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RAMAN SPECTROSCOPIC STUDY OF THE DEHYDRATION BEHAVIOUR IN APOPHYLLITE

INTRODUCTION

The dehydration process of apophyllite has been studied since their discovery in the late eighteenth century. The crystal structure of apophyllite was first determined by Taylor & Nàray-Szabo (1931) and next refined many times (e.g. Colville et al. (1971), Rouse et al. (1978)). Apophyllite, $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH})\cdot 8\text{H}_2\text{O}$ is an unusual layer silicate with puckered sheets laying parallel to (001). They are made up of alternate rings of four silicon-oxygen tetrahedra that are pointed up and down the c-axis, respectively. The layers are connected together through Ca-coordination of silica oxygen and through K- coordination of water molecules.

The DTA curve of apophyllite shows two distinct endothermic peaks centred at about 325 and 450°C, respectively. A multi-stage dehydration process is typical for minerals with different structural sites of water molecules. The refinement of apophyllite structure provides no evidence for existence of two different structural environments and indicates unequivocally that only one site of H_2O can exist. There are different explanations for the present of the two endothermic peaks. Marriner et al. (1990) connects the first stage of apophyllite dehydration with such loss of the water proportion which result only in minor distortion of the crystal lattice. At the second one the total structure collapses into an amorphous material. Stàhl (1987, 1993) described that process as a two step reaction. The first step leads to $n(\text{H}_2\text{O}) \approx 7$ with preservation of tetragonal symmetry. The second one is connected with continued dehydration, resulting in a collapse of Ca and K coordination and formation of non-diffracting amorphous phase.

In order to try to explain this problem the Raman spectroscopic study was carried out on thin slabs of fluorapophyllite from Poona, India. Each sample was heated to obtain a definite stage of dehydration of apophyllite and was analyzed on a Dilor Micro Raman spectrometer with a 514.5 nm argon ion laser. It focuses the size of the laser beam to about 5 μm on the surface of the sample.

RESULTS AND DISCUSSION

Continued dehydration experiments on the thin slabs were carried out in a resistance furnace in air, during controlled periods of time, with subsequent rapid

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cooling to room temperature. The degree of dehydration was measured by means of weighting of the slabs before and after heating. Unpolarized Raman spectra of apophyllite and its partially dehydrated forms were collected on the (001) surface of the slabs at different points (see Fig. 1). When the weight loss reached 11% only amorphous form was recorded (Fig. 1d). The continuous dehydration of apophyllite up to this value is shown on Fig. 1b and 1c. These spectra are simple superpositions of the spectrum of amorphous apophyllite phase (Fig. 1d) and their crystalline form (Fig. 1a). The process of recrystallization of amorphous form of apophyllite to wollastonite above 700°C is shown on Fig. 1e and 1f.

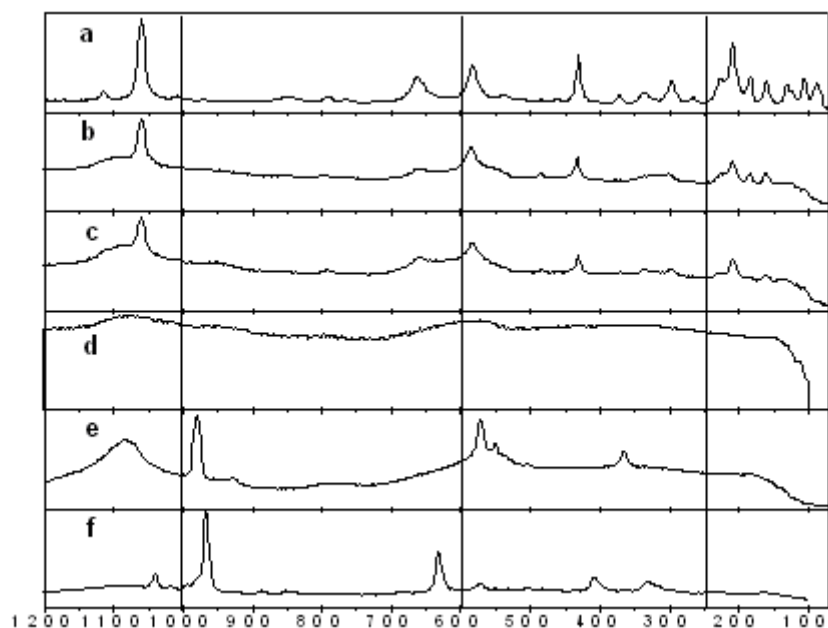


Fig. 1. Unpolarized (VV + VH) Raman spectra of apophyllite (a), its partially dehydrated (b and c) and non-diffracting amorphous form and also spectra of recrystallization products of apophyllite at 700°C (e) and 820°C (f); scale in cm^{-1} .

The data obtained allows described the dehydration process as a one step reaction. The destabilization of K and Ca coordinations results in the crystal structure collapse into the amorphous structure. The transition to an amorphous form, initially on the outside surfaces of the apophyllite crystal will trap a certain part of the molecule water inside forming a diffusion barrier. The diffusion process of water through the amorphous part gives rise to the second endothermic peak on the DTA curve.

The Raman spectra of amorphous structure of apophyllite (Fig. 1c and Fig. 2a) and its melted equivalent (Fig. 2b) are very similar. The major bands observed in these samples were assigned to various structural units according to McMillan (1984) interpretation. The strongest band at about 1070 cm^{-1} corresponds to symmetric silicon-oxygen stretching vibrations of silicate tetrahedral units with one

non-bridging oxygen (\equiv SiO unit). The other one at about 950 cm^{-1} corresponds to units with two non-bridging oxygen ($=\text{SiO}_2$). The low-frequency bands ($700\text{-}500\text{ cm}^{-1}$) are assigned to inter-tetrahedral Si–O–Si linkages in groups more polymerized than SiO_4 units. The fully polymerized tetrahedral network $=\text{Si}=\text{}$ has strong asymmetric band in the $500\text{-}400\text{ cm}^{-1}$ region (see Fig. 2c)

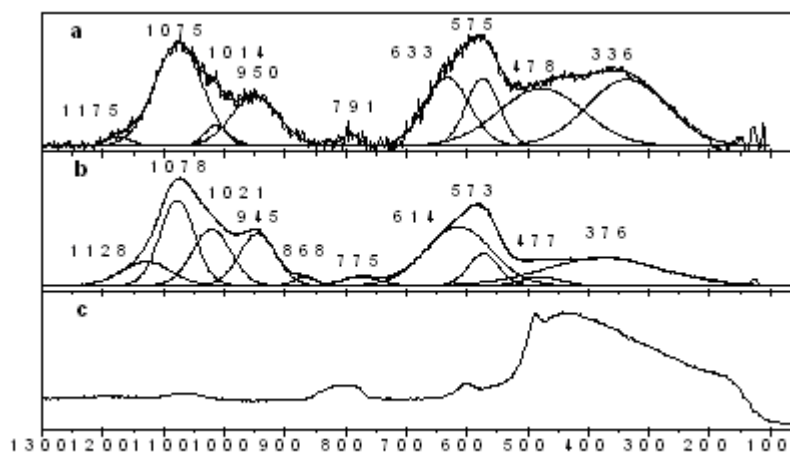


Fig. 2. Fitted Gaussian lines of unpolarized spectra of apophyllite heated to 600° (a) and melted at 1550°C (b); c- spectrum of vitreous SiO_2 ; scale in cm^{-1} .

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