

## **PETROLOGICAL AND MINERALOGICAL CHARACTERIZATION OF KA'OJE (KEBBI STATE, NIGERIA) MANGANESE ORES**

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### **ABSTRACT**

*Samples from two different locations in Ka'oje (Kebbi State, Nigeria) were mineralogically characterized. Obtained petrographs and micrographs were analyzed to establish optical and microstructural behaviours of the samples and their respective minerals. Ores' chemical formations, constituent minerals' compositions and proportions were investigated using energy dispersed X-Ray fluorescence spectrometry (ED-XRFS). The results showed the anisotropy of the ores which are of secondary deposition, combining ferruginous and metallurgical manganese ore types with dominant oxide manganese minerals.*

*Keywords: Anhedral, Absorption, Supergene-enrichment, Interstitial-quartz and Manganese.*

### **1.0 INTRODUCTION**

Mineral/Ore usually contains various elements of different stable chemical compounds (minerals) in varied proportions to be revealed by characterization processes of that ore. The unwanted components are considered as gangues to be separated and may be discarded during beneficiation exercises. (Gaudin, 1992 and Higgins, 1993). The beneficiation of manganese ores centers on separating manganese minerals as valuables from the available gangues.

Manganese as an element was first recognized by Carl Wilhelm Scheele, a Swedish chemist, in 1774. In the same year, J.G. Gahn isolated the metal. It is a light pinky-gray metal which melts at 1260°C and has a specific gravity of 7.4. (Olsen et al, 2007). Its major use can be either in steel making as an alloying element to modify strength, toughness and hardness or as a

deoxidizer and desulphuriser. Manganese is destined for sedimentary deposits and it is the 12<sup>th</sup> most abundant element in the Earth crust, occurring in oxides, sulphides, carbonates and silicates forms. Pyrolusite (MnO<sub>2</sub>), Hausmannite (MnO.Mn<sub>2</sub>O<sub>3</sub>), Manganosite (MnO), Manganite (MnO(OH)), Alabandite (MnS), Hauerite (MnS<sub>2</sub>), Rhodocrosite (MnCO<sub>3</sub>) and Rhodonite (MnSiO<sub>3</sub>) are some of the known ones. (Olsen et al, 2007). Vast terrestrial manganese ore deposits (Corathers, 2007 and Thomas, 2000) have been discovered in Nigeria; from Kebbi to Kaduna, Katsina, Yobe and Cross-River states. Ores of less than 30% Mn are low grade ones, 45 to 48% are medium whereas 50 to 56% Mn are considered high grade ores. (Stanton, 1972).

The Characterization exercise on Ka'oje manganese ores of Kebbi state serves as a prelude to beneficiation of the ore to be used subsequently in steelmaking feed materials. This investigates the chemical formation, compositions and proportions of constituent

minerals and their elements (major, minor and trace elements) present in the ores. This can be achieved in a thorough petrology and microstructures study of the ores through methods such as X-ray diffraction analysis, X-ray refraction analysis, Inductively Coupled Plasma Optical Electron Spectroscopy and Atomic Absorption Spectroscopy (AAS). (Olubambi and Potgieter, 2005).

## 2.0 LITERATURE REVIEW

A high content of manganese in alloy steel in the presence of carbon increases the wearing resistance of such alloy steel substantially; it can increase its tensile strength by 100N per mm<sup>2</sup> for every percent increase in Mn from 3 to 8%. Manganese precipitates in the crust mainly as oxides and carbonates, while its hydrides, silicates and sulphides are rare sedimentation accumulations. These occurrences are common in Mn<sup>++</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> ions. Mn<sup>++</sup> is predominant in magmatic rocks while Mn<sup>4+</sup> is predominant among the manganese compounds of sedimentary cycle of supergene enrichment. (Stanton, 1972). The sedimentary, secondary deposition of supergene enrichment is derived from solutions carrying manganese and iron which were precipitated in the crust. Sources of which could probably be volcanic deposits and colonized tufts representing part of the leached host rocks. (Wadsley and Samson, 2007).

### 2.1 Manganese ore associated minerals

Manganese minerals have been found notably associated, in its ores, with minerals of iron, silicon, aluminium, magnesium, calcium and barium. (Dexter, 2003).

### 2.2 Physical and chemical behaviours of manganese

#### *Manganese as a transition element*

Manganese, as a d-block element, is the fifth element in the first transition series (Table 1) having its 3d orbital partially filled with five electrons.

**Table1. : The first transition series**

21Sc	Ti	V	Cr	25Mn	Fe	Co	Ni	Cu	Zn
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Atoms of the metals in the first transition series have one or two 4s electrons and partially filled 3d orbital which is responsible for their colours, except the colourless zinc atom and scandium ion (Sc<sup>3+</sup>). This position makes manganese minerals to reflect very few to none light vibrations, while in some instances all light vibrations are absorbed and the manganese mineral appears black.

#### *Oxidation states*

In the electronic configuration 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>5</sup> 4s<sup>2</sup> of manganese, the last seven electrons (3d<sup>5</sup> 4s<sup>2</sup>) can be used in various ways during bonding. This avails Mn the most ability it has in bonding ranging from +VII to 0 oxidation states. The highest oxidation state is obtained if all the seven are used up in bonding. The oxidation +II state is the most stable in acidic solution. In alkaline solution however, Mn<sup>2+</sup> is readily oxidized to MnO<sub>2</sub>. (Lee, 1996).

#### *Magnetic character*

Minerals of manganese are paramagnetic unlike magnetic iron minerals. A high-intensity magnetic field will therefore be required to attract the manganese minerals. (Gaudin, 1992).

## 2.3 Ore Mineralogy and characterization

Detailed mineralogy with proper understanding of ore morphology, minerals association, phases and behaviours is required to properly characterize an ore.

#### *Microstructure analysis:*

The determination of minerals distribution, grain sizes, and minerals locking characteristics can be achieved from the microstructure of an ore. Micrographs of various magnifications are produced using ore/metallurgical (reflected light) and petrographic (transmitted light) microscopes with camera attached from thin and polished sections of samples. (Wills, 2005).

Petrographic microscopy (Transmitted Polarized Light Microscopy)

Transmitted Polarized light microscopy offers a wealth of information. Information on absorption colour and boundaries between minerals of differing refractive indices are obtainable. The technique exploits optical properties of anisotropy to reveal detailed information about the structure and composition of materials, which are invaluable for identification and diagnostic purposes. The technique of polarizing microscopy exploits the interference of the split light rays, as they are re-united along the same optical path to extract information about these materials. This, perhaps, is best known for its metallurgy/geological applications-primarily for the study of minerals in rock thin sections.

#### *Thin Section*

Slices between one and 40 micrometers thick are used for transmitted light observations. Specimens are mounted between the slide and the cover slip using a mounting medium whose composition will depend on the chemical and physical nature of the specimen.

#### *Polished sections*

Representative specimens are prepared size by size, ground, sectioned and polished to mirror finishing.

#### Composition analysis

X-Ray diffractometry (XRD), X-Ray fluorescent (XRF), Inductively Coupled Plasma-Optical Emission Spectrometer, analytical method and Atomic Absorption Spectrometry (AAS) are mostly used for this purpose. (Madsen, 2007 and Pan, 2005).

### **3.0 Methodology and Experimental Design**

#### **3.1 Field of Study**

Ka'oje lies within Latitude 11.2°N and Longitude 4.13°E (figure 1). Ore deposits are away from each other in hundreds of meters.



**Figure 1: Map showing Ka'oje**

#### **3.2 Sample Collection**

The trip to the Ka'oje ore deposits was facilitated by The National Geological Survey Agency, Abuja. Samples were collected from five different locations. The random selections covered both surface and mid (4-5m depth) layers of the deposits.

#### **3.3 Ore Petrology**

◆ Ore origin and physical properties: Ore samples were physically examined to establish origin, physical properties as well as Magnetic property.

##### **3.3.1 Petrographic analysis (Thin section)**

► Cutting: Specimens were prepared for good results by careful cutting of samples to cuboids shapes of approximate 5 × 2.5 × 1cm dimension. After mounting, the Specimens were ground down and hand finished to the thicknesses between 25-30 micrometers as thin sections.

► Slices preparation: Slices of about 40 micrometers thick (plate 2) are used for the transmitted light observations. Specimens were mounted between the slide and the cover slip using a synthetic mounting medium.

► Petrography: Two polarizing filters were in a polarizing microscope - the polarizer and analyzer. Observations in the plane-polarized light revealed details of the optical relief of the specimens, which was

manifested in the "visibility" of boundaries. Examinations of transparent or translucent materials in plane-polarized light were similar to those seen in natural light until the specimens were rotated about the optical axis of the microscope when changes in the brightness and/or the color of the material were noticed as cross-polarized. Petrographs of the viewed fields were captured at magnification  $\times 10$ .

### 3.4 Microstructure analysis:

Representative samples (S1 and S5) were cut from the run-off mine ore bulks, mounted, ground and polished. The cut samples were mounted (plate 6) in Bakelite for easy handling, followed by progressive grinding on grades of silicon carbide (SiC) impregnated emery paper (240-600grits) sizes using water as coolant. Samples were then pre-polished with 1000grit silicon-carbide powder. A rotating cloth pad impregnated with  $1\mu\text{m}$  size alumina polishing powder (APP) was used in polishing with light pressure. Final polishing followed using  $0.05\mu\text{m}$  APP suspended in distilled water. Etching was considered not necessary as a result of the clarity of structures obtained from the polished samples. The structures were photographically recorded with the attached camera on the Binocular

metallurgical microscope 'Metallux II' and operated between 9-12V and at various magnifications. (Plates 7- 8).

### 3.5 Chemical Analysis

#### 3.5.1 X-Ray Fluorescence Spectrometry (mineralogical)

MiniPal4 ED-XRF machine was used to identify the mineralogical assembly and determine concentrations of major, minor and trace elements present in the ore samples. Samples were ground and sieved to  $75\mu\text{m}$  particle size. A 4g mass of the sieved samples were intimately mixed with 1g of lithium tetra borate binder ( $\text{Li}_2\text{B}_4\text{O}_7$ ) and pressed in a mould under  $15.5\text{-}23.3\text{ Kg/m}^2$  to pellets. The pressed pellets were dried at  $110^\circ\text{C}$  for 30 minutes in an oven to get rid of moisture. The samples were finally stored in desiccators for analysis, ran with calibrations and the elements concentrations present in them were displayed by the spectrometer.

### 4.0 Results and Discussion

#### 4.1 Sample collection

About 178Kg samples were collected from the field in five locations within Ka'oje. (Plate 1)

#### 4.2 Ore petrology:

Observed pertinent physical properties of the ore samples are contained in Table 2.

**Table 2: Samples' physical properties**

Sample	Origin	Specific Gravity	Colour	Streak	Transparency	Cleavage	Magnetic Property
S1	Sedimentary	2.82	Brownish Black	Dark brown	Opaque	Good	Poor
S5	Sedimentary	2.78	Black	Brownish Black	Opaque	Good	Poor

#### 4.2.1 Petrography and Microstructure Analysis

##### Specimens Preparation:

Prepared Thin-section slides for petrographic analysis are shown in Plate 2.

Ground specimen slices of approximately 35micrometers were mounted between glass slides and cover slips.

##### Petrographic Microscopy:

Random cross-sections of slides were viewed under plane and crossed polarized light. Different fields were captured at magnification  $\times 10$  (plates 3 and 4). Dual-band of vertical network of alumina-silicate (blue-to-white) with interstitial quartz (brown) crystals shows clearly. Opaque manganese mineral with haemetite inclusions

stand out .Haematite shows characteristic transparent reddish thin edges. The distribution of subhedral alumina-silicate in the characteristic pleochroic blue to white colour with average relief suggests the presence of kyanite. Dark colour of manganese mineral dominates the field with little haemetite (reddish edge), Plate 3. Anhedral quartz crystals (grayish-white) and interstitial blue coloured alumina-silicate are clearly seen. The manganese minerals appear opaque (black) with haematite inclusions. Haematite shows characteristic transparent reddish thin edges. Quartz in undulose extinction while alumina-silicate appears whitish-brown, Plate 4, the above confirmed (Dexter, 2003) that:

- 1 Manganese minerals formed with insignificant alumina-quartz intergrowth
- 2 Alumina-silicate minerals co-exist in the ore bulk
- 3 The four major minerals are clearly identified with their optic characteristics.
- 4 Manganese is present in oxide form
- 5 Haematite is present

### 4.3 Microstructure analysis:

#### 4.3.1 Polished sections

##### Plate 7:

Interstitial alumina-quartz (dark gray patches) and iron mineral (yellowish white) distributed in the less-stressed manganese mineral network. Well formed dominant manganese grains mostly surrounded by quartz at the boundaries. More alumina-quartz and iron minerals to the top left of the micrograph.

Clear manganese mineral grains and grain boundaries. The grains are homogeneous without alterations or inclusions. Thus, dominant manganese minerals formed with no inclusions and interstitial iron minerals also exist without inclusions. The secondary deposition during the sedimentary circle produced high supergene enrichment of the manganese ore. (Steven, 2005 and Alfthan, 2007).

##### Plate 8:

Discontinuous iron-mineral distribution within stressed manganese minerals network and with little or no manganese intergrowth. The manganese mineral network was gently stressed. (Steven, 2005)

#### 4.3.2 Grain Size Determination:

Geometric-Statistical method: Tables 3a and 3b present grain sizes statistics from plate 7 for S5 and plate 8 for S1.

**Table 3a: S5 manganese mineral grain sizes in cm.**

Grain No	Repetitions						Row mean(r) (cm)	Actual size* (µm)
	I	Ii	Iii	Iv	V	Vi		
1	0.626	0.668	0.584	0.543	0.647	0.501	0.595	30
2	0.522	0.522	0.626	0.731	0.501	0.668	0.595	30
3	0.543	0.230	0.271	0.313	0.230	0.397	0.330	17
4	0.501	0.397	0.407	0.376	0.459	0.355	0.416	21
5	0.334	0.188	0.313	0.355	0.355	0.271	0.303	15
6	0.250	0.250	0.209	0.250	0.209	0.167	0.223	11

\*Magnification = 200

Ground average grain size = 4.1mm

= 20microns.

Table 3b: S1 iron mineral grain sizes in cm.

Grain No	Repetitions						Row mean(r) (cm)	Actual size* (µm)
	I	Ii	Iii	Iv	V	Vi		
1	0.167	0.125	0.125	0.146	0.167	0.164	0.149	7.45
2	0.230	0.250	0.230	0.209	0.250	0.209	2.300	11.48
3	0.147	0.104	0.125	0.250	0.209	0.250	0.167	9.04
4	0.146	0.125	0.146	0.146	0.125	0.125	0.138	6.78
5	0.146	0.125	0.250	0.146	0.209	0.146	0.175	8.52

Magnification = 200

Ground average grain size = 1.73mm

= 8.65 microns.

#### 4.4 Chemical Analysis:

##### 4.4.1 X-Ray Fluorescence Spectrometry (XRFS)

The ED-XRFS results are presented in tables 4 and 5

Table 4: S1 ED-XRF Results

Sample S1	% Al <sub>2</sub> O <sub>3</sub>	% SiO <sub>2</sub>	% P <sub>2</sub> O <sub>5</sub>	% SO <sub>3</sub>	% K <sub>2</sub> O	% CaO	% TiO <sub>2</sub>	% V <sub>2</sub> O <sub>5</sub>	% Cr <sub>2</sub> O <sub>3</sub>	% MnO <sub>2</sub>	% Fe <sub>2</sub> O <sub>3</sub>	% NiO
	16.01	21.60	0.31	*ND	0.07	1.49	1.16	0.03	0.08	31.01	19.07	0.08
	% CuO	% ZnO	% SrO	% BaO	% As <sub>2</sub> O <sub>3</sub>	% La <sub>2</sub> O <sub>3</sub>	% ZrO <sub>2</sub>	% PbO	% MgO	% Na <sub>2</sub> O	% Sc <sub>2</sub> O <sub>3</sub>	
	0.01	0.05	ND	0.43	ND	ND	0.13	ND	0.24	0.09	0.007	

Table 5: S5 ED-XRF Results

Sample S5	% Al <sub>2</sub> O <sub>3</sub>	% SiO <sub>2</sub>	% P <sub>2</sub> O <sub>5</sub>	% SO <sub>3</sub>	% K <sub>2</sub> O	% CaO	% TiO <sub>2</sub>	% V <sub>2</sub> O <sub>5</sub>	% Cr <sub>2</sub> O <sub>3</sub>	% MnO <sub>2</sub>	% Fe <sub>2</sub> O <sub>3</sub>	% NiO
	13.58	10.65	0.30	ND	0.06	2.05	0.74	0.06	0.06	54.96	11.06	0.12
	% CuO	% ZnO	% SrO	% BaO	% As <sub>2</sub> O <sub>3</sub>	% La <sub>2</sub> O <sub>3</sub>	% ZrO <sub>2</sub>	% PbO	% MgO	% Na <sub>2</sub> O	% Sc <sub>2</sub> O <sub>3</sub>	
	0.06	0.05	ND	0.06	0.17	ND	ND	0.02	0.26	0.03	0.02	

(\*ND = NOT DETERMINED)

Alumina-silica/corundum-quartz occurred as kyanite combination in all the ore samples in a substantial concentration. Manganese mineral concentration ranged between 31 and 54%. The iron mineral concentration ranged between 11.06 and 19.07. Ore sample S1 satisfied ferruginous manganese ore type, while sample S5 met the metallurgical manganese ore type requirements. (Olsen et al, 2007).

Calcium and Titanium minerals (oxides) occurred as minor ore constituents. While oxides of P, S, K, V, Cr, Ni, Cu, Zn, Sr, Ba,

As, La, Zr, Pb, Mg, Na, and Sc occurred as trace minerals. (Thomas, 2000 and Lee, 1996).

## 5.0 CONCLUSION

1. The manganese ores are anisotropic with high relief under polarized light.
2. The enrichment of Kao'je Manganese Ore deposits is secondary, combining ferruginous and metallurgical manganese ore types, each at a separate location.
3. Among the constituent major

- minerals (alumina, silica, haematite and manganese minerals) in the ores, manganese mineral dominated.
4. Alumina-silicate exists mostly in homogeneous bands, a good condition for better liberation in the beneficiation stage.
  5. The ores are pyrolusite associated majorly with kyanite, haematite and quartz.

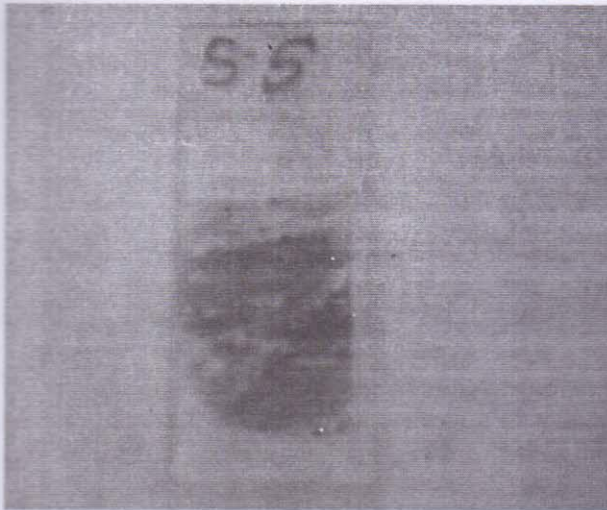
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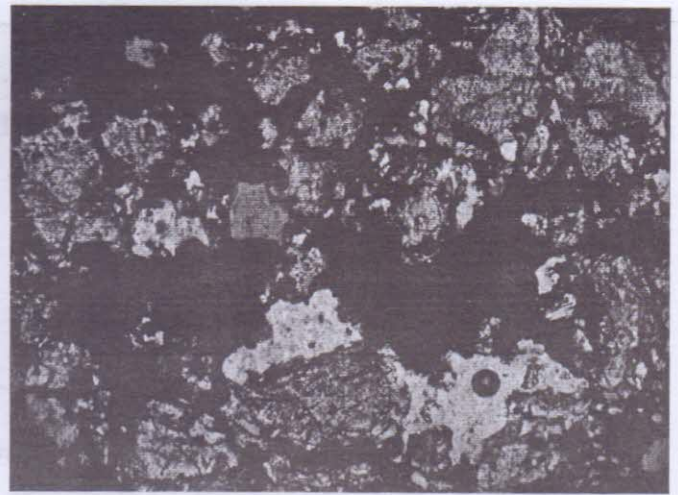
**Plates:**



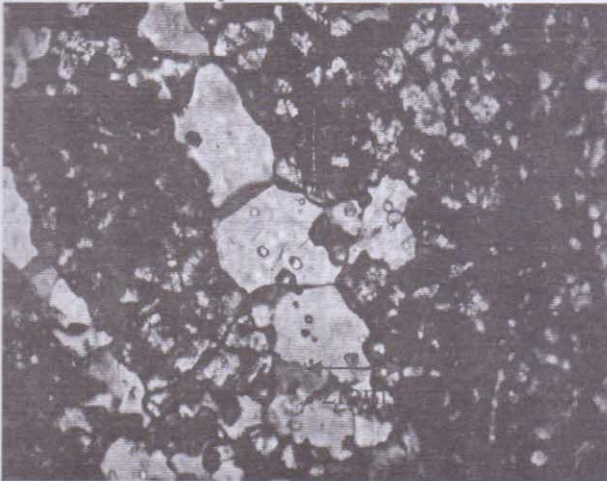
**Plate 1: Collected ore samples.**



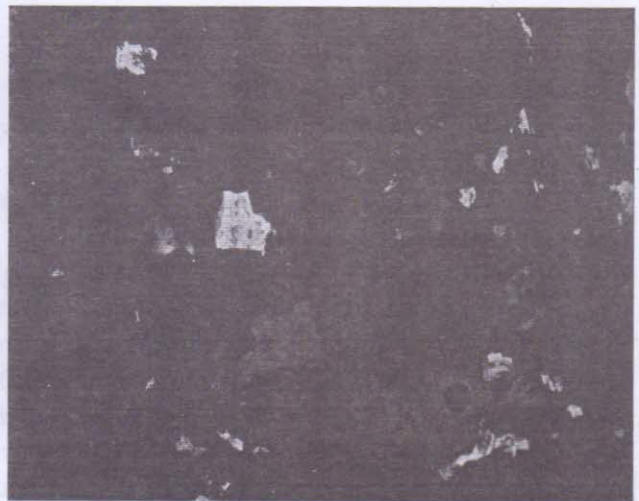
*Plate 2: S5 Sample slide*



*Plate 4a: Micrograph of S5 under plane polarized Light (different. field). 10x*



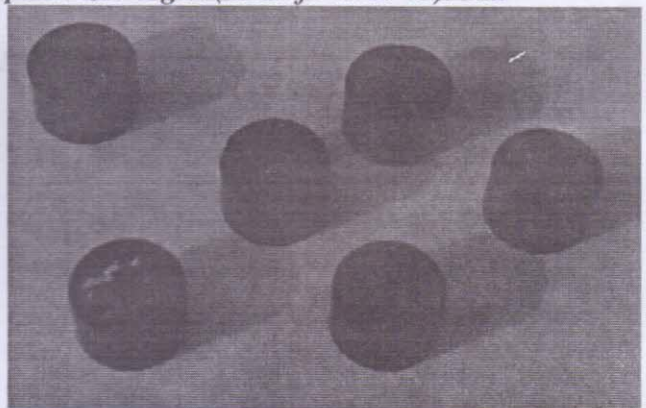
*Plate 3a: Micrograph of S1 under Plane polarized Light x10*



*Plate 4b: Micrograph of S5 under crossed polarizer Light (same field as 4a). 10x*

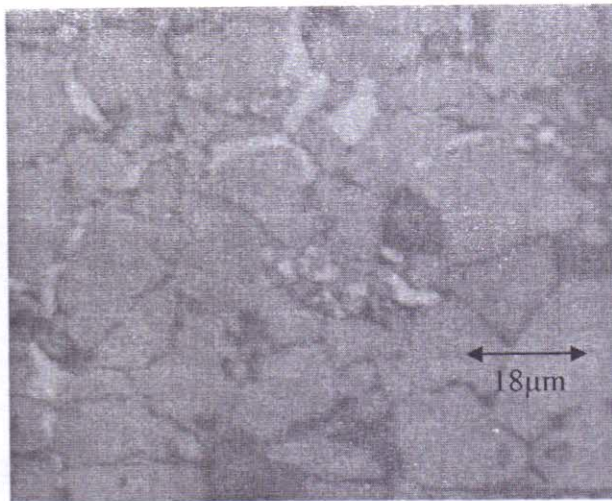


*Figure 3b: Micrograph of S1 under crossed polarizer Light (same field as 3a)*

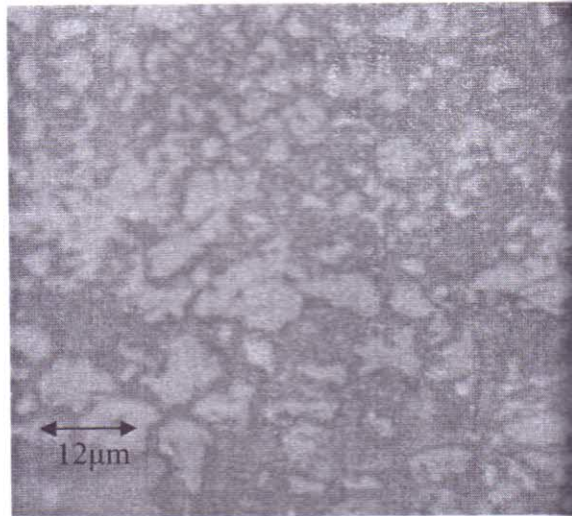


*Plate 6: Polished and mounted samples for photomicrography*





*Plate 7: Micrograph of S5 Structure.200x*



*Plate 8: Micrograph of S1 Structure. 200x*

