the oxygen compound. If a comparison is done between sulfide and oxide material, an enlargement has been observed in a and b cell parameters of the sulfur doped material. Although Tamura et al. [40] reported that a=b≅3.83A° for Pb-1223 oxide, when we carried out a complete substitution, we observed an enlargement in both a and b lengths, (a≅b=5.94A°), which is close to the unit cell dimension of PbS. This enlargement in a and b cell parameters is expected, as the ionic radius of sulfur (1.70A°) is larger than that of oxygen (1.40A°). Formation of superstructure for these type of materials (more than two atoms) is common. The formation of a perovskite structure may be possible with sulfide ions making the cubic, or a tetragonal symmetry similar to the known Pb-Sr-Ca-Cu-O homologous system. On the other hand, Wu et al. [41] stated that the basic structure of Pb-Sr-Ca-Cu-O is isostructural to the Tl- or Hg-based superconductors. This structure is constructed by a rock salt block. Wu et al.[41-42] by Rietveld analysis found that "Pb"-1223 phase has a tetragonal symmetry whereas "Pb"-1212 has an orthorhombic crystal structure with pseudo-tetragonal symmetry. Also they reported a commensurate superstructure was found for "Pb"-1212 $((Pb_{0.5}Cu_{0.3}Sr_{0.2})Sr_2(Ca_{0.6}Sr_{0.4})Cu_2O_y)$ and an incommensurate superstructure for "Pb"-1223 $((Pb_{0.5}Cu_{0.25}Sr_{0.25})Sr_2(Ca_{0.87}Sr_{0.13})_2Cu_3O_9)$ phase that is B face centered.

In this study, $Pb_2Sr_2CaCu_{3-y}S_x$ obtained has a distorted (monoclinic) rock salt (NaCl) superstructure and the superstructure should be formed from the two rock salt blocks since the c cell parameter is doubled compared to cubic PbS structure.

Apart from X-Ray diffraction, SEM and EDX analysis, IR and conductivity measurements were also carried out. In EDX analysis (Fig.3.4.), oxygen could not be detected. In Infrared spectrum, no peaks were observed (Fig.3.5.) due to sulfate anion or M-O stertching vibrations in the range studied (4000-400 cm^{-1}). This would be a proof of the absence of oxygen in the samples. Frequencies caused by M-S stretching vibrations occur below 400 cm^{-1} [30]. It is also significant for us to know, if by this method we can prepare oxygen free sulfide materials. To find the correct amount of sulfur in the $Pb_2Sr_2CaCu_3S_x$ samples, elemental analysis was done which gave x=6.5. According to this result, the chemical formula should be $Pb_2Sr_2CaCu_3S_{6.5}$. This shows the reduction of Cu^{2+} to Cu^{1+} and Cu^{o}. However, if

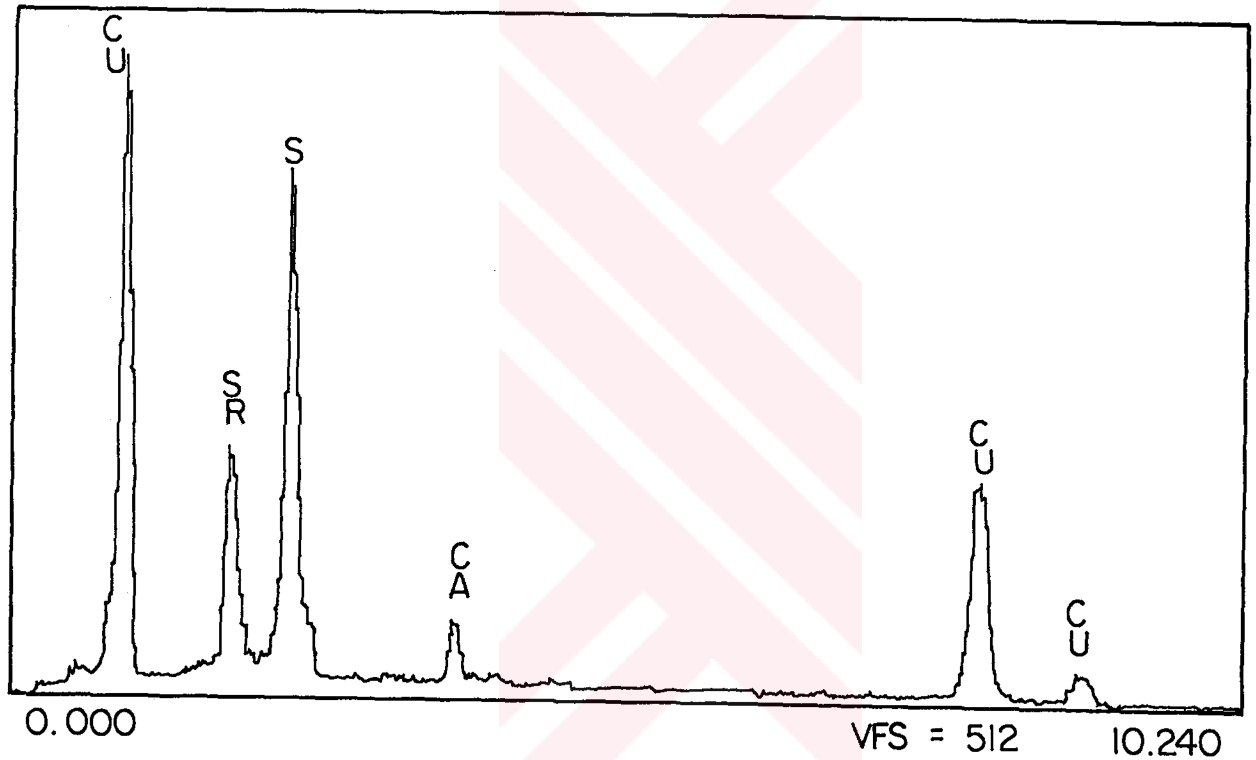

Fig. 3.4. EDX Spectrum of $Pb_2Sr_2CaCu_{3-y}S_x$ (Sample No.3D)

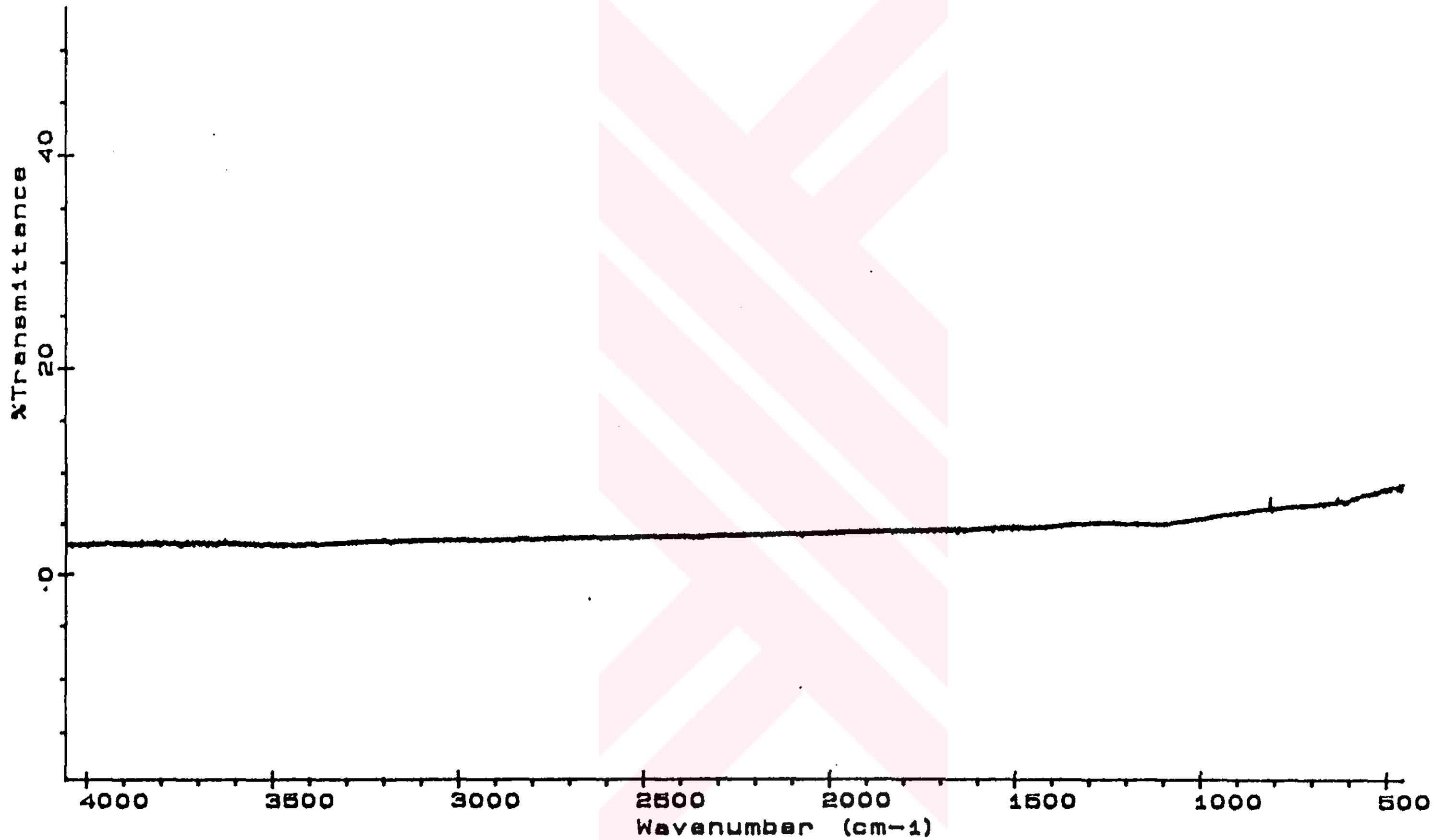

Fig.3.5. IR Spectrum of $Pb_2Sr_2CaCu_{3-y}S_x$ (Sample No. 3D)

there is a formation of $Cu_{2-x}S$ phase, the formula should change. The proposed formula could be $Pb_2Sr_2CaCu_{1.5}S_6$ + $Cu_{1.5}S$ or something similar. In $Pb_2Sr_2CaCu_{1.5}S_6$ and $Cu_{1.5}S$, the copper ions should be both in the form of Cu^{2+} and Cu^{+1}. So the formula may be written as $Cu_{2-x}S$. The JCPDS data (Card No.33-486) fits to the unindexed $Cu_{2-x}S$ lines in the pattern 3D. It was indexed in the orthorhombic system (Table 3.2.) as given in the literature where, for example, Cu_2S, chalcocite, has orthorhombic structure (pseudo-hexagonal) [78].

Conductivity measurements are done by using four probe technique, designed in our laboratory [28]. The sample showed metallic behavior in temperature range of liquid nitrogen (Fig. 3.6).

In the literature, basically partial sulfur substitution had been studied since total substitution causes multiphases with degradation of superconductivity. In our case we also confirmed that the superconductivity was destroyed at high sulfur substitution by forming $Cu_{2-x}S$ crystals. However, in contrast to Taylor et al. [57] who stated that complete substitution caused semiconductivity, our material showed metallic behavior with appreciable room temperature resistance.

The results obtained from the above mentioned experiments were not very clear and satisfying. Is the PbS structure accidental or are these compounds really contain PbS as a separate entity. If the structure is indeed fcc, for a meaningful explanation it

Table 3.2.

X-Ray Powder Diffraction Data of $Cu_{2-x}S$

Orthorhombic (a=7.9065, b=7.8223, c=11.078)

Rad CoKα

Sample $Cu_{2-x}S$		**Cu_7S_4 (JCPDS Card No: 33-489)**		
d_{obs}	**I/I_o**	**d_{obs}**	**I/I_o**	**hkl**
3.92	3	3.92	5	112
3.36	15	3.36	25	211
		3.34	25	103,121
3.21	30	3.21	40	202
3.20	35	3.19	9	022
2.789	50	2.780	55	220
		2.769	15	004
2.690	20	2.697	25	221
		2.619	20	104
2.544	15	2.538	25	031
2.384	15	2.384	30	302
2.168	35	2.173	35	124
2.143	9	2.145	10	321

Table 3.2. (continued)

2.075	15	2.068	11	313
2.049	25	2.056	20	133
1.978	25	1.977	25	400
1.965	100	1.962	100	224
1.959	80	1.953	40	040
1.907	15	1.909	15	304
		1.8813	10	323
1.7980	20	1.7960	15	142
1.6906	5	1.6965	2	305
1.6845	10	1.6784	15	422,206
1.6692	15	1.6698	10	026
1.6391	3	1.6336	1	126
1.5913	2	1.5918	2	423
1.5548	6	1.5565	10	325
1.4459	3	1.4454	2	343

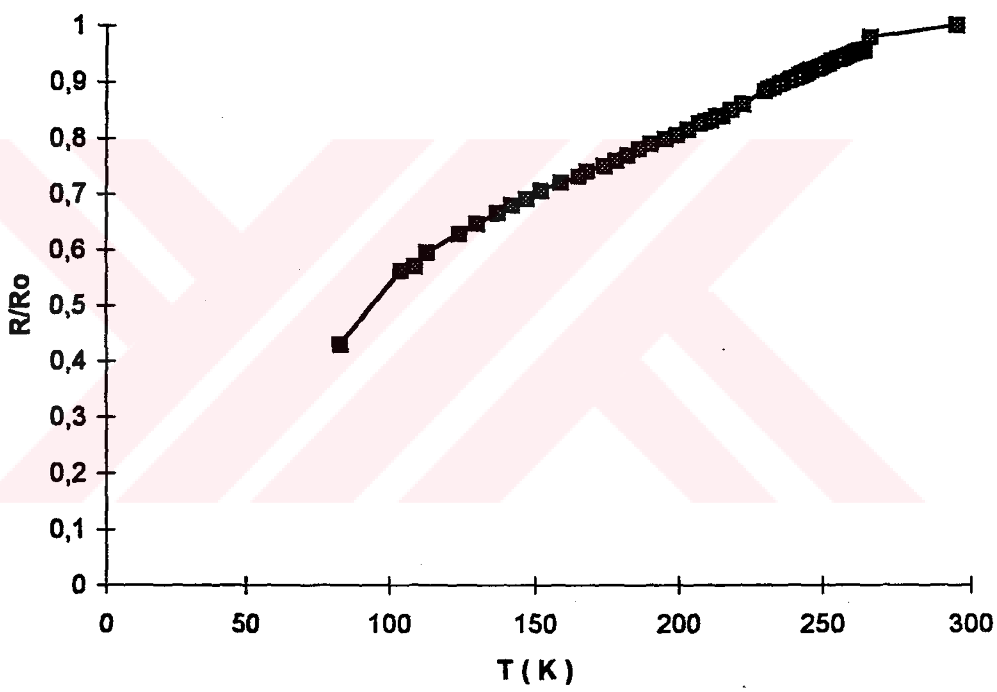

Fig. 3.6. Resistivity Measurement of $Pb_2Sr_2CaCu_{3-y}S_x$ (Sample No. 3D)

should be suggested that Pb and S forms the array of the parent cubic structure and the remaining cations go to the available cation positions (holes) alternatingly. Certainly, as there are four different cations each with different radius, it is difficult to observe simple cubic structure. Thus, observation of a distortion from cubic to tetragonal, orthorhombic or monoclinic structure with $a \cong b \cong c$ and $\beta \cong 90$ is reasonable.

3.2. Sulfidization of mixtures containing different amount of PbO

To be able to answer to the questions arose earlier and to make things more clear, several experiments were performed. First of all, we wished to see the effect of changing the concentration of Pb in the samples. In other words, the PbS structure may be due to lead sulfide alone and the remaining cations either form another phase or stay unreacted in the background and could not be detected by X-Ray powder diffraction. With this purpose, the amount of lead in the samples was stoichiometrically changed and the following mixtures

$2\ Sr(NO_3)_2 + CaO + 3\ CuO$ (Sample 3C)

$0.5\ PbO + 2\ Sr(NO_3)_2 + CaO + 3\ CuO$ (Sample 3B)

$PbO + 2\ Sr(NO_3)_2 + CaO + 3\ CuO$ (Sample 3A)

$2\ PbO + 2\ Sr(NO_3)_2 + CaO + 3\ CuO$ (Sample 3D)

were sulfidized and extraordinary results were obtained. Interestingly enough, PbS structure remained same even in the sample where Pb is absent. For the compound (3C), $Sr_2CaCu_3S_x$, we observed an X-Ray diffraction pattern similar to PbS (Fig 3.7.,

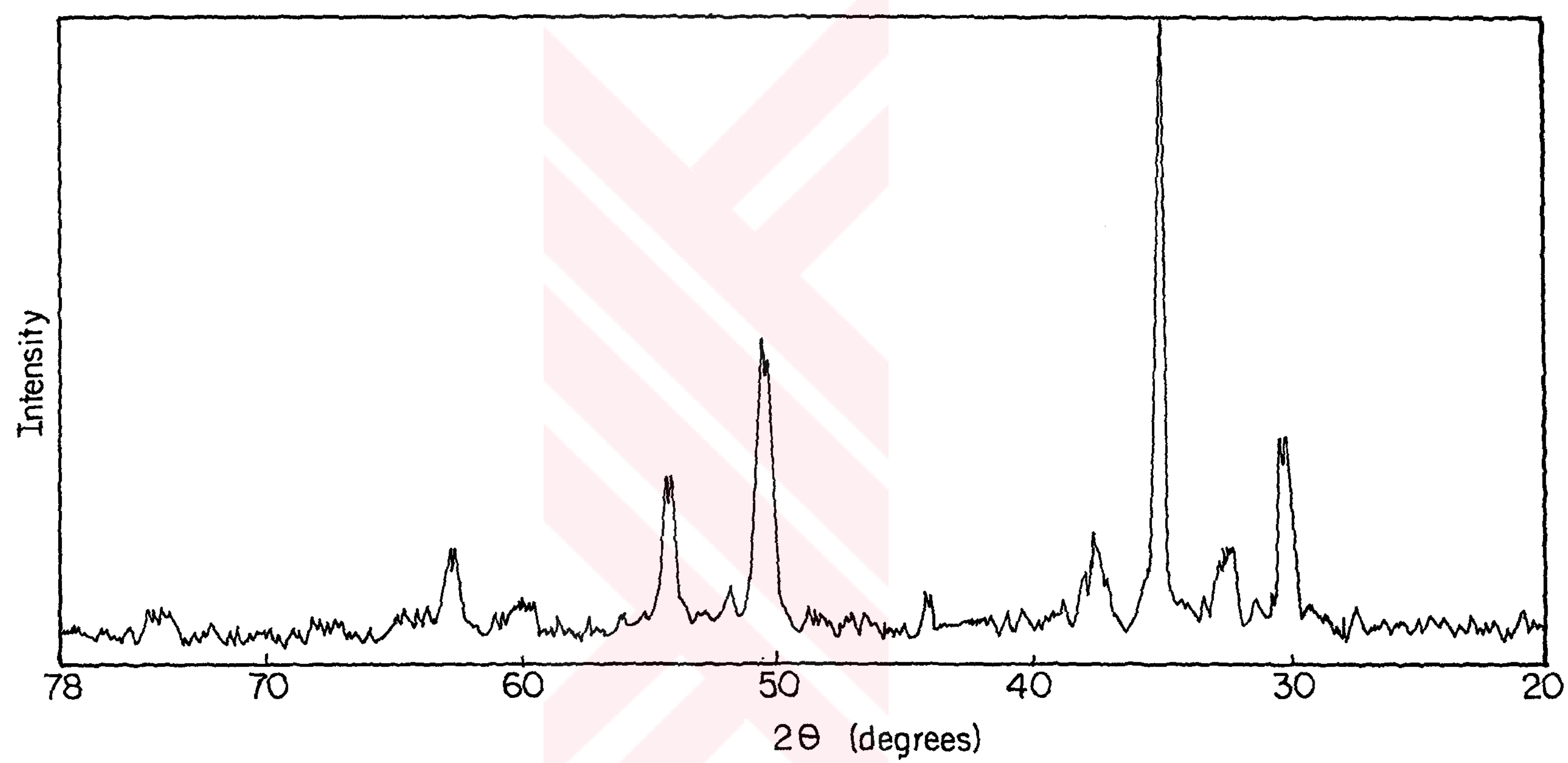

Fig. 3.7. X-Ray Powder Diffraction Pattern of $Sr_2CaCu_3S_x$ (Sample No 3C)

Table 3.3.

X-Ray Powder Diffraction Data of $Sr_2CaCu_{3-y}S_x$

Monoclinic (a=5.9583, b=5.95036, c=11.89A° β=90.19°)

Rad CoKα

Sample No: 3C $Sr_2CaCu_{3-y}S_x$			**PbS (JCPDS Card No: 5-592)**		
d_{obs}	**I/I_o**	**hkl**	**d_{obs}**	**I/I_o**	**hkl**
3.44	25	11-2			
3.43	22	112	3.43	84	111
2.976	100	020	2.969	100	200
2.098	75	204	2.099	57	220
1.798	14	31-2			
1.795	10	13-2			
1.787	10	116	1.790	35	311
1.718	18	224			
1.713	19	22-4	1.714	16	222
1.483	12	31-5	1.484	10	400

Table 3.3.). The other important outcome is that d =1.96 A° peak was present in all of the diffraction patterns which may be taken as the evidence of the formation of another phase. Based on the observations and discussions above, it can be deduced that $Cu_{2-x}S$ is formed in all of the samples making them multiphasic. The diffraction pattern of $Cu_{2-x}S$ in $Sr_2CaCu_3S_x$ is given in Table 3.2. $Sr_2CaCu_3S_x$ was also indexed as distorted NaCl (monoclinic) superstructure like $Pb_2Sr_2CaCu_{3-y}S_x$.

$Sr_2CaCu_3S_x$ (3C), was subjected to EDX, SEM. In SEM picture, $Cu_{2-x}S$ crystals are seen at the surface of the pellet (Fig 3.8), showing the multiphase formation for $Sr_2CaCu_3S_x$ nominal composition. Similar to IR (Fig. 3.9), also in EDX (Fig.3.10.) no oxygen could be detected.

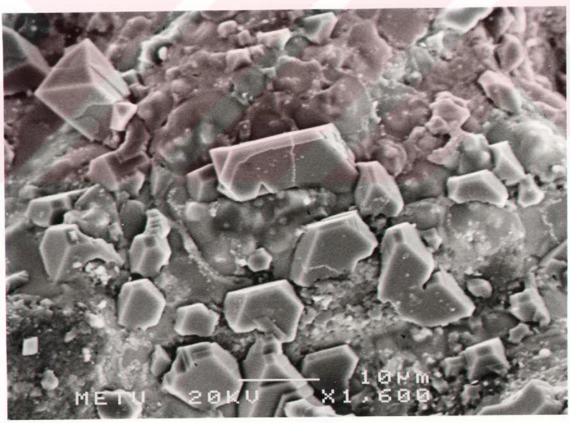

Fig. 3.8. SEM Micrograph of $Sr_2CaCu_3S_x$ (Sample No 3C)

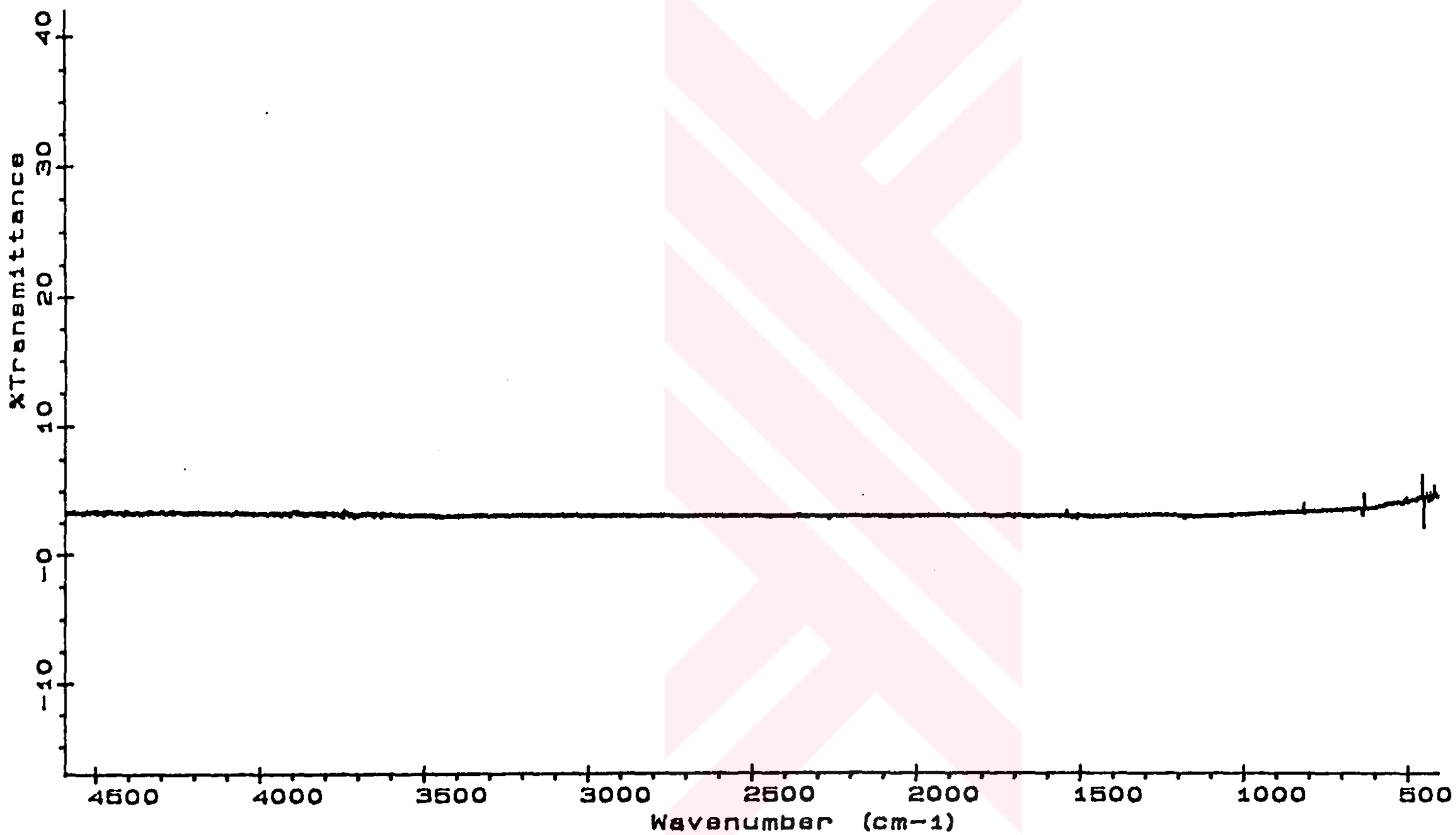

Fig.3.9. IR Spectrum of $Sr_2CaCu_3S_x$ (Sample No. 3C)

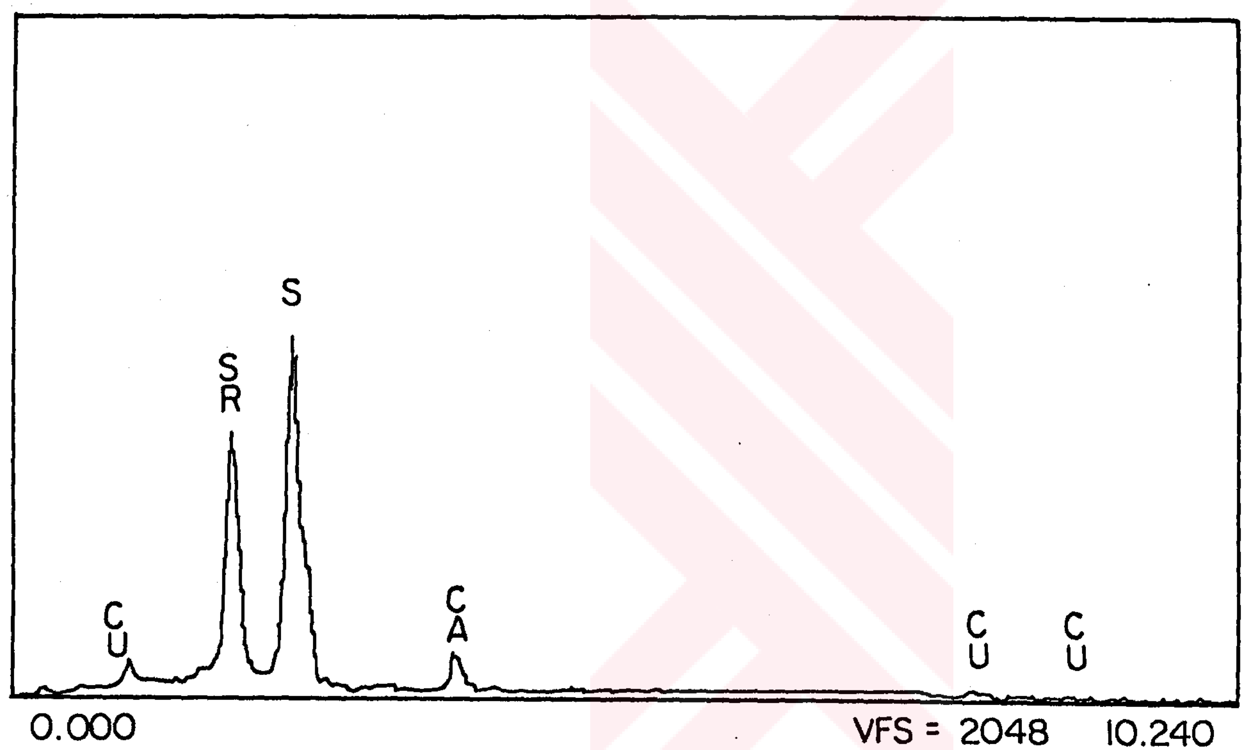

Fig. 3.10. EDX Spectrum of $Sr_2CaCu_3S_x$ (Sample No. 3C)

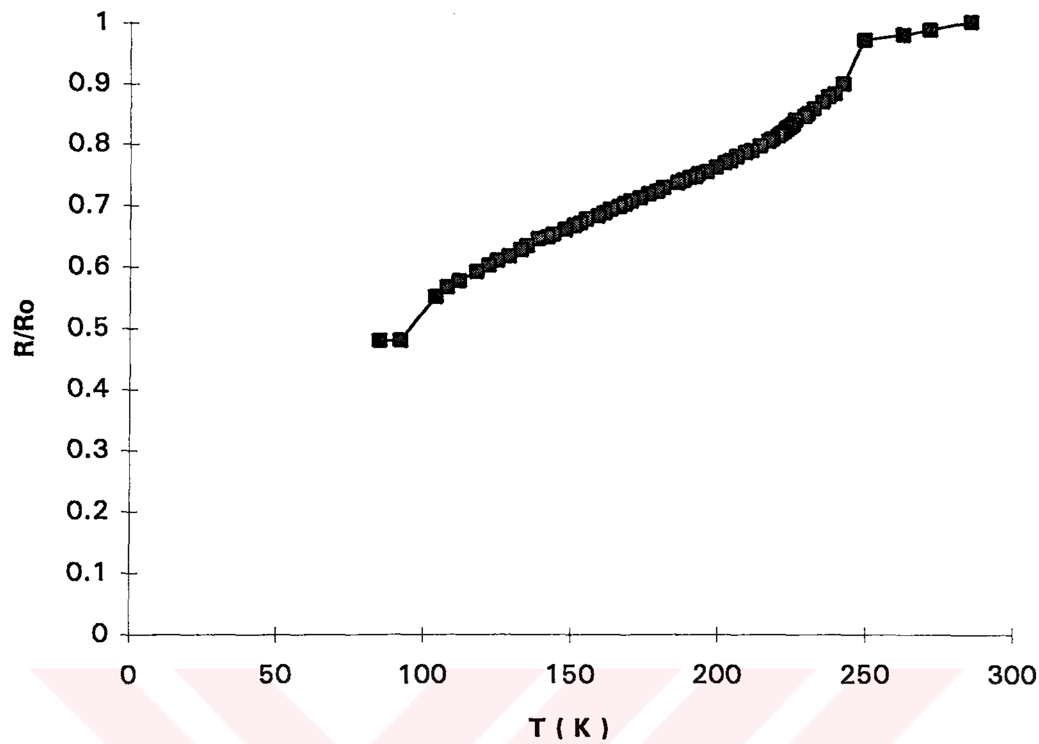

Fig. 3.11. Resistivity Measurement of $Sr_2CaCu_3S_x$ (Sample No 3C)

Conductivity measurement is also carried out for $Sr_2CaCu_3S_x$ and like $Pb_2Sr_2CaCu_3S_x$, this sample also exhibited metallic behavior (Fig.3.11.).

If partial substitution had been studied instead of complete substitution, we could probably observe single phase materials. Thus going from $Pb_2Sr_2CaCu_3S_x$ (3D) to $PbSr_2CaCu_3S_x$ (3A) (Fig.3.12.), $Pb_{0.5}Sr_2CaCu_3S_x$ (3B) (Fig.3.13.) and finally to $Sr_2CaCu_3S_x$, (3C) we observed the increase in intensity of the other phases but the

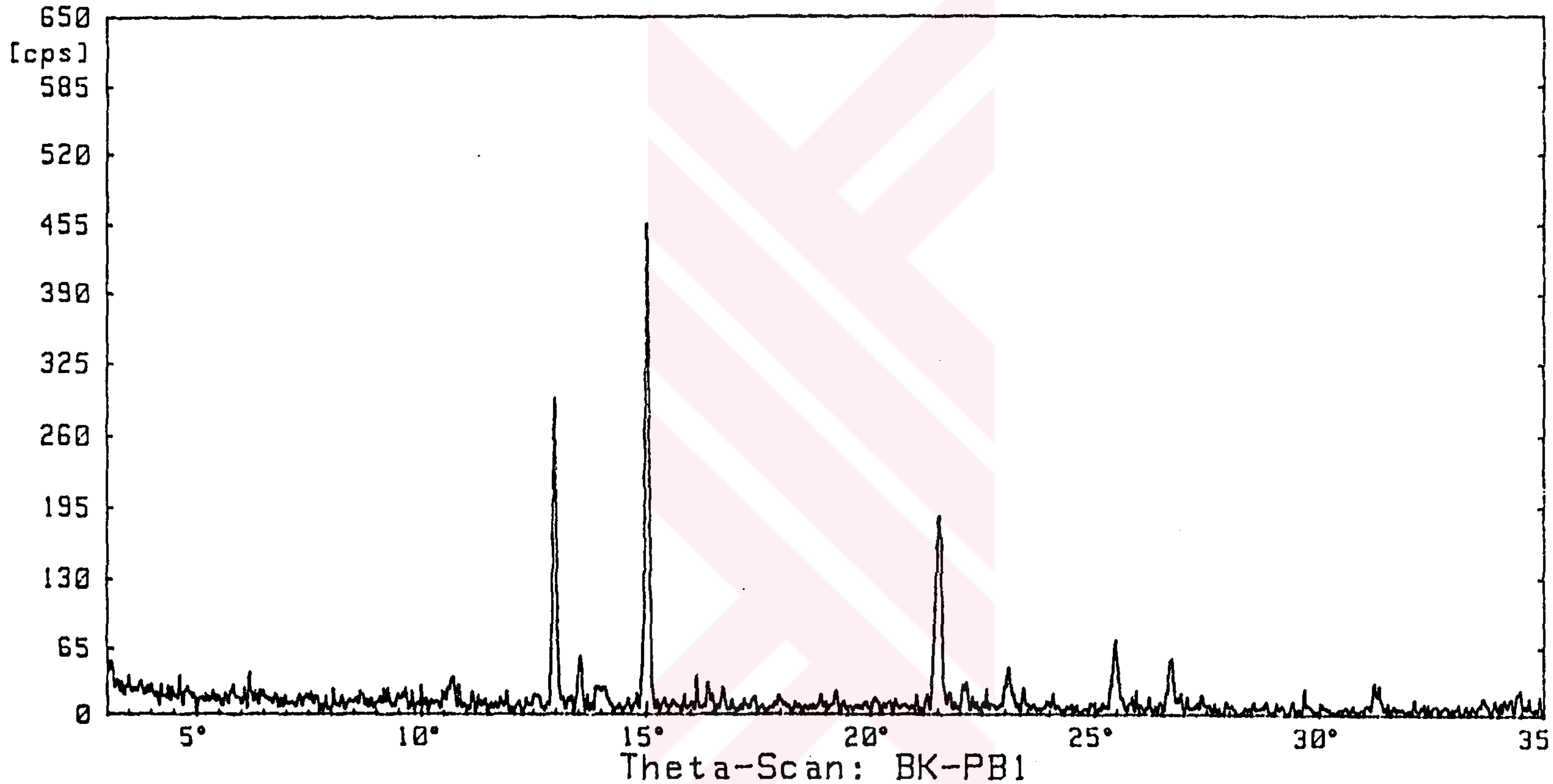

Fig.3.12. X-Ray Powder Diffraction Pattern of $PbSr_2CaCu_3S_x$ (Sample 3A)

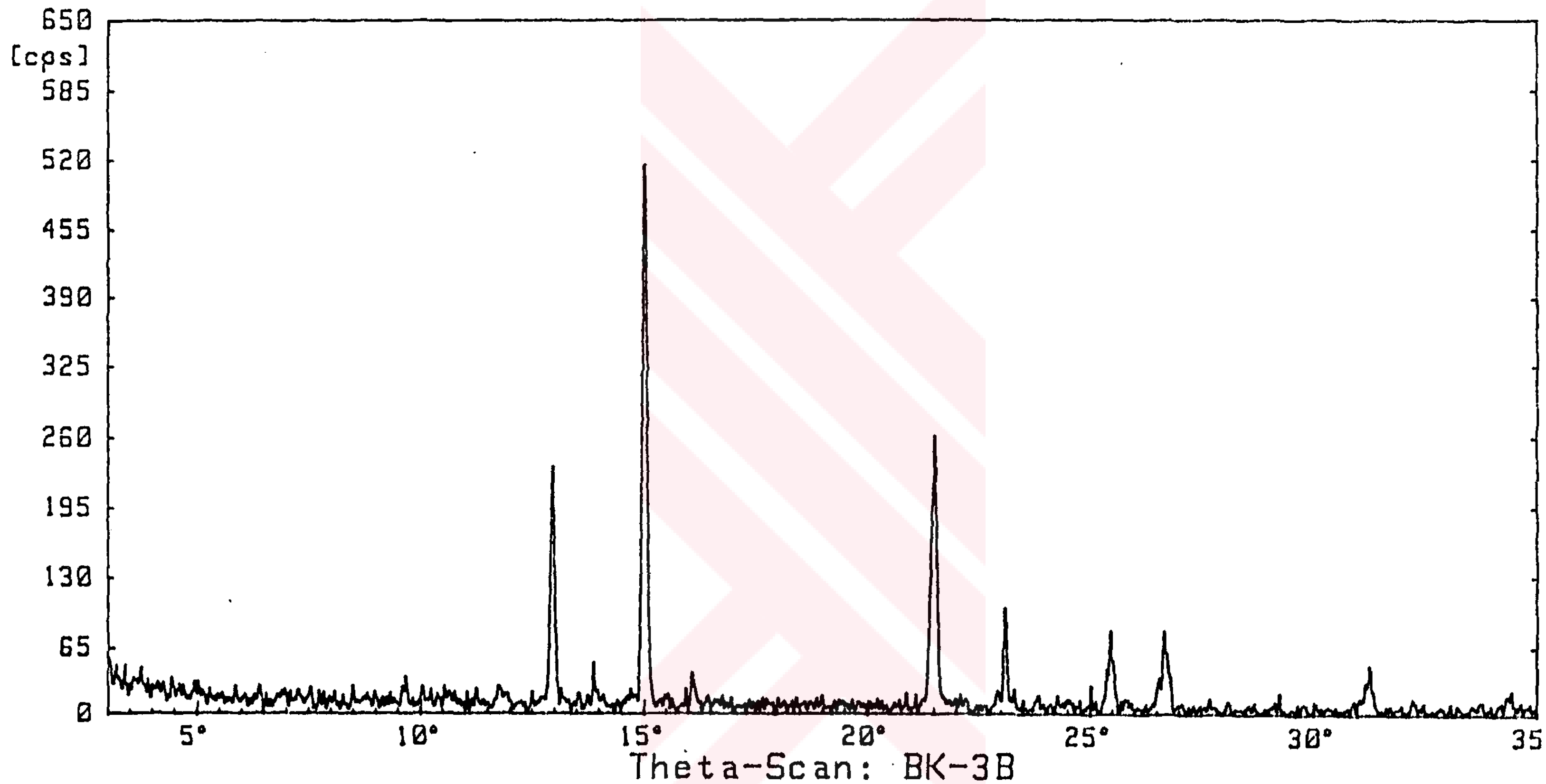

Fig.3.13. X-Ray Powder Diffraction Pattern of $Pb_{0.5}Sr_2CaCu_3S_x$ (Sample 3B)

main structure remained to be PbS crystal structure. Actually, there is a shift in the d-values compared to PbS (JCPDS Card No 5-592) which is expected because the presence of four cations in the sample increases the dimensions of the unit cell. Another feature which has been observed was that these ions did not crystallize in another crystal structure but somehow was stable in PbS structure.

3.3. Sulfidization of mixtures containing different amounts of $Sr(NO_3)_2$

In order to find the contribution of the atoms to the crystal structure or to the formation of other phases, different possibilities have been studied. In an effort to understand the effect of Sr in the crystal structure $Pb_2SrCaCu_3S_x$, $Pb_2Sr_3CaCu_3S_x$ and $Pb_2Sr_4CaCu_3S_x$ were synthesized apart from the parent material $Pb_2Sr_2CaCu_3S_x$ by sulfidizing the following mixtures.

$2PbO + Sr(NO_3)_2 + CaO + 3CuO$ (Sample No 4H)

$2PbO + 3Sr(NO_3)_2 + CaO + 3CuO$ (Sample No 4F)

$2PbO + 4Sr(NO_3)_2 + CaO + 3CuO$ (Sample No 4G)

When we compare the three X-Ray powder diffraction patterns (Fig.3.14.), the most important difference among them is the shift to higher d-values as the number of atoms increases. As the unit cell dimensions increase with increasing number of atoms, this is an expected result. Probably, in all the samples there was a formation of $Cu_{2-x}S$ phase. In the IR spectrum sulfate peaks could not be detected, so all the oxygen should be substituted by sulfur. It is convenient to think that in all the

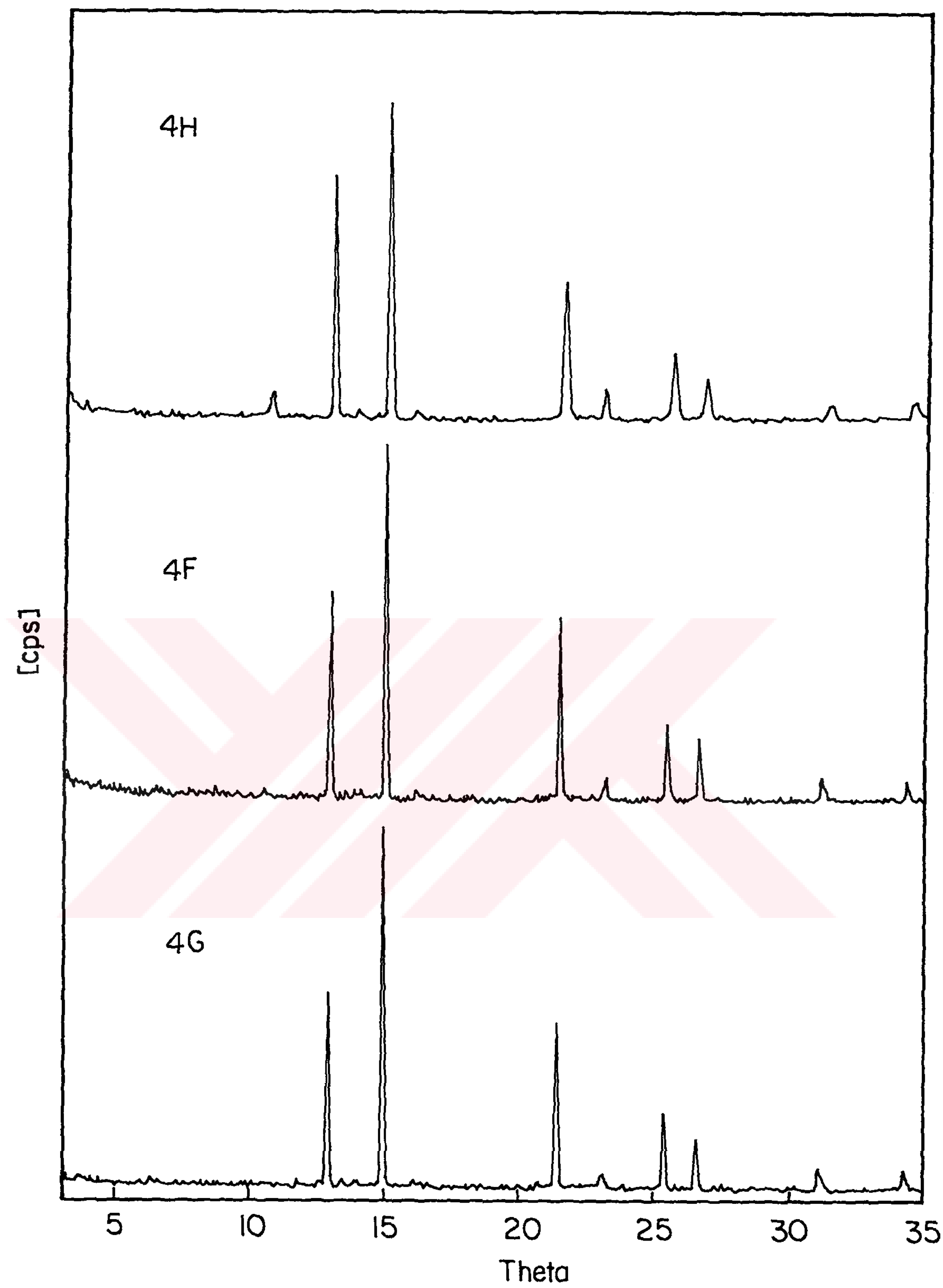

Fig. 3.14. X-Ray Powder Diffraction Patterns of $Pb_2SrCaCu_3S_x$ (Sample No. 4H), $Pb_2Sr_3CaCu_3S_x$ (Sample No. 4F) and $Pb_2Sr_4CaCu_3S_x$ (Sample No. 4G)

different stoichiometries were studied, there is not a change in crystal structure since PbS peaks are always dominant. We can propose that a layered or a superstructure was formed, therefore the cations are in the holes and they cannot be detected by X-Ray diffraction method. Besides, the change in Sr content (as the ratio increases from 1 to 4) does not induce a distortion in the observed PbS crystal structure.

3.4. Sulfidization of binary mixtures of IIA or IIA and Cu Compounds

The other possibilities include Sr_2CaS_x, $Sr_2Cu_3S_x$ and $CaCu_3S_x$ ternary sulfides. To investigate these possibilities the following mixtures were sulfidized.

$2Sr(NO_3)_2 + CaO$ (Sample No 4A)

$2Sr(NO_3)_2 + 3CuO$ (Sample No 4B)

$CaO + 3CuO$ (Sample 4C)

In the X-Ray powder pattern of the product of the 2 $Sr(NO_3)_2$ + CaO sulfidizing reaction (4A), two phases were observed; which have yellow and white colours. In their X-Ray and IR spectra SO_4^{2-}formation (oxidation from S^{2-} to S^{6+}) was evident . The SO_4^{2-} present (Fig.3.15.) is mainly in the form of $SrSO_4$. The powder appearing white is mostly $SrSO_4$ with very minor amount of SrS. On the other hand, the yellow powder has almost equal amounts of SrS and $SrSO_4$. The striking observation from these powder patterns are that any calcium compound could not be observed. It should be in the form of either CaS or $CaSO_4$. Actually, Ca was present but due to its low atomic scattering factor and atomic weight it was not easy to differentiate

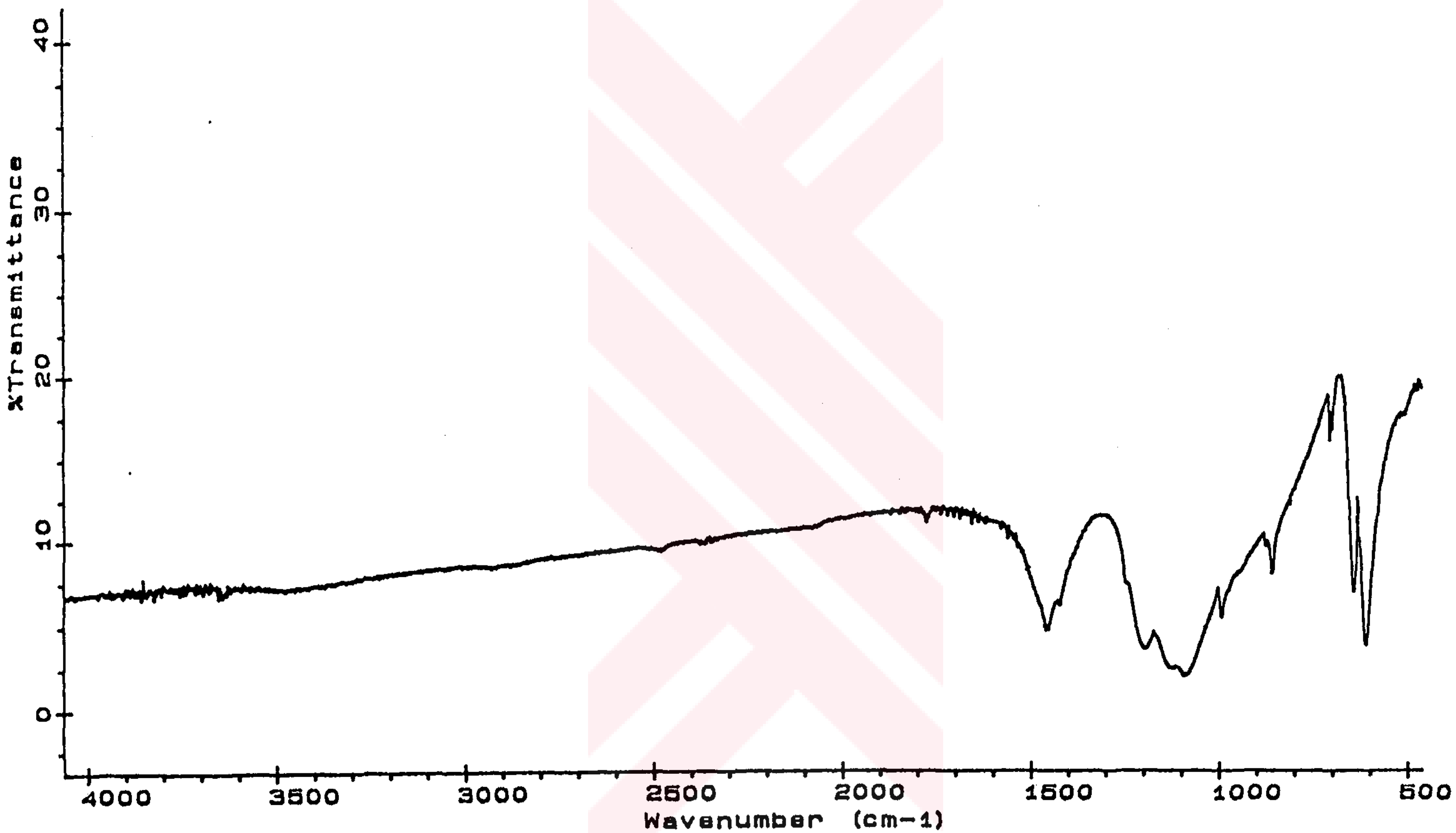

Fig.3.15. IR Spectrum of Sr_2CaS_x(Sample No. 4A)

calcium compound peaks from the background. What we can conclude from these result is that strontium and calcium together does not form a stable phase.

$2Sr(NO_3)_2$ + 3CuO sulfidizing reaction gave a product which had an X-Ray diffraction pattern mainly consisting of SrS peaks with very strong intensities. $Cu_{2-x}S$ is also formed with very weak intensities. Thus two phases are clearly visible, and SO_4^{2-} peaks cannot be observed in IR. Again it is seen that strontium and copper together do not form a stable phase.

The last of the tried ternary sulfides is $CaCu_3S_x$ which was attempted to prepare through CaO + 3CuO (4C) sulfidizing reaction. Here again multiphase formation is evident. These are CaS, CuS and possibly $CaSO_4$. However, in the IR spectrum SO_4^{2-} peaks were not observed. Thus there should be other phases present which have X-Ray diffraction pattern almost overlapping with $CaSO_4$.

The results of all these experiments, in a way showed us that neither Ca and Sr, nor Sr and Cu or Ca and Cu form stable ternary sulfides under sulfidizing gas atmosphere for five hours heating period at 800° C. So in $Pb_2Sr_2CaCu_3S_x$ phase that we prepared, the peaks observed in the powder pattern are not due to ternary phase formation.

3.5. Sulfidization of CaO, $Sr(NO_3)_2$, PbO and CuO

(Synthesis of the Sulfide Compounds of the Initial Reactants)

When CaO was sulfidized under the same experimental conditions pure CaS is obtained. The X-Ray diffraction pattern (Fig. 3.16) and Infrared spectrum (Fig. 3.17) of CaS obtained are given. In Table 3.4. the first five d-spacings of CaS are listed and compared with the d-spacings in the JCPDS Card.

Table 3.4. d-spacings of CaS; $4CaO + COS + CS_2 + CO + 1/2S_2 \rightarrow 4CaS + 3CO_2$ where a = 5.69 A°, Fm3m

CaS (Sample No 4D)		**JCPDS Card No 4-484**		
d (A°)	**I/I₀**	**d (A°)**	**I/I₀**	**hkl**
3.28	1	3.28	1	111
2.847	100	2.846	100	200
2.013	70	2.013	70	220
1.717	1	1.717	1	311
1.645	20	1.644	21	222

The first five d-spacings observed in X-Ray powder diffraction pattern (Fig. 3.18.) of SrS synthesized are given in Table 3.5. However, $Sr(NO_3)_2$ does not yield pure SrS but contaminated with some $SrSO_4$ present in the sample. The IR spectrum (Fig. 3.19.) obtained was the same as $SrSO_4$ given in literature. The formation of $SrSO_4$ could be eliminated by sulfidizing for longer time.

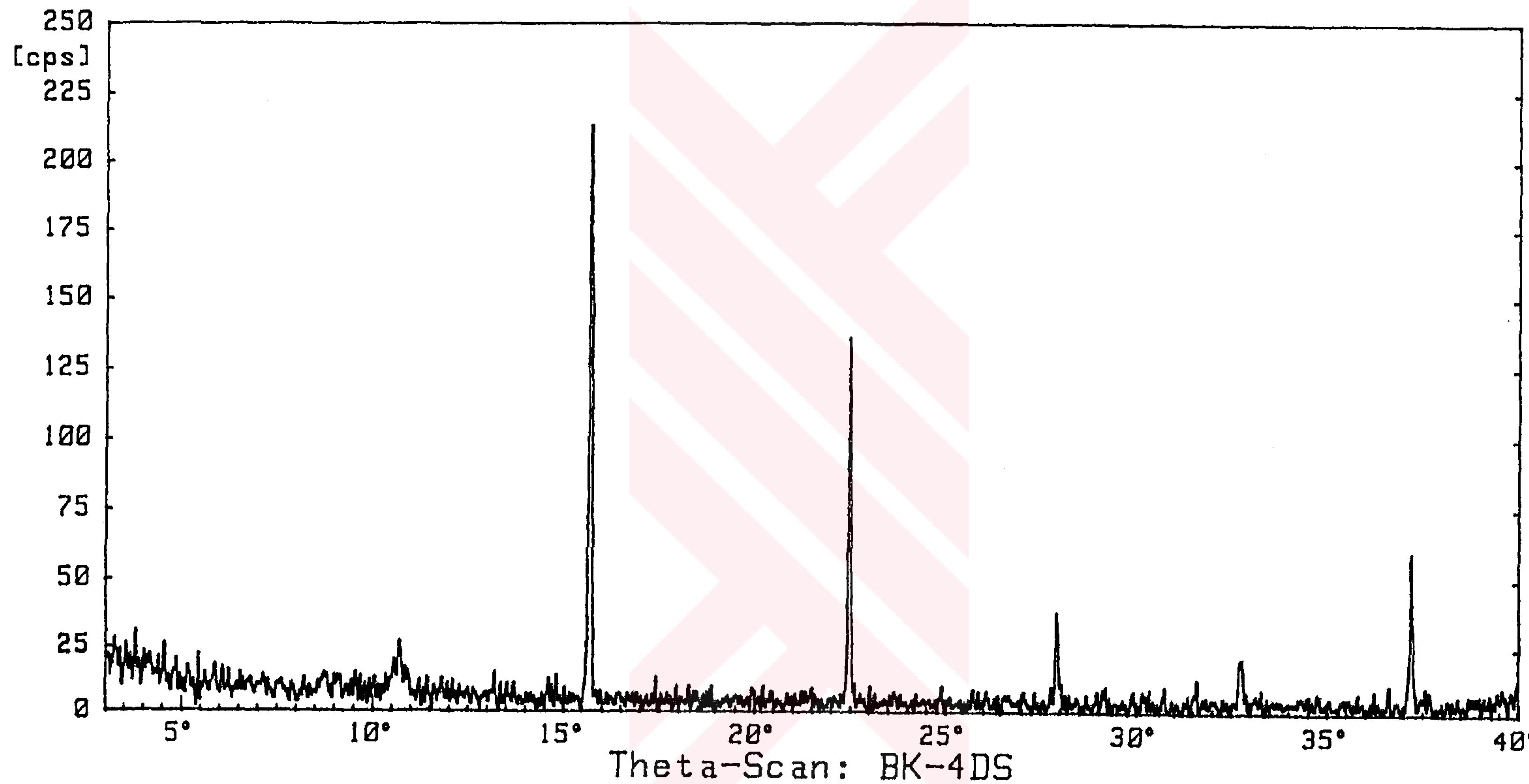

Fig.3.16. X-Ray Powder Diffraction Pattern of CaS (Sample 4D)

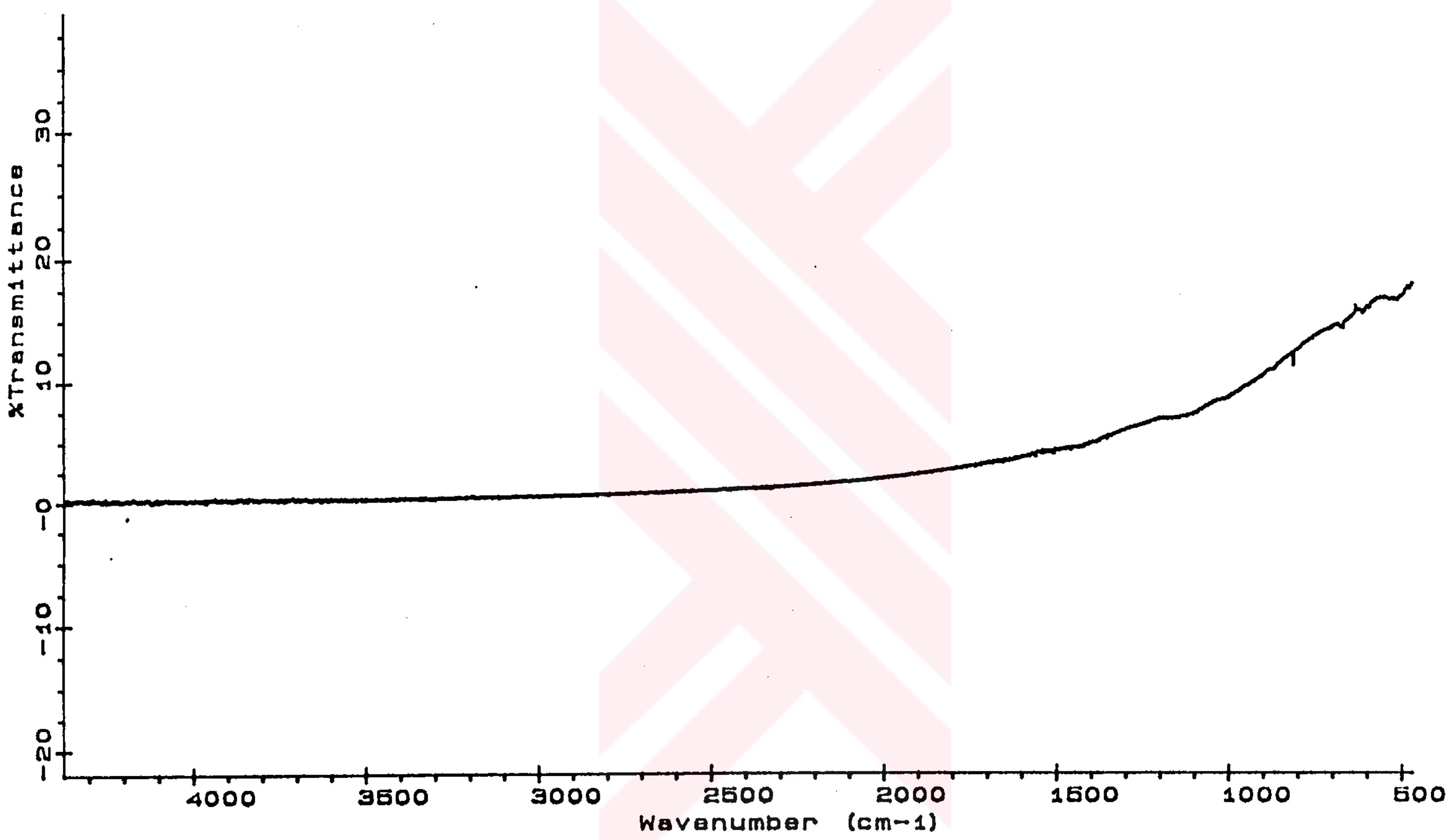

Fig.3.17. IR Spectrum of CaS (Sample No. 4D)

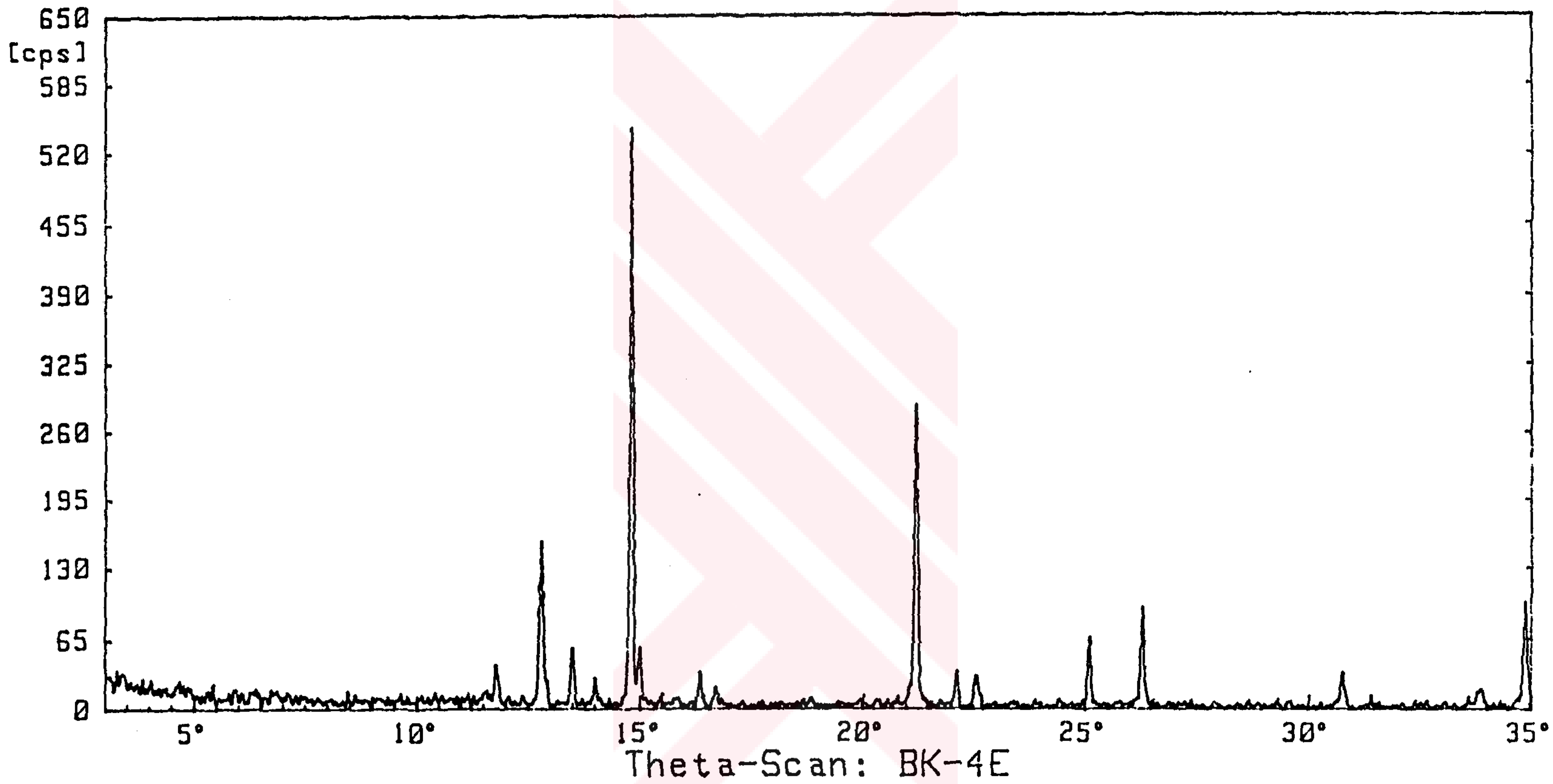

Fig.3.18. X-Ray Powder Diffraction Pattern of SrS (Sample 4E)

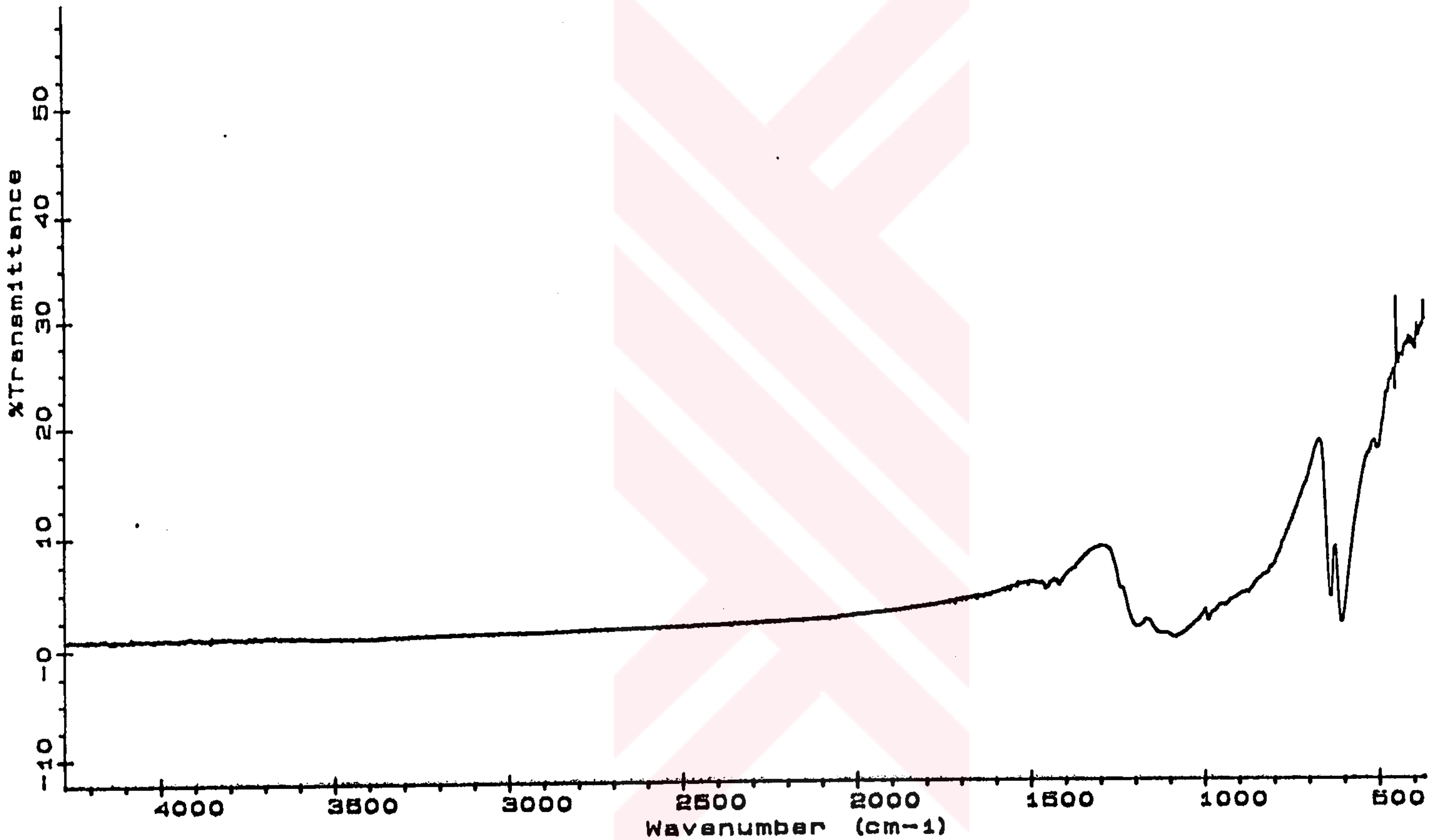

Fig.3.19. IR Spectrum of SrS (Sample No. 4E)

Table 3.5. d-spacings of SrS; $4Sr(NO_3)_2 + COS + CS_2 + 5CO + 1/2S_2 \rightarrow 4SrS + 7CO_2 + 8NO_2$

where a = 6.02 A°, Fm3m

SrS (Sample No 4E)		JCPDS Card No 8-489		
d (A°)	I/I$_o$	d (A°)	I/I$_o$	hkl
3.4796	35	3.479	30	111
3.002	100	3.007	100	200
2.1301	50	2.129	50	220
1.816	15	1.814	14	311
1.739	20	1.738	16	222

PbS was synthesized from the sulfidization of PbO at 800°C for an hour. One hour of reaction time was sufficient to obtain single phase PbS (Fig 3.20.). The IR spectrum (Fig. 3.21.) taken between 4000-400 cm^{-1} did not show presence of sulfate group. In Table 3.6., the d-spacings are given that entirely matches the JCPDS Card of PbS.

Table 3.6. d-spacings of PbS; $4PbO + COS + CS_2 + CO + 1/2S_2 \rightarrow 4PbS + 3CO_2$

where a = 5.936 A°, Fm3m

PbS (Sample No 4I)		JCPDS Card No 5-592		
d (A°)	I/I$_o$	d (A°)	I/I$_o$	hkl
3.432	86	3.429	84	111
2.972	100	2.969	100	200
2.10	67	2.099	57	220
1.791	45	1.79	35	311
1.714	23	1.714	16	222

As it is known, there are many different structures of copper sulfide. In these structures copper can be either in Cu^{1+} or Cu^{2+} state. Since in our reaction system the sulfidizing gases have reducing property as well, it is expected that copper should be

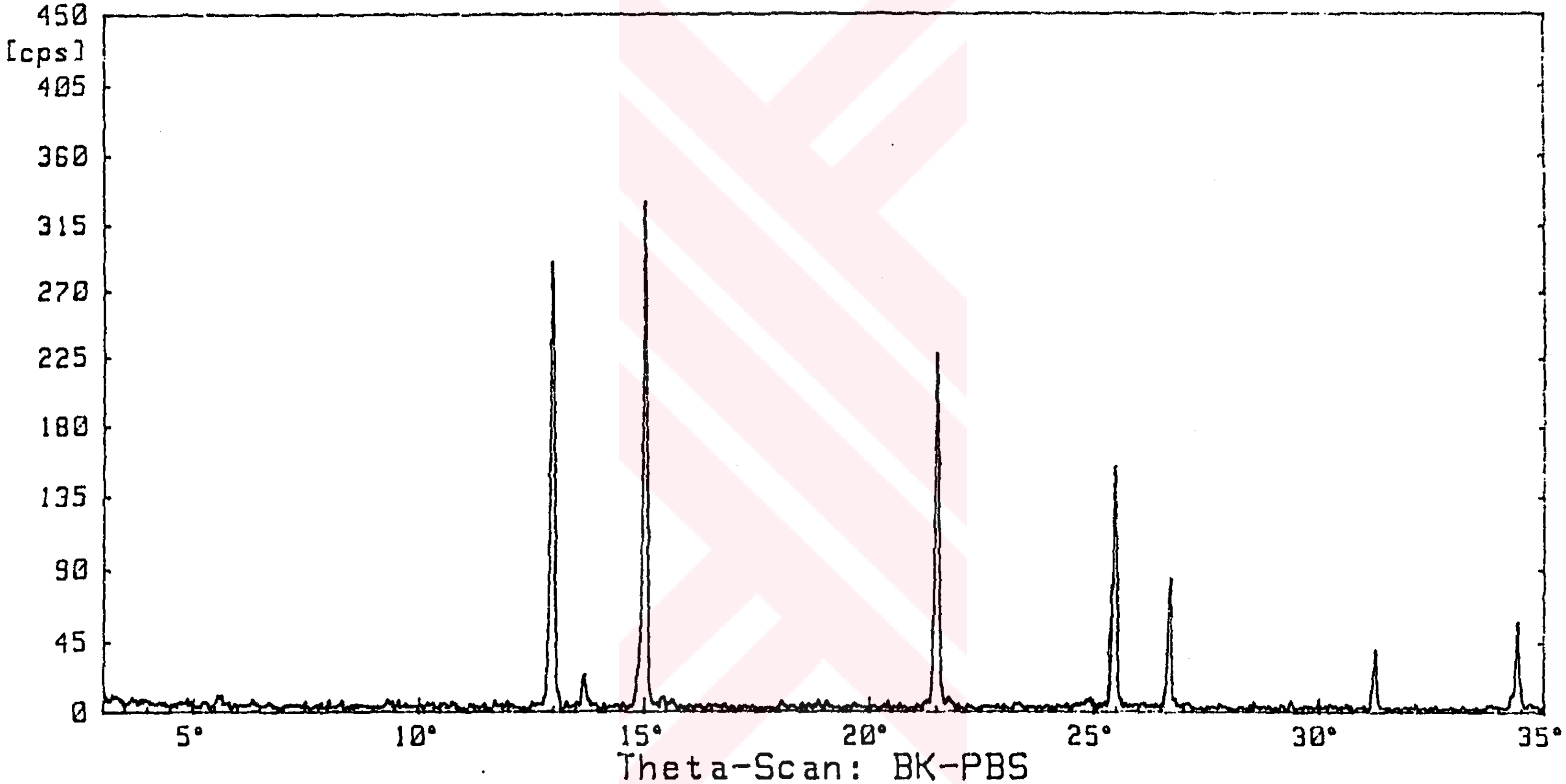

Fig.3.20. X-Ray Powder Diffraction Pattern of PbS (Sample 4I)

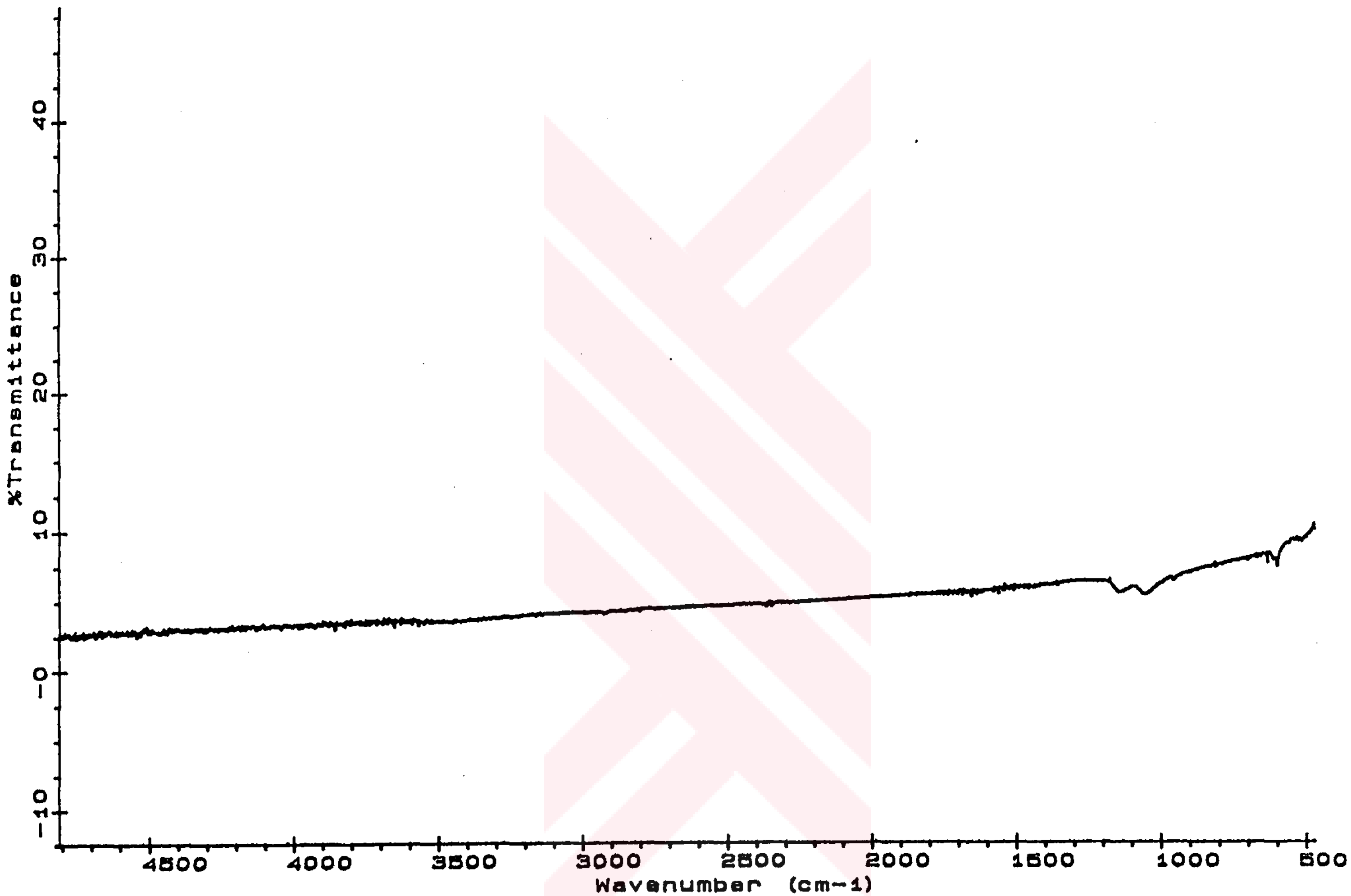

Fig.3.21. IR Spectrum of PbS (Sample No.4I)

in Cu^{+1} state. Another possibility is the formation of both oxidation states resulting in nonstoichiometry. The X-Ray powder pattern obtained from the sulfidization of CuO (Fig. 3.22.) was exactly matching $Cu_{7.2}S_4$ JCPDS card. This can also be written as $Cu_{2-x}S$ showing the presence of both oxidation states. IR spectrum (Fig. 3.23.) of this sample did not show any remaining oxide.

Table 3.7. d-spacings of $Cu_{7.2}S_4$; $7.2CuO + COS + CS_2 + 4CO + 1/2S_2 \rightarrow Cu_{7.2}S_4 + 6CO_2$

where a = 5.57 A°, Fm3m

$Cu_{7.2}S_4$(Sample No 4J)		**JCPDS Card No 24-61**		
d (A°)	**I/I$_o$**	**d (A°)**	**I/I$_o$**	**hkl**
3.22	48	3.216	40	111
2.789	50	2.785	68	200
1.971	100	1.969	100	220
1.681	25	1.679	14	311
1.393	10	1.392	3	400

3.6. Sulfidization of binary mixtures of Pb with IIA compounds (Preparation of Ternary Sulfide Compounds)

$Pb_{1-x}Sr_xS$ and $Pb_{1-x}CaS$ are given in the literature as the pseudobinary semiconducting compounds. They exist as single phase for all values of x [15,78]. They are useful for p-n junction devices, and their thin films could offer a low-cost technology for solar cells. Therefore the sulfidization of following mixtures were investigated.

$2PbO + 2Sr(NO_3)_2$ (Sample No 4K)

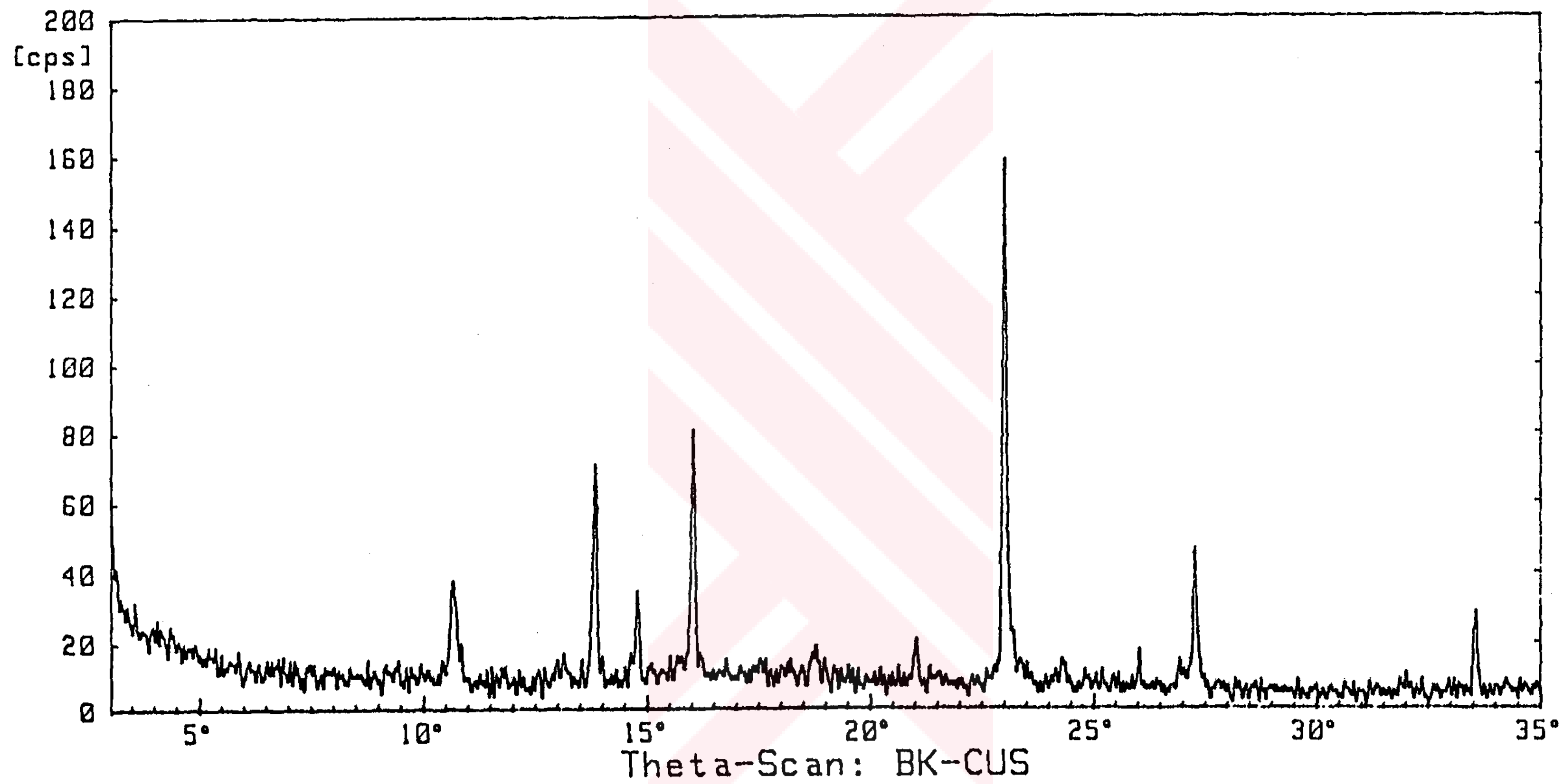

Fig.3.22. X-Ray Powder Diffraction Pattern of $Cu_{7.2}S_4$ (Sample 4J)

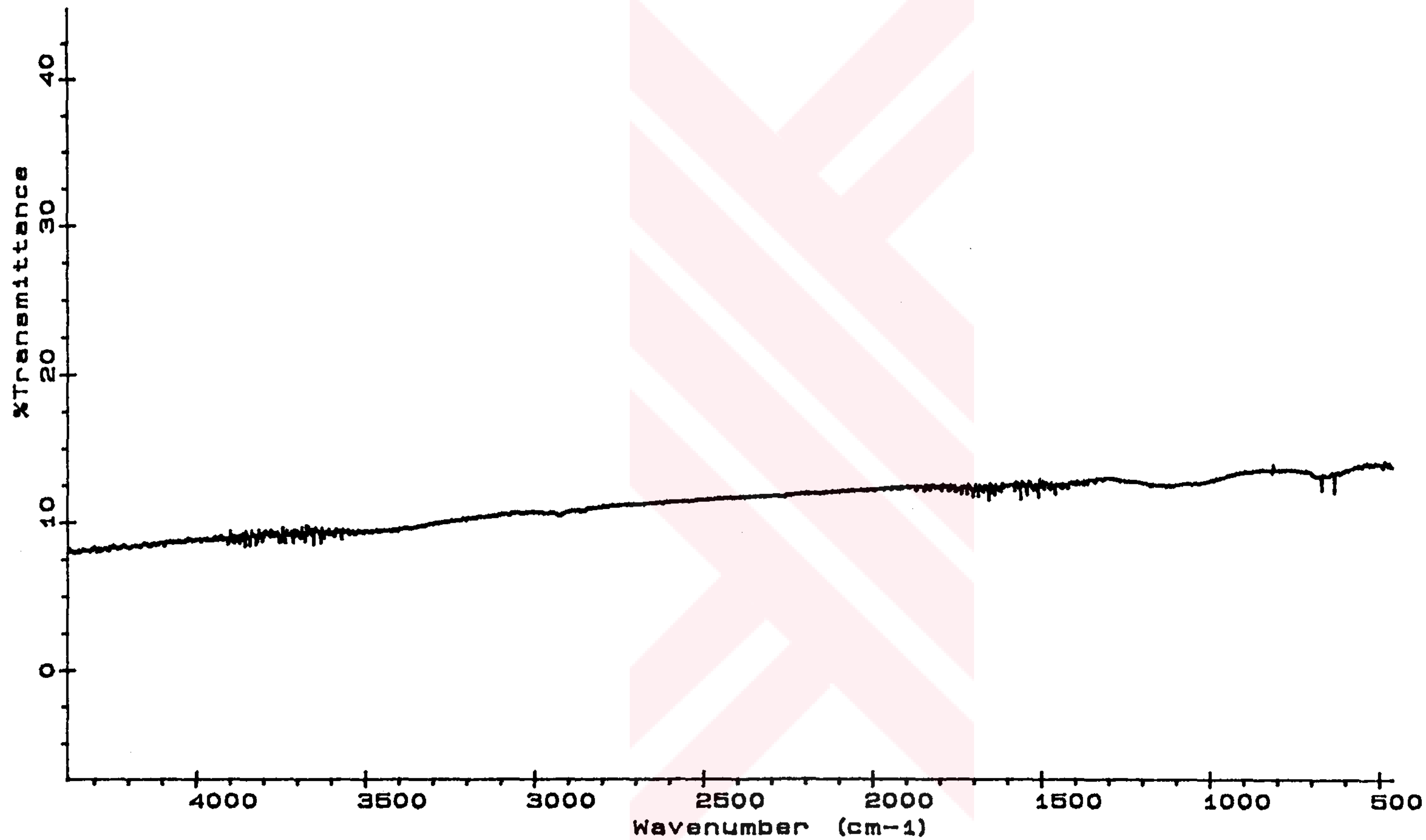

Fig.3.23. IR Spectrum of $Cu_{7.2}S_4$ (Sample No.4J)

2PbO + CaO (Sample No 4L)

The X-Ray diffraction pattern of $Pb_2Sr_2S_x$ mainly showed peaks similar to PbS peaks with a slight increase in d-values. This is possible as there are more atoms in this structure than simple PbS. In IR very small amount of sulfate is observed, and the very weak peaks in X-Ray indicate presence of another unknown phase.

For Pb_2CaS_x (4L), there is a higher degree of oxidation compared to $Pb_2Sr_2S_x$ (4K). This might be due to vacuum failure in the reaction system. During this study we should be very careful since there might be some cloggings in the system due to elemental sulfur formation.

Pb_2CaS_x, too, gave PbS peaks, but compared to $Pb_2Sr_2S_x$ the shift in d-values was less. This can be attributed to the fact that Sr has larger ionic radius than Ca, which causes a larger unit cell. Some weak unknown phases are also present in Pb_2CaS_x powder pattern.

3.7. Sulfidization of mixtures containing different IIA compounds

(Preparation of Quaternary Sulfide Compounds)

To investigate the effect of IIA elements the following mixtures have been sulfidized.

2PbO + 2Sr$(NO_3)_2$ + 3CuO (Sample No 5D)

2PbO + CaO + 3CuO (Sample No 5C)

These two products obtained by the reactions given above also crystallizes like PbS rock salt structure. Besides, sulfate phases were observed in IR spectra. The interesting feature was that the quaternary sulfides showed a shift to higher d-values compared to the ternary sulfides obtained in this section, $Pb_2Sr_2S_x$ and Pb_2CaS_x. Therefore, this increase in lattice parameters compared to corresponding ternary compounds, showed that the excess cations, really enter into the crystal lattice. For example, if we compare Pb_2CaS_x and $Pb_2CaCu_3S_x$, as there is an increase in the lattice parameters, it can be predicted that copper is indeed incorporated into the lattice. This increase is due to the presence of more atoms in the unit cell [57].

This enlargement is obvious in most of the samples, indicating that the atoms present can altogether form a stable structure. Unfortunately, this does not prevent the multiphase formation. As a result, it can be suggested that atoms only partially make the PbS like crystal structure and the remaining atoms are either sulfidized to form a corresponding sulfide or oxidized to give sulfate compounds.

3.8. Sulfidization of Pb-1212 and Pb-1223 materials

In the literature, the closed formula of Pb-based Y free oxide superconductors were given as Pb-1212 and Pb-1223. Therefore, for the final set of experiments, sulfidization of these materials according to the given atomic ratio have been attempted as given below.

$PbO + 2Sr(NO_3)_2 + CaO + 2CuO$ (Sample No 6A)

$PbO + 2Sr(NO_3)_2 + 2CaO + 3CuO$ (Sample No 7A)

The resulting X-Ray powder diffraction patterns (Fig.3.24. and 3.25.) were compared with the $Pb_2Sr_2CaCu_{3-y}S_x$ material and in this case again PbS d-spacings were observed. The formation of $Cu_{2-x}S$ was detected with its strong peak at d=1.96A°. In IR spectra, no sulfate group was visible which showed that complete substitution of O by S was achieved. These results may indicate that if complete substitution is tried, $Cu_{2-x}S$ crystals will form.

In the X-Ray powder diffraction pattern of Pb-1223, there were splittings in the d-spacings. These splittings may be a result of formation of another phase like the one found by Tamura et al. [40] for Pb-1223 nominal composition.

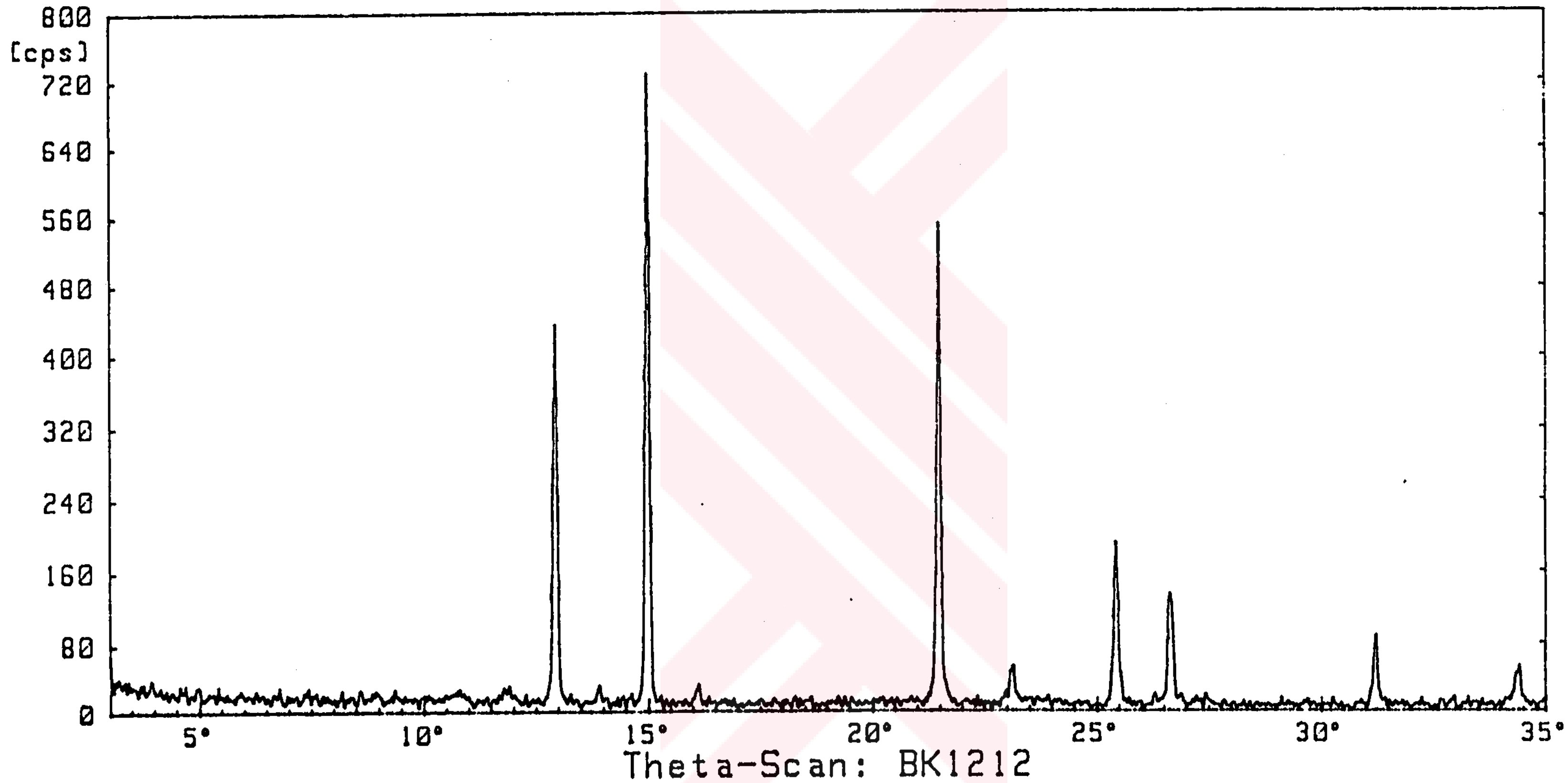

Fig.3.24. X-Ray Powder Diffraction Pattern of Pb-1212 (Sample 6A)

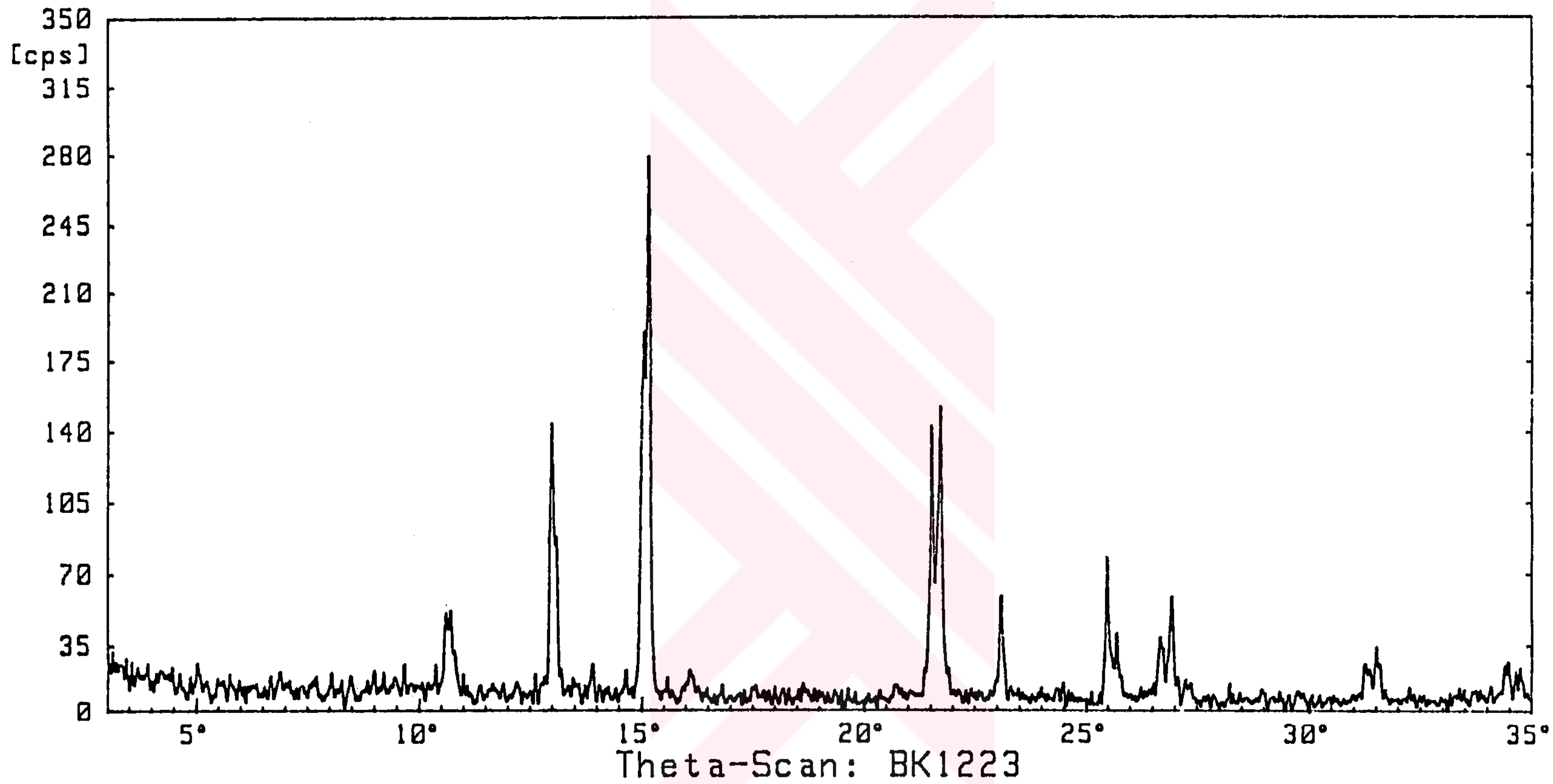

Fig.3.25. X-Ray Powder Diffraction Pattern of Pb-1223 (Sample 7A)

CHAPTER 4

CONCLUSION

The synthesis of $Pb_2Sr_2CaCu_{3-y}S_x$ and other related sulfides were done by using solid-gas reaction. The sample obtained was characterized by using X-Ray powder diffractometer, IR Spectroscopy, SEM, EDX, four probe resistivity measurement and elemental analysis for sulfur. The significant outcome of most of the experiments is that the X-Ray powder patterns of them were similar or in some cases entirely matches to that of PbS JCPDS Card No. 5-592.

When $Pb_2Sr_2CaCu_{3-y}S_x$ was indexed, although a and b cell parameters were very close to the cell parameter of PbS which has face centered cubic structure, it is seen that the c parameter was almost doubled. This indicates the formation of a superstructure. However, this structure is not a simple cubic superstructure but is rather a distorted rock salt superstructure of monoclinic crystal system. It is known that rock salt structures have monoclinic superstructure for complex sulfides [1].

The superstructure formation is common for oxides of these type of materials that contain many atoms [40-42]. As a result, the corresponding sulfides could also form a superstructure.

The exact positions of the atoms were not easy to predict, only suggestions can be done without a single crystal analysis. As a result we can suggest that the PbS structure obtained was not due to only Pb and S but all the cations present in the sample exchange positions with Pb and contribute to the crystal structure.

The monoclinic superstructure formation was also seen in sample that had no Pb ($Sr_2CaCu_3S_x$). The powder pattern was again similar to that of PbS. The a and b cell parameters of $Sr_2CaCu_3S_x$ is a little less than a, b cell parameters of $Pb_2Sr_2CaCu_{3-y}S_x$. This is due to the fact that the former sample contains more atoms than the latter that increases the unit cell.

The increase in cell parameters of sulfur doped sample is an evidence for complete substitution of O by S. The oxide material was found to have a and b cell parameters equal to 3.83A° [40], whereas sulfur doped material synthesized had a≅b≅5.94A°. As the ionic radius of S^{2-} is greater than O^{2-}, this result is meaningful. By looking at the enlargement in unit cell dimensions, it can be said that sulfur really enters into the crystal lattice. On the other hand, $Cu_{2-x}S$ phase formation is observed for every sample. Thus, it can be concluded that sulfur indeed goes to crystal lattice and replaces all the oxygen however it also forms another phase with copper.

All the samples containing copper a characteristic d =1.96A° peak was always present, being very weak in intensities in some cases. The samples without copper did not have this peak. Based on this observation, it can be suggested that this d =1.96A° peak may be the evidence for copper forming a secondary $Cu_{2-x}S$ phase. Thus, $Cu_{2-x}S$ crystals always formed in all of the samples studied. Nonetheless, this does not mean that copper does not enter into the parent crystal. Only, partially incorporated and the remaining copper crystallizes as $Cu_{2-x}S$ as seen in the SEM photograph given in Fig 3.2. and Fig. 3.11.

Complete substitution of oxygen by sulfur can be considered to be achieved also by examining IR spectrum and EDX micrographs. Not even a trace amount of oxygen could be detected by them.

$Pb_2Sr_2CaCu_{3-y}S_x$ and $Sr_2CaCu_3S_x$ were found to be metallic when subjected to four probe resistivity measurement. Taylor et al. [57] reported that complete substitution caused semiconductivity. In contrast to it, our sulfur doped samples showed metallic behavior in liquid N_2.

In this study, various stoichiometries of Pb-Sr-Ca-Cu-S system were tried. It was seen that the crystal structures were almost the same for all of them. That is the X-Ray powder diffraction patterns were all matched the PbS powder pattern.

In this specially designed solid-gas system, various single phase binary, ternary, quaternary and other complex sulfides can be synthesized.

In the literature, the preparation of sulfides are given either by solid state route or by sulfidizing the oxide precursors with H_2S gas at high temperatures. This former reaction is carried out in a quartz tube. The disadvantage of this method is not only the production of mixed phases but also danger arising from the heating with H_2S gas. Our method of synthesis is different from the ones given in literature where a solid gas reaction is involved. This system produces sulfidizing and reducing gas mixture that provides the medium for obtaining mixed valent compounds which was reported to be necessary for superconductivity.

The following lines of development might be suggested:

1) Single crystals of the compound $Pb_2Sr_2CaCu_3S_x$ should be prepared to understand the exact crystal structure.

2) Rietveld analysis must be used to determine the atomic positions.

3) SEM pictures of both surface and bulk should be taken in order to make a comparison and to observe if $Cu_{2-x}S$ crystals were indeed only at the surface.

4) Conductivity measurement of samples 3D, $Pb_2Sr_2CaCu_{3-y}S_x$, and 3C, $Sr_2CaCu_{3-y}S_x$, should be carried out at liquid He temperature to investigate the possibility of superconductivity.

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