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Thermal effects on the electrical properties of Potassium Nitrate: Polyvinyl Alcohol Composite Films

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This manuscript describes the experimental results of the potassium nitrate (KNO_3): polyvinyl alcohol (PVA) composite thick films. To explain the nature of ferroelectric phase (phase III) of potassium nitrate (KNO_3), the composite films of potassium nitrate with polyvinyl alcohol containing equal weight percentage have been prepared by solvent-cast methods. Temperature dependence characteristics of the dc electrical conductivity of these samples have been investigated. The Current versus Voltage (I-V) characteristics exhibit the polarization current at room temperature, which reveals the existence of ferroelectricity in these composite films. Current versus Temperature (I-T) measurements have been performed to identify the ferroelectric phase transition in KNO_3: PVA composite films.

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1. Introduction

Ferroelectric composite films especially ferroelectric ceramic-polymer composites in the range of nanoscale characterization have remarkable applications in multidirectional fields of engineering, science and technology [1]. To study the ferroelectric, pyroelectric, piezoelectric and dielectric behavior of the ferroelectric materials; the composite films have better performance [2-8]. The composite materials have been produced using mixtures of ceramic as filler in polymer matrix. The fillers are included in the matrix in order to modify its physical properties in a high range. The filler such as PZT, $BaTiO_3$, $PbTiO_3$ SBT, BST, SBN, BFO, BST/G, $KNbO_3$, $NaNO_2$, $CsNO_3$& $(NH_4)_{0.39}K_{0.61}NO_3$ ceramics are currently in current focus and their composite films with polymers such as PVDF, PVF & PVA have been prepared and investigated in past [9-16].Composite materials with piezo-, pyro- properties have been gain enormous attention due to the potential to produce these films with tailored properties such, enhancement of ferroelectricity, lowering of operating voltage, flexibility etc. Therefore, the polymer-ferroelectric composite materials are emerging as a new class of electronic and dielectric materials. These composites can find vast tremendous and technological applications; such as ferroelectric capacitor, MEMS, ferroelectric memory devices etc. [2-16].

Recently, the ferroelectric properties of composite films have gained much interest due to the formation of thin and large area composite films [1-16]. Potassium Nitrate (KNO_3) is well known ferroelectric materials and to study the stability of ferroelectric phase (phase III), the extensive research work have been carried out [9, 10, 17-23].

Polyvinyl Alcohol has amorphous nature as well as in semi crystalline form depending upon the method of preparation. It reported x-ray diffraction peaks at $2\theta=11.4$, 19.4 and 40.4^o corresponds to the crystalline phase [9, 10]. It has crystallinity due to the strong intermolecular interaction and hydrogen bonding between the PVA chains [24-30]. Development and characterization of PVA based ferroelectric composite films have been found an emerging method to improve the properties [9-16, 30]. KNO_3: PVA composite films with improved electrical properties may offer a viable alternative for the applications in the field of memory devices, ferroelectric capacitor, MEMS etc. Earlier, the ferroelectric properties of KNO_3: PVA composite films have been studied by our research group [9-16].

PVA and KNO_3 both are soluble in water; therefore, we focused on the composite films of both the materials by the solvent cast method, which is commonly used for the fabrication of ceramic/polymer composite films. Comparison to the results obtained in pure PVA and KNO_3 revealed that the ferroelectric phase (phase III) in KNO_3 is stable at room temperature due to admixture of KNO_3 at50 wt. % ratio in PVA. Hence, we intend to investigate the thermal effect on the electrical properties of KNO_3: PVA composite films.

Preparation of the solvent-cast composite film: The purified powders of potassium nitrate (Aldrich USA) and PVA were used for the preparation of composite films. For a particular composition (50% by weight), the composite powder mixture of an equal amount weighing (100mg) was dissolved in double distilled water and stirred well while being heated at 40°C on a hot plate magnetic stirrer [9, 10, 32]. The composite solution of PVA and KNO_3 was spread onto the ultra clean glass plate and covered by a glass bell jar for four days for drying. After the solvent cast composite film has formed, it was easily removed from the glass plate and kept in a vacuum oven for 6 hrs at 60°C to remove the excessive moisture from the composite film. Further to remove the wrinkles and for the homogeny, the composite film was pressed in a stainless steel die at 100°C and stress 250 Kg/cm^2 for 60s and cooled down to room temperature using melt-press techniques. The thickness of the composite film was measured to be 30-60μm. The circular indium electrodes having an area of ~0.25 cm^2 on both the sides of the composite film were deposited in a chamber at the pressure of 2×10^{-5}mbar. The prepared composite film were poled at the following poling conditions for better performance i.e. poling temperature (T_p)=130 °C, poling voltage (V_p)= 30 V and the poling time (t_p)= 20 min.

2. Results and discussions

2.1 DC Electrical Conductivity of KNO_3: PVA Composite

The dc electrical conductivity variation with temperature has been found to provide knowledge of the phase transition in KNO_3 [33-37]. The dc conductivity studies on single crystal KNO_3 shown anomalies at about 130°C on heating and about 124°C and 108°C on cooling. These measurements gave the activation energies of phase I, II and III as 0.89, 1.38 and 0.78 eV respectively [37, 39].

Table 1. The activation energies calculated for different phases during heating and cooling modes in the composite films.

Mode	Temperature Range (°C)	Phase	Activation Energy (eV)
Heating	37.5 →128	II→I	0.14~0.72
Heating	130°→155	II	~0.55
Cooling	107 →90	III	~0.85
Cooling	60 →37.5	II+III	0.18~0.48

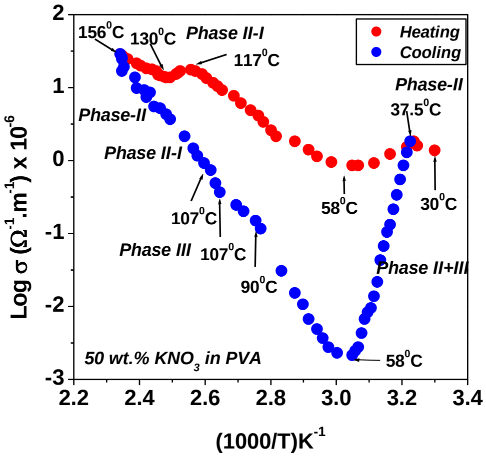

Fig. 1. DC conductivity versus 1000/T plot of the composite films.

The electrical conductivity in KNO_3: PVA composite was calculated using the relation:

$$\sigma = \frac{I.d}{A.V} \qquad (i)$$

Where, σ, I, d, A and V are the electrical conductivity, current, sample thickness, electrode area and applied voltage respectively.

The conductivity was evaluated after the application of 10 V dc as a function of temperature for 50wt.% KNO_3: PVA composite sample for both the heating and cooling modes. The temperature of the sample was varied at constant heating rate of 5°C/min using a temperature programmer attached to specially designed furnace. Fig. 1 depicts the plot of log σ versus T^{-1}.

Initially the composite is assumed to contain mixed phases II and III of KNO_3 as revealed by the X-ray and Raman studies [40-44]. During heating cycles both the phases II and III seem to coexist up to about 58°C and in the temperature range 58 to 117°C, phase III converts to phase II and exists up to temperature 128°C. Further heating converts phase II to phase I in the temperature interval 128 to 135°C [45]. At temperature 130⁰C the ferroelectric to paraelectric transition occur as obtained by DSC measurements. It is envisaged that during the cooling mode, phase I converts to phase III in the temperature range 107 to 58°C. The phase III seems to exist in the temperature interval 98 to 55°C. However, the curve again shows a sharp drop in conductivity in the temperature range 58to 37°C, which may indicate that some of phase III is converted to phase II and then up to room temperature both the phases III and II coexist. The Raman studies on KNO_3 in the past also show similar temperature ranges of the phase transformations and the coexistence of phases II and III. The thermal expansion studies on KNO_3 films also showed a transition peak of phase III to phase II near 62°C [37-39].

Table 2.DSC parameters of pure KNO_3, pure PVA and composite films.

Heating Modes (Endothermic Reactions)			Cooling Modes (Exothermic Reactions)	
Sample	Phase Trans. Temp. (˚C)	ΔH (mJ/mg)	Phase Trans. Temp. (˚C)	ΔH (mJ/mg)
Pure KNO_3	132.1	+61.1	114.4 100.8 94.9	-31.8 -18.8
Pure PVA	218	+21.7	178.2˚C	-18
KNO_3: PVA film	132.4 210.4	+22.8 +19.9	114.3 176.6	-12.1 -10.2

Table 2 shows the results of DSC measurements of PVA film, KNO_3 powder and PVA: KNO_3 composite film for heating and cooling cycles. The DSC scan of the composite film shows two peaks appearing at 132.4°Cand 210.4°Cin the heating mode. The 132.4°Cpeak corresponds to the conversion of phase-II to phase-I. This matches with the single peak at 132.4°C in the DSC scan of $KNO_{3,}$ which is known to occur due to the transition of phase II and / or phaseIII to phase I [22]. The peak at210.4°C corresponds to the melting of PVA [9, 10, 30]. The transition observed at 114.3°C can be attributed to the transformation of phase I to phase III of KNO_3 as in case of other composites. The exothermic DSC measurements indicate that the composite samples with composition ≤ 50wt. % KNO_3 mainly possess ferroelectric phase III near room temperature. The nucleation of phase II from phase III of KNO_3 in the composite is suppressed due to the presence of PVA.

The composite may contain crystallites of different sizes and in all probability some of the small crystallites of phase III may convert to phaseII. Therefore possibly the phases II and phase III coexist in the lower temperature range. The X-ray experiments also support the existence of crystallite distribution in the composite. The DSC endothermic experiments also show transition peak of phase II to phase I at 130°C during heating [22, 31]. On the other hand, the exotherm DSC experiments shows peak of phase I to phase III in the temperature interval 107 to 90°C. This temperature range of the exothermic DSC experiment is different from that observed from conductivity experiment. This may be due to different nature and sensitivity of the experiments; however, both the experiments do show the existence of phase transitions in the composite sample. The temperature dependent of dc electrical conductivity (σ_{dc}) and activation energy (E_a) can be expressed by the following Arrhenius equation [36, 38],

$$\sigma_{dc} = \sigma_o exp\left(-\frac{E_a}{k_b T}\right) \qquad \text{(ii)}$$

Where,$\sigma_{o,} k_b$ and T are pre-exponential factor, Boltzmann constant, and temperature respectively. The activation energies were calculated in different temperature ranges of the log σ versus T^{-1} in KNO_3:PVA composite film as shown in Fig. 1 during heating and cooling modes and the corresponding results are shown in Table 1. These values are lower than observed by other workers in pure KNO_3 [36, 38]. The different form of phases assumed to be present in various temperature ranges are also given in Table 2. Several reports indicate that oxygen vacancies are mobile charged point defects in bulk perovskite titanate materials. The activation energies ~ 0.6 eV for oxygen vacancy migration have been reported [44]. The electrical conductivity studies also exhibit the temperature ranges of the phase transformations as obtained in the DSC and the dielectric investigations [22, 31]. The electrical conductivity studies also support the coexistence of phases II and phase III in the composite films.

2.2 Current-voltage characteristics

The I-V characteristics of the 50 wt.% composite films have been carried out at room temperature as shown in Fig. 2. The voltage was swept from 0 to +21 V in the forward bias. The sharp peak was observed at + 11 V. This sharp peak indicates the predominant switching current due to the polarization in the composites at room temperature. The value of initial rise in current with applied voltage may be due to the orientation of domain which creates the ferroelectric polarization in the field direction. The peak voltage in the I-V curve arises in the vicinity of the coercive field at which the majority of the ferroelectric domains switched in field directions. Further then at the peak value, the decrease in current is due to the decline in domain contribution. The voltage corresponding to the sharp peak has been taken as the coercive voltage by many researchers. The value of E_c (≈ 3.2 kV/cm) obtained from the I-V characteristics was less than the E_c (≈ 4.62 kV/cm) obtained from the hysteresis loop measurement as published in our previous research work [22-31].

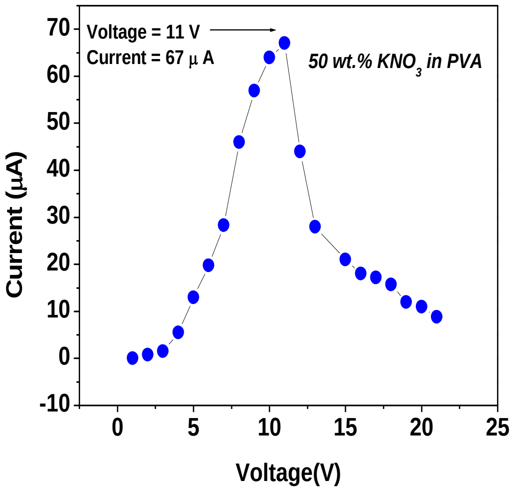

Fig. 2. Current- Voltage (I-V) characteristics of KNO_3: PVA composite films at room temperature.

2.3 Current vs. Temperature (I-T) characteristics of the composite film

The temperature dependence of I-T measurements of optimized composite film has been studied. Fig.3 shows the sharp peak at the increased value of temperature up to temperature (T=118°C) and the value of corresponding current is (I=58μA)and above this temperature (T=130°C), the value of corresponding current is (I= 40μA) during heating mode. This indicates the transition of ferroelectric phase in to paraelectric phase of KNO_3 in the composite films. The variation of peak current of I-T characteristics of the composite films is due to the existence of the polarization switching current.

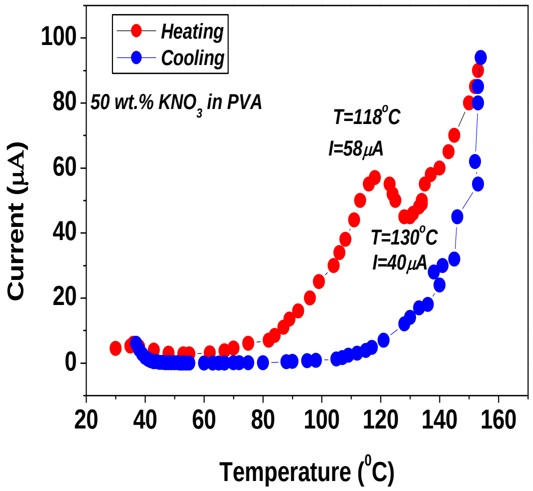

Fig. 3. Current vs. Temperature (I-T) characteristics of KNO_3: PVA composite films.

The Curie temperature obtained from the DSC measurements strongly supports the ferroelectric peak temperature as obtained from these measurements. In the cooling mode, there is no peak observed at this temperature range, it means that the co-existence of the paraelectric and ferroelectric phase up to room temperature.

2.4 Current vs. Temperature (I-T) Characteristics of the pure KNO_3:

The temperature dependence of I-T measurements of pure KNO_3 in pellet form has been studied. Figure shows the sharp peak at the increased value of temperature up to temperature (T=115°C) and the value of corresponding current is (I= 1.22μA) and above this temperature (T=130°C), the value of corresponding current is (I= 0.52 μA) during heating mode. This indicates the transition of ferroelectric phase in to paraelectric phase of KNO_3 in the composite films. The variation of peak current of I-T characteristics of the composite films is due to the existence of the polarization switching current. The Curie temperature obtained from the DSC measurements strongly supports the ferroelectric peak temperature as obtained from these measurements. In the cooling mode, there is a peak observed at the temperature T=115°C, it indicates the ferroelectric phase III of KNO_3, which is confirmed by the DSC measurements at this temperature.

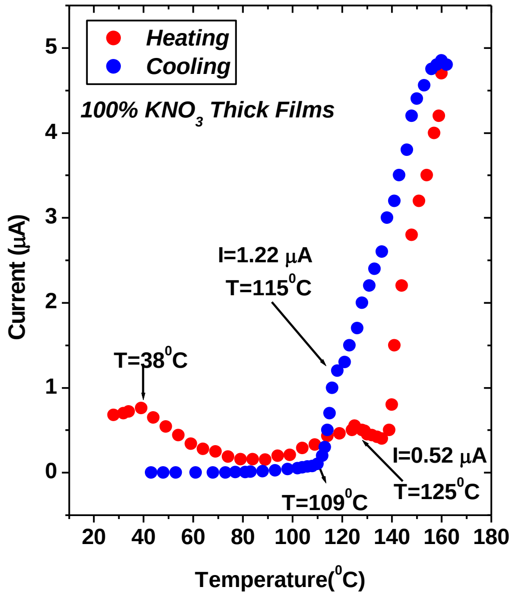

Fig. 4. Current vs. Temperature (I-T) characteristics of pure KNO_3.

2.5 Dissipation factor (tan δ) vs. temperature characteristics

Fig. 5 shows the variation of dissipation factor (tan δ) with temperature for the 50 wt.% composite films at the frequency 1 kHz. This plot indicates that the tan δ increased with rising in temperature during heating mode.

The increase value of dissipation factor of the composite film is due to the intermolecular / interfacial electrical polarization mechanism occurred in the composite film. At temperature ~ 130°C, the value of dissipation factor has been found to be 0.5 and increased up to 6.5 at temperature ~ 150°C. In cooling mode, there is n peak observed up to room temperature.

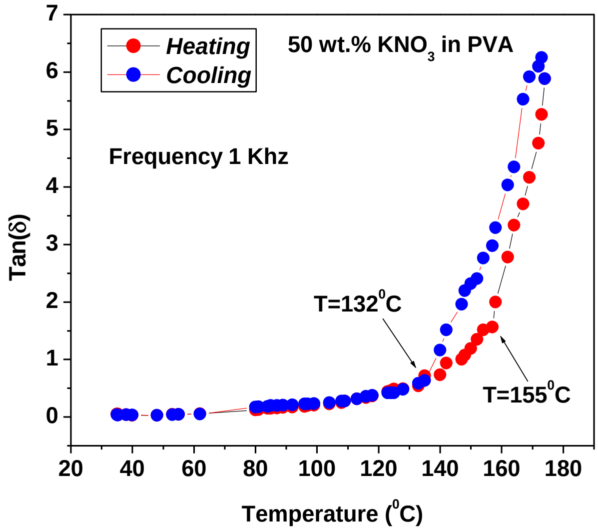

Fig. 5. Dissipation factor (tan δ) vs. temperature of the composite films.

3. Conclusions

The KNO_3: PVA composite films show the ferroelectric polarization current as observed by the I-V measurements at room temperature. I-T characteristics indicate the ferroelectric to paraelectric phase transition near the transition temperature of potassium nitrate in the composite films: The results of DC electrical conductivity supports to identify the different phases of potassium nitrate and corresponding value of activation energies. Dissipation factor (tan δ) plots for composite film exhibit the phase transition.

References

[1] M. Dawber, K. M. Rabe, J. F. Scott, Rev. Mod. Phys. **77,** 1083 (2005).

[2] V. Annapu Reddy, Navneet Dabra, J. S. Hundal, N. P. Pathak, R. Nath, Science of Advanced Materials**6** (5), 1043 (2014).

[3] K. P. Jayadevan, T. Y. Teng, J. Mat. Sci.: Mat. in Electr. **13**, 439 (2002).

[4] J. F. Scott, Ferroelectric memories, Springer-Verlag Berlin Heidelberg, Germany (2000).

[5] V. Annapu Reddy, Navneet Dabra, J. S. Hundal, N. P. Pathak, R. Nath, Science of Advanced Materials, **6**(6), 1228 (2014).

[6] V. Annapu Reddy, Navneet Dabra, J. S. Hundal, N. P. Pathak, R. Nath, Science of Advanced Materials, **6**(2), 235 (2014).

[7] B. Hilczer, Jan Kulek, E. Markiewicz, M. Kosec, Ferroelectrics **293**,253(2003).

[8] C. K. Chiang, R. Popielarz, Ferroelectrics**275**, 1 (2002).

[9] N. Dabra, J. S. Hundal, K. C. Sekhar, A. Nautiyal, R Nath, IEEE Trans. on Ultra., Ferro., and Freq. Cont. **56** (8),1627 (2009).

[10] N. Dabra, J. S. Hundal, K.C. Sekhar, A. Nautiyal, R Nath, J. of Amer. Cera. Soc. **92**(4), 834 (2009).

[11] A. Nautiyal, K. C. Sekhar, N. P. Pathak, R. Nath, N. Dabra, J. S Hundal, J. of App. Phy. A:Mater. Sci. & Pro. **99**(4), 941 (2010).

[12] A. Nautiyal, K. C. Sekhar, N. P. Pathak, R. Nath, N. Dabra, J. S Hundal, Ferroelectric Letters Section **38**, 51 (2011).

[13] N. Kumar, Navneet Dabra, J. S. Hundal, R. Nath, Ferroelectric Letter Section **40**(4-6), 108 (2013).

[14] NavneetDabra, J. S. Hundal, Dae-Yong Jeong, Baljinder Kaur, A. Nautiyal, V. Annapu Reddy, R. Nath, Materials Focus: **2**(6), 454 (2013).

[15] A. Nautiyal, Navneet Dabra, J. S. Hundal, N. P. Pathak, R. Nath, IEEE Dielectric and Electrical Insulation 2014 (accepted).

[16] Annapu Reddy.V., K. C. Sekhar, Navneet Dabra, A. Nautiyal, J. S. Hundal, N. P. Pathak, R. Nath, ISNR Materials Science Volume 2011, Article ID 142968 (2011) (doi:10.5402/2011/142968).

[17] S. Sawada, S. Namura, S. Fujii, J. Phys. Soc. Japan **13**, 1549(1958).

[18] J. P. Nolta, N. W. Schubring, Phys. Rev. Lett. **9**, 285 (1962).

[19] J. P. Nolta, N. W. Schubring, R. A. Dork, J. Chem. Phys. **42**, 508 (1965).

[20] S. Sawada, S. Nomura, Y. Asao, J. Phys. Soc. Japan **16**,2486 (1961).

[21] Neeraj Kumar, R. Nath, Polymer Engineering & Science- : John-Wiley and Sons; 2012.

[22] Neeraj Kumar, R. Nath, Advanced Materials Research, **403-408**, 607 (2012).

[23] Neeraj Kumar, R. Nath, J. Appl. Phys. **97**, 024105 (2005).

[24] J. Ruiz, A. Mantecon, V. Cadiz, J. Polymer Science: Part B: Polymer Physics **41**, 1462 (2003).

[25] K. E. Strawwhecker, E. Manias, Macromolecules, **34**, 8475(2001).

[26] Xiao-Dong Ma, Xue-Feng Qian, Jie Yin, Zi-kang Zhu, J. Mater. Chem. **12**, 663 (2002).

[27] K. E. Strawwhecker, E. Manias, Chem. Mater: **12**, 294300).

[28] M. Avella, M. E. Errico, R. Rimedio, J. Mat. Sci., **39**, 6133(2004).

[29] P. Frubing, M. Wegener, R. Gerhard- Multhaupt, A. Buchsteiner, W. Neumann, L. Brehmer, Polymer **40**, 3413(1999).

[30] S. A. Khairy, S. S. Ibrahim, J. Phys. D: Appl. Phys. **28**, 1919 (1995).

[31] K. C. Sekhar, R. Nath, J. Appl. Phys. **102**, 044114

(2007).

[32] Neeraj Kumar, R. Nath, Ferroelectrics Journal, **329**, 85 (2005).

[33] F. M. Herman, Encyclopedia of polymer science and technology, 3rd ed.(Wiley, New York**8**, p.401, 2003.

[34] G. Rohrer, S. Narayan, L. McMillan, A. Kulkarni, J. Vac. Sci. Technol. A **6**, 1756 (1988).

[35] Helinando P. de Oliveira,Celso P. de Melo, J. Appl. Phys. **101**, 084113 (2007).

[36] H. F. Mark, Encyclopedia of Polymer Science and Technology, Vol. **2**, John Wiley & Sons. Inc., Hoboken, New Jersey, pp. 438-458 (2003).

[37] A. Man Singh, A.M. Smith, J. Phys. D: Appl. Phys. **4**, 1792 (1971).

[38] F. EL-Kabbany, S. Taha, E. H. EL-Khawas, J. Mater. Sci. **24**, 1819(1989).

[39] A. Man singh, A. M. Smith, J. Phys. D: Appl. Phys. **4**, 560 971).

[40] J. F. Scott, Ming-sheng Zhang, R. Bruce Godfrey, C. Araujo, L. McMillan, Phys. Rev. B.**35**, 4044(1987).

[41] M. Balakanski, M. K. Teng, M. Nusimovici, Phys. Rev. **176**, 1098 (1968).

[42] D. Liu, F. G. Ullman, J. R. Hardy, Phys. Rev. B.**45**, 2142(1992).

[43] R. Murugun, A. Ghule, H. Chang, J. Appl. Phys.**86**, 6779(1999).

[44] V. N. Belomestnych, A. P. Hrolenko, On the Data of Ultra Acoustics and Heating Physics”, XI Session of the Russian Acoustical Society, Moscow, Nov. 19-23, (2001).

[45] Ruey-Ven Wang, P. C. Mclntyre, J. Appl. Phys.**97**, 023508 (2005).

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