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FAR INFRARED PROPERTIES OF FLUORAPATITE

Nikolić P.M., +Roys W.B., Blagojević V.

Institute of Physics, Electrotechnical Faculty Belgrade University and +Department of Physics Nottingham University, 11000 Belgrade, P.O.Box 57,Yugoslavia.

ABSTRACT

Far infrared reflectivity measurements for fluorapatite have been done using polarised light. Six oscillators were observed in the range between 40 and 400 cm^{-1} for $\vec{E}\perp\vec{c}$ and three oscillators for $\vec{E}||\vec{c}$. The experimental results have been numerically analysed and the optical parameters obtained.

1. INTRODUCTION

Fluorapatite (FAPT) is a mineral with the chemical formula $Ca_5(PO_4)_3F$. Its structure belongs to the hexagonal[1)] space group C^2_{6h}. Ionic forces in FAPT are dominant and consist of connected discrete ions of Ca,F and PO_4. Four Ca ions (CaI) have point symmetry C_3 with PO_4 ions which are oriented in such a way that 6 atoms of oxygen are the nearest neighbours of Ca. The fifth Ca ion (CaII) has four O atoms and one F ion as the nearest neighbours. The fluoride ions are aligned parallel to the $\vec{c}$ axis.

When Nd^{+3} is added to FAPT, there is a well known lasers effect. Because of this effect large single crystals of FAPT have been grown by the Czochralski method[2,3)].

The lattice vibration of FAPT has already been investigated. Raman[4)] and infrared active modes[5)] were determined in the range between 100 and 1100 and 400-1100 cm^{-1}, respectively. Arhipenk et al[5)] have compared the experimental results with a theoretical expression which gives all lattice modes for (PO_4) ions in the centre of the Brillouin zone

$$\Gamma(PO_4^{-3}) = 6A_g + 3A_u + 3B_g + 6B_u + 3E_{1g} + 6E_{1u} + 6E_{2g} + 3E_{2u}$$

In this work experimental results for room temperature reflectivity are given in the far infrared range for natural mineral and synthetic single crystal of FAPT. During the measurements polarised light was used for both $\vec{E}||\vec{c}$ and $\vec{E}\perp\vec{c}$.

2. EXPERIMENTAL

Mineral FAPT which was transparent but slightly yellow was used for far infrared reflectivity measurements where a Beckman

Fourier spectrometer (FS 720) was employed. In figure 1 and 2 these reflectivity diagrams are given as a function of the wavenumber for two $\vec{E}\perp\vec{c}$ and $\vec{E}||\vec{c}$, respectively. It is obvious that there are at least six ascillators for the first case and only three oscillators when $\vec{E}||\vec{c}$.

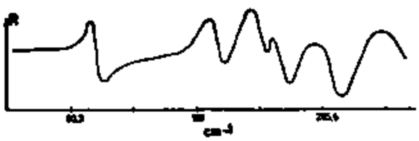

Fig.1. Far infrared reflectivity of fluorapatite for $\vec{E}\perp\vec{c}$.

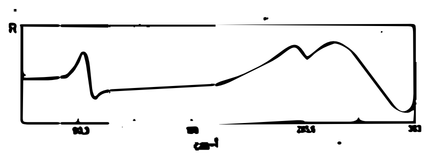

Fig.2.Far infrared reflectivity of fluorapatite for $\vec{E}||\vec{c}$.

The experimental results were numerically analysed using a four parameter model[6,7] which was introduced by Gervais and Piriou. The computing procedure is rather long and complicated for $\vec{E}\perp\vec{c}$ because we had to fit the values of 25 optical parameters (four parameters for each oscillator) plus the infinity dielectric constant. At the beginning we found rough approximations of the mentioned 25 parameters using a modified program which was kindly given to us by Gervais. Then a proper fitting procedure of the reflectivity curve was carried out. For this purpose a model of the Simplex subroutine was used and the details of this are given elsewhere[8].

In table 1 are given the best values of the fitted parameters--transverse (ω_{TO}) and longitudinal (ω_{LO}) optical modes and their damping factors (γ_{TO} and γ_{LO}, respectively).

The quality of this fitting procedure was checked by plotting together experimental and theoretical curves in the same figure. This is done for $\vec{E}\perp\vec{c}$ in figure 3.

In figure 4 the change of the real and imaginary parts of the complex dielectric function for $\vec{E}\perp\vec{c}$.are given

Table 1. Optical parameters used to fit far infrared reflectivity spectra of fluorapatite. Frequencies and damping factors are expressed in units of cm^{-1}.

	$\vec{E}\perp\vec{c}$	$\varepsilon_\infty = 7.1$			$\vec{E}\parallel\vec{c}$			$\varepsilon_\infty = 5.3$
Osc	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}	ω_{TO}	γ_{TO}	ω_{LO}	γ_{LO}
I	103	3.78	113	7.41	96	11.8	100	10.1
II	197	5.27	207	8.66	264	10.4	277	41.9
III	226	5.37	239	7.21	300	23.3	362	32.2
IV	244	8.63	254	7.98				
V	274	16.2	297	9.16				
VI	319	6.18	357	35.1				

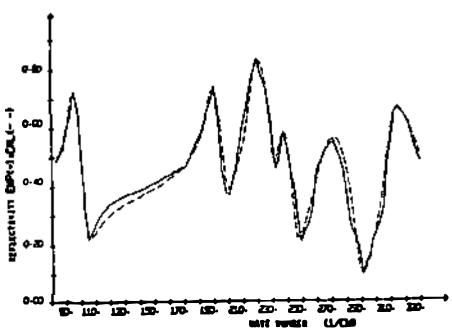

Fig.3. Far infrared reflectivity of fluorapatite. The solid line was calculated using the oscillator parameters given in table 1. The broken line represents the experimental results, for $\vec{E}\perp\vec{c}$.

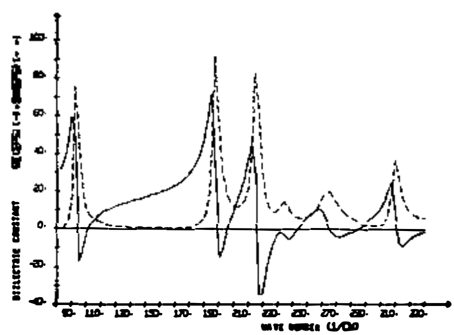

Fig.4. The real "RE(EPS)(—)" and imaginary "IM(EPS)(--)" parts of the complex dielectric function for $\vec{E}\perp\vec{c}$.

3. ANALYSIS AND DISCUSSION OF RESULTS

Using the literature data[4,5] one would expect nine active infrared modes for PO_4^{-3} ions at the centre of the Brillouin zone. Unfortunately the complete factor group analysis of the Γ point lattice modes for FAPT is not calculated yet so it is not possible to find out the exact number of either Raman or infrared active modes.

In our case nine oscillators were observed - six for $\vec{E}\perp\vec{c}$ and three for $\vec{E}\parallel\vec{c}$. In addition, according to our previous report[9] there are at least 5 more active infrared modes in the infrared range. Using our experimental far infrared data one could expect that ionic resonances from Ca and F ions would be in the far infrared range.

If we consider the way of change of the optical dielectric constant it is possible to say that ionic forces are much greater parallel to the c axis compared with perpendicular to the c axis.

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