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XANES AS A TOOL FOR ESTIMATION OF Fe AND Ti IONIC STATE IN RAW MATERIALS USED IN PIGMENTS PRODUCTION

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The quantitative analysis of the phase contents in raw materials used for white pigment production (TiO_2), is very important for the proper adjustment of chemical reactions conditions. The composition of minerals varies depending on the location where they are collected. Ilmenites are valuable natural sources of titanium and titanium compounds, widely used in industry of white pigments production. In the process of TiO_2 production by sulphate method, reaction of titanium raw material with sulphuric acid is the first step of the process, which is highly exothermic and should be properly adjusted to avoid an explosion. Knowledge of elemental, chemical and phase composition has a large influence on efficiency, safety, kinetics of reaction and the quality of products. The materials have complicated morphology and this is a reason that usually the content of elements measured by conventional electron probe microanalysis (EPMA) or X-ray fluorescence analysis is given, after averaging, as a content of the most typical simple oxides, which does not fit to the real contents of oxygen in the material. Moreover, none of the oxides is observed in the diffraction and the oxidation state of some elements in the formal formula of oxides ascribed to the mineral can be different than that one in the compounds present in mineral.

Therefore, several complementary methods were used in the present study for characterisation of the mineral ilmenite. The X-ray powder diffraction (XRD), EPMA as well as X-ray absorption (XANES) were applied to analyse the samples of mineral ilmenite. From X-ray microanalysis we would like to get not only information about elements contents, including the oxygen, but also information about the possible phase content. Next, the microanalysis results were compared with the results of the XRD and refined to achieve the

overall agreement. Finally, the dominant elements observed in the microanalysis, were found with the proper proportions in the phases detected by the XRD. The bonding of the atom in the particular chemical compound forces the ionic state of the element. The X-ray absorption spectrum (XAS) is a fingerprint of the given chemical compound. To check the ionic state of elements, the spectra for K and L-edges of most important elements in the mineral ilmenite (Fe and Ti) and reference samples were studied.

The K-absorption edges of Fe (Fig. 1) and Ti were measured in the HASYLAB at the A1 station. The measurements were performed for mineral ilmenite and for reference samples of hematite (Fe_2O_3) and rutile (TiO_2). The spectra of L-edges of Ti and Fe were collected at the Advanced Light Source in Lawrence Berkeley National Laboratory, at the 6.3.1 station. Reference sample of ilmenite and iron oxides were measured at BESSY U41 PGM station Berlin, Germany. These data provide information about $2p$ and $3d$ unoccupied electron states in compounds, respectively.

The position of edges is closely related to the ionic state of the element in the compound and the energy shift of the edge can be used in estimation of the element valence in a new compound. The energy positions of the K-edges (p -states) of Fe and Ti in ilmenite mineral are very close to that of trivalent iron (Fe^{3+}) in hematite (Fig. 1) and four-valence titanium (Ti^{4+}) in rutile. This finding does not support valence of Fe^{2+} in ilmenite resulting from charge balance of anions and cations.

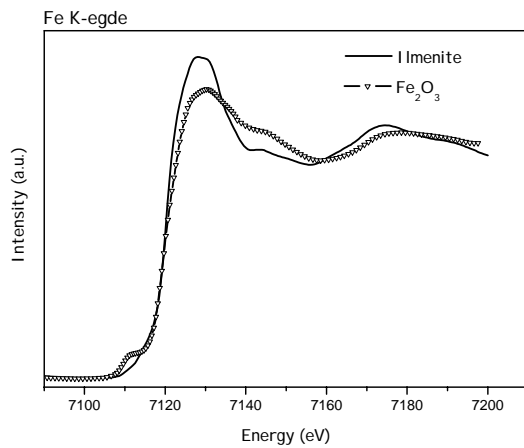


Figure 1. Fe K-edge of mineral Ilmenite and hematite (Fe_2O_3).

In the L-edges of ions of 3d metals usually a lot of structures can be observed which are well described by multiplet atomic theory with the inclusion of the crystal field. The multiplets structure changes significantly with varying number of 3d electrons. Besides the shift to the higher energy with higher valency, the spectral shape does change significantly, which makes determination of the valency straightforward. In Figure 2 the L-edges of Fe in mineral ilmenite and different reference materials are presented. The significant differences between spectra can be observed. This fact may indicate that in ilmenite the 3d electrons are responsible for chemical bond of Fe atoms.

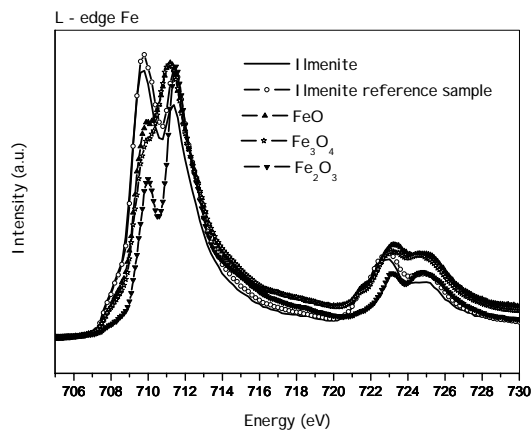


Figure 2. Fe L-edge in ilmenite and several reference samples.

In the L-edges of Ti (Fig. 3) we do not observe that pronounced changes in the position of edges in mineral ilmenite and reference samples what prove the Ti^{4+} valence.

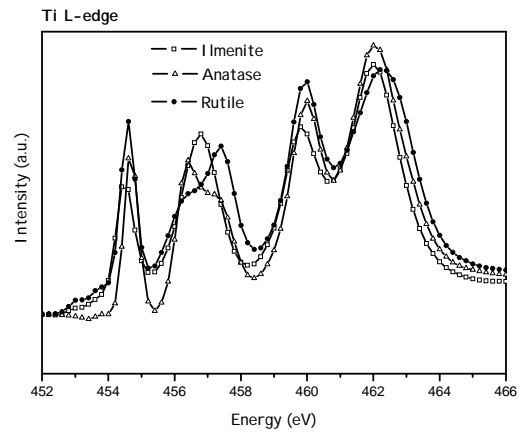


Figure 3. Ti L-edge in ilmenite and TiO_2 in structure of rutile and anatase.

The nature of Fe bonding in the synthetic and mineral ilmenite will be discussed and the L spectra of iron from reference compounds used for quantitative estimation of phase content applying the principal elements content method (XANDA program). An example of fitting procedure is shown in Figure 4.

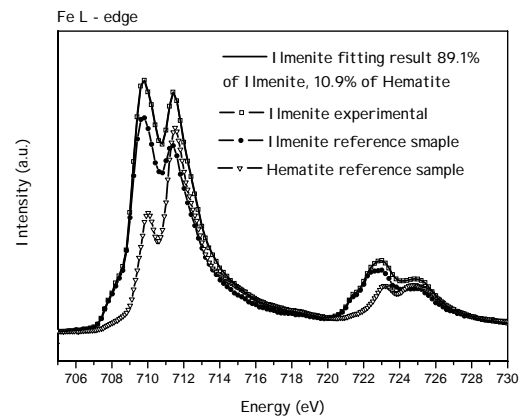


Figure 4. Fe L-edge of mineral ilmenite, two reference samples and the result of fitting.

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