

## 1.5.14

**High-pressure phase transition in natural marcasite**

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We report here for the first time, the high-pressure induced phase transition in natural marcasite at room temperature. Marcasite and pyrite occur along with fire clays, sand stone and carbonaceous matter in sedimentary sequences in lignite deposits of Neyveli. Formations associated with the Neyveli Lignite belong to Miocene Cuddalore Group.

Our experimental studies on the characterization of this sulphide-rich samples show that the top level of lignite band consists of marcasite-rich sulphide and the content of marcasite is found to decrease with the increase of depth. In the present study we report the high-pressure electrical resistivity, high-temperature DTA and FT-IR spectroscopic measurements on few selected samples from this borehole. The Marcasite-rich samples show a pressure-induced irreversible marcasite-to-pyrite phase transition at 4 to 6 GPa at room temperature. Pure marcasite exhibits the transition at 6 GPa. The samples were characterized by XRD, FT-IR-spectroscopic and DTA/TG methods.

The samples above the lignite bed (TL-2 and TL-6) exhibit seven exothermic peaks at 230, 332, 415, 480, 540, 600, 657 degree C. in the temperature of investigations (30-1000 degreeC). These values are in close agreement with the data published for pure-marcasite. The samples from the middle level (ML-4 and ML-10) show one strong exothermic at around 733 K and two distinct sharp endothermic peaks at 860 K and 923 K, indicating the enrichment of pyrite content and also decrease in the marcasite content in the samples.

Fourier-transform infrared spectroscopic measurements (at room-temperature) on the sample TL-2 showed four absorptions bands at 419, 396, 353, 325  $\text{cm}^{-1}$  while the sample ML-10 showed only three IR absorption bands at 410, 345, 290  $\text{cm}^{-1}$  all of these corresponding to pure pyrite vibrational modes. These change of absorption bands could be explained on the basis of the structural difference between the marcasite (space group O (2/m, 2/m, 2/m)) and pyrite (space group I(2/m-3)).

The chemical analyses of the samples and the structural data indicate that the formation temperature of sulphide rich deposits is around 673 K.

## 1.5.15

**Exploration of structural phase transitions in transition metal oxides of the titanite structure type**

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The structural topology of the mineral titanite is characterized by chains of corner sharing transition metal cation coordination octahedra. If the direction of these chains is set parallel to the [001] direction, the aristotype structure is described in space group C2/c. This structure type is formed by a large variety of compounds and it can distort to several possible ground state structures, depending on the particular crystal chemistry.

So far the known transition metal compounds with this structural topology and general stoichiometry  $\text{AMOXO}_4$  involve the cations  $\text{A}=\text{Ca, Sr, Na, Li, M}=\text{Ti, Nb, Ta, Zr}$  and  $\text{X}=\text{Si, Ge, Al, P}$ . Several different types of displacive structural phase transitions have been observed in these compounds using X-ray diffraction, differential scanning calorimetry and solid state NMR-spectroscopy. The transition  $\text{P2}_1/\text{c} - \text{C2}/\text{c}$ , which is well documented for titanite, involves an off-centering shift of the transition metal cation and occurs in several of these compounds over a wide range of critical temperatures. While the critical temperature is 487 K in titanite itself, transition temperatures of 231 K, 439 K, 560 K and 588 K have been observed in  $\text{LiTaOGeO}_4$ ,  $\text{LiTaOSiO}_4$ ,  $\text{SrTiOGeO}_4$  and  $\text{CaTiOGeO}_4$  respectively. In other known compounds of this type, such as  $\text{NaTiOPO}_4$  and  $\text{NaNbOGeO}_4$ , the transition temperatures are expected to be raised above the respective stability limit of the material and therefore only the ordered structure is observable.

Two compounds do not transform to a  $\text{P2}_1/\text{c}$  low temperature structure however:  $\text{CaZrOGeO}_4$  is triclinic at room temperature and transforms to the monoclinic aristotype structure near 500K, while the low temperature structure of  $\text{CaTaOAlO}_4$  has space group symmetry  $\text{P2}_1/\text{n}$  in the above setting.

Possible driving forces of the respective structural instabilities are discussed based on these observations.