POLYMORPHOUS TRANSFORMATIONS OF EDINGTONITE AT LOW TEMPERATURE AND HIGH PRESSURE

Goryainov S.V. *(Institute of Mineralogy and Petrography, Novosibirsk, Russia)*
Kurnosov A.V. *(Institute of Inorganic Chemistry, Novosibirsk State University, Novosibirsk, Russia)*
svg@uiggm.nsc.ru; fax:+7(3832)33-27-92; phone: +7(3832)33-24-06

Key words: *edingtonite, zeolite, Raman spectra, IR spectra, generation of second harmonics, high pressure, ferroelectrics, phase transtion*

As rule, molecules H_2O are isolated in structure of natrolite group (edingtonite is member of the group), and the channels are narrow, resulting to low mobility of water in the channels. The exception is edingtonite, in which H_2O-H_2O bonds are available. In result, edingtonite differs by high mobility of H_2O, comparable with that in wide-porous zeolites.

Edingtonite is ferroelectrics lower temperature of para-ferroelectric transition (which depends on water content) and demonstrates anomalies of various properties at low *T* [1]. Edingtonite is analogue of classical Rochelle salt due to coincidence of space group $P2_12_12$ and presence of two sub-lattices of H_2O. In present work, we planned to study low-T phase transition (PT) in edingtonite by methods of IR and Raman spectroscopy and generation of second harmonics (GSH), and also to find the suggested PT at high pressures (analogue of low-T ferroelectric transition), and to investigate the stability of crystal structure of edingtonite up to amorphization, which earlier was observed in other silicates [2-4].

Edingtonite ($Ba_{0.97}$ $Na_{0.03}$ $K_{0.04}$) [$Al_{1.98}$ $Si_{3.02}$ O_{10}] 3.69 H_2O (Bohlet, Sweden) exhibits considerable anomalies of IR spectra in low-frequency range at low T (Fig. 1,2). Maximum of intensity of anomalous IR bands is observed in natural edingtonite at -124 ^oC and in deuterated one at -113 ^oC.

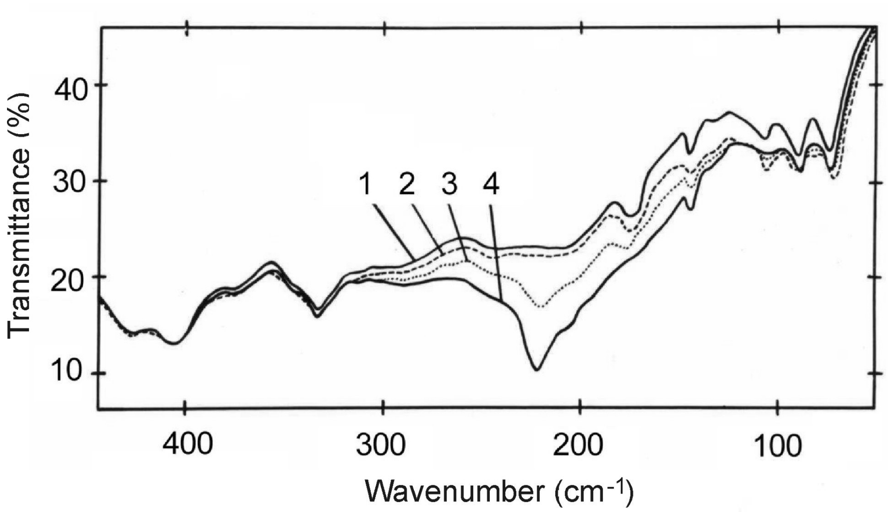


Fig. 1. IR transmittance spectra of partially dehydrated edingtonite at low temperature: (1) –152 ^oC, (2) -86 ^oC, (3) -106 ^oC, (4) -124 ^oC.

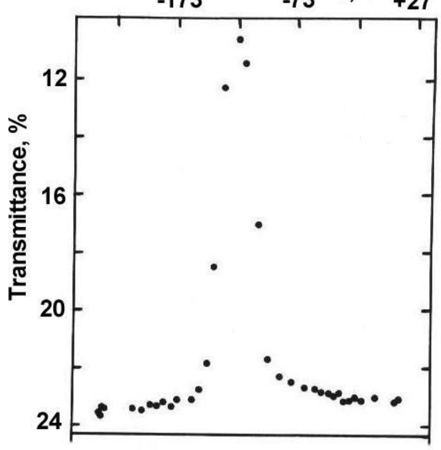
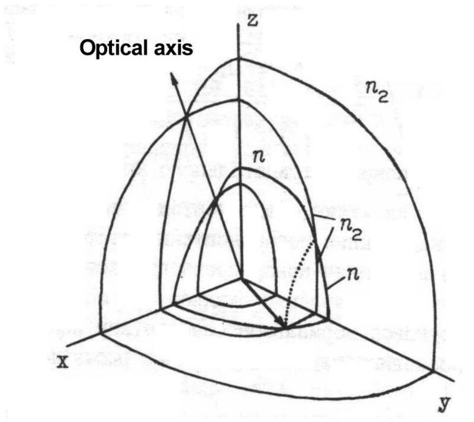


Fig. 2. Temperature dependence of IR transmittance of anomalous band of partially dehydrated edingtonite at 220 $см^{-1}$.

Fig. 3. Directions of synhronism of collinear coherent waves of generation of second harmonics for optically negative crystal for intersection of surfaces of excited beam n and second harmonics beam n_2.



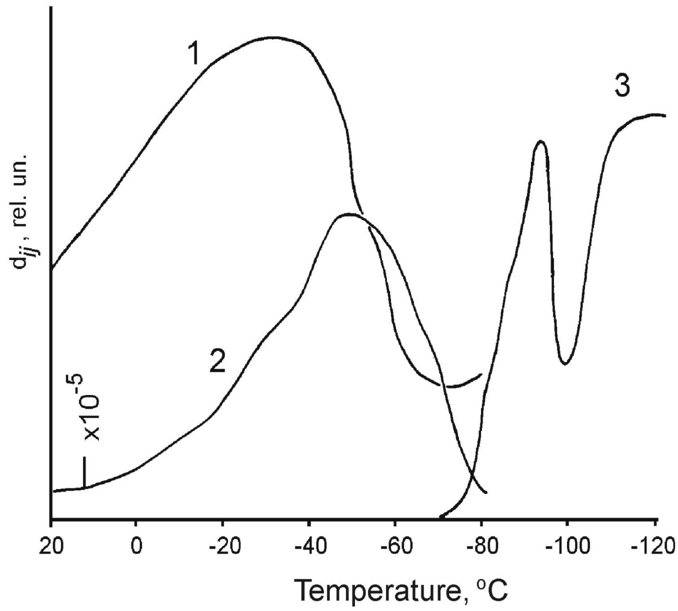


Fig. 4. Temperature dependence of the intensity of the components of the tensor d_{ij} of edingtonite measured by second-harmonic generation: 1 - d_{36}, 2 - close to direction of synchronism, 3 - d_{31}.

The most intense anomalous band at 220 cm^{-1} is not shifted with deuteration. The form of this vibration of framework corresponds to a strong deformation of cavity around water molecules.

Condition for synhronism of collinear coherent waves at generation of second harmonics for optically negative crystal is presented in Fig. 3.

The appearance of d_{31} component of generation of second harmonics at low temperatures (below –70 °C) is in agreement with the P2 (c-axis) space group. The present investigation of SHG component d_{31} of edingtonite (Fig. 4) proves that three transitions are available at low temperatures: 1. para-to-ferro-electric transition at –70 °C; 2. ferro-to-antiferro-electric transition at –95 °C; 2. antiferro-to-ferro-electric transition at –105 °C.

It was shown that in edingtonite there is direction of coherent collinear waves for generation of second harmonics that may lead to possible application edingtonite as nonlinear element.

Bands of Raman spectra exhibit the linear dependences on pressure. The spectrum type, characterized by band form, intensities and number of bands, are not changed within this pressure range measured. Rate of strongest Raman O-T-O bending band at 532 cm^{-1}, which is "breathing" mode of 4-membered rings, is equal to 4.3 cm^{-1}/GPa. We conclude that in the pressure range up to 6.4 GPa there is no phase transition connected with symmetry change or with any significant structural change. No sign of amorphization, viz. widening of bands and decreasing of band intensity, was evident.

Results of the works are following:

- observation of anomaly of IR bands in low-frequency range,
- determination by GSH space group of edingtonite *P*112 at low T,
- finding of direction of coherent collinear waves for generation of second harmonics that leads to perspective of application edingtonite as nonlinear element,
- determination by GSH several transformations,
- confirmation by Raman spectroscopy the stability of edingtonite crystal up to 6.4 GPa.

This work was supported by the RFBR (02-05-65313, 01-05-65373 grants) and CRDF (REC-008 grant).

References:

[1] *I.A. Belitsky et al.* Phys. Chem. Minerals 18 (1992) 497.
[2] *N.N. Ovsyuk, S.V. Goryainov*. Phys. Rev. B 60(21) (1999) 14481.
[3] *Ph. Gillet, J.-M. Malezieux, J.-P. Itie*. Am. Miner. 81 (1996) 651.
[4] *S.V. Goryainov, M.B. Smirnov*. Eur. J. Mineralogy 13 (2001) 507.

Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21)'2003
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/term-8e.pdf
Published on July 15, 2003