



## Electroacoustic properties of various types of quartz in the finely dispersed state

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An electroacoustic echo method for studying the high-frequency (HF) electrical and elastic properties of piezoelectric materials in a finely dispersed state is described. The characteristics and relaxation time of electroacoustic echo for natural and artificial quartz powders are determined. Natural one is represented by the following types: smoky quartz, citrine, amethyst, recrystallized, granular and columnar. It is shown that natural quartz (especially citrine), has a higher electromechanical coupling coefficient than artificial quartz. The amplitudes of HF electric field are determined, at which the saturation mode of the echo signals is observed.

**Keywords:** *artificial and natural quartz, electroacoustic echo, relaxation time and echo parameters, powder.*

## Электроакустические свойства различных типов кварца в мелкодисперсном состоянии

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Описан метод электроакустического эха для исследования высокочастотных (ВЧ) электрических и упругих свойств пьезоэлектрических материалов, находящихся в мелкодисперсном состоянии. Определены характеристики и время релаксации электроакустического эха для порошков из природного и искусственного кварца. Природный представлен следующими типами: дымчатый кварц, цитрин, аметист, перекристаллизованный, гранулированный и шестоватый. Показано, что природный кварц (особенно цитрин) имеет значение коэффициента электромеханической связи большее, чем у искусственного кварца. Определены амплитуды ВЧ электрического поля, при которых наблюдается режим насыщения сигналов эха.

**Ключевые слова:** *искусственный и природный кварц, электроакустическое эхо, время релаксации и параметры эха, порошок.*

### Introduction

Piezoelectric materials are an integral part of electronics and electrical equipment used for domestic and industrial purposes, such as ultrasonic piezoelectric transducers, resonators, sensors, drives, transformers (Shujun Zhang et al., 2018; F. Li et al., 2018; Heywang et al., 2008; S. Troler-McKinstry et al., 2018; Park and Shrout, 1997). The development and use of elements and devices of functional electronics based on new piezo- and pyroelectric materials is currently an important and rapidly developing area of HF and microwave technology (Iwazaki et al., 2015; Hackenberger et al., 2019; Moreira et al., 2011). Among many different types of piezoelectric materials, quartz crystals are the most widely used traditional piezoelectric materials in practice (Mohammadi, 2015; Kotov et al., 2020). A distinctive feature of functional electronics is the performance of operations on radio signals in the absence of traditional discrete elements: capacitors, resistors, transistors, etc. Radio signals are processed as a result of the interaction of electromagnetic radiation with the special physical properties of the solid medium in which this radiation propagates. A special place among

these areas is occupied by functional acoustoelectronics, which, due to its great technical capabilities, finds wide practical application. Elements of acoustoelectronics are widely used, for example, as resonators for surface acoustic waves in cell phones. Acoustoelectronics widely uses the excitation of acoustic oscillations and waves when a piezoelectric material is placed in an electromagnetic field. The measurement of acoustic parameters, such as piezoelectric constants and electromechanical coupling coefficient, the quality factor of oscillations of piezoelectric bodies, the amplitude of the signal saturation field, have become the most sensitive, and sometimes the only possible methods for determining the nature of materials (Kotov et al., 2020). One of the most important properties of quartz crystals is an infinitely high-quality factor of vibrations and a wide band of operating frequencies of the piezoelectric transducer. Therefore, the most efficient devices of functional acoustoelectronics can be built on a wide class of quartz with various impurities. A wide variety of physical properties of crystals is created by nature itself, which in natural conditions creates many different piezoelectric crystals that cannot yet be

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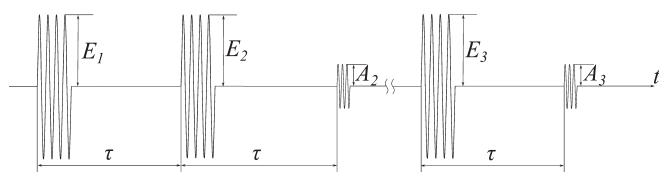
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created artificially (Kotova et al., 2018; Chen Mulan et al., 2021). This article presents the results of our study of high-frequency (HF) piezoelectric properties and quality factor of electroelastic oscillations of different types of natural quartz in comparison to similar properties of artificial quartz. Here, we also consider possible mechanisms and methods for enhancing the piezoelectric properties and increasing the quality factor of electroelastic vibrations, for example, by introducing impurities when growing quartz crystals in artificial conditions.

### Methodology and technique of the experiment

A convenient method for studying the electrical and elastic properties of piezoelectric materials can be the electroacoustic echo (EAE) method (Kajimura, 1982; Shutilov et al., 1985). The EAE method consists in the occurrence of an electrical response after excitation of an ensemble of piezoparticles (powder) by radio pulses of an electric field (Fig. 1). The EAE method allow studying

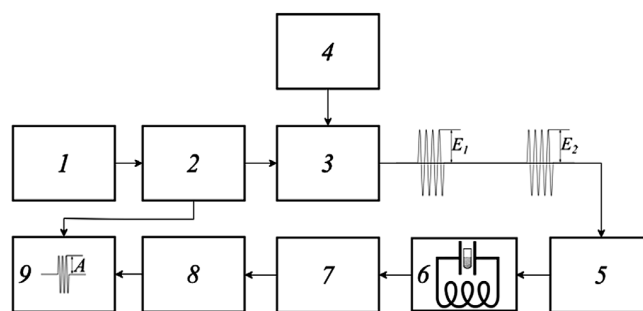


**Fig. 1.** Time sequence of radio pulses of the electric field  $E_1, E_2, E_3$  and two- and three-pulse echo signals  $A_2, A_3$

**Рис. 1.** Временная последовательность радиоимпульсов электрического поля  $E_1, E_2, E_3$  и сигналов двух- и трёхимпульсного эха  $A_2, A_3$

the HF electrical and elastic properties of materials at high amplitudes of electric fields and elastic deformations that are unattainable by other methods. With its help, it is possible to study the nonlinear electrical and elastic properties, the distribution of surface charges, defects and their mobility in particles, which manifest themselves in large samples only in a weak form (Shutilov et al., 1985). For effective excitation of elastic oscillations of piezoparticles, it is necessary that the acoustic resonance condition be satisfied, under which the particle sizes should be of the order of the elastic wave length in the material under study. Two- and three-pulse electroacoustic echoes in piezoparticle powders are observed in the time intervals during which the sound is attenuated in the studied material. This time for solids does not exceed a fraction of a second; therefore, the available standard equipment for observing nuclear quadrupole resonance (NQR) satisfies all the requirements imposed on the duration, amplitude of radio frequency pulses, and the amplitude of weak receiving electrical signals emitted by piezoelectric powder.

In this work, studies of two- and three-pulse electroacoustic echoes in quartz powders were carried out with pulsed panoramic spectrometer ISP-1. The main blocks of the ISP-1 spectrometer are shown in Fig. 2. The ISP-1 spectrometer has the following parameters: operating frequency range  $f = 1 \div 20$  MHz, radio pulse duration  $0.1 \div 100$   $\mu$ s, voltage applied to the parallel oscillatory circuit  $0.1 \div 3$  kV.



**Fig. 2.** Block diagram of the ISP-1 spectrometer for studying two- and three-pulse electroacoustic echoes in piezoelectric powders: synchronization unit (1), time interval unit (2), radio pulse shaper-amplifier (3), sinusoidal signal generator (4), matching device (5), a measuring device in the form of an inductor with a capacitor (6), a receiver with a signal amplifier (7), an attenuator (8), an oscilloscope for observing signals (9).

**Рис. 2.** Блок-схема спектрометра ИСП-1 для исследования двух- и трёхимпульсного электроакустического эха в пьезоэлектрических порошках: блок синхронизации (1), блок временных интервалов (2), формирователь-усилитель радиоимпульсов (3), генератор синусоидальных сигналов (4), согласующее устройство (5), измерительное устройство в виде катушки индуктивности с конденсатором (6), приёмник с усилителем сигналов (7), аттенюатор (8), осциллограф для наблюдения сигналов (9)

As a rule, an oscillatory circuit consists of an inductor, measuring and trimmer capacitors. To study the electroacoustic echo, the substance under study is placed between the plates of the measuring capacitor. The time interval from the end of the exciting radio pulses to the moment of observation of echo signals, in which it is impossible to observe electroacoustic responses, is 10–20  $\mu$ s. In this work, all studies of quartz powders were carried out at room temperature  $T = 300$  K. In experiments on the study of electroacoustic echo in quartz, the frequency of the electric field was  $f = 16.5$  MHz, the duration of all radio pulses of the electric field was  $\Delta t = 4$   $\mu$ s. The amplitude of the electrical response of the two-pulse echo was determined depending on the voltage across the capacitor with the sample at a constant interval between the first two radio pulses  $\tau = 30$   $\mu$ s and between the second and third radio pulses  $T_p = 1$  ms. From the obtained dependence of the amplitude of the two-pulse echo on the interval between radio pulses  $\tau$ , the relaxation time of the two-pulse echo  $T_2$  was determined and from this the quality factor of the electroelastic vibrations of quartz particles of the powder  $Q = f \cdot T_2$  was found.

### Sample preparation, characterization and composition

All experiments on the study of different quartz were performed on powder samples with particle sizes of 75–125  $\mu$ m. Powders with these particle sizes were obtained using a set of measuring sieves with mesh sizes of 75 and 125  $\mu$ m.

The selected sizes of powder particles corresponded to half the length of the elastic half-wave in the materi-

**Table 1.** Content of impurity elements,  $10^{-4}$  wt. %  
**Таблица 1.** Содержание примесей в кварце,  $10^{-4}$  мас. %

Elements / Элементы		Al	Ti	K	Mg	Na	Fe	Li	Cu	Mn
Quartz types / Типы кварца	Smoky / Дымчатый кварц	32.4	17.1	18.8	3.8	3.9	5.4	0.6	0.6	0.2
	Citrin / Цитрин	222	13.1	7.5	1.7	2.5	no	19.2	0.5	0.1
	Amethyst / Аметист	27.3	4.5	2.6	1.2	1.9	no	4.1	0.9	0.1
	Recrystallized / Перекристаллизованный	51	16.3	4.5	4.7	9.9	no	4.5	0.5	0.2
	Granular / Гранулированный	384	24.2	27	25	21.5	19.5	0.08	1.3	0.5
	Columnar / Шестоватый	79	21.8	23.1	8.5	30	5.8	0.2	0.4	0.2

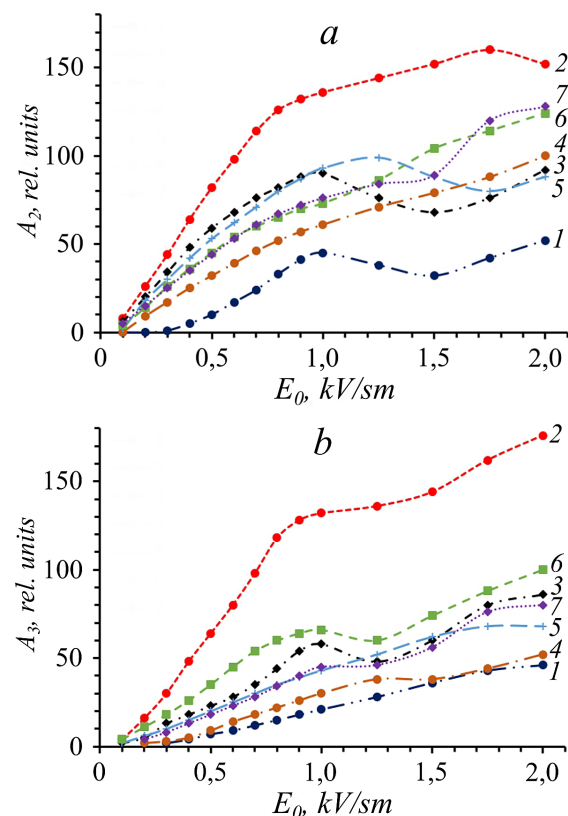
al under study  $l \approx \lambda/2 = V/2f$ , where  $\lambda$ ,  $V$ ,  $f$  – the length, velocity, and frequency of the elastic longitudinal (or transverse) wave (Shutilov et al., 1985). Taking into account the fact that in our experiments the frequency of the electric field was equal to  $f=16.5$  MHz, and the velocity of the transverse wave in quartz was  $V = 3.9158$  m·s<sup>-1</sup>. For this speed, the length of the elastic wave will be  $\lambda = 237.3$   $\mu$ m. It is known that the fulfillment of the acoustic resonance condition corresponds to the effective excitation of electroelastic vibrations of particles and better observation of electroacoustic echo signals from powder piezoparticles. The resulting powder with a volume of 0.2 cm<sup>3</sup> was poured into an ampoule 3 cm long and with an outer diameter of 0.6 cm. After that, the powder was subjected to high-temperature heating at 600 K for an hour with air being evacuated from the powder ampoules to a pressure of  $10^2$  Pa. After this procedure, the powder ampoules were sealed. Vacuumization of heated powders was carried out in order to clean the surface of quartz particles from water molecules and OH hydroxyl groups. The vacuum in the sealed ampoule with the powder also contributed to a decrease in the damping of elastic vibrations of powder particles by air molecules during the study.

All types of quartz that were used to study the electroacoustic echo were selected in the Subpolar Urals (Russia). Along with silicon oxide, they contain various impurities to a large extent. In the Subpolar Urals (Russia), a variety of vein quartz is widely developed, which is used as a technical raw material. Table 1 shows the average content of impurities for various types of quartz, most of which were taken from the hydrothermal quartz veins of the Lyapino anticlinorium. Impurities of Al, Cu, Fe, Mg, Mn atoms were determined by the spectral method at the Institute of Geology of the Komi Scientific Center of the Ural Branch of the Russian Academy of Sciences (Syktyvkar, Russia), and impurities of Na, Ka, Li atoms were determined at St. Petersburg Mining University (St. Petersburg, Russia) (Kotova et al., 2018).

### Experimental results and discussion

Figure 3 shows the amplitude dependences of two- (a) and three-pulse (b) electroacoustic echo in powders obtained from different types of quartz. It can be seen from Fig. 3 that the dependences of the two- and three-pulse echo on the electric field strength  $A_2(E_{02})$ ,  $A_3(E_{03})$  have linear and non-linear sections. For the linear section at the electric field amplitude  $E_0 < E_{02max}$ ,  $E_{03max}$  a linear increase in the amplitude of the two- and three-pulse electroacoustic echo is observed depending on the electric field strength. The second region at  $E_0 > E_{01max}$ ,  $E_{02max}$  corresponds to the nonlinear region, in which it

is possible to distinguish areas of saturation and decay of the amplitudes of the echo signals. The areas of saturation of the echo amplitude can be associated with the area of saturation of the permittivity of quartz crystals. The observed segments of the decay of the amplitudes of the  $A_2$ ,  $A_3$  echo can be caused by the breakdown of the elastic oscillations of quartz particles at high amplitudes of the electric field (Kajimura, 1982) due to a change in the natural frequency of the elastic oscillations. The decrease in the  $A_2$  amplitude in the region of the two-pulse echo decay is the least observed for artificial quartz, which indicates small excited amplitudes of elastic oscillations of powder particles compared to the amplitude of oscil-



**Fig. 3.** Dependences of the amplitude of two- (a) and three-pulse (b) echo on the amplitude of the HF field for different types of quartz: artificial (1), smoky (2), citrine (3), amethyst (4), recrystallized (5), granulated (6), columnar (7)

**Рис. 3.** Зависимости амплитуды двух- (а) и трёхимпульсного (б) эха от амплитуды ВЧ поля для разных типов кварца: искусственного (1), дымчатого (2), цитрина (3), аметиста (4), перекристаллизованного (5), гранулированного (6), шестоватого (7)





**Table 2.** Characteristics of electroacoustic echo of powders of different types of quartz  
**Таблица 2.** Характеристики электроакустического эха порошков разных типов кварца

Characteristics / Характеристики		$Q \cdot 10^{-3}$	$T_2$ , ms	$A_{2max}$ , rel.unit	$A_{3max}$ , rel.unit	$E_{02max}$ , kV/cm	$E_{03max}$ , kV/cm	K, rel.unit
Quartz type / Типы кварца	Artificial / Искусственный	3.64	0.22	35	45	2.0	1.0	1
	Citrin / Цитрин	36.4	2.2	40	80	1.0	1.0	2.1
	Smoky / Дымчатый	32.2	1.95	130	125	0.95	0.9	1.3
	Amethyst/Аметист	9.8	0.59	35	95	1.3	2.0	1.4
	Recrystallized / Перекристаллизованный	16.8	1.02	60	50	1.7	1.7	1.4
	Granular / Гранулированный	14.0	0.85	60	65	0.9	1.0	1.31
	Columnar / Шестоватый	5.6	0.34	40	85	1.0	1.3	1.1

lations of particles from natural quartz. The highest values of the tangent of the slope of the  $A_{2max}(E_{02})$  curves in the linear section of 0.3–0.8 kV/cm are observed for smoky and granular quartz (Table 2), which corresponds to their large values of the electromechanical coupling coefficient compared to other quartz. To observe a three-pulse echo, the time of excitation of the powder by the third radio pulse  $T_p$  must be less than the decay time of the elastic oscillations of the particles or the two-pulse echo  $T_2$ , the values of which are given in Table 2. In the Table 2, the following designations were used  $A_{2max}$  and  $A_{3max}$  — the maximum amplitude of the two- and three-pulse echo in the linear section,  $E_{02max}$ ,  $E_{03max}$  — the amplitude of the electric field at which saturation of the amplitude of the two- and three-pulse echo signals begins,  $tg\alpha$  — the tangent of the slope of the  $A_2(E_{02})$  curve in the linear section 0.3–0.8 kV/cm. The maximum amplitude of the three-pulse echo is observed for smoky quartz, and then for citrine and recrystallized quartz, which indicates their large decay times of elastic oscillations of particles. A large value of the relaxation time of electroelastic vibrations of powder particles is typical for citrine and almost the same for smoky quartz, which is most likely due to the highest uniformity of the surface of the powder under study (Table 1), for example, the absence of mineral impurities and textural and structural features, which leads to a decrease in sound attenuation  $\alpha$ . In granular quartz, the relaxation time is half that of citrine. Here it is also possible to talk about the influence of texture-structural impurities and the presence of mineral impurities in the total volume of the sample, for example, mica. Granular quartz has a fine-grained structure, various microstructural defects of grains are present: almost all quartz grains are presented as subindividuals with characteristic wavy or cloudy extinction, and there are also various microdefects in the form of mineral impurities. That is, we can conclude that the powders of granulated and recrystallized quartz are the most “non-monomineral”, which leads to a decrease in the relaxation time compared to other natural quartz samples.

Table 2 shows the ratios of the electromechanical coupling coefficients K for artificial quartz and other types of quartz. When evaluating the ratio for the electromechanical coupling coefficients K, it was taken into account that the amplitude of the two-pulse electroacoustic echo  $A_2$  at the same parameters of the HF electric field depends on the material parameters as follows  $A_2 \sim T_2 K_3$ . Amethyst quartz has the weakest high-frequency piezoelectric effect among all studied natural quartz.

## Conclusion

The method of two- and three-pulse electroacoustic echo for the study of piezoelectric materials, including varieties of quartz, which are in a finely dispersed state, is described. The values of relaxation times and parameters of electroacoustic echo in quartz powders, consisting of particles with sizes of 75–125  $\mu\text{m}$ , are obtained. Powders obtained from artificial and natural quartz, including vein quartz from the Lyapinsky anticlinorium (Subpolar Urals, Russia), were studied. The relative values of the electromechanical coupling coefficient for natural types of quartz are obtained and the amplitudes of the HF electric field are determined, at which the electroacoustic echo signal saturation mode is observed. It is shown that most of the natural quartz has a value of the electromechanical coupling coefficient greater than that of artificial quartz. Citrine is characterized by the highest value of the coefficient of electromechanical coupling K, and columnar quartz has the closest value of K to artificial quartz. It is shown that among the studied quartz powders, granular and recrystallized are characterized by the shortest relaxation time compared to other natural quartz samples, which is primarily due to the presence of mineral impurities in the quartz aggregate and, accordingly, in the powder, as well as with textural and structural features. The saturation region of the two- and three-pulse echo amplitudes for most quartz is in the range of 0.9–1.3 kV/cm, except for artificial and recrystallized quartz, for which this value is 1.7–2 kV.

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