# PHASE AND MICROSTRUCTURE OF CHROMITE: A DIFFERENT APPROACH

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## ABSTRACT

Chromite ores are basically classified on basis of $Cr_2O_3$ content and Cr to Fe ratio in a sample. The higher content of Cr increases the value of the ore but this is greatly affected by the presence of impurities in form of silicates, oxides or hydroxides. The present study was performed to analyze the impurities of chromite ore collected from Prangghar (Mohmand agency), Pakistan. From x-ray diffractormeter analysis a single phase (magnesiochromite-ferroan, ICDD card # 09-0353) was identified. SEM/EDX analysis along with metallurgical microscopy images were in partial agreement with XRD, as some impurity phases were also identified. In spite of these impurities, mostly silicates, the ore was best suited for metallurgical industry due to its high Cr content.

## 1. INTRODUCTION

Normally chromite occurs in nature with an ($AB_2O_4$) cubic spinel structure (Fd3m)[1-3]. Here A and B are metal ions of 2+ and 3+ valance state and occupy tetrahedral and octahedral sites respectively. Figure 1 shows the $AB_2O_4$ spinel structure[4-5]. Natural chromite being a cubic spinel compound has a formula unit $(Mg,Fe^{2+})O(Cr,Al,Fe^{3+})_2O_3$[3]. In chromite the tetrahedra of oxygen atoms surround divalent metal ions and the octahedra of oxygen surround chromium ions[6]. At the A and B sites of naturally occurring chromite, the substitution of $Fe^{+2}$ by Mg and Cr by Al and even by $Fe^{+3}$ in lower proportion occurs depending upon the type of minerals which are usually found with the chromite, thus describing the presence of serpentines, chlorites, olivine and other minerals[7]. For industrial use chromite minerals are classified into different grades by the total amount of $Cr_2O_3$ present and Cr to Fe ratio. The general grade wise classification of chromite ores is as follow:

i) metallurgical grade with $Cr_2O_3$ content above 46–48% and Cr/Fe ratio above 3; and 25% alumina and magnesia together

ii) chemical grade with $Cr_2O_3$ content above 44% and Cr/Fe ratio above 1.5%

iii) refractory grade with $Cr_2O_3$ between 30 and 40% and Cr/Fe ratio between 2 and 2.5 and above 63% of $Cr_2O_3$ and $Al_2O_3$ together. The properties of the chromite mineral for refractory grade are improved by the content of magnesia[8-9].

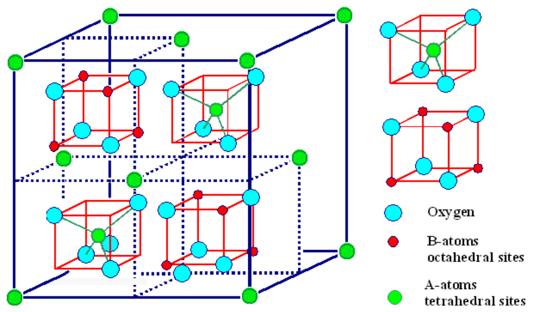


Figure 1. An $AB_2O_4$ spinel structure[1].

A higher proportion of chromium increases the heat resistance of the mineral, but this can be modified by the type and relative amount of the impurities. For example, the presence of silicates causes a decrease in the melting point, so liquid phases can appear at relatively lower temperatures, provoking breakage and decomposition of the product, and have strong influence over their possible applications. Depending upon the type and geological area of occurrence of the chromite ore. Table 1 gives different types of impurities found in the chromite ore[7]. Since the impurities play a vital role in determining the application of a specific chromite ore in either metallurgical, chemical or refectory industry, the identification and characterization of ore and its impurities becomes very much essential. In this study a sample of chromite from Prangghar (Mohmand agency), Pakistan, was investigated for impurities and major phase identification and therefore most probable application of this chromite in industry.

## 2. EXPERIMENTAL

Sample was properly cleaned with standard laboratory grade iso-propanol then dried in a hot air oven (Thermo-scientific Fearas-605, USA). For X-ray diffractormeter (XRD) the sample was ground using stainless steel pestle and mortar. For metallurgical microscopy, the sample was cut into thin section and polished with 0.25μ diamond paste (Allied High Tech, USA). Chemical etching for metallurgical microscopy was done with 40% HF fumes for 60 seconds. The same sample was Ag-coated in vacuum evaporator for scanning electron microscopy (SEM).

XRD was performed using a Bruker AXS D8 Discover X-Ray Diffractometer under the following conditions, scanning angle $2\theta = 5^{o}$ to $60^{o}$, step size of $0.02^{o}$, count time = 1sec; X-ray tube operating voltage and current was kept at 40kV and 40mA respectively. Target source used was $Cuk_{\alpha}$ ($\lambda$=1.5406Å). Metallurgical microscopy images (MMI) were taken at 10x magnification using an Olympus PMG-3 (Japan) inverted metallurgical microscope equipped with an Olympus DP-12 digital camera. A JEOL, JSM-5910 (Japan) scanning electron microscope coupled with an Energy Dispersive X-ray Spectroscopy (EDX) was used to take secondary electron images (SEI). The EDX was performed using INCA-200, Oxford Instruments UK.

Table 1. Impurities of different sorts found in chromite ores.

| | | | |
|---|---|---|---|
| **Mineral Groups in Chromite ore** | **Silicates** | Olivine | Olivine |
| | | Pyroxene | Diopside |
| | | Serpentine | Antigorite |
| | | Amphybole | Tremolite-anctinolite |
| | | Chlorite | Pennine-clinochlore-kammererite-rhodochrome |
| | | Talc | Talc |
| | | Montomoril | Nontzonite |
| | | Granite | Uvarovite |
| | **Oxy salts** | Carbonate | Calcite- dolomite- magnesite-hydromagnesite |
| | **Sulfur compounds** | Sulphide | Chalcopyrite |
| | **Oxides and hydroxides** | Corandum- ilmenite | Hematite |
| | | Spinel | Chloropicotite- ferrochromepicotite-hercynite- magnetite |
| | | Rutile | Rutile |
| | | Quartz | Alpha quartz- chalcedony- opal- semi opal |
| | | Brucite | Brucite- nemolite |
| | | Hydrotalcite | Brugnatellite |
| | | Goethite | Goethite- hydrogoethite- limonite |

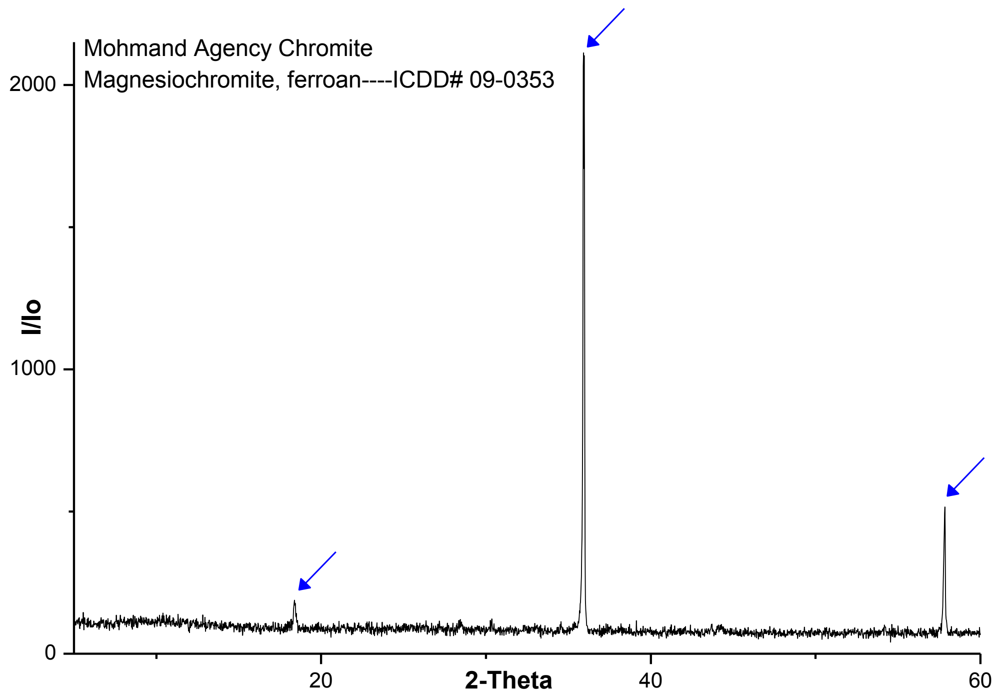


Figure 2. The XRD pattern of the Mohmand agency chromite, the data has possible match with ICDD card # 09-0353.

## 3. RESULTS & DISCUSSION

### Phase analysis

The XRD data for the sample showed mainly 3 major peaks as shown in Figure 2. The pattern was matched with magnesio-chromite-ferroan ((Mg, Fe) (Cr, Al)$_2$ O$_4$), ICDD card # 09-0353. According to the ICDD card data the spinelunder investigation has a cubic structure and almost all the iron is in form of $Fe^{2+}$ [3]; however, a slight difference between the d-values of the first peak and that of the database was observed. The difference could be attributed to the change in the geological location of specimen used in ICDD database, as it has been reported to be from Cribou pitt, Coleraine Tp. Quebec, Canada; having the composition: $Cr_2O_3$= 55.51%, $Al_2O_3$= 14.03%, $Fe_2O_3$= 3.79%, FeO= 11.35%, MgO= 14.83% and minor Si, Ti, Ca and Mn related compounds[10]. The EDX analyses carried out were in agreement with XRD for the major compound; but some impurity phases were also detected.

### Microstructural analysis

MMI showed four different type of grain morphologies marked with G, H, I & J suggesting a different phase for each, however that was not the case when compared to SEM/EDX analyses. Figures 3(b,d) and 3(a,c) show the metallurgical microscopy images and SEI's of the same area respectively. MMI of samples when compared with SEM/EDX analysis revealed that both G and H represented the same phase. The difference in grain morphology (grain G being more continuous than H) might be due to over etching of one region with respect to other. EDX of grains I and J showed them as impurities but of different sort, this could also be seen in color contrast of SEI's (Figure 3(a, b)) as I was darker and J had whitish touch. EDX analyses of each grain in Figure 3(a, b) are given in Table 2. Some previous studies[3, 7, 8] suggest that such type of impurities mainly represent silicate phase. On the basis of previous studies conducted[7] the impurity containing uranium was proposed to be uvarovite, as it is the

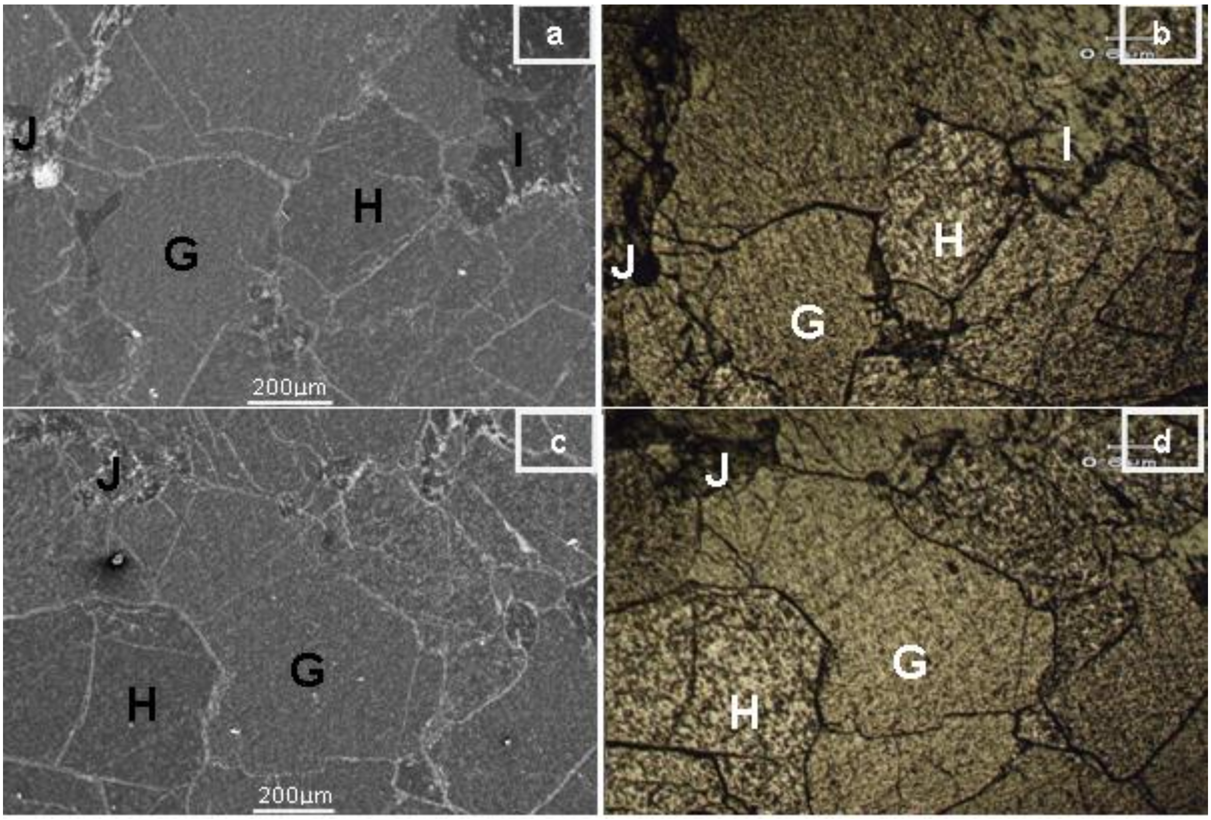


Figure 3. (a,c and (b,d) showing the SEI and MMI of the same regions respectively. EDX analysis suggested that the grains G and H represent chromite ore and I represent silicate impurities.

Table 2. EDX analyses in weight% of the G, H, I and J grains shown in Figure 3(a, b).

| Elements \ Grain | G | H | I | J |
|---|---|---|---|---|
| **Mg wt%** | 13.44 | 11.52 | 24.65 | 27.03 |
| **Al wt%** | 12.36 | 13.09 | 2.93 | 4.89 |
| **Si wt%** | - | - | 59.78 | 40.07 |
| **Ca wt%** | - | - | 15.31 | 4.30 |
| **Cr wt%** | 59.01 | 57.82 | 2.34 | 5.55 |
| **Fe wt%** | 15.41 | 17.57 | - | 4.42 |
| **U wt%** | - | - | - | 13.75 |

only uranium containing silicate impurity in chromite. Over all the grayish yellow color of the sample in MMI has been attributed to the presence of $Fe^{2+}$ [3].

## CONCLUSION

The XRD data in light of SEM/EDX analyses allowed us to deduce that the mineral was essentially made of pure chromite spinel (Magnesiochromite-ferroan) with ICDD # 09-0353. The SEM/EDX and MMI data comparison showed that there were three phases as compared to four in MMI. The impurity phases could not be characterized properly due to lack of experimental data from XRD, but based on SEM/EDX the impurities could be mainly attributed to silicates family with one of them being uvarovite based on the literature available.

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