

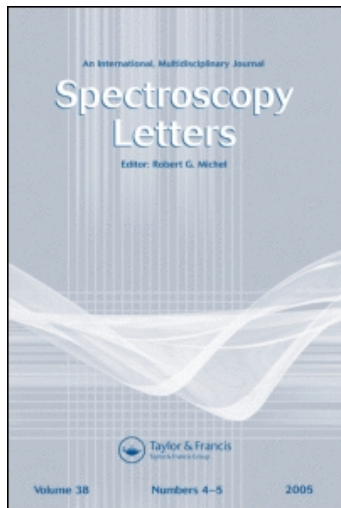
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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

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O. Czupinski^a; G. Bator^a; R. Jakubas^a

^a Faculty of Chemistry, University of Wrocław, Wrocław, Poland

To cite this Article Czupinski, O. , Bator, G. and Jakubas, R.(2000) 'Infrared Studies on Structural Phase Transition in $[N(CH_3)_4]_3Bi_2Br_9$ ', Spectroscopy Letters, 33: 2, 269 – 282

To link to this Article: DOI: 10.1080/00387010009350076

URL: <http://dx.doi.org/10.1080/00387010009350076>

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INFRARED STUDIES ON STRUCTURAL PHASE TRANSITION IN $[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Br}_9$

Key words: FT-IR, phase transition, tetramethylammonium.

O. Czupiński, G. Bator and R. Jakubas*

*Faculty of Chemistry, University of Wrocław, Joliot-Curie 14
50-383 Wrocław, Poland*

Abstract. FT-IR ($4000 - 400 \text{ cm}^{-1}$) spectroscopy was used for the study of the phase transition at 183 K in $[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Br}_9$. The changes in the spectra confirmed the presence of the phase transition of first order type at 183 K. The most spectacular changes in the vicinity of the phase transition are found for the stretching CH_3 and skeletal NC_4 modes. The mechanism of the phase transition of the order-disorder type is believed to be connected with the reorientation motions of the tetramethylammonium cation.

* author to whom the correspondence should be addressed

INTRODUCTION

$[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Br}_9$ belongs to the family of crystals of general formula $[\text{NH}_{4-n}(\text{CH}_3)_n]_3\text{Y}_2\text{X}_9$ (where $\text{Y} = \text{Sb}^{+3}, \text{Bi}^{+3}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$) [1-3]. Monomethyl-, dimethyl and trimethylammonium halogenoantimonates(III) revealed ferroelectricity [4-6]. The numerous studies like X-ray, dielectric, and NMR performed on these crystals showed that the polar properties were due to the ordering of the cationic sublattice [7]. In the case of the tetramethylammonium derivatives the freezing of the rotational motion of the cations possessing spherical symmetry did not lead to the long-range order of the ferro- or antiferroelectric type. In spite of the fact that all tetramethylammonium halogenoantimonates(III) and bismuthates(III) were isomorphous at room temperature ($\text{P6}_3/\text{mmc}$ -space group) they exhibited a different sequence of phase transitions and physical properties [8]. $[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Cl}_9$ revealed weak pyroelectric properties ($P_s \approx 10^{-5} \text{ C m}^2$) below $T_c = 152 \text{ K}$ [9]. $[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Br}_9$ underwent one structural phase transition of first order type at 183 K . No polar properties were found in the low temperature phase, however, the optical studies on this crystal revealed the ferroelasticity below 183 K [9]. The Proton Magnetic Resonance (^1H NMR) [10] and Nuclear Quadrupolar Resonance (NQR) [10] studies on tetramethylammonium analogues indicated that the mechanism of the phase transitions was governed by the reorientational motions of the organic cations.

In order to obtain more information about the molecular mechanism of structural phase transition at 183 K in $[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Br}_9$ (TEMABB) the vibrational study of the polycrystalline sample using FT-IR spectroscopy ($4000 - 400 \text{ cm}^{-1}$) in the temperature range $100 - 300 \text{ K}$ has been performed.

EXPERIMENTAL

The FT-IR spectra were recorded on the 205 NICOLET spectrometer between $4000 - 400 \text{ cm}^{-1}$ with the resolution of 2 cm^{-1} . The temperature study in the range $100 - 300 \text{ K}$ of FT-IR spectra were carried out with the Graseby Specac variable temperature cell where liquid nitrogen was used as coolant. The Unipan temperature controller type 660K was applied to stabilize the temperature. The temperature of the sample was maintained at an accuracy of 1 K . The samples for spectroscopic measurements were prepared as a suspension in Nujol or Perfluorolube medium.

The multifunctional GALACTIC GRAMS/386 program was used for analysis of the spectroscopic data.

RESULTS AND DISCUSSION

The infrared spectra of [N(CH₃)₄]₃Bi₂Br₉ (TEMABB) were recorded in the frequency region related to the internal vibration of the tetramethylammonium cations (TEMA). The observed wavenumbers at temperature 300 K (phase I) and at 109 K (phase II) and their assignments are collected in Table 1.

The assignments are based on the comparison with the infrared spectra of the other tetramethylammonium compounds [2, 11, 12]. The temperature dependence FT-IR studies allow checking out the influence of the change in the dynamical state of the TEMA cations on the internal vibration of them. Usually the splitting of the bands related to the methyl CH₃ and skeletal N-C₄ vibrations as well as the change in their intensities and band width are expected.

The temperature evolution of the infrared spectra in the region of the asymmetric $\nu_a(\text{CH}_3)$ and symmetric $\nu_s(\text{CH}_3)$ stretching vibration is shown in Fig. 1. At room temperature the asymmetric band $\nu_a(\text{CH}_3)$ is observed at 3027 cm⁻¹. The asymmetry is probably the results of an overlapping of two bands. At lowest temperature (109 K) at least four bands in the region of asymmetric CH₃ stretching vibration region may be distinguished. The analysis of the temperature dependence of wavenumbers revealed that the splitting appears at temperature related to the structural phase transition of the first order type in TEMABB at 183 K (see Fig. 2). The effect of this phase transition is observed also in the changes of the intensities of the bands at 3031 and 3022 cm⁻¹ with temperature (see Fig. 3). It is interesting that the intensity of the band at 3031 cm⁻¹ rapidly increases below 183 K, whereas the intensity of the second band (at 3022 cm⁻¹) decreases. The FWHM (full width at half maximum) of both bands decreases in the phase transition which is typical for the transition in which the freezing of the molecules motion takes place (see Fig. 4). The decreasing of the band intensity at T_c is related to the splitting of the band and indicates the differentiation of the cations in the low temperature phase. This is additionally supported by the fact that the number of the $\nu_{as}(\text{CH}_3)$ bands is double below T_c in comparison to that at room temperature. Taking into account the NQR results of Ishihara *et. al.* [3] and observation of the ferroelastic domains by Jakubas *et. al.* [9] in the low temperature phase of TEMABB the possible phase transition from hexagonal to monoclinic phase is postulated.

In Fig. 5-6 there are displayed the evolution of the bands assigned to the CH₃ asymmetric and symmetric deformation, $\delta(\text{CH}_3)$ and N-C₄ skeletal vibrations. Fig. 7 presents the temperature dependencies of the frequencies of the CH₃ deformation modes. Fig. 8 shows the changes with temperature of the FWHM values of the N-C₄ skeletal mode.

TABLE I
Wavenumbers (cm^{-1}), Relative Intensities and Tentative Assignments of the FT-IR Bands Arising from the Internal Vibrations of the Tetramethylammonium Cations in TEMABB at 109 and 300 K.

Phase II 109 K	Phase I 300 K	Description	
3038 <i>w</i> 3031 <i>m.</i> 3022 <i>m.</i> 3018 <i>w</i>	3031 <i>m</i> 3022 <i>m</i>	ν_5	CH_3 asymmetrical stretching
2963 <i>w</i> 2951 <i>w</i>	2953 <i>w</i>	ν_1	CH_3 symmetrical stretching
2855 <i>w</i> 2808 <i>w</i> 2764 <i>w</i> 2747 <i>w</i>	2749 <i>w</i>	ν_{14}	CH_3 symmetrical stretching
2547 <i>w</i> 2506 <i>w</i> 2474 <i>w</i> 2356 <i>w</i>	2580 <i>w</i> 2509 <i>w</i> 2478 <i>w</i> 2360 <i>w</i>		
1480 <i>m.</i> 1477 <i>m.</i>	1480 <i>m.</i>	ν_{10}	CH_3 asymmetrical deformation
1440 <i>m.</i> 1432 <i>vw</i> 1424 <i>w</i> 1417 <i>vw</i> 1409 <i>w</i>	1444 <i>w</i> 1414 <i>vw</i>	ν_{15} ν_{16}	CH_3 asymmetrical deformation CH_3 symmetrical deformation
1292 <i>w</i> 1287 <i>m.</i> 1268 <i>vw</i>	1288 <i>m.</i>	ν_2	CH_3 symmetrical deformation
949 <i>vs</i>	949 <i>vs</i>	ν_{18}	Skeletal triply-degenerate
732 <i>w</i> 725 <i>m.</i>	723 <i>m</i>	ν_3	Skeletal non-degenerate

vs - very strong, *s* - strong, *m.* - medium, *w* - weak, *vw* - very weak.

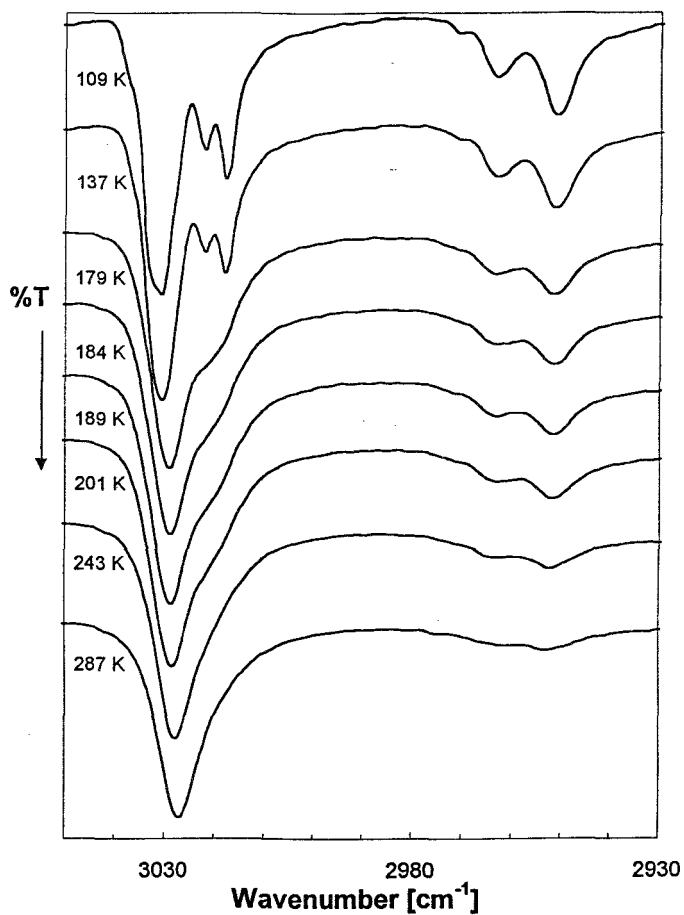


Fig. 1 Temperature evolution of the CH_3 asymmetric and symmetric stretching modes.

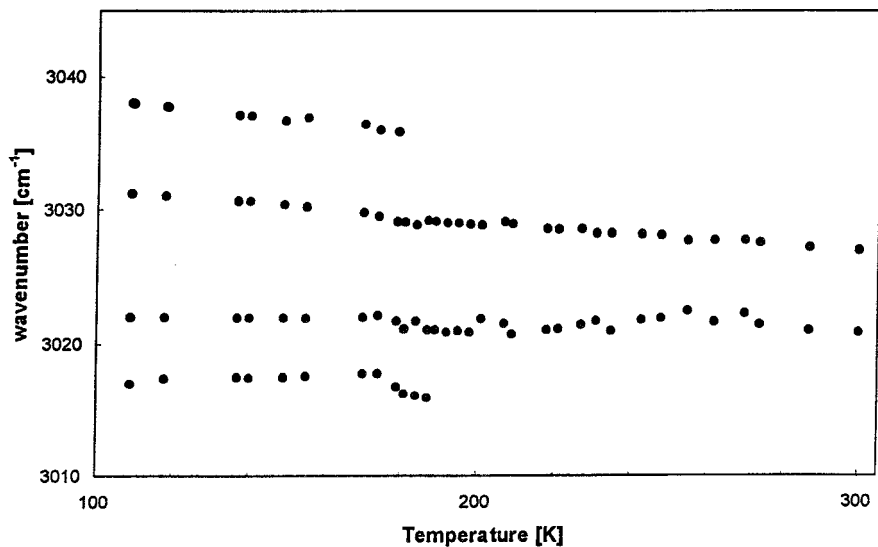


Fig. 2. Temperature dependence of the frequencies of the CH₃ asymmetric modes.

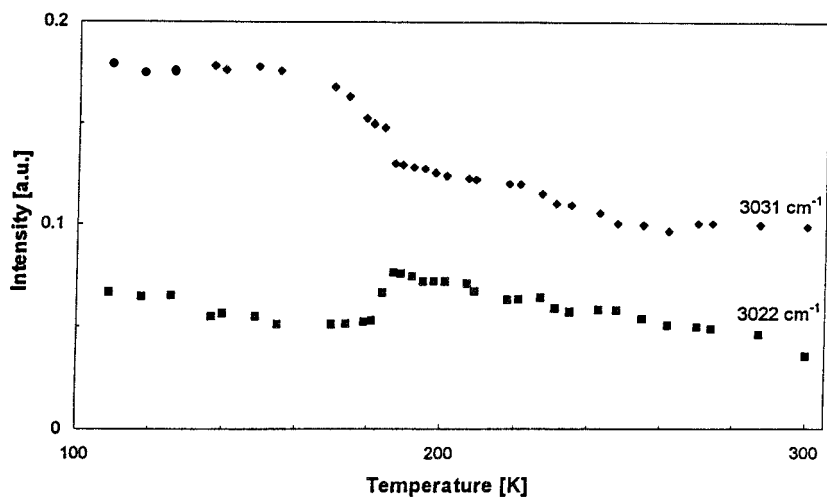


Fig. 3. Temperature variation of the intensity for the CH₃ asymmetric stretching modes.

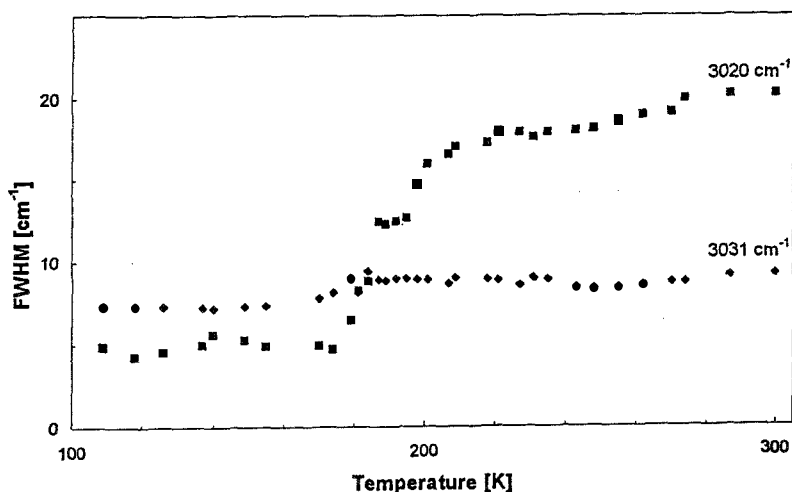


Fig. 4. Temperature variation of the FWHM of the assigned to the CH₃ asymmetric stretching modes.

It is clearly seen that these three bands at room temperature in the region between 1400 and 1500 cm⁻¹ split into at least 8 bands in the low temperature phase. This supports the supposition that the dynamical state of TEMABB cations changes when the crystal undergoes the phase transition at 183 K and the cations differentiate below T_c . The narrowing of the bands in the region of N-C₄ skeletal mode may suggest the change in the motional state of the TEMA cations.

The important changes observed at various temperatures in the infrared spectra of TEMABB for most internal modes of the cation clearly indicate an alteration in the motional state of this cation when the phase transition at 183 K is crossed.

We focus our attention on bands at 955 cm⁻¹ (112 K) and at 949 cm⁻¹ (112 K). The temperature dependencies of the FWHM values, which are proportional to the damping coefficients of the mentioned above modes, are shown in Fig. 9. Since these components represent the contribution from the disordered NC₄ group we follow the analysis by Carabatos-Nedelec and Backer which is based on the theory used for the damping associated with an order-disorder mechanism [13]. In this model the jumping of the molecule from one orientation to another (as it was found in the case of [(CH₃)₂NH₂]₃Sb₂Cl₉ [14]) can be treated as a self-diffusion mechanism responsible for the orientational disorder.

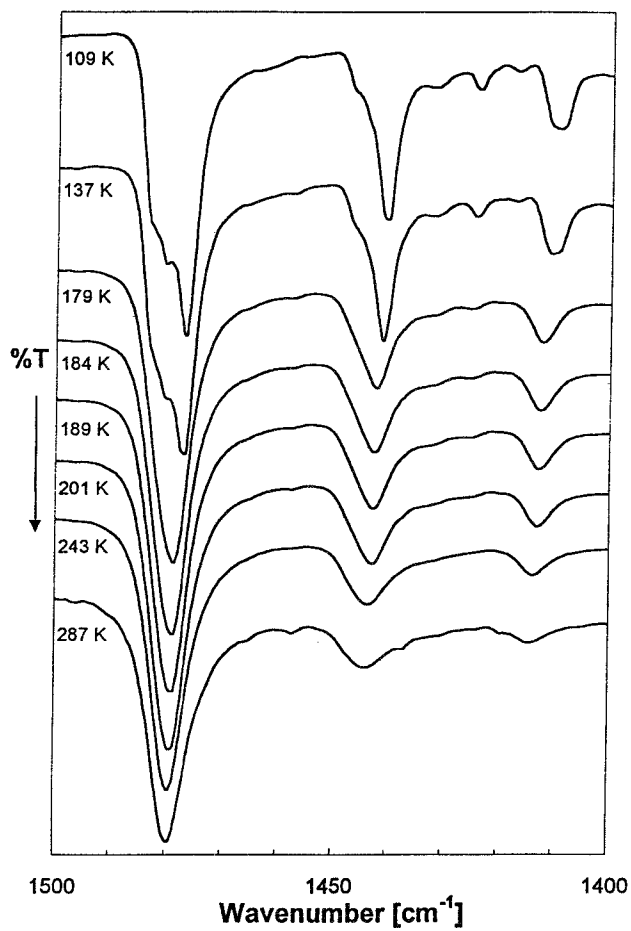


Fig. 5. Temperature evolution of the CH_3 asymmetric and symmetric deformation modes.

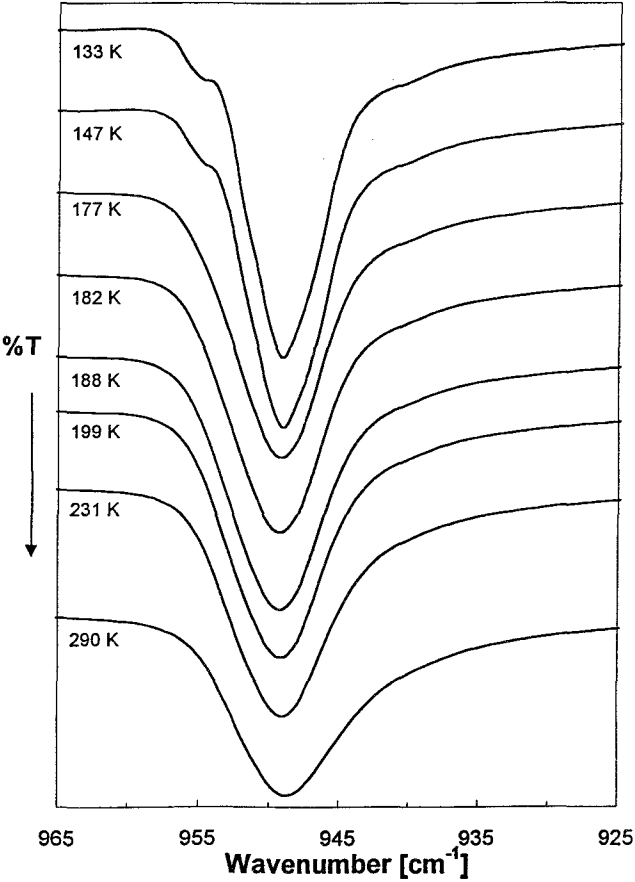


Fig. 6. Temperature evolution of the N-C₄ skeletal mode.

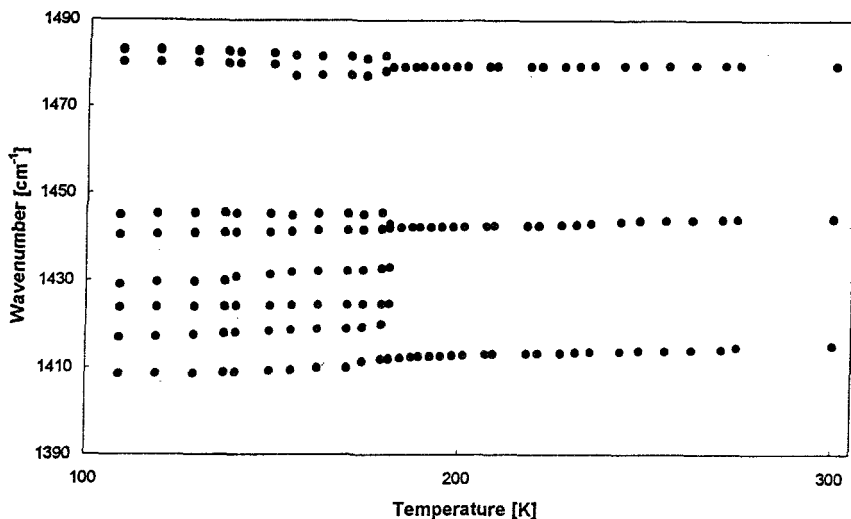


Fig. 7. Temperature dependence of the frequencies of the CH₃ deformation modes.

The orientational correlation time is the mean reorientational time of the cations to jump from one potential well to another, it is given by

$$\tau_r = \tau_o \exp(U/k_B T) \quad (1)$$

where τ_o is a magnitude and U the height of the potential barrier.

The temperature dependence of the bandwidth, that is, its damping is described by the equation:

$$\Gamma(\omega) = (a + bT) + C \frac{\tau_R}{1 + \omega^2 \tau_R^2} \quad (2)$$

in which first linear part corresponds to the vibrational relaxation or the anharmonicity and the second term represents the thermal orientational mechanism of diffuse nature. ω in the eqn. (2) is the frequency of a particular phonon mode. Since in this case τ_R is expected to be long in the low temperature phase and $\omega^2 \tau_R^2 \gg 1$ so that the eqn. (2) is reduced to

$$\Gamma = (a + bT) + c \exp(-U/k_B T) \quad (3)$$

in which a , b , c and U are parameters to fit. The fitted parameters for the analysed bands (955 and 949 cm⁻¹ at 112 K) are listed in Table 2.

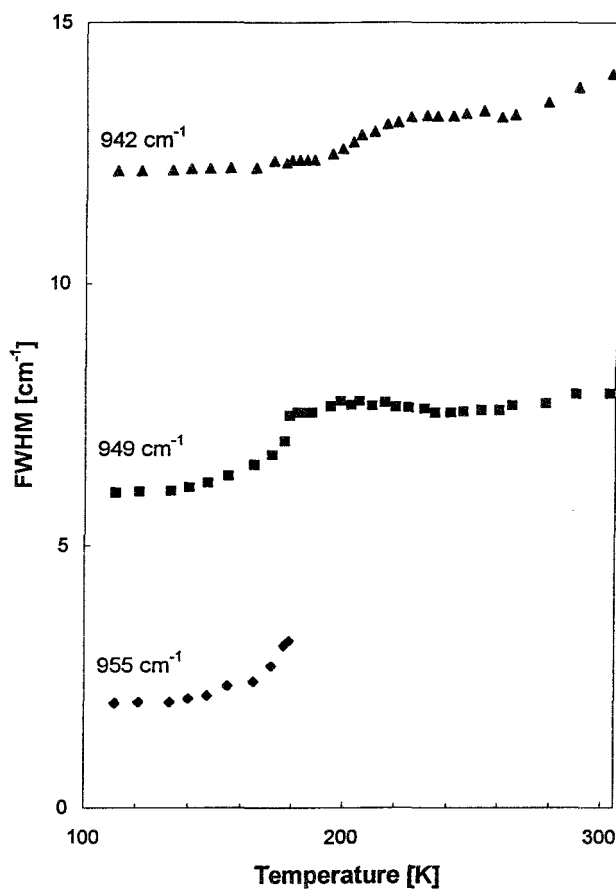


Fig. 8. Temperature variation of FWHM of the assigned to the N-C₄ skeletal mode.

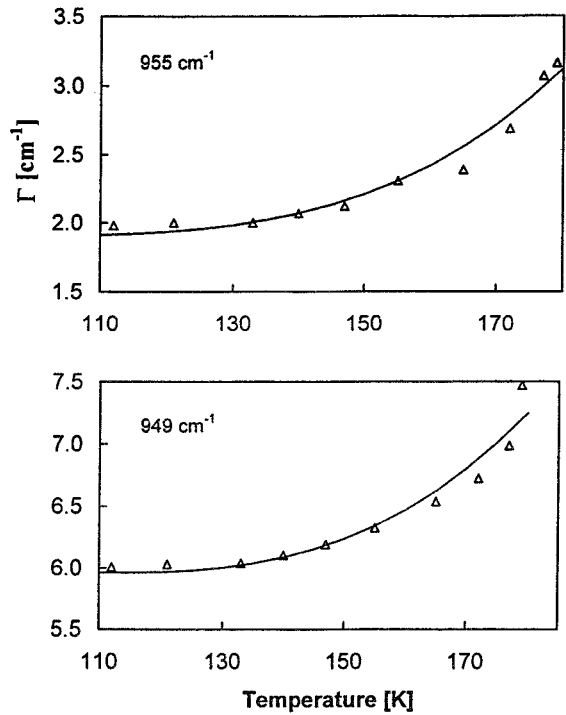


Fig. 9. Temperature dependencies of the damping coefficients of the bands at 955 cm^{-1} and 949 cm^{-1} (112 K) for TEMABB.

TABLE 2.

The Fitted Parameters a , b , c and U , for the Temperature Dependence of the Damping Coefficient, Γ .

Parameter	955 cm^{-1}	949 cm^{-1}
a/cm^{-1}	1.92	6.33
$b/\text{cm}^{-1}\text{K}^{-1}$	$-2.28 \cdot 10^{-4}$	$-3.57 \cdot 10^{-3}$
c/cm^{-1}	1003	837
U/eV	0.104	0.098

The most important parameter e.i. the barrier height, U , obtained as a fit value is reasonable and comparable to that found for the other alkylammonium cation of the similar size [15].

CONCLUSION

1. The structural phase transition at 183 K is clearly reflected in the temperature evolution of the infrared spectra of the $[N(CH_3)_4]_3Bi_2Br_9$ crystal.
2. The temperature changes of the internal vibration modes of the tetramethylammonium cations confirmed their contribution to the phase transition mechanism of an order-disorder type.

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Date Received: April 13, 1999

Date Accepted: August 20, 1999