T7 - MINERALS

T7 - P131

CRYSTAL STRUCTURE DETERMINATION OF NEW PHASE Ni_2SbTe_2 FROM KUNRATICE NEAR ŠLUKNOV (CZECH REPUBLIC)

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The new unnamed nickel antimonide telluride, Ni_2SbTe_2, was founded as 6 μm grain by Vavřín and Frýda (1998) at the Kunratice Cu-Ni deposit. This ternary phase is in close association with melonite; this assembly is included in pyrrhotine. The crystal structure was determined from synthetic analogue prepared using silica glass tube method. The stechiometric amounts of Ni, Sb and Te were loaded into silica tubes and sealed under vacuum. They were then heated in a programmable furnace at 400 °C, 800 °C for three weeks. The experiments were terminated either by quenching in a cold water bath or by slow cooling.

The crystal structure of Ni_2SbTe_2, prepared at 800 °C (terminated by quenching), determined from X-ray single diffraction data, is hexagonal, NiAs type with lattice parameters a = 3.9108(2) Å, c = 5.2489(3) Å, space group $P6_3/mmc$. The antimony and tellurium atoms occupy the crystallographic position 2*c*; the position 2*a* is occupied by nickel atoms.

The crystal structure of Ni_2SbTe_2, prepared at 400 °C (terminated by slow cooling to 50 °C within the intervals of 22 hours), originally described by Reynolds et. al. (2004), refined from X-ray single diffraction data, is hexagonal with lattice parameters a = 3.9110(2) Å, c = 15.696(1)Å , space group $P6_3/mmc$. The antimony and tellurium atoms occupy different crystallographic positions, antimony 2*c* and tellurium 4*f*.

The situation in the case of crystal structure of Ni_2SbTe_2, prepared at 400 °C (terminated by quenching) is more complicated. The X-ray powder diffraction pattern corresponds to the disorder (high temperature) phase, nevertheless diffraction profiles of 201 and 110 lines are asymmetrical. This asymmetry disappears in powder pattern of Ni_2SbTe_2 prepared at 800 °C (Figure 1,2). It was possible to observe weak reflections near 1/3 and 2/3 of the distance between the sharp diffractions on the photographs of reciprocal planes *h0l* obtained from electron diffraction (SAED). These weak diffractions systematically shifted from 1/3 to the left and from 2/3 to the right, i.e. closer to the sharp diffractions. The phase Ni_2SbTe_2 forms at 400 °C a solid solution with end members having the composition of 42.1 % Ni, 13.0 % Sb, 44.9 % and 43.0 % Ni, 28.4 % Sb, 28.6 % Te (at. %).

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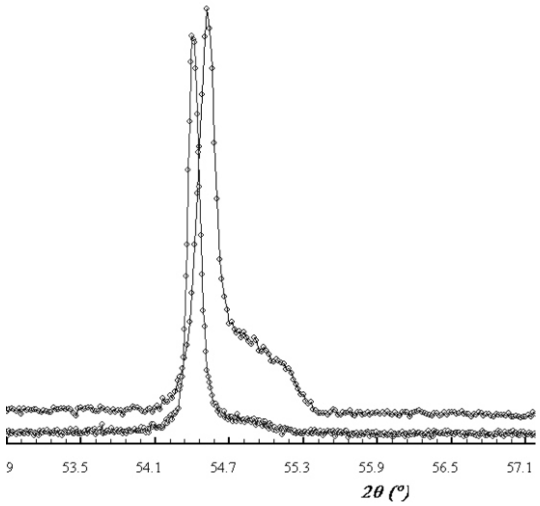

Figure 1: Diffraction profil 110 line of Ni_2SbTe_2 prepared at 400 °C (above) and at 800 °C, Co rad.

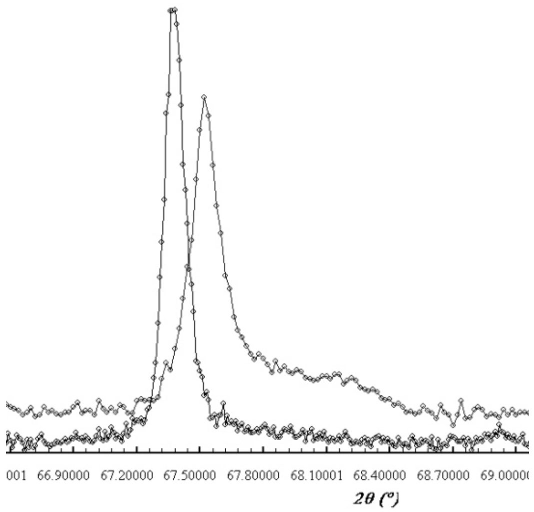

Figure 2: Diffraction profil 210 line of Ni_2SbTe_2 prepared at 400 °C (above) and at 800 °C, Co rad.

T7 - P132

MODEL OF DISORDER AND STRUCTURE REFINEMENT OF ILLITE

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The term illite, introduced by Grim in 1937 [1], refers to an aluminum-potassium mica-like, non-expanding, dioctahedral mineral, present in the clay fraction (under 4 m). Together with kaolinite, clorite and illite-smectite mixed-layers (I-S), illite is one of the four major constituents of argillaceous sedimentary rocks. Illite generally crystallizes in the monoclinic system, like other micas. Its structure is very similar to 2:1 mica structure, with two tetrahedral sheets and one octahedral between, to build up the T-O-T sheet [2].

According to Rosenberg [3], an approximate formula for illite can be written as:

$$K_{0.88}Al_2(Si_{3.12}Al_{0.88})O_{10}(OH)_2$$

deduced both by experimental studies [4, 5], and by studies on natural materials [6] With respect to muscovite, in illite there is a lower K content, due to the lower substitution of Si with Al in the tetrahedral site.

Illite presents extensive structure disorder likely due to shifts and rotations between the layers: this contributes to the anisotropic broadening of peaks width in the diffraction pattern. One of the major problem concerning illite studies is finding of a pure sample. The sample utilized in this work is pure and occurs in a mine from the Tokaji mountains region, Hungary. The aim of this study is to investigate the structure model and structure disorder of this pure illite sample. In order to do this, DIFFaX [7] has been utilized for the preliminary simulation of the XRPD pattern, and DIFFaX+ [8] for the refinement of the structure. The result obtained with DIFFaX+ will be cross checked with WILDFIRE© [9]. Figure 1 shows the observed XRPD pattern of the pure illite sample.

We are actually in the process to test a number of different models and to obtain the best results for our sample.

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T7 - P133

STRUCTURE AND MICROTEXTURE OF HIGHLY HYDRATED NATURAL CLAYS BY MEANS OF SAXS AND MET ANALYSIS

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The main objective of this study is to specify the hydration mechanism of soil clays coming from Tunisia, in particular according to their mineralogical characteristics and stress history and to compare these clays with that from clay deposit such as Wyoming montmorillonite. The fraction < 2 μm of these clays was separated and was then subjected to a cycle of desiccation (3,2 to 10^5 kPa) then to a controlled rehydration up to 3,2 kPa. The study of their organization at high water contents was carried out with TEM by replacing water with an expoxy resin on the sample initially hydrated. The structural and textural characteristics during drying and rewetting was determined by mean of Small Angle X-ray Scattering (SAXS). Observations with the MET indicated that soil clays present an organisation in aggregates with different levels of solid phase assembly (layers, crystals, aggregates). The particles had different facieses according to their mineralogical nature and their layer charge and location. The particles were more rectilinear when their layer charge increased. SAXS results showed that their size evolved during drying-wetting cycles so that it was not possible to define a particle which was characteristic of the clay independently of its stress history. This observation remained valid for the Wyoming montmorillonite but, in this case, the particles had homogeneous hydrated layer spacing and were easily curved assemblies on contact with water. The comparison of SAXS results and MET observations showed that in the range of high water contents, the main part of water was retained inter particle pores and its amount and localisation varied considerably as a function of the stress history. Contrary to Wyoming montmorillonite, in interstratified clays, the interlayer hydration is partly reversible. This study demonstrates that for understanding and predicting the behaviour of clays, in particular those in soils developed from sediments, it is necessary to refer to the layer charge localisation and to the energy history of the material, which determine a part of the swelling mechanism, especially for clays exposed to natural conditions.

T7 - P134

INCRUSTATION OF PRECIOUS STONES IN DENTAL APATITE

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From the X to VI centuries B.C., the incrustations of precious stones in dental apatite were commonly practiced in ancient Mexico. According to several authors [1-3] pyrite, hematite, jadeite and turquoise were typically used for this purpose. The technique probably consisted in practicing a cavity on the tooth surface (of anterior teeth) by mean of a drill-like tool and perhaps the helping of powdered quartz with water as an abrasive. The stone was then fixed by using an adhesive like *copal* [2] or calcium phosphate-based cement [3]. With regard to this, Swedish scientist S. Linné cited by Fastlicht [1, 4] pointed out the following: “It is no concern of mine to judge if this is praiseworthy but I have heard prominent specialists express their surprise when observing that this cement has kept its purpose after 1,500 years. While today, despite of our advanced technology, it does not even last the life of a patient.” At present, dental inlays (silver-based alloys) can last almost 8 years, and despite that one do not obtain a real adherence between these inlays and the dental tissue; alloys inlays are frequently used today because of their cheapness and longest permanence in the mouth. On the contrary, in the case of ceramic inlays (i.e. metal free porcelain) an interface between tooth and the inlay is created using phosphoric acid, adhesives and, for instance, dual cement. Both surfaces are joined together creating an UV-polymerized thin hybrid layer (i.e. polymethyl-methacrylate). Ceramic metal free inlays present an approximate life of 10 years [5] and have the advantage of be very aesthetic and cosmetic; but they are not very resistant to rupture and are very expensive.

In this work, we consider that a composite adhesive made-up by *copal* and powdered apatite (from tooth or bone) was used in ancient Mexico for dental incrustations. Two facts support this statement: first, the work reported by Fastlicht and Pompa y Padilla [1, 2] where the presence of powdered apatite has been detected by X-ray diffraction experiments, also they consider very seriously the presence of *copal* even if it has not been completely confirmed and identified yet [1]. The second fact is narrated in the amazing book written by F. Martínez Cortés entitled *Sticky-materials, Gums and Resins in Prehispanic Mexico* [3]. In this book one can read that *copal* was the basis of the sticky-materials employed to elaborate several wonderful pieces such as the granite mask discovered in Malinaltepec, Guerrero, Mexico, and decorated with small fragments of turquoise platelet-like stones. We have considered the last as an evidence that *copal* would be known as a suggestive sticky-material to stick precious stones such as turquoise or others to the dental tissue. We have reproduced our assumption in modern dental pieces using *copal*, powdered apatite and some precious stones such as turquoise. The preferred crystal orientation of apatite crystals was characterized by X-ray powder diffraction data. With the knowledge of the relative orientation of apatite crystals with respect to the surface to be in contact with the incrustation surface by mean of the *copal*-based adhesive, we have tried to investigate the mechanism in which the adhesive properties of *copal* works. For this purpose, we have also performed some analyses with FTIR (infrared spectroscopy) and LVSEM (low vacuum scanning electron microscopy).

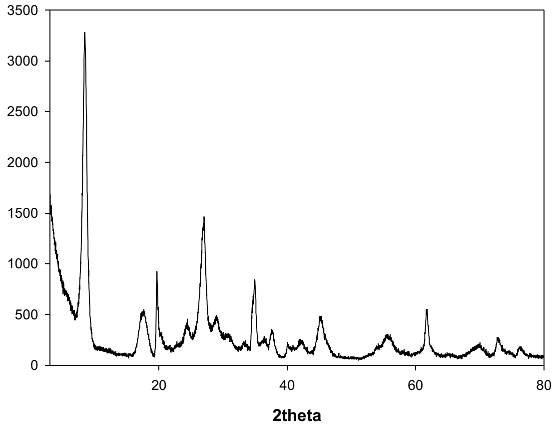

Figure 1. Observed pattern of the Hungarian illite in the range 3-80 °2 .

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