Effect of Uniaxial Pressure on the Infrared Spectra of (NH₄)₂SO₄ Crystals

V. I. Stadnyk, N. A. Romanyuk, and N. R. Tuzyak
Franko Lviv National University, ul. Universitetskaya 1, Lviv, 79005 Ukraine
e-mail: vasylstadnyk@ukr.net
Received July 31, 2006

Abstract—The infrared reflectance spectra of a mechanically free or uniaxial-pressure-confined (NH₄)₂SO₄ crystal were studied for the first time in the spectral range 800–1700 cm⁻¹ in three crystallographic directions. Using the Kramers–Kronig relations, the dispersion and pressure dependences of the following quantities are obtained: the index of refraction n, the real (ε₁) and imaginary (ε₂) parts of the permittivity, the frequencies of longitudinal (ωₖLO) and transverse (ωₖTO) optical vibrations, the damping constant γ, and the oscillator strength f of the mechanically free or clamped (NH₄)₂SO₄ crystal. A considerable change in the main reflection bands with pressure was observed, which is due to the effect of uniaxial pressure on the NH₄ and SO₄ tetrahedral frames.

PACS numbers: 78.30.Am, 78.20.Hp
DOI: 10.1134/S1063783407040166

1. INTRODUCTION

Ammonium sulfate (AS) (NH₄)₂SO₄ crystals are nonpolar at room temperature and belong to the orthorhombic space group Pnma. They undergo a phase transition (PT) below Tₛ = 223 K without changing the number of formula units in the unit cell (Z = 4) and become ferroelectrics belonging to space group Pna₂₁ [1, 2]. The PT is accompanied by a significant jump in strain. Below Tₛ, the spontaneous polarization Pₛ decreases and changes sign near 85 K [3, 4]. This indicates that there are several temperature-dependent contributions to Pₛ coming from different sublattices and that these contributions compensate for one another near 85 K [4, 5].

Comprehensive structural studies of the para- and ferroelectric phases in AS crystals made it possible to determine the ordering elements in the structure [6]. The NH₄(1), NH₄(2), and SO₄ groups were considered possible disordered elements. The corresponding structural models for the paraelectric phase have been analyzed and compared. It has been concluded that the SO₄ tetrahedrons have a single equilibrium position in the paraelectric phase and move in a single-minimum potential with a rather high amplitude.

Radio-frequency spectroscopic studies have shown that there is an intense change in the orientation of the ammonium ions, that the structurally nonequivalent ions are deformed both in the para- and ferroelectric phases [7], and that the PT is of the order–disorder type.

Preliminary studies of the IR reflectance spectra of the AS crystals have shown [8, 9] that, in the range of internal ion oscillations (400–4000 cm⁻¹), there are three distinct bands whose frequencies increase as the temperature decreases to Tₛ. However, the effect of external fields on the infrared spectra of AS crystals has not been studied.

Earlier, the effect of uniaxial pressure on the spectral and temperature dependences of the index of reflection of a number of isomorphic AS crystals was studied and it was shown that the electronic subsystem of these crystals is very sensitive to pressure, which is manifested in a considerable shift of the intense bands in the energy spectrum of the ultraviolet and infrared oscillators [10].

Therefore, it is of interest to study the effect of uniaxial pressure on infrared spectra in order to determine its selective influence on the dynamics and spatial orientation of the individual building blocks of AS crystals.

2. EXPERIMENTAL

The effect of uniaxial pressure on the IR spectra of AS crystals was studied on a UR-20 spectrophotometer. Special equipment was used to apply uniaxial pressure. The UR-20 setup is a prism-based automated spectrophotometer, which makes it possible to perform measurements in the range 400–5000 cm⁻¹ (2–25 µm).

AS crystals were grown from a water solution on cooling. The orientation of the samples was determined by conoscopic figures using a polarizing microscope.
3. RESULTS AND DISCUSSION

Figure 1 shows the IR reflectance spectra of a (NH₄)₂SO₄ crystal recorded at room temperature in the range 800–1700 cm⁻¹ for three directions of light polarization. Two distinct bands with a significant dispersion are observed in this spectral range (Table 1).

The spectral range 10–400 cm⁻¹ corresponds to lattice oscillations of NH₄⁺ [11], which are responsible for the ferroelectric state of the crystal studied, while the spectral range 400–4000 cm⁻¹ corresponds to internal oscillations of the NH₄⁺ and SO₄²⁻ ions. In this frequency range, two distinct bands with maxima at 1155–1164 cm⁻¹ (band II, which is the most intense) and at 1445–1461 cm⁻¹ (band III) are observed in the three polarization directions in the reflectance spectra of the AS crystal.

According to group theory, the free radical of the tetrahedral structure has T₄ symmetry and nine internal modes: a single longitudinal mode (ν₁), a double transverse mode (ν₂), a triple longitudinal mode (ν₃), and a triple transverse mode (ν₄), of which only the ν₂ and ν₄ modes are IR active [12]. The ν₁ and ν₂ modes in the crystal split into nondegenerate modes and also become IR active. The modes with ν₂ = 968–986 cm⁻¹ and ν₃ = 1155–1164 cm⁻¹ correspond to oscillations of the SO₄ tetrahedron, whereas the mode with ν₄ = 1445–1461 cm⁻¹ corresponds to oscillations of the NH₄ tetrahedron.

It was established that the application of uniaxial pressure along the crystallographic directions has a significant effect on the IR reflectance spectra of the (NH₄)₂SO₄ crystal (Fig. 1), changing both the intensity and the positions of the maxima of the basic reflection peaks. Thus, for the light polarization E || X and a uniaxial pressure σₓ, the intensity of band II increases by about 10% and its maximum shifts to lower energies by δν₂ ~ 5 cm⁻¹ for σₓ = 100 bar (δλₓ/δσₓ ~ 4 × 10⁻⁴ μm/bar). For band III, similar pressure dependences are found: the intensity of this reflection band increases by about 5%, and the reflection peak shifts to lower energies by δν₃ ~ 4 cm⁻¹ for σₓ = 100 bar (δλₓ/δσₓ ~ 3 × 10⁻⁴ μm/bar).

For the light polarization E || Y and a uniaxial pressure σᵧ, the intensity of reflection band II also increases by about 12% but its maximum shifts to higher energies by δν₂ ~ 4 cm⁻¹ for σᵧ = 100 bar (δλᵧ/δσᵧ ~ 3 × 10⁻⁴ μm/bar). The intensity of band III increases, and its peak shifts to higher energies by δν₄ ~ 3 cm⁻¹. For the light polarization E || Z with pressure applied in this direction, the intensities of bands II and III increase most significantly (by ~15 and 11%, respectively); in this case, the bands shift to shorter wavelengths by δν₂ ~ 3 cm⁻¹ and δν₄ ~ 4 cm⁻¹, respectively.

Using the reflection spectra and the Kramers–Kronig relations, we analyzed the effect of pressure on the spectral dependences of the optical constants: index of refraction n and the real (ε₁) and imaginary (ε₂) parts of the permittivity of the AS crystal along three crystallographic axes (Figs. 2–4). An abrupt increase in the index of refraction was observed near the absorption bands: δn/δλ ~ 5.441 (band II) and 1.362 μm⁻¹ (band III). The change in the index of refraction far from the absorption band corresponds to normal dispersion (δn/δλ < 0). The normal dispersion in this region is

Table1. Pressure-induced changes in the positions of the reflection bands (in cm⁻¹) of a (NH₄)₂SO₄ crystal at room temperature (σₓ ~ 100 bar)

<table>
<thead>
<tr>
<th>Directions of the field E and pressure σ</th>
<th>ν₃</th>
<th>ν₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ = 0</td>
<td>σ = σₓ</td>
</tr>
<tr>
<td>X</td>
<td>1164</td>
<td>1159</td>
</tr>
<tr>
<td>Y</td>
<td>1160</td>
<td>1164</td>
</tr>
<tr>
<td>Z</td>
<td>1155</td>
<td>1158</td>
</tr>
</tbody>
</table>