doi: 10.15407/ujpe62.08.0679

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PACS 62.20.D-

ELASTIC PROPERTIES OF SUBSTITUTIONAL SOLID SOLUTIONS $In_xTl_{1-x}I$ AND SOUND WAVE VELOCITIES IN THEM

Elastic properties of substitutional solid solutions $In_xTl_{1-x}I$ have been studied. The corresponding Young modulus, shear modulus, and compression modulus are calculated theoretically. The dependence of the elastic properties of the $In_xTl_{1-x}I$ solid solution on the content x within the interval $0.375 \leq x \leq 1$ is analyzed. The velocity of sound propagation in examined specimens is studied experimentally. The obtained data are used to calculate the elastic coefficient C_{22} for $In_xTl_{1-x}I$. The theoretical results are found to be in good agreement with experimental data.

K e y w o r d s: substitutional solid solutions, elastic constants, piezoelectric transducer, ultrasonic waves.

1. Introduction

Practical interest to substitutional solid solutions (SSSs) $In_xTl_{1-x}I$ is, first of all, associated with a possibility to use them as a basis for the creation of either narrow-band optical filters in a wide spectral range or detectors of ionizing radiation [1–4]. Substitutional solid solutions are characterized by a continuous variation of their lattice parameters. This fact considerably expands the application scope of those crystals. However, the influence of a mechanical loading on the crystals, which is important for practical applications of examined specimens, remains obscured. We have not found any theoretical or experimental works in the literature that would concern the study of elastic properties of $In_xTl_{1-x}I$ substitutional solid solutions.

In this work, we present the results of calculations of the elastic constants, compression modulus B_0, Young modulus Y_0, and shear modulus C' for the researched crystals. Experimental values for the elastic constant C_{22} and the velocity of sound propagation in $In_xTl_{1-x}I$ are reported for the first time. The experimental data are compared with the theoretically calculated values.

2. Experimental Technique

The crystals of $In_xTl_{1-x}I$ were synthesized from binary single-crystalline compounds TlI and InI taken in equimolar ratios. The crystals were grown up by the Bridgman–Stockbarger method in quartz ampoules located in a vertical furnace with a temperature gradient of 1 °C/mm. During the crystal growth process, an ampoule was moved through the crystallization zone at a rate of 3 mm/h. In the case of $In_{0.4}Tl_{0.6}I$, the growth temperature was equal to 450 °C. As the InI content increased, the growth temperature was lowered, down to 430 °C for $In_{0.9}Tl_{0.1}I$. The growth stage lasted for 48 h. Then the grown crystals were annealed in the same furnace for 24 h at a temperature varying from $T = 190\,°C$ for $In_{0.4}Tl_{0.6}I$ to $T = 130\,°C$ for $In_{0.9}Tl_{0.1}I$.

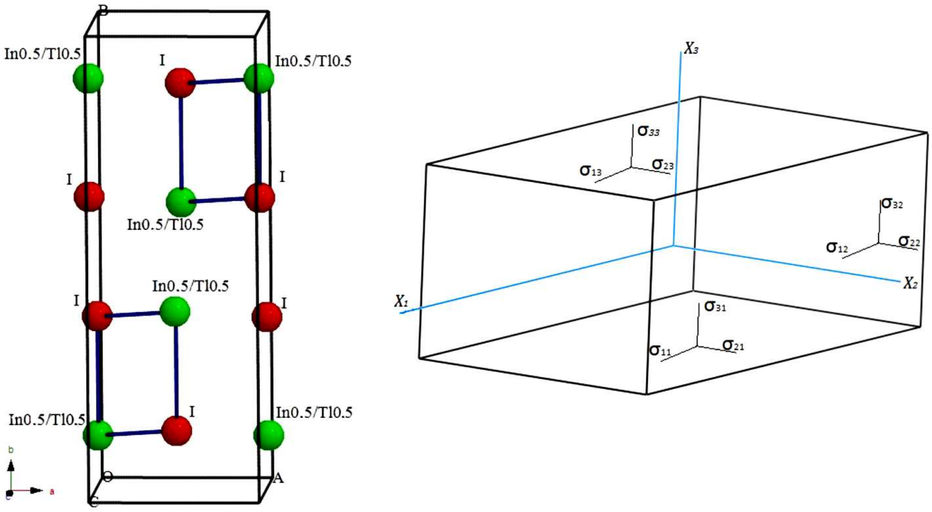

Fig. 1. Schematic of a unit cell in the substitutional solid solution $\mathrm{In}_x\mathrm{Tl}_{1-x}\mathrm{I}$ (a) and the strain components σ_{ij} at the edges of a unit cube (b)

X-ray structural researches were performed on a spectral complex STOE Transmission Diffractometer System STADI P at room temperature, T = 297 K. As research specimens, we used powders obtained by grinding $\mathrm{In}_x\mathrm{Tl}_{1-x}\mathrm{I}$ single crystals in an agate mortar [4–6].

The band structure of $\mathrm{In}_x\mathrm{Tl}_{1-x}\mathrm{I}$ substitutional solid solutions was determined from first principles, by using the norm-preserving method of nonlocal pseudopotential. The calculation procedure was described in works [7–11] in detail.

The total energy of crystals was calculated self-consistently in the framework of the density functional theory (DFT). The electron energies and concentrations were determined from the Kohn–Sham equations [12]. The method of generalized gradient approximation (GGA) was used to describe the exchange-correlation potential. The representation of this potential was taken in the Perdew–Burke–Ernzerhof (PBE) form [13, 14]. Calculations were carried out for a $2 \times 2 \times 1$ superlattice.

The velocity of sound propagation in $\mathrm{In}_x\mathrm{Tl}_{1-x}\mathrm{I}$ was studied with the use of an ultrasonic method known as the Papadakis method [15, 16]. It is based on the determination of the time interval needed for a sound wave to transit from the piezoelectric transducer to the crystal face and backward. The velocity was calculated by the relation

$$\vartheta = 2Nfl, \qquad (1)$$

where N is the difference between the numbers of two coincident reflected pulses, f the synchronization frequency, and l the crystal size along the wave propagation direction. This method is rather exact, because its sensitivity to velocity variations amounts to about 10^{-5}–10^{-6} times the velocity magnitude [16]. The signal generation frequency amounted to 10 MHz, and the diameter of a piezoelectric transducer to about 3 mm. Under those conditions, a correction to the velocity magnitude from diffraction effects did not exceed 2% [16].

3. Results and Their Discussion

Substitutional solid solutions $\mathrm{In}_x\mathrm{Tl}_{1-x}\mathrm{I}$ crystallize into a layered orthorhombic structure with the $Cmcm$ (D_{2h}^{17}) space-group symmetry. The layered structure of specimens includes two layers of the sandwich type and four formula units per unit cell. The layers are oriented normally to the crystallographic b-axis. A unit cell is depicted in Fig. 1.

Elastic properties of solids are important for both fundamental researches and practical applications. They are governed by interatomic forces acting on atoms, when the latter are displaced from their equilibrium positions. The pseudopotential method allows the calculations of the total energy to be carried out for arbitrary crystalline structures. Therefore, we can deform the obtained equilibrium structure, determine the total energy of the crystal, and use the obtained results to find the elastic constants. The elastic constants are proportional to the second-order coefficient in the polynomial expansion of the total energy as a function of the strain parameter δ. In calculations, only small deformations were taken into consideration, which did not exceed the crystal elasticity limit.

Under such deformations, the lattice symmetry remains orthorhombic, but the cell volume changes. Knowing the total crystal energy and its variation at the strain δ, it is possible to determine nine elastic constants from the following equations:

$$\begin{aligned}
&E(V,\delta) = E(V_0,0) + V_0(\tau_1\delta + C_{11}\delta^2/2),\\
&E(V,\delta) = E(V_0,0) + V_0(\tau_2\delta + C_{22}\delta^2/2),\\
&E(V,\delta) = E(V_0,0) + V_0(\tau_3\delta + C_{33}\delta^2/2),\\
&E(V,\delta) = E(V_0,0) + V_0(2\tau_4\delta + 2C_{44}\delta^2),\\
&E(V,\delta) = E(V_0,0) + V_0(2\tau_5\delta + 2C_{55}\delta^2),\\
&E(V,\delta) = E(V_0,0) + V_0(2\tau_6\delta + 2C_{66}\delta^2),\\
&E(V,\delta) = E(V_0,0) + V_0\Big[(\tau_1-\tau_2)\delta + \\
&+ \frac{(C_{11}+C_{22}-2C_{12})\delta^2}{2}\Big],\\
&E(V,\delta) = E(V_0,0) + V_0\Big[(\tau_1-\tau_3)\delta + \\
&+ \frac{(C_{11}+C_{33}-2C_{13})\delta^2}{2}\Big],\\
&E(V,\delta) = E(V_0,0) + V_0\Big[(\tau_2-\tau_3)\delta + \\
&+ \frac{(C_{22}+C_{33}-2C_{23})\delta^2}{2}\Big].
\end{aligned} \tag{2}$$

The elastic constants C_{12}, C_{13}, and C_{23} are determined as linear combinations of already obtained constants.

In this work, we present the elastic constants C_{11}, C_{22}, C_{33}, C_{44}, C_{55}, C_{66}, C_{12}, C_{13}, and C_{23} for substitutional solid solutions $In_xTl_{1-x}I$ ($0.125 \leq x \leq 0.375$) and the velocities of sound propagation calculated on their basis. The results obtained are quoted in Table 1. The dependences of elastic constants on the content x are exhibited in Fig. 2. Note that, with the growth of the TlI component content, the elastic constants demonstrate a qualitatively similar behavior. Hence, a conclusion can be drawn that the growth of the Tl content in substitutional solid solutions $In_xTl_{1-x}I$ gives rise to the enhancement of

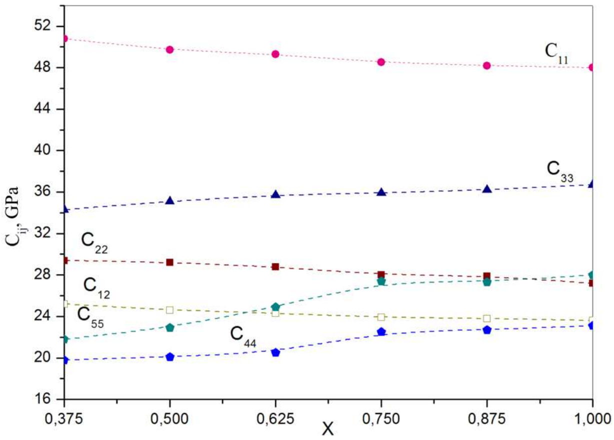

Fig. 2. Dependences of elastic constants on the composition content x in the substitutional solid solution $In_xTl_{1-x}I$

the material strength in all directions except in the *ac*-plane.

Knowing the elastic constants, it is possible to determine the compression modulus B_0, [100] Young modulus Y_0, and shear modulus C' by the formulas [8, 17, 18]

$$\begin{aligned}
&B_0 = (C_{11}+C_{12})/3,\\
&Y_0 = (C_{11}+2C_{12})(C_{11}-C_{12})/(C_{11}+C_{12}),\\
&C' = (C_{11}-C_{12})/2.
\end{aligned} \tag{3}$$

The values obtained for B_0, Y_0, and C' are quoted in Table 2. The dependences of those quantities on the content x are shown in Fig. 3.

It is worth to note that the values of the parameters B_0, Y_0, and C' monotonically grow with the Tl content. The compression modulus determines the resistance of the medium to a uniform compression. Therefore, the increase of B_0 with the inclusion of TlI allows us to assume that the substitutional solid

Table 1. **Elastic constants for various TlI component contents in substitutional solid solutions $In_xTl_{1-x}I$ (in GPa units)**

x	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
1	48.0	27.2	36.7	23.1	28.0	22.5	23.6	31.0	18.8
0.875	48.0	27.9	36.2	22.7	27.3	22.7	23.8	27.8	19.1
0.75	48.5	28.0	35.9	22.5	27.4	22.8	23.9	26.6	19.9
0.625	49.3	28.8	35.7	20.5	24.9	23.1	24.3	22.9	20.3
0.5	49.7	29.2	35.1	20.1	22.9	23.4	24.65	22.3	20.7
0.375	50.8	29.4	34.3	19.8	21.8	23.5	25.2	20.8	21.8

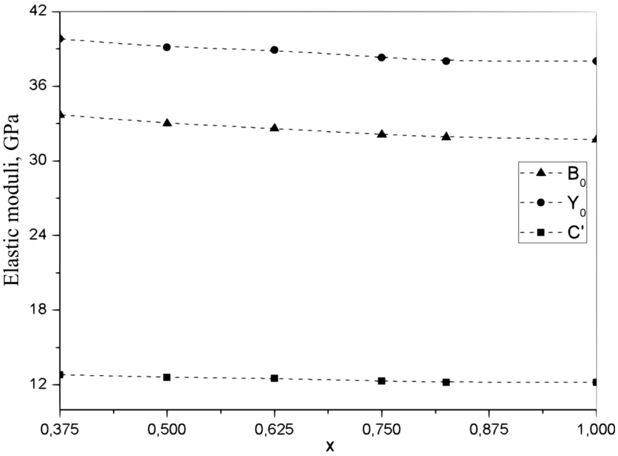

Fig. 3. Dependences of the compression modulus B_0, [100] Young modulus Y_0, and shear modulus C' on the composition content x in the substitutional solid solution $In_xTl_{1-x}I$

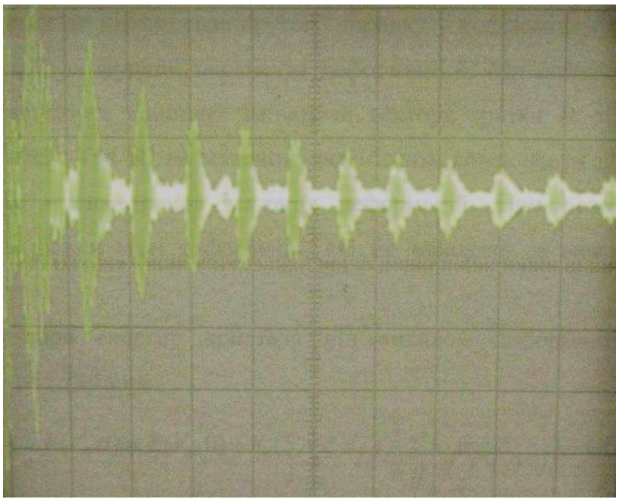

Fig. 4. Sequence of ultrasonic echo pulses in the $In_{0.5}Tl_{0.5}I$ crystal

solution $In_xTl_{1-x}I$ becomes less compressible. The Young modulus is an indicator of the material stiffness. Hence, the growth of Y_0 allows us to assume that the examined material becomes more robust to a bending or to a deformation under the action of an applied force. The shear modulus is determined as the ratio between the shear stress and the shear deformation. The growth of C' in the substitutional solid solutions $In_xTl_{1-x}I$ testifies that this material becomes more rigid.

The Papadakis method was used to experimentally study the velocity of ultrasonic wave propagation in the substitutional solid solutions $In_xTl_{1-x}I$ with $x = 0.9$, 0.6, 0.5, and 0.4.

Layered crystals are easily cleaved along the layers, whereas, for the researches to be carried out in the directions along the layer plane, crystals should be subjected to a special grinding. In this work, the velocity of ultrasonic waves propagating normally to the crystal b-axis was measured. The working surface of bulk specimens had the same orientation as the crystallographic ac-plane. The axis c was perpendicular to the cleavage plane, and the axis b was oriented perpendicularly to the ac-plane.

Ultrasonic waves were excited in the crystals by means of piezoelectric transducers fabricated from a $LiNbO_3$ crystal. Longitudinal ultrasonic waves were excited, by using the plates of the $Y + 36°$-cut of this crystal. The piezoelectric transducers generated

Table 2. **Compression modulus B_0, [100] Young modulus, and shear modulus C' for various TlI component contents in substitutional solid solutions $In_xTl_{1-x}I$**

x	B_0, GPa	Y_0, GPa	C', GPa
1	31.7	38.0	12.2
0.875	31.9	38.0	12.2
0.75	32.1	38.3	12.3
0.625	32.6	38.9	12.5
0.5	33.0	39.1	12.6
0.375	33.7	39.8	12.8

Table 3. **Experimental and theoretical values of the elastic constant C_{22} and the sound propagation velocity in substitutional solid solutions $In_xTl_{1-x}I$**

x	C_{22}, GPa, theor.	$\vartheta_\perp$, km/s, theor.	$\vartheta_\parallel$, km/s, theor.
1	27.2 ± 0.9	2.64	1.49
0.875	27.9 ± 0.6	2.61	1.48
0.75	28.0 ± 0.7	2.57	1.46
0.625	28.8 ± 1.7	2.54	1.44
0.5	29.2 ± 1.0	2.51	1.42
0.375	29.4 ± 1.1	2.49	1.41

x	C_{22}, GPa, expt.	$\vartheta_\perp$, km/s, expt.
0.9	28.3	2.254
0.6	30.2	2.238
0.5	30.6	2.214
0.4	31.4	2.206

a signal corresponding to a series of reflected acoustic pulses with decreasing amplitudes (Fig. 4).

The time interval between the pulses amounted to 4.2 μs. The crystal thickness was equal to 4.65 mm. Therefore, the velocity of ultrasound wave propagation perpendicularly to the b-axis in the $In_{0.5}Tl_{0.5}I$ crystal was equal to 2.214 km/s. The velocities of sound propagation in substitutional solid solutions $In_xTl_{1-x}I$ are quoted in Table 3. Taking the crystal density into account [4], from the Cristoffel equation, we can calculated the elastic constant C_{22}:

$$C_{22} = \rho\vartheta^2. \tag{4}$$

Using the classical procedure described in work [19], we can theoretically calculate the velocity values for transverse and longitudinal waves propagating in the crystal. The propagation velocity of transverse waves (parallel to the ac-planes of the layers) is determined by the formula

$$\vartheta_\perp = \sqrt{\frac{Y_0}{\rho}}, \tag{5}$$

where ρ is the crystal density. On the other hand, the propagation velocity of longitudinal waves (perpendicular to the cleavage plane) is determined, by using the shear modulus:

$$\vartheta_\parallel = \sqrt{\frac{C'}{\rho}}. \tag{6}$$

By comparing the obtained results with experimental data for various layered crystals (GaS, GaSe, TiS_2, $TiSi_2$) [20, 21], one can see a larger anisotropy of elastic properties for orthorhombic indium compounds, in particular, for directions lying in the plane of crystal layers. Furthermore, the velocity of sound propagation between the crystal layers, $\vartheta_\perp$, is higher than perpendicularly to them, $\vartheta_\parallel$, which decreases as the TlI content grows.

4. Conclusions

The stress energy was calculated for nine deformations of the crystal lattice, and the results obtained were used to determine the components of the tensor of elastic constants. Those values were used to calculate the compression modulus B_0, [100] Young modulus Y_0, and shear modulus C', as well as their dependences on the TlI component content in substitutional solid solutions $In_xTl_{1-x}I$. A strong anisotropy of the compression modulus along the crystallographic axes was revealed.

On the basis of elastic constants, the propagation velocities of longitudinal and transverse sound waves in the examined specimens were calculated. The propagation velocity of ultrasonic waves along the ab cleavage plane in substitutional solid solutions $In_xTl_{1-x}I$ was measured. On the basis of experimental values, the elastic constant C_{22} was calculated. Theoretical and experimental values are in good agreement. Therefore, the selected technique can be used as a basis for further researches of the physical properties of substitutional solid solutions $In_xTl_{1-x}I$.

1. A. Franiv, O. Bovgyra, O. Savchyn. Electron and phonon spectra of $In_xTl_{1-x}I$ substitutional solid solutions. *Ukr. J. Phys.* **51**, 269 (2006).
2. Ya.O. Dovhyi, S.V. Ternavska, A.V. Franiv, O.V. Bovgyra, O.V. Savchyn. Raman spectra of $In_x xTl_{1-x}I$ substitutional solid solutions. *Funct. Mater.* **12**, 503 (2005).
3. Xu Zhao-Peng, Wang Yong-Zhen, Zhang Wei, Wang Qian, Wu Guo-Qing. First-principle study on the effects of Tl doping on the band gap and the band-edge of optical absorption of InI. *Acta Phys. Sin.* **63**, 147102 (2014).
4. A.I. Kashuba, S.V. Apunevych. Phonon spectrum of crystals of substitutional solid solutions $In_xTl_{1-x}I$. *Zh. Nano Elektron. Fiz.* **8**, 01010 (2016) (in Ukrainian).
5. A. Kashuba. Concentration dependence of the energy gap width in substitutional solid solutions $In_xTl_{1-x}I$. *Visn L'viv. Univ. Ser. Fiz.* No. 50, 3 (2015) (in Ukrainian).
6. A.I. Kashuba, O.V. Bovgyra, A.V. Franiv, S.V. Apunevych. Argand diagrams and oscillator forces of the $In_{0.5}Tl_{0.5}I$ crystal. *Fiz. Khim. Tverd. Tila* **17**, 350 (2016) (in Ukrainian).
7. M.I. Kolinko, O.V. Bovgyra. Band energy diagram of indium bromide. *Ukr. J. Phys.* **46**, 707 (2001).
8. A. Bellouche, A. Gueddim, S. Zerroug, N. Bouarissa. Elastic properties and optical spectra of $ZnS_{1-x}O_x$ dilute semiconductor alloys. *Optik* **127**, 11374 (2016).
9. Y. Abed, F. Montaghni. Simulation investigations of structural, electronic, optical and elastic properties of the $Cu_xTi_{1-x}O_2$. *Nanosci. Nanotechnol.* **6**, No. 4, 62 (2016).
10. R.M. Martin. Elastic properties of ZnS structure semiconductors. *Phys. Rev. B* **1**, 4005 (1970).
11. F. Kalarasse, B. Bennecer. Structural and elastic properties of the filled tetrahedral semiconductors LiZnX (X = N, P, and As). *J. Phys. Chem. Solids* **67**, 846 (2006).
12. P. Hohenberg. Inhomogeneous electron gas. *Phys. Rev.* **136**, 864 (1964).
13. P. Perdew, K. Burke, M. Ernzerhof. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).

14. I.V. Semkiv, B.A. Lukiyanets, H.A. Ilchuk, R.Yu. Petrus, A.I. Kashuba, M.V. Chekaylo. Energy structure of β'-phase of Ag_8SnSe_6 crystal. *J. Nano-Electron. Phys.* **8**, 01011 (2016).
15. O.G. Vlokh, O.M. Mokryi, A.V. Kityk. Device for measuring ultrasound velocity in solid and liquid media. Author sertificate No. 1608432 USSR (1990).
16. E.P. Papadakis. Ultrasonic phase velocity by the pulse-echo-overlap method incorporating diffraction phase corrections. *J. Acoust. Soc. Am.* **42**, 1045 (1967).
17. *Handbook Series on Semiconductor Parameters.* Edited by M. Levinshtein, S. Rumyantsev, M. Shur (World Scientific, 1999), Vol. 2.
18. N. Bouarissa, S. Saib. Elastic modulus, optical phonon modes and polaron properties in $Al_{1-x}B_xN$ alloys. *Curr. Appl. Phys.* **13**, 493 (2013).
19. S.I. Mudryi. *Acoustic Methods of Substance Analysis* (Lviv Nat. Univ. Publ. Center, 2008) (in Ukrainian).
20. Y. Honma, M. Yamada, K. Yamamoto. Elastic constants of GaS and GaSe layered crystals determined by Brillouin scattering. *J. Phys. Soc. Jpn.* **52**, 2777 (1983).
21. P. Ravindran, L. Fast, P. A. Korzhavyi *et al.* Density functional theory for calculation of elastic properties of orthorhombic crystals: Application to $TiSi_2$. *J. Appl. Phys.* **84**, 4891 (1998).

Received 15.12.16.

Translated from Ukrainian by O.I. Voitenko

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ПРУЖНІ ВЛАСТИВОСТІ ТА ШВИДКІСТЬ ПОШИРЕННЯ ЗВУКУ В ТВЕРДИХ РОЗЧИНАХ ЗАМІЩЕННЯ $In_xTl_{1-x}I$

Р е з ю м е

Подано результати дослідження пружних властивостей твердих розчинів заміщення $In_xTl_{1-x}I$. Теоретично розраховано значення модуля Юнга, модуля зсуву та об'ємного модуля пружності. Аналізується залежність зміни пружних властивостей залежно від компонентного складу твердого розчину $In_xTl_{1-x}I$ в межах концентрації $0{,}375 \leq x \leq 1$. Експериментально досліджено швидкість поширення звуку в досліджуваних зразках. На основі одержаних значень розраховано пружну константу C_{22}. Наведено порівняння теоретичних та експериментальних значень, які добре узгоджуються.