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Ferroelectric phase transition in thiourea:KBr composites studied with optical second-harmonic generation

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We present results of an experimental study on the effect of the inclusion of ferroelectric thiourea particles in paraelectric amorphous KBr on the ferroelectric phase transition. The phase transition as a function of temperature has been observed with optical second-harmonic generation (SHG) of infrared light. The Curie temperature T_c shows a minimum as a function of the volume fraction x of thiourea in the composites at $x=0.4$. We describe the experimentally observed density dependence of the Curie temperature in a phenomenological mean-field model. © 1995 American Institute of Physics.

I. INTRODUCTION

The interest in composite materials has increased dramatically in recent years, due to developments in technology and the discovery of new physical phenomena in composite systems, such as anomalous dielectric behavior, percolation phase transitions, and high- T_c superconductors. The study of composite samples consisting of finite size particles embedded in host materials with different dielectric properties is a rapidly developing field.^{1,2} The ability to control the properties of the composites by changing the compound structure has strongly increased the technological interest in composites.

The length scales present in these systems, which are large compared to atomic length scales, allow a classical description of the interactions present in the samples. The theoretical difficulties in describing these systems often forces one to use an effective-medium approximation (EMA).³ One of the objections to EMA is that correlations between particles in the composites are neglected. Mean-field theory for the dielectric constant of a disordered system of polarizable particles leads to the well-known Clausius-Mossotti formula.⁴ When applied to a suspension of finite size spheres this results in the Maxwell-Garnett formula.⁵ Recent theoretical and numerical studies² of composites consisting of dielectric spheres randomly dispersed in a homogeneous background of different dielectric constant, show significant deviations from the Clausius-Mossotti formula.

In this paper we present a study on the density dependence of the properties of a composite material, consisting of a powdered ferroelectric material embedded in an amorphous paraelectric host material near the ferroelectric phase transition. For the study, we chose the well-known ferroelectric thiourea, $\text{SC}(\text{NH}_2)_2$, and the paraelectric KBr, for thiourea shows drastic changes of the nonlinear properties over the ferroelectric phase transition,⁶⁻⁸ and KBr is convenient for it has a low plasticity pressure.

In many ferroelectrics the origin of ferroelectricity is associated with structural phase transitions, where a symmetry breaking occurs. This symmetry breaking, specifically from a centro-symmetric to a noncentro-symmetric crystal structure can be studied with optical second-harmonic generation (SHG), for in the dipole approximation SHG is forbidden when a center of symmetry is present in the structure of the crystal.⁹ Thus structural phase transitions can be observed as drastic changes in the measured SHG signal.

II. PROPERTIES OF THIOUREA

An elaborate study of the structure properties and dielectric constant of thiourea as function of temperature and electric field can be found in the article of Goldsmith and White.⁶ At ambient pressure and temperature, thiourea has an orthorhombic lattice structure and shows a number of phase transitions as a function of temperature. The first phase transition takes place at $T_c = 168$ K, from the ferroelectric phase (phase I) to an incommensurate structure (phase II).^{7,8} The point group of the ferroelectric phase is C_{2v}^2 ($P2_1ma$)⁷ which has no center of symmetry. At 173 K, thiourea shows a phase transition from the incommensurate structure (phase II) to a second ferroelectric phase (phase III), where the spontaneous polarization is much weaker compared to phase I. At 179 K the structure changes from ferroelectric to a second incommensurate structure (phase IV),^{7,8} while at $T_i = 202$ K thiourea shows a phase transition from phase IV to the paraelectric phase V. The point group of the paraelectric phase is D_{2h}^{16} ($Pnma$)⁷ which has a center of symmetry.

The incommensurate structures are essentially centro-symmetric, but show a modification of the unit cell with a modulation period of a number of unit cells. The spontaneous polarization in phase I and III is directed along $[010]$. Measurements of the birefringence of thiourea reveal strong interdependence with the structural phase transitions.¹⁰ Maxima in the static dielectric constant appear at T_i and T_c .^{6,8} A distinct maximum occurs at 177 K and is connected with the second ferroelectric phase (phase III).⁶

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FIG. 1. Illustration of the experimental setup. Optical beams are drawn as solid lines, electronic connections are drawn as dashed lines.

FIG. 2. SHG signal as a function of temperature, measured on pure thiourea powder in a complete temperature cycle. The arrows indicate the direction of the scan.

III. SAMPLE PREPARATION

The materials used are thiourea and potassium bromide (KBr), which are separately milled with an impact mill to an average particle size of $25 \mu\text{m}$ and a particle size distribution of $\approx 10 \mu\text{m}$ width, as was observed by microscopic inspection. The thiourea particles are transparent and show all the features of the raw single crystals, thus they have not been amorphized by the milling process. At a chosen volume ratio, the powders of thiourea and KBr are well mixed and compressed with a hydraulic press to a pressure of 5 kbar, at which KBr becomes amorphous and the homogeneously distributed thiourea particles are embedded after releasing the pressure, as was observed by microscopic inspection.

We have obtained composite samples of different volume fractions of thiourea powder, homogeneously distributed in amorphous KBr. As a function of temperature samples of pure KBr show no detectable optical SHG signal, thus KBr is applicable as a host material for the thiourea particles. Before measurements are performed, the samples are thoroughly annealed at 393 K for 24 h to efficiently reduce the effects of internal strain in the samples. Without annealing the samples the Curie temperature changes with every temperature cycle, while with annealing we obtain a reproducible T_c .

IV. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. The output of a Q-switched Nd:YAG laser impinges on a sample in a homebuilt liquid-nitrogen cryostat. The output of the laser consists of 650 mJ pulses of 2 ns duration (FWHM) at 1064 nm wavelength with a repetition rate of 20 Hz. The beam is attenuated to 4 mJ per pulse to prevent damage and heating of the sample. The part of the beam split off by the attenuators is used to monitor the pulse energy during the measurements.

The sample is mounted on a copper head containing a manganin-wire heater and a platinum resistance thermometer placed right below the sample. The temperature of the head is adjustable from 77 to 330 K with a 0.5 K accuracy. The temperature-scale calibration is accurate within 1 K.

The SHG signal produced by the sample is collected by a parabolic mirror and projected towards the entrance slit of a triple-grating spectrometer. The spectrometer projects the second-harmonic light to a microchannel plate intensified CCD (Princeton Instruments ICCD-576/SB). The collection efficiency of the second harmonic light is estimated to be ≈ 0.01 . The ICCD detector integrates the SHG signal over all its pixels, and is thus effectively used as a very sensitive single-channel detector. The ICCD is gated with a 20 ns electronic gate pulse, synchronized to the arrival of the pulsed SHG signal through use of a digital-delay pulse generator as a trigger for the Q-switch of the laser and the gate-pulse generator.

V. EXPERIMENTAL RESULTS

We have measured the SHG signal as function of temperature on samples of pure thiourea powder and with samples of different volume fractions of thiourea in the composites. The SHG signal is corrected for the background due to dark count of the detector, and for the fluctuating fundamental laser power.

In Fig. 2 we show the result of a measurement on pure thiourea powder over a complete temperature cycle. At the observed phase transition, the SHG signal decreases nearly three orders of magnitude. By defining the Curie temperature T_c as the bending point of the logarithmic SHG signal curve with increasing temperature we obtain $T_c = 168 \text{ K}$ for pure thiourea, in very good agreement with the value quoted in the literature.⁶⁻⁸

A pronounced hysteresis with respect to temperature is observed to occur in the SHG signal. The width of the hysteresis with respect to temperature is 8 K for pure thiourea powder, as taken from the temperature difference between the half-maximum points in the logarithmic SHG curve. The incommensurate structures of thiourea, which occur between 168 and 173 K (phase II), 179 and 202 K (phase IV), and the paraelectric phase (phase V) show no significant SHG signal.

FIG. 3. SHG signal as a function of scaled temperature measured on different volume fractions of thiourea in the composites with KBr. The inset indicates the volume fractions that are investigated. The arrows indicate the direction of the scan.

In Fig. 3 we show the SHG signal obtained by performing the SHG measurement over a complete temperature cycle for different volume fractions x of thiourea in the composite. The temperature range of each curve is scaled with respect to the observed transition temperature according to $(T - T_c)/T_c$, where T_c is obtained from each scan as the bending point of the logarithmic SHG curve. The strength of the SHG signal for different volume fractions does not show a functional dependence on the volume fraction x . They are equal within a factor 1.5. As shown in Fig. 3, the curves of the SHG signal show a scaling behavior in the direction of increasing temperature. The pronounced hysteresis observed shows a maximum and minimum width of 25 and 18 K, respectively, and does not depend systematically on the volume fraction.

Time-dependent measurements below T_c of the SHG signal for different volume fractions show a nearly exponential behavior of the SHG signal to an equilibrium value with an exponential decay time of 5 min. In all the measurement the time between adjacent temperature points was 5 min.

In Fig. 4 we show the observed Curie temperature for different volume fractions of thiourea in the composite with KBr. The Curie temperature T_c shows a surprising minimum at a volume fraction $x \sim 0.4$ of thiourea in the composites. The error bars drawn in Fig. 4 result from the inaccuracy in calibration of the temperature reading, and from the inaccuracy in the determination of T_c . The estimated error is ± 3 K. In Sec. VII we will introduce a phenomenological model which describes the observed behavior of T_c .

VI. DISCUSSION

For pure thiourea powder, with an average particle size of 25 μm , we observe a first order phase transition at $T_c = 168$ K, equal to the T_c of bulk crystal thiourea. The reduced size of the crystallites does not alter the order of the transition nor the Curie temperature. Significant effects are only expected to occur at much smaller particle sizes.¹¹

FIG. 4. Experimentally determined phase-transition temperature as a function of volume fraction of thiourea in the composite with KBr. In the figure the electrostatic energy $W(x)$ is drawn as the solid line using $\epsilon_{\text{KBr}} = 15$, $\epsilon_{\text{thio}} = 100$ and $\Gamma\Psi = -5500$ J. The model describing $W(x)$ and the variables Γ and Ψ are explained in Sec. VII.

As a function of temperature, the molecular nonlinear susceptibility $\chi^{(2)}$ decreases slowly due to the increasing thermal motion of the molecules, explaining the gradual decrease of the SHG signal in the single phase region below and above T_c . The collapse of $I(2\omega)$ with three orders of magnitude over the phase transition cannot be attributed to $\chi^{(2)}$, because the polarizability of the molecules does not change drastically.⁶ The change in the symmetry of the crystal unit cell of thiourea (see Sec. II) from noncentrosymmetry to centro-symmetry accounts for the collapse of $I(2\omega)$ over the phase transition.

The ferroelectric phase III of thiourea, which occurs between 173 and 179 K, is not observed in the pure powder with optical SHG, although the transition from phase II to phase III is caused by a structural phase transition.⁶ This structure is absent in the phase diagram of the thiourea powder, probably caused by the reduced size of the thiourea crystallites. Because the spontaneous polarization in phase III is known to be almost three orders of magnitude smaller than in phase I, we can expect the SHG signal to be much smaller compared to $I(2\omega)$ measured in phase I.

The maximum SHG signal measured on the composite samples is weaker than measured on pure thiourea powder, but does not show a systematic dependence on the volume fraction of thiourea in the composites. Due to the presence of KBr between the thiourea particles, the refractive-index mismatch compared to thiourea in vacuum is reduced. This allows the fundamental and second harmonic light to travel deeper into the sample and reduces the back scattering of the light. The refractive-index mismatch still causes the incoming light to scatter and hence limits the depth to which the light can travel into the sample. For smaller volume fractions x of thiourea in the samples, this depth becomes larger and therefore also the volume that is probed optically. These effects counterbalance, explaining the absence of a functional dependence on the volume fraction of the maximum SHG signal.

Above T_c the SHG signal measured is attributed to the occurrence of SHG on the interface of the thiourea particles with vacuum or with the KBr environment where the symmetry is broken.¹²

The average width of the hysteresis with respect to temperature in the SHG signal as measured on the composite samples, is much larger than the width of hysteresis as measured on pure thiourea. As a result of the separation of the thiourea particles by the KBr matrix the particles are no longer strongly coupled neighboring particles. Individual particles of different size will have different transition temperatures and thus the size distribution is reflected in the increase of the width of the hysteresis. Because the width does not depend systematically on the volume fraction of thiourea the effect of separation of the thiourea particles by the KBr matrix occurs already in slightly diluted samples. The scaling behavior of the SHG curves in the direction of increasing temperature indicates the presence in all the composite samples of the same mechanism which drives the phase transition.

The most striking feature observed in the composites of thiourea in KBr is the strong dependence of the transition temperature T_c on the volume fraction x , and the occurrence of a minimum in this curve at $x=0.4$, as shown in Fig. 4. In the limit of pure thiourea samples, T_c increases to the Curie temperature of pure thiourea powder. In the limit of one crystallite embedded, T_c does not decrease to zero because it is an individual system.

VII. PHENOMENOLOGICAL MODEL

In order to interpret the occurrence of the minimum in T_c , we introduce a phenomenological model in which we calculate the work W per ferroelectric thiourea particle necessary to form the polarization of the sample. We separate three terms; W_1 is the work necessary to polarize one thiourea particle, W_2 is the work necessary to polarize the composite environment of the polarized particle by its field, and W_3 the work necessary to polarize the entire sample. The work is calculated by

$$W = -\frac{1}{2} \int_{\text{space}} \frac{1}{\epsilon_0(\epsilon_r - 1)} P^2 d\tau, \quad (1)$$

where $\mathbf{P}$ is the polarization present in the volume of integration, ϵ_r is the relative static dielectric constant of the material in the volume of integration, and $d\tau = dx dy dz$. The work is set equal to zero for the nonpolar phase of the particles.

We associate the spontaneous polarization $\mathbf{P}$ of the thiourea particles and of the entire sample with a field, according to

$$\mathbf{P} = \epsilon_0(\epsilon_r - 1)\mathbf{E}. \quad (2)$$

Integration over the particle volume results in

$$W_1 = \Psi \frac{1}{(\epsilon_{\text{thio}} - 1)}, \quad \Psi = \frac{-2\pi a^3 P_s^2}{3\epsilon_0}, \quad (3)$$

where P_s is the spontaneous polarization of the thiourea particle at the phase transition, ϵ_{thio} is the relative static dielectric constant of thiourea at the phase transition, and a is the particle radius.

The work associated with the polarization of the composite environment by the electric field of ferroelectric particle is calculated by performing Eq. (1) over the area outside the particle, using the expression for the field of a point dipole¹³ with $\mu = 4\pi/3 a^3 \mathbf{P}$ as the dipole moment. The effective relative dielectric constant of the environment of the dipole is given by the Maxwell-Garnett⁵ expression

$$\frac{\epsilon_{\text{eff}}}{\epsilon_{\text{KBr}}} = \frac{1 + 2x\beta}{1 - x\beta}, \quad \beta = \frac{\epsilon_{\text{thio}} - \epsilon_{\text{KBr}}}{\epsilon_{\text{thio}} + 2\epsilon_{\text{KBr}}}, \quad (4)$$

where ϵ_{KBr} is the relative static dielectric constant of the paraelectric KBr. The calculation results in

$$W_2 = 2\Psi \frac{(\epsilon_r - 1)}{9\epsilon_r^2}. \quad (5)$$

We calculate the work associated with the spontaneous polarization of the entire sample by diluting pure thiourea with KBr and calculating Eq. (1) over a large spherical sample with radius R under the condition, $a \ll R$. This energy is divided by the number of particles $N = xR^3/a^3$. The spontaneous polarization of the entire sample depends linearly on the volume fraction of thiourea in the samples, for x is a measure of the number of particles. The calculation results in the following expression:

$$W_3 = \Psi \frac{x}{(\epsilon_r - 1)}. \quad (6)$$

The minimum in T_c can be understood in terms of two competing effects present in the composite samples. First, the coupling of the dipole to the external field caused by the surrounding ferroelectric crystallites tends to increase as the volume fraction of thiourea increases (W_3), i.e., the interparticle distance decreases. Secondly, the polarization of the environment of the dipole by its dipole field tends to decrease as the effective dielectric constant of the environment is increased (W_2). These two counteracting effects balance at the minimum in T_c . When the particle size a is further reduced, the self-energy of a ferroelectric particle is reduced thus the T_c in the limit of very low x decreases. The minimum in T_c can then be expected to move to lower x for the polarizing effect of the particle is reduced with decreasing particle size.

The dependence of T_c on x is related to the electrostatic interaction energy W , where $W(x) = W_1(x) + W_2(x) + W_3(x)$, for the free-energy F will contain W as calculated in the model. T_c is determined as the temperature where the two stable phases (polarized and nonpolarized) of F have equal energy, as is shown in a plot of the power series expansion of F in terms of the polarization P for a first order transition.¹⁴ W contains a term P^2 in the prefactor Ψ . As x is altered W is changed according to W_2 and W_3 , thus the prefactor of the P^2 term in the expansion of F . In order to re-establish the equality of energy of the two stable phases of

FIG. 5. Electrostatic energy $W(x)$ for different values of the relative dielectric constant ϵ_{thio} of thiourea, where $\epsilon_{\text{KBr}}=3$. $\epsilon_{\text{thio}}=20, 40, 100, 200, 10^3, 10^4$ respectively. The curves have been scaled to a common point at $x=1$.

F the temperature has to be changed. As for $x=1$ we obtain $T_c=168$ K, $T_c(x)$ can be evaluated according to,

$$k_b \Delta T_c(x) = \Gamma \Delta W(x), \quad (7)$$

where k_b is the Boltzmann constant and the prefactor Γ is the proportionality constant between ΔT_c and $\Delta W(x)$. $W(x)$ is fixed to the T_c of the pure thiourea powder. Using $\epsilon_{\text{KBr}}=3$ from high frequency powder capacitance measurements,⁴ the model converges to a minimum in T_c near $x=0.25$ for increasing ϵ_{thio} , and this minimum remains almost fixed for $\epsilon_{\text{thio}} > 10^2$. Thus we can use $\epsilon_{\text{thio}} \approx 10^4$ which is the value measured right below T_c for single-crystal thiourea in the direction of the spontaneous polarization [010].^{6,8} A good fit is obtained for $\epsilon_{\text{thio}}=100$, $\epsilon_{\text{KBr}}=15$, and $\Gamma\Psi=-5500$ J, shown in Fig. 4 as the solid line. $W(x)$ is shown in Fig. 5 for a number of values of ϵ_{thio} . Note the convergence of the minimum for increasing ϵ_{thio} . The prefactor $\Gamma\Psi$ can be used

to calculate the dipole moment, i.e. the spontaneous polarization of the ferroelectric thiourea particles once the proportionality constant Γ is known.

In conclusion, embedding of the powdered ferroelectric in a paraelectric KBr host strongly changes the Curie temperature, and even gives rise to a striking minimum as function of the volume fraction. In future research one could study the effects of using smaller particle size and different host materials with different dielectric constant on the minimum in the Curie temperature as a function of the volume fraction of the ferroelectric, in order to obtain a clearer picture of the composite and of the validity of the model.

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