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Some Electric Properties of Doped Single Crystals of Rochelle Salt

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Single crystals of Rochelle salt containing Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Co^{2+}, N^{2+}, Cd^{2+}, Cl^-, and OH^- impurities at differing concentrations have been submitted of testing for ferroelectric and piezoelectric properties. Crystal samples have been used for the recording of the dielectric hysteresis loop at $+3^0$ C, for the measurements of the temperature dependence of the dielectric contanat ε_x in a weak field in the temperature range comprising both Curie points, and for the measurements of the temperature dependence of the piezoelectric modulus d_{14} by means of weak force in the temperature range around the upper Curie point.

The limits of the approximate concentrations of the impurities, at which changes in the measured properties occur, have been determined. The observed changes are discussed on the basis of papers and reports published earlier. The influence of the impurities is specific in relation to their species.

INTRODUCTION

There are comparatively few reports dealing with the influence of heteromorphous impurities on the electric properties of Rochelle salt single crystals. First to investigate the problem were Thorp and Buckley[1], who examined the effect of Cu^{2+} ion and boric acid. Chormonov should be mentioned here[2–4] since he investigated the effect of purifying Rochelle salt single crystals as well as the influence of aluminium impurity. Chormonov also tested the influence of traces of Al, Cu, Si, Ca and Rb mixture on electric properties. The next author to deal with B, Cu and Mo impurities was Eisner[5, 6]. The above authors were mainly interested in ferroelectric and piezoelectric properties in the temperature range covering both Curie points. Eisner also examined the influence of irradiation on the electric properties of Rochelle salt. All these investigations were mainly qualitative. A more thorough analysis of the phenomena was provided by Zheludev, Yurin *et al.*, as a result of the research into the properties of irradiated single crystals and single crystals doped with Cu^{2+} ions. The first paper on this problem was published in 1957[7] and the completed investigations were reported in 1964[8].

The aim of our work was to examine ferroelectric and piezoelectric properties of a greater number of crystals prepared previously[9, 10] containing various impurity ions in various concentrations, the influence of which had not been tested until now.

EXPERIMENTAL

Recording of the dielectric hysteresis loops

As the dielectric hysteresis loop provides the most readily observed characteristic of ferroelectric properties, this was first recorded for doped crystals by means of the well-known method of Sawyer and Tower[11]. The recording was performed on plate samples 1.4 × 1.4 × 0.24 cm, of X-90 orientation. We tried to avoid differences in the size of the samples, especially in the thickness, which did not vary by more than 0.01 cm. In the cases of crystals with a higher concentration of doping it was necessary to cut plates with smaller surfaces

TABLE I:

The influence of impurities on the electrical properties of Rochelle salt monocrystals. (No) the ordinar number, (S) the sign of the crystal with the symbol of the impurity atom, crystals without checked doping are marked WD-1 and WD-2; (C_s) the impurity concentration [equivalent/unit cell]; ($\varepsilon_x = f(t)$) the temperature dependence of the dielectric constant; ($d_{14} = f(t)$) the temperature dependence of the piezoelectric modulus. Crystals which have been tested are denoted by a cross.

No	S	C_s	Change in dielectric hysteresis loop		Change in $\varepsilon_x = f(t)$		Change in $d_{14} = f(t)$	
1	WD-1		+	Practically no change	+	Slight differences	+	Practically no change
2	Ca-1		+					
3	Ca-2		+				+	
4	Ba-1		+					
5	Ba-2	$2 \cdot 10^{-6}$	+				+	
6	Cd-1	$4 \cdot 10^{-6}$	+					
7	Cd-2	$4 \cdot 10^{-6}$	+					
8	Cl-3	$8 \cdot 10^{-6}$	+				+	
9	Co-1	$3 \cdot 10^{-5}$	+					
10	Cr-1	$3 \cdot 10^{-5}$	+					
11	Cr-2	$4 \cdot 10^{-5}$	+				+	
12	Fe-1	$6 \cdot 10^{-5}$	+		+			
13	Cd-3	$6 \cdot 10^{-5}$	+					
14	Ni-1	$6 \cdot 10^{-5}$	+					
15	Mn-1	$7 \cdot 10^{-5}$	+		+			
16	Co-2	$8 \cdot 10^{-5}$	+			In most cases there is a fall in the maxima and a decrease in their separation	+	
17	Fe-2	$2 \cdot 10^{-4}$	+	Specific change according to the kind of impurity	+		+	The maximum of the function decreases or changes position
18	Ni-3	$4 \cdot 10^{-4}$	+		+			
19	Mn-2	$4 \cdot 10^{-4}$	+		+			
20	Cr-3	$5 \cdot 10^{-4}$	+		+			
21	Co-3a	$1 \cdot 10^{-3}$	+		+			
22	Fe-3	$3 \cdot 10^{-3}$	+		+			
23	Mn-3	$3 \cdot 10^{-3}$	+		+			
24	OH-2		+		+		+	
25	WD-2		+		+		+	

in order to avoid nonhomogeneous regions. The plates were cut from the middle of single crystals, so that various impurity concentrations originating from various, pyramids of growth were equally represented. Electrodes were prepared by the evaporation of gold under a reduced pressure of $4 \cdot 10^{-4}$ mm, Hg. The distance between the gold source and the sample was 8 cm, the time of the evaporation was 5 seconds, and the total time of the evacuation did not exceed 3 minutes so that dehydration of the sample was avoided. Before the recording hysteresis loops all the samples were kept together at room temperature. During the recording the samples were thermostated at 3^0 C. Prepolarization took place in a field of 1000 V/cm and at a frequency of 50 Hz. The error in determining the ferroelectric parameters amounted to $\pm$ 10%.

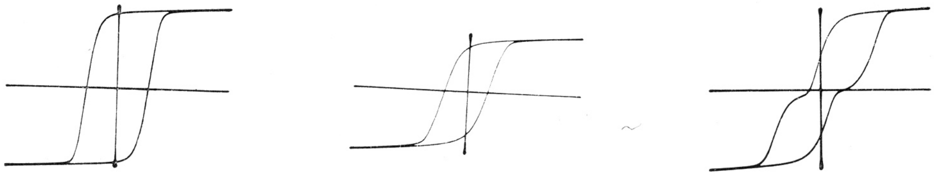
The loops were recorded for all the doped crystals listed in Table I. The loopes for the crystals without controlled doping were recorded simultaneously. One of these crystals, WD-1, had been prepared from p. a. substance, while the other, WD-2, had been grown in conditions for technical purity with unknown impurity content.

Measurement of the dielectric constant ε_x in a weak field

A *UM-3* bridge (made in USSR) was used to measure the temperature dependence of ε_x. The electric field of the crystal condenser was 0.4 V/cm at a frequency of 1 KHz. The accuracy of the measurements is ± 5%. The measurements were carried out in the temperature interval of $+27^0$ C to -16^0 C, proceeding from the higher temperature to the lower. The cooling rate was about 0.01^0 C per minute for temperatures close to the Curie points and was 10 to 20 times faster at more distant temperatures. The measurements were discontinued at room temperature (about 15^0 C) and resumed the following day. The accuracy of the temperatures taken in the vicinity of the Curie points was $\pm$ 0.05^0 C, and in other regions $\pm$ 0.5^0 C. The ε_x measurements were taken only for the crystal which had shown some change in the course of loop recording. Those were the systems with impurity content over $8 \cdot 10^{-5}$ equivalents per unit cell. Systems with smaller impurity content were also measured for comparison as well as the WD-1 and WD-2 systems. A list of the measured crystals is found in Table I. The same samples were used for the measurements of the dielectric constant and for loop recording.

Measurement of the piezoelectric modulus d_{14}

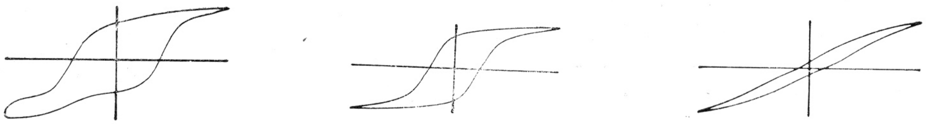
The piezoelectric modulus d_{14} was determined statically by means of the direct effect of a 45 p force. The maximal field strength formed in the crystal did not exceed 2 V/cm. The potential difference was measured with a quartz electrometer SG-1M and the capacity of the crystal element was measured with the UM-3 bridge. The accuracy of the determined moduli is $\pm$ 10%. The measurents were performed in the range around the upper Curie point, proceeding from higher to lower temperatures. The cooling rate was about 0.01^0C/min in the vicinity of the Curie point and the accuracy of the measurements was $\pm$ 0.15^0 C. Samples of *X*-45 orientation which had also been cut from the middle of single crystals were used for the measurements. The surfaces of the samples were about 1.0×1.1 cm an the thickness along the x axes 0.8 cm. The electrodes had been evaporated *in vacuo*. Since a greater quantity of homogeneous crystal material is necessary for such samples, it was not possible to measure piezoelectricity on the crystals with higher concentrations



a) WD-1
$P_{\max} = 820$, $P_S = 770$
$E_K = 280$

b) WD-2
$P_{\max} = 860$, $P_S = 780$
$E_K = 240$

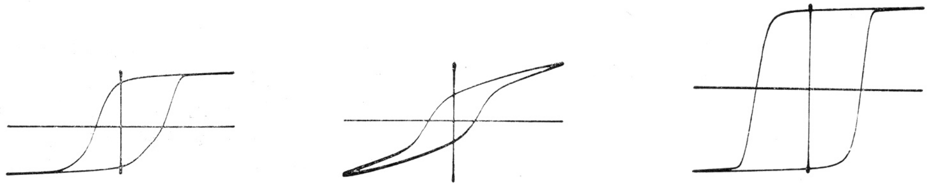
c) Fe-2
$P_{\max} = 820$, $P_S = 760$
$E_K = 220$



d) Fe-3
$P_{max} = 570$, $P_S = 940$
$E_K = 390$

e) Mn-2
$P_{\max} = 700$, $P_S = 630$
$E_K = 204$

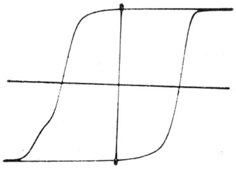
f) Mn-3
$P_{\max} = 260$, $P_S = 170$
$E_K = 110$



g) Cr-3
$P_{\max} = 810$, $P_S = 740$
$E_K = 290$

h) Co-3a
$P_{\max} = 240$, $P_S = 150$
$E_K = 210$

i) Ni-3
$P_{\max} = 830$, $P_S = 790$
$E_K = 460$



j) OH-2
$P_{\max} = 620$, $P_S = 780$
$E_K = 540$

Fig. 1: The dielectric hysteresis loops of Rochelle salt single crystals with and without doping. The y axis represents the maximum polarization ($P_{\max}$) [stat C/cm^2], and the x axis the maximum field of 1000 [volt/cm], frequency 50 Hz. (P_S) is the spontaneous polarization obtained by extrapolation, (E_K) the coercive field. The signs of the crystals are the same as used in Table 1. Temperature 3^{0}C.

of doping, from which it was difficult to cut the required parallelepiped owing to the altered habit and crystal defects. The crystals on which the measurements of d_{14} were carried out are marked by cross in the last column of Table I.

RESULTS

The results obtained from the hysteresis loops are shown in Fig. 1. Only those recordings showing some change will be discussed here. Fig. 1*a* represents the loop of the pure WD-1 crystal which has been taken to serve as standard in the analysis of the other loops. It is interesting to note the difference between this and the loop in Fig. 1*b* belonging to the technically pure crystal WD-2. An unknown impurity in the crystal causes the loop to lose the right angle and causes a delay in the saturation of polarization.

Figs. 1*c* and 1*d* show the recordings of the loops of single crystals doped with iron. The loop of the single crystal Fe-2 reveals a typical »double loop« where the separation has not been completed. This modification of the loop was described and explained by Eisner and Yurin. There is no evidence that the spontaneous polarization is greately affected, while the coercive force is somewhat lessened. The coercive force was measured at the widest part of the positive and the negative sides, respectively, of the separated loop. As for the loop of the single crystal Fe-3, its irregular shape is the consequence of nonuniform distribution of impurities in the sample which includes the pyramids varying greatly in the concentration of iron. The parts of the sample with high concentration yielded the separated »double loop« so that in the field of 1000 V/cm saturation did not occur. The remaining parts of the sample with minimum impurity concentration give a normal loop in the middle. Our loop reflects all the effects in which the influence of the lower concentration is predominating so that the result is a triple loop which could be traced out but which did not shape completely until a stronger field had been applied. The assymmetry of the loop is a consequence of the assymmetry of antiparallel domains. That is, the crystal sample, namely, was not perfectly homogeneous.

Single crystals containing manganese, Mn-2 and Mn-3, yielded utterly different loops. The Mn-2 loop (Fig. 1*e*) indicates a decrease in spontaneuos polarization, which is even more pronounced in Mn-3 (Fig. 1*f*). In the latter loop the coercive force has also been weakened. A 1000 V/cm field is just enough for saturation to take place. The formation of a double loop (narrowing in the middle) is hardly noticeable. The loops of single crystals containing manganese are stable against the influence of the field, their parameters, do not change and only the Mn-3 loop straightens and loses the narrow part.

The Cr-3 crystal also yielded a modified loop (Fig. 1*g*). A decreased spontaneous polarization can be observed, as well as a shift in the direction of the x axis, evidence for the existence of an inner field, and an increase in the coercive force. When the sample was allowed to »rest« for a longer period of time at 18^0 C and the loop then recorded, it was observed to be narrower in the middle. Under even a short influence of the field the above effect was lost. At 3^0 C the effect of narrowing was practically lost, and the shift of the loop became much more pronounced.

Fig. 1*h* shows the loop of the single Co-3*a* crystal. The presence of cobalt causes a decrease in spontaneous polarization, whereas the diminution of the coercive force is negligible. The system containing cobalt is rather unstable.

Under the influence of the alternate field the loop presently changed shape. In Fig. 1*h* the loop was recorded immediately after the field had been applied. When the field was applied for a longer period of time the loop widened and both parameters rapidly increased.

The loops of single crystals Ni-3 and OH-2 shown in Figs. 1*i* and 1*j* do not reveal any particular change in the magnitude of spontaneous polarization. These loops are distinguished only by great coercive forces. The small deviation in the OH-2 loop is interpreted by the beginning of an asymmetric separation of the loops (due to asymmetry of antiparellel domains and the beginning of »monoclinization« under the influence of the impurities).

The main features of the temperature functions of ε_x and d_{14} for the measured crystals are given in Table I. The data concerning the magnitude, position and distance between the maxima of the functions of ε_x are shown in Table II. The distance between the maxima of the temperature functions of ε_x which, according to Yurin, only seemingly represents the magnitude of the ferroelectric interval, differed from one sample to another. For a better illustration we have presented in Table II the changes in the distance between the maxima for all the systems as the difference from that for the pure WD-1 system. The maximum values of d_{14} are given in Fig. 2. while those temperature functions of d_{14} which show changes are plotted in Fig. 3. In addition to the functions measured for the crystals Fe-2 and OH-2 we have also recorded, for comparison's sake, the function measured for the single crystal WD-1.

TABLE II.

Maximum values of the dielectric constant of pure and doped single crystals of Rochelle salt. (ε_{xh}) the maximum at the higher temperature, (ε_{xd}) the maximum at the lower temperature, (t_h) and (t_d) the maximum temperatures [^{0}C], ($\triangle$ f. i.) the change of the temperature interval between the achieved maxima [^{0}C]. Other symbols as in Table I.

S	C$_S$	ε_{xh}	t_h	ε_{xd}	t_d	$\Delta f. i$
WD-1		4900	24,4	3600	—18,7	0
WD-2		2900	24,7	2300	—18,2	—0,2
Fe-1	$6 \cdot 10^{-5}$	3600	24,5	3300	—18,6	0
Mn-1	$7 \cdot 10^{-5}$	5400	24,3	3600	—19,0	+0,7
Fe-2	$2 \cdot 10^{-4}$	2000	25,2	1600	—19,15	+1,25
Ni-3	$4 \cdot 10^{-4}$	4300	24,2	2300	—18,7	—0,2
Mn-2	$4 \cdot 10^{-4}$	1900	24,2	1500	—18,5	—0,4
Cr-3	$5 \cdot 10^{-4}$	2300	24,3	1800	—18,7	—0,1
Co-3a	$1 \cdot 10^{-3}$	1600	24,2	360	—18,5	—0,4
Fe-3	$3 \cdot 10^{-3}$	1900	24,2	1200	—18,2	—0,7
Mn-3	$3 \cdot 10^{-3}$	580	21,9	450	—17,35	—0,9
OH-2		2400	22,9	2100	—18,0	—0,85

DISCUSSION

Let us first consider the results obtained from the recordings of the dielectric hysteresis loops. The effect of »monoclinization«, which is revealed in the formation of the double loop, was only observed for crystals containing iron.

For single crystals doped with alkali, manganese and chromium, this effect was hardly noticeable, and it failed completely to appear in all other cases. Nevertheless the concentration of impurities in the single crystals of Mn-3 and Co-3*a* did not differ greatly from the concentration of copper in Yurin's single crystal, or from the concentration of iron in our crystal Fe-3. However, the state of »monoclinization« in Cr-3 and Mn-3 is extremely unstable. A short application of the 1000 V/cm alternate field regulated the state completely, while Yurin could achieve the same effect with irradiated crystals or with copper doped crystals only by heating the crystals or by the lengthy application of a strong alternate field. We can also speak of the influence of impurities on the ferroelectric parameters indicated by the loops. All the crystals with higher impurity concentration show a drop of decrease in spontaneous polarization, which is particularly pronounced with Co-3*a* and Mn-3. While the Mn-3 is stable in this respect, Co-3*a* undergoes a modification through the influence of the field and the spontaneous polarization and coercive field increases. As regards the coercive field, it can be seen that this is increased in all the crystals which were grown with the addition of alkali — Cr-3, Co-3*a*, Fe-3, Ni-3 and especially so in the crystal OH-2. The only crystal with a higher concentration

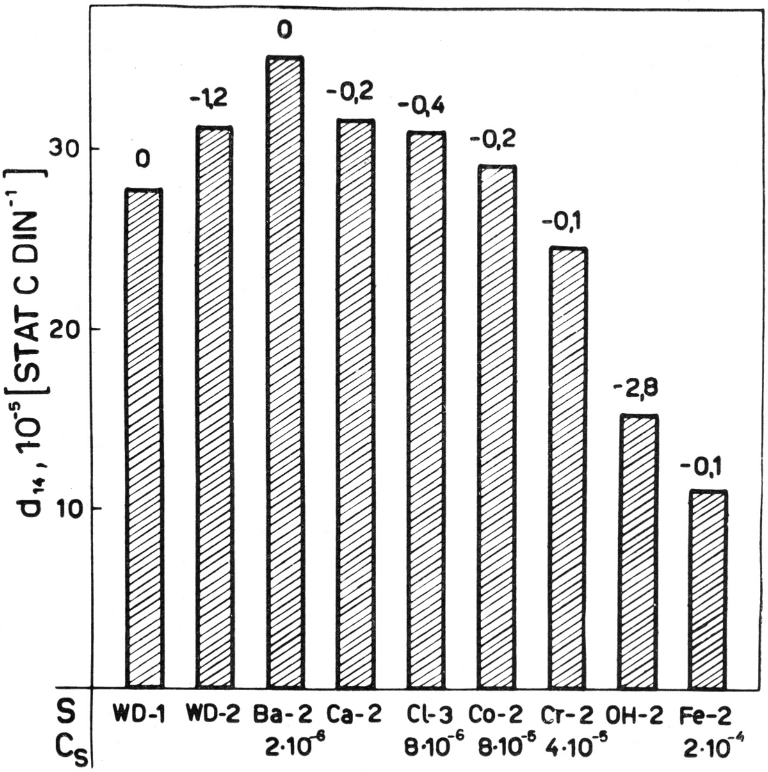


Fig. 2: Maximum values of the piezoelectric modulus d_{14} of pure and doped single crystals of Rochelle salt. The meaning of the symbols are as in Table 1. The differences in temperature [^{0}C] of the achieved maximum are recorded at the top of each column.

of doping, which was prepared without alkali addition (Mn-3), shows a considerable decrease in the coercive force.

As can be seen from these results the phenomena caused by impurities are rather complex. Those described so far by other authors could be confirmed by our results in a few cases only. If, in the interpretation of the phenomena, we start from Yurin's theory, which was based on qualitative results for the irradiated crystal and the copper doped crystal, it must be assumed that there are great differences in the kinetics of distribution of the doping centres for the various doping species. In the same way the concentration of impurity needed for a particular modification of the ferroelectric state greatly depends on the kind of impurity.

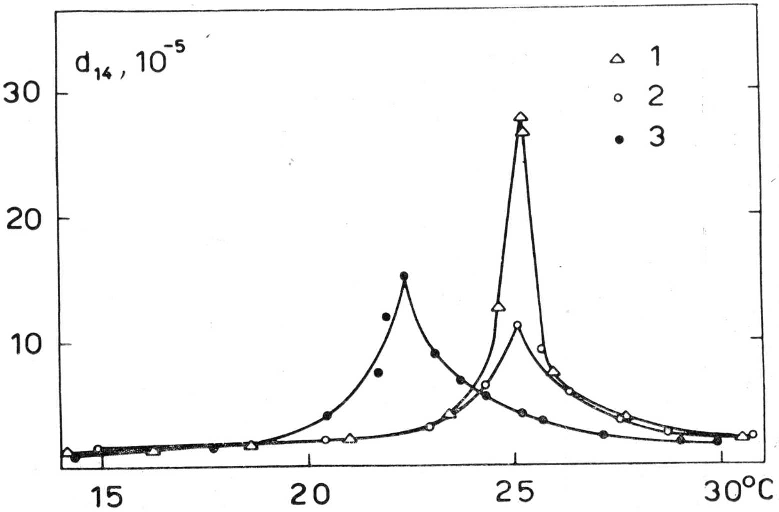


Fig. 3: Temperature dependence of the piezoelectric modulus d_{14} [stat C/din] of pure and doped single crystals. (1) WD-1, (2) Fe-2, (3) OH-2. For the signs of crystals see Table I.

If we analyze the results of the measurements of the temperature function ε_x in a weak field, we shall notice the general tendency for a decrease in the maxima on increasing the concentration of impurity. This decrease is typical of certain kinds of impurities. Another phenomenon is the diminution of the temperature interval between both peaks with an increase in the doping concentration. There are a few exceptions here, the first is shown by Mn-1, whose interval is even wider than that of WD-1. These properties are rather sensitive, so that it is quite plausible that the Mn-1 with minimal content of doping is »purer« than the »pure« crystal. A considerable deviation is found for Fe-2 and to a slightly lesser extent for Cr-3. These experiments have generally confirmed the phenomena observed by other authors on crystals with other dopings. If we exclude Fe-2 and take Mn-1 as basis, it can be said that in the case of our systems the concentration of doping up to $3 \cdot 10^{-3}$ equivalents per unit cell diminishes the interval between both peaks by as much as 1.6^0 C.

In the analysis of the results of the d_{14} measurements we use Fig. 2. Taking into account the error in the measuraments it may be said that the first seven systems practically do not differ. A conspicuous change occurs only with OH-2 and Fe-2 *i. e.* with the systems whose impurity concentration exceed $8 \cdot 10^{-5}$ equivalents per unit cell. A more significant shift in the maximum is found for the technically pure samples of WD-2 and OH-2. These phenomena are also in agreement with the facts known so far on the influence of impurities on piezoelectric properties of Rochelle salt.

Finally, it is worth mentioning that, regardless of the same conditions under which the crystals were prepared and the same conditions of measurement, we have drawn a comparison between the samples with different domain structures. When investigating the influence of irradiation, measurements were always carried out on one and the same sample. The other factor to be taken into consideration is the importance of knowing the exact concentration of impurities in the samples. The C_s magnitude which we have been using is very approximate since it represents a rounded mean value of impurity concentration in the whole crystal. The large number of systems which we have studied prevented a more thorough examination, so that this report contain only general information.

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IZVOD

Neka električna svojstva dopiranih monokristala Seignetteove soli

M. Topić

Monokristali Seignetteove soli s primjesama Ca^{2+}, Ba^{2+}, Cr^{3+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cl^- i OH^- u raznim koncentracijama podvrgnuti su ispitivanju senjetoelektričnih i piezoelektričnih svojstava. Na kristalnim uzorcima izvršeno je snimanje dielektrične histerezne petlje kod $+3^0$ C, mjerenje temperaturne zavisnosti dielektrične konstante ε_x u slabom polju u temperaturnom intervalu koji zahvaća obje Curieve tačke, i mjerenje temperaturne zavisnosti piezoelektričnog modula d_{14} upotrebom slabe sile u temperaturnom dijapazonu oko gornje Curieve tačke.

Određene su granice približnih koncentracija primjesa iznad kojih dolazi do promjena u izmjerenim svojstvima. Diskutira se o uočenim promjenama na bazi dosad objavljenih radova. Utjecaj primjesa je specifičan u odnosu na njihovu vrst.

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