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Glass-forming liquid kinetics manifested in a KTN:Cu crystal

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The relaxation processes in pure and copper-doped potassium tantalate niobate (KTN) were investigated by dielectric spectroscopy over a wide frequency and temperature range. In the copper-doped KTN above the ferroelectric phase transition temperature, a relaxation process was observed to behave according to the Vogel-Fulcher-Tammann model. This process was not observed in the pure KTN crystal. Following the Adam-Gibbs theory of glass-forming liquids, this behavior was attributed to a cooperative rearrangement of dipolar clusters that are formed by off-center niobium ions around the copper impurity ions. This interpretation was substantiated by the observed difference in the configurational entropy between Cu-doped KTN and pure KTN crystals derived from differential scanning calorimetry measurements.

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The nature of the glass state and the mechanism of the glass transition are considered one of the "deepest and most interesting unsolved problems in solid state theory".[1]

The material systems in which glass-forming kinetics were observed require supercooling below the melting point, where the relaxation processes of the supercooled liquid are much slower than the cooling rate. This leads eventually to the glassy transition where the material is frozen in an amorphous rather than crystalline state. Glass-forming phenomena have been observed and investigated in a variety of liquids.[2] We henceforth present glass-forming kinetics manifested in the cooperative behavior of copper impurities embedded in a potassium tantalate niobate (KTN) crystal.

KTN crystals ($KTa_{1-x}Nb_xO_3$) are ferroelectric perovskites that display both displacive-like and order-disorder-like properties.[3–6] It was found that for $x > 0.2$ the ferroelectric phase transition is first order occurring at $T_c \approx 682x + 33.2$ (Ref. 7). It was also found that at the ferroelectric phase transition the crystal structure is transformed from cubic to tetragonal. Further cooling incurs two additional structural transitions: tetragonal to orthorhombic and orthorhombic to rhombohedral.[7] Copper-doped KTN crystals have been shown to exhibit a strong photorefractive effect.[8] In particular it was shown that at the paraelectric phase of KTN:Cu the photorefractive gratings are voltage controlled,[8] making this material a suitable medium for electroholographic applications.[9]

For several decades dielectric spectroscopy methods were found to be an effective tool for the study of relaxation processes in glass-forming liquids.[10] In general, the relaxation time of the simplest relaxation process incurred by the transition between two states separated by an energy barrier E_a is given by the Arrhenius law

$$\tau = \tau_0 \exp(E_a/k_B T), \tag{1}$$

where k_B is the Boltzman constant, T is the temperature, and τ_0 is a prefactor corresponding to the minimum lifetime of the process at the high-temperature limit. The temperature dependence of the relaxation times of glass-forming systems was found to deviate from the Arrhenius behavior and to follow the Vogel-Fulcher-Tammann (VFT) equation

$$\tau = \tau_0 \exp[E_{\mathrm{VFT}}/k_B(T - T_{\mathrm{VFT}})], \tag{2}$$

where E_{VFT} is the VFT energy[11] and T_{VFT} is the ideal glass transition temperature (Vogel temperature) at which the relaxation time becomes infinite. It is regarded as the characteristic temperature of the dynamic glass transition.[10,11] The prefactor τ_0 here is not identical to τ_0 of Eqs. (1). As proposed by Adam and Gibbs[12] (AG), in glass-forming liquids viscous flow occurs by cooperative rearrangements of clusters of particles. Each cluster is supposed to be acting independently of other similar clusters in the system, but it is assumed that the minimum size of such an independent cluster is temperature dependent. This leads to

$$\tau = \tau_0 \exp(A/TS_c), \tag{3}$$

where A is a constant and S_c is the configurational entropy. If S_c goes to zero at a finite temperature ((i.e., $S_c = a[(T - T_k)/T]$, where T_k is the Kauzmann temperature representing the minimum in configurational entropy of the system under investigation),[2] the VFT equation is obtained with $T_{\mathrm{VFT}} = T_k$. Hence VFT relaxation is an indication of glass-forming behavior. It has been observed in different material systems[2,10] and was also observed in relaxor ferroelectrics, such as potassium lithium tantalate and lead scandium tantalate.[13,14]

In this paper we present results of the investigation of the dielectric relaxation in pure and copper-doped KTN crystals. We shall focus in particular on a relaxation process that occurs exclusively in the copper-doped KTN at the paraelectric phase. Two KTN crystals were investigated by both dielectric spectroscopy and differential scanning calorimetry (DSC). The crystals were grown by us using the top-seeded solution growth method.[15] The Ta/Nb ratio in both crystals was estimated by electron microprobe analysis and was found to be approximately 62/38 per mole. The first crystal (crystal No. 1) was doped with copper. The doping level was 2% in the flux yielding approximately 1.5×10^{-4} per mole in the grown crystal. The second crystal (crystal No. 2) was a pure KTN crystal. Samples of $1 \times 1 \times 2$ mm^3 were cut from the grown bole along the crystallographic [001] axes. The x-y faces of the samples (perpendicular to the growth direc-

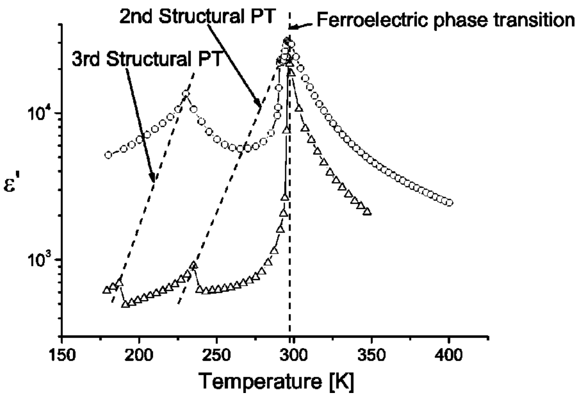

FIG. 1. The dielectric permittivity measured at 12 Hz: ○, crystal No. 1 (Cu-doped KTN); Δ, crystal No. 2 (pure KTN). The ferroelectric phase transition is at 295.6 K for both crystals, whereas the second structural phase transition is at 235 K for crystal No. 2, compared to 291.1 K for crystal No. 1.

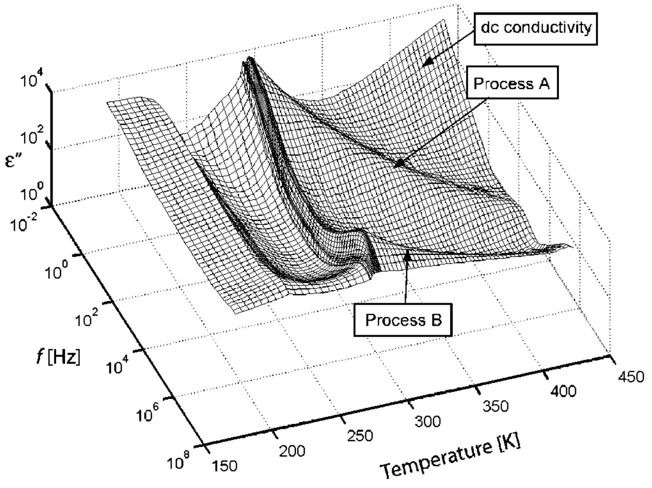

FIG. 2. The dielectric losses $[\mathrm{Im}(\varepsilon^*)]$ of crystal No. 1 (Cu-doped KTN).

tion z) were polished and coated with gold electrodes. Separate samples from the same bole were prepared without electrodes for DSC measurements.

The complex dielectric permittivity $\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)$ was measured in the frequency range of $10^{-2}-10^6$ Hz and the temperature interval 133–473 K. The estimated accuracy in temperature stabilization is better than 0.1 K and in the range of frequencies measured the error in $\tan(\delta)$ of the dielectric values is less than 10^{-4} (Ref. 16). The crystals were cooled from 297 K to 190 K with a temperature step of 4 K. In the region of the phase transition, 292–297 K, the temperature step was reduced to 0.5 K. Reheating from 190 K to 440 K was done with a step of 5 K. As before, in the region of the ferroelectric phase transition the step was reduced to 0.5 K. For the DSC measurements the cooling and heating rates were 5 K/min in an interval ranging from 373 K to 220 K.

The dielectric permittivity (ε') of both samples, measured at 12 Hz, is presented in Fig. 1. The three structural phase transitions typical to KTN (Ref. 7) are apparent in both crystals. In particular, in crystal No. 1 the ferroelectric (cubic-to-tetragonal) transition occurs at 295.6 K, whereas the tetragonal-to-orthorhombic and orthorhombic-to-rhombohedral transitions occur at 291.1 K and 230 K, respectively.

The three-dimensional landscape of the dielectric losses as a function of temperature and frequency of crystal No. 1 is presented in Fig. 2. The complex dielectric response of crystal No. 1 can be described in terms of a number of distributed dynamic processes separated by different frequency and temperature ranges. In the paraelectric phase, above 295.6 K, there is a thermally activated process (process A) starting in the low frequencies at the phase transition and shifting towards higher frequencies as the temperature increases. The quantitative nature of process A was established by examining the temperature dependence of τ^A, obtained as the inverse value of the characteristic frequency $f_m(T)$ along the crest representing process A in the $\varepsilon''(T,f)$ landscape.[17] Quantitative examination of the temperature dependence of τ^A for process A revealed that it follows the Arrhenius curve (1) with an activation energy of $E_a^A=0.94\pm0.01$ eV and the high-temperature limit of the relaxation time $\tau_0^A=1.7\pm0.4\times10^{-15}$ s. At the high-temperatures region process A was found to be correlated with well-pronounced dc conductivity. The dc conductivity σ was found to follow Arrhenius behavior—namely, $\sigma=\sigma_0\exp(-E_\sigma/k_BT)$, with an activation energy of $E_\sigma=0.9\pm0.01$ eV and the high-temperature limit of conductivity $\sigma_0=42\pm7$ s m^{-1}. The fact that both process A and the dc conductivity are Arrhenius in form with similar activation energies suggests that both processes originate from the same physical mechanism. Since the Nb-O bond is covalent in nature with bond energy of 12.10 eV (Ref. 18), the dc conductivity is most likely provided by electron mobility. An additional process (process B) that transcends through all the three phase transitions and was found to be non-Arrhenius was observed in crystal No. 1 and was not observed in crystal No. 2. The dynamic features of process B can be extracted from the temperature dependence of relaxation time τ^B obtained as inverse value of characteristic frequency f_m in the same manner as for process A (see Fig. 3). Note first that the three phase transitions are evident in the relaxation time picture (see also Fig. 1), and each delineates a change in its behavior. In the high-temperature range, down to 354 K, process B exhibits an Arrhenius behavior with the activation energy $E_a^B=0.37\pm0.01$ eV and $\tau_0^B=2.8\pm0.9\times10^{-12}$ s. At $T_x=354$ K process B changes its behavior to a VFT process in which τ^B is given by Eq. (2) with VFT temperature $T_{\mathrm{VFT}}=228$ K and $E_{\mathrm{VFT}}=0.02$ eV.

Following the onset of the ferroelectric phase transition τ^B decreases until it reaches a minimum at 264 K, exhibiting a small cusp at the second (tetragonal-to-orthorhombic) phase transition. Upon further cooling τ^B increases until it reaches a maximum at the third (orthorhombic to rhombohedral) transition at 230 K.

As process B was observed only in crystal No. 1 (see Fig. 4) it must be attributed to the presence of the Cu impurities embedded at random in the KTN crystal. The Arrhenius nature of the process at elevated temperature above 354 K indicates normal relaxation of the independent Cu$^+$ ions. These

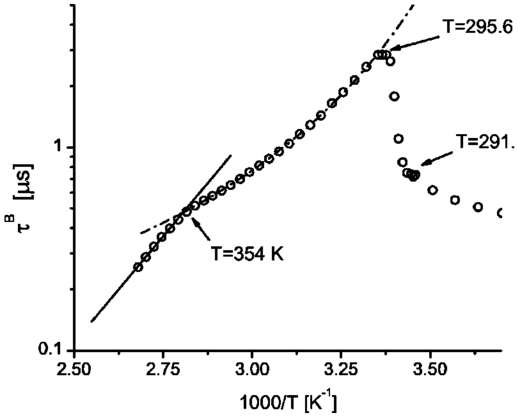

FIG. 3. The relaxation time (τ_B) versus inverse temperature for process B in the paralectric phase of crystal No. 1. The symbols correspond to the experimental data, the solid line represents the Arrhenius law (1), and the dash-dotted line represents the VFT law (2).

ions are significantly smaller than the K^+ site in which they reside. (The radii of the Cu^+ and the K^+ are given by 0.71 Å and 1.53 Å, respectively.) The Cu^+ ions can therefore hop between the eight symmetrical minima of their potential well. Indeed, the energy of activation of $E_a^B = 0.37$ eV corresponds to activation energies for the hopping of transition metal ion impurities in $KTaO_3$ (Ref. 19).

As pointed out above, the VFT relaxation that occurs here as the crystal is cooled down towards the phase transition is characteristic to glass-forming liquids. According to the AG theory, this behavior originates from the cooperative rearrangement of some clusters. It is well established that in KTN at the paraelectric phase the Nb^{5+} ions are displaced from the center of inversion of the unit cell.[4] These displacements form a dipolar cluster with a correlation length that increases as the system is cooled towards the ferroelectric phase transition. We propose that the cooperative relaxation that is observed at $T < 354$ K is produced by the interaction between such dipolar clusters that are formed around the relaxing Cu^+ ions and act as the rearranging clusters in the AG model. Adopting the formalism of AG (Ref. 12) the minimum cluster size z is related to the rate of relaxation $P(T,z)$ by

$$P(T,z) \propto \exp\left(-z\frac{\Delta\mu}{k_B T}\right). \qquad (4)$$

As pointed out above, the Kauzmann temperature T_k and the chemical potential $\Delta\mu$ can be equated to T_{VFT} and E_{VFT}, respectively.

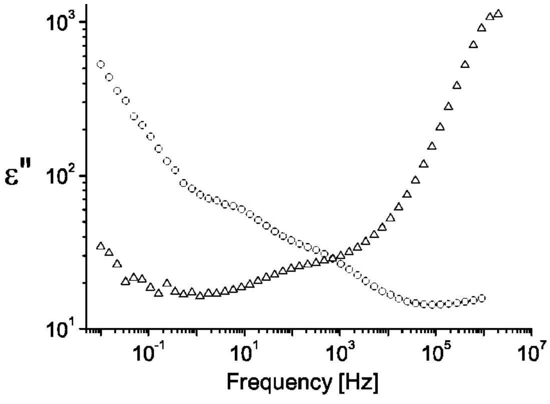

FIG. 4. A comparison of the dielectric losses measured at $T = 250$ K: Δ, crystal No. 1 (KTN doped with Cu ions); ○, crystal No. 2 (pure KTN).

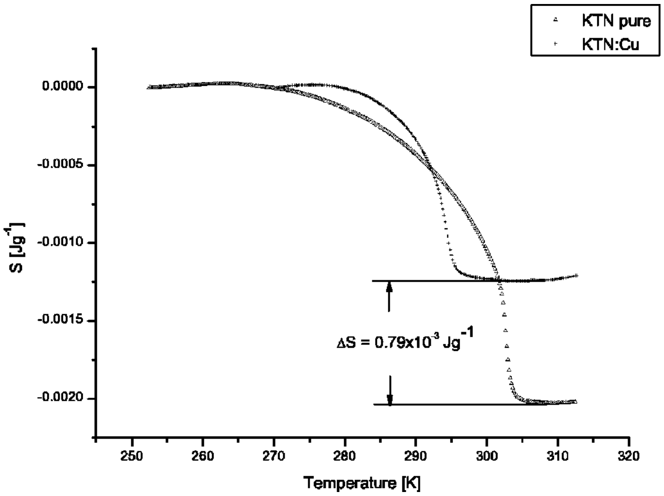

FIG. 5. The entropy as a function of temperature for crystals No. 1 and No. 2, as they pass through the ferroelectric phase transition. The difference is attributed to the contribution made to configurational entropy by the presence of Cu ions in the crystal lattice.

Let us define the VFT region of process B as the temperature region spanned between the temperature at which $\tau^B(T)$ deviates from the Arrhenius model—namely, $T_x = 354$ K and the ferroelectric phase transition temperature $T_c = 295.6$ K. Fitting the VFT model to the experimental results of τ^B in the VFT region yields $T_k = 228$ and $\Delta\mu = 0.02$ eV. Identifying the temperature at which τ^B deviates from the Arrhenius model with the onset of cooperativity yields a minimum cluster size given by

$$z = \frac{T_x}{T_x - T_k} = 2.8. \qquad (5)$$

This coincides well with an estimation of the minimum size of the dipolar cluster formed around the nearest-neighbor Nb^{5+} ion given by

$$[Nb^{5+}]^{-1} = [0.38]^{-1} \approx 2.63.$$

At elevated temperatures ($T > 354$ K), the Nb^{5+} ions hop at random between equivalent minima of their potential within their site in the unit cell. As the phase transition is approached these ions form a dipolar cluster around the Cu^+ ions that are randomly distributed far apart from each other. These clusters are at first with a minimum size containing only the Nb^{5+} ions that are closest to the Cu^+ ion. As the phase transition is approached further, the crystal softens and the cluster size around the Cu^+ ion grows accordingly. These are the rearranging clusters of the AG theory.

An independent assessment of the validity of the AG interpretation to the Cu^+-induced relaxation (process B) was provided by direct estimation of the configurational entropy.

The latter was derived from DSC measurements in the vicinity of the ferroelectric phase transition. It is well known that the configurational entropy can be evaluated from the heat capacitance of the crystal by the integral

$$S_C(\Delta T) = \int_{\ln T_1}^{\ln T_2} [C_p(\ln T) - C_P(\text{base line})] d(\ln T), \quad (6)$$

where T_1 is the onset and T_2 is the completion of the phase transition, and $C_P(\text{base line})$ is the extrapolated base line heat capacitance in the temperature interval.[20] The results for the pure KTN crystal (No. 2) and the copper-doped KTN crystal (No. 1) are presented in Fig. 5. The resulting difference was found to be $\Delta S = 0.79 \times 10^{-3}$ J g^{-1}. Normalized to the Cu ion content we have per Cu ion $\Delta S_{\mathrm{Cu}} = 2.068 \times 10^{-21}$ J ≈ 0.013 eV. This result is good agreement with $\Delta\mu = 0.02$ eV derived from fitting the VFT model to $\tau^B(T)$, given the spatial variation of the Cu concentration in the crystal.

At the onset of the ferroelectric phase transition the Cu^+ ions are frozen and no longer constitute the seed of the relaxation process. In this respect the ferroelectric phase transition "quenches" the glass-forming liquid.

Below the phase transition the dipolar clusters surrounding the Nb^{5+} ions merge to yield the spontaneous polarization of the (now ferroelectric) crystal, and due to the strong crystal field, the off-center potential minima of the Cu^+ ions are no longer symmetrical.

Thus, in conclusion one may summarize the physical picture of the relaxation dynamics in KTN crystal doped with Cu ions in the following way: In the paraelectric phase as the ferroelectric phase transition is approached, the Nb^{5+} ions form dipolar clusters around the randomly distributed Cu^+ impurity ions. The interaction between these clusters gives rise to a cooperative behavior according to the AG theory of glass-forming liquids. At the ferroelectric phase transition the cooperative relaxation of the Cu^+ ions is effectively "frozen."

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[1] P. W. Anderson, Science **267**, 1615 (1995).
[2] C. A. Angel, Science **267**, 5206 (1995).
[3] R. Comes *et al.*, Ferroelectrics **12**, 3 (1976).
[4] Y. Yacoby, Z. Phys. B **31**, 275 (1978).
[5] M. D. Fontana, G. Metrat, J. L. Servoin, and F. Gervais, J. Phys. C **17**, 483 (1984).
[6] M. D. Fontana, H. Idrissi, and K. Wojcik, Europhys. Lett. **11**, 419 (1990).
[7] C. H. Perry, R. R. Hayes, and N. E. Tornberg, in *Proceeding of the International Conference on Light Scattering in Solids, 1975*, edited by M. Balkansky (Wiley, New York, 1975), p. 812.
[8] A. J. Agranat, V. Leyva, and A. Yariv, Opt. Lett. **14**, 1017 (1989).
[9] A. J. Agranat, in *Infrared Holography for Optical Communications, Topics in Applied Physics*, Vol. 86, edited by P. Boffi, P. Piccinin, and M. C. Ubaldi (Springer-Verlag, Berlin, 2003), p. 129.
[10] F. Kremer and A. Shönhals, in *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Shönhals (Springer-Verlag, Berlin, 2002), p. 99.
[11] M. D. Ediger, C. A . Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13 200 (1996).
[12] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[13] J. Toulouse, B. E. Vugmeister, and R. Pattnaik, Phys. Rev. Lett. **73**, 3467 (1994).
[14] B. E. Vugmeister and H. Rabitz, Phys. Rev. B **57**, 7581 (1998).
[15] R. Hofineister, S. Yagi, A. Yariv, and A. J. Agranat, J. Cryst. Growth **131**, 486 (1993).
[16] User's Manual, Alpha High Resolution Dielectric Analyzer, Novocontrol GmbH, 1999.
[17] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949), p. 74.
[18] A. Villesuzanne, C. Elissalde, M. Pouchard, and J. Ravez, Eur. Phys. J. B **6**, 307 (1998).
[19] K. Leung, Phys. Rev. B **65**, 012102 (2001).
[20] R. K. Pathria, *Statistical Mechanics* (Butterworth-Heineman, Oxford, 1996), p. 15.