



# Phase transitions in tris-sarcosine calcium chloride (TSCC) to 14 GPa

Authors: Z.X. Bao, V. Hugo Schmidt, and F.L. Howell

This is an Accepted Manuscript of an article published in [Ferroelectrics](#) on [date of publication], available online: <http://www.tandfonline.com/10.1080/00150199308222452>

Z.X. Bao, V.H. Schmidt, and F.L. Howell, "Phase transitions in tris-sarcosine calcium chloride (TSCC) to 14 GPa," *Ferroelectrics* 145, 241-245 (1993).

<http://dx.doi.org/10.1080/00150199308222452>

Made available through Montana State University's [ScholarWorks](#)  
[scholarworks.montana.edu](http://scholarworks.montana.edu)

# PHASE TRANSITIONS IN TRIS-SARCOSINE CALCIUM CHLORIDE (TSCC) TO 14 GPa

Z. X. BAO,<sup>†</sup> V. H. SCHMIDT and F. L. HOWELL<sup>‡</sup>

*Department of Physics, Montana State University, Bozeman, MT 59717 USA*

*(Received December 2, 1992)*

The capacitance of samples of tris-sarcosine calcium chloride (TSCC) has been measured at room temperature at pressures up to 14 GPa. A diamond anvil cell was employed to control the pressure. Experimental results indicate that TSCC undergoes two phase transitions, near 1.3 GPa and 4.1 GPa.

*Keywords: high pressure, diamond anvil cell, ferroelectric*

## I. INTRODUCTION

Tris-sarcosine calcium chloride (TSCC),  $(\text{CH}_3\text{NHCH}_2\text{COOH})_3\text{CaCl}_2$ , exhibits a ferroelectric (FE) phase transition at  $T_c = 127$  K.<sup>1</sup> It has attracted considerable interest because of its very weak spontaneous polarization associated with sarcosine ion ordering in its pseudo-hexagonal but actually orthorhombic<sup>2</sup> Pnma structure. Recent work includes dielectric dispersion,<sup>3</sup> Brillouin scattering,<sup>4-6</sup> infrared studies,<sup>7</sup> nuclear magnetic resonance (NMR),<sup>7,8</sup> and electron paramagnetic resonance (EPR).<sup>9,10</sup> The EPR results have been interpreted in terms of incommensurate modulation of the structure. The Brillouin scattering frequency versus temperature results near the FE transition show anomalies related to the weak spontaneous polarization. Another effect related to the weak polarization is an internal bias, whose strength is dependent on crystal quality, and which is evidenced by increase of ac dielectric permittivity upon applying a dc field of the correct polarity.<sup>11</sup>

Although TSCC is hydrogen-bonded, its deuterated crystal DTSCC shows almost no shift in  $T_c$ , unlike  $\text{KH}_2\text{PO}_4$  in which deuteration raises  $T_c$  from 123 to 223 K. This is because the hydrogen bonds are of the intrinsically asymmetric N—H . . . O type, in which the protons are always closer to the nitrogens. Instead of hydrogen ordering, the sarcosines order below  $T_c$ . However, partially replacing Cl by Br lowers  $T_c$  and eventually suppresses the FE transition altogether.

Fujimoto *et al.*<sup>12-14</sup> investigated deuterated and brominated crystals. More recently, dielectric<sup>15</sup> and NMR<sup>8,16</sup> studies of DTSCC have been made. Electron-nuclear double resonance experiments have been performed<sup>17</sup> on a fully bromine-substituted crystal (TSCB), and it was found that at 4.2 K the crystal still has the paraelectric (PE) Pnma structure. Finally, soft modes were studied in TSCC and mixed crystals  $\text{TSCC}_{1-x}\text{B}_x$  by laser and infrared spectrometry.<sup>18</sup>

The temperature ( $T$ ) versus pressure ( $p$ ) phase diagram for TSCC is shown in

---

<sup>†</sup>On leave from Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.

<sup>‡</sup>On leave from Department of Physics, University of North Dakota, Grand Forks, ND 58201.

Figure 1. Two features of interest were found by Schmidt<sup>19</sup> in his measurements made up to 0.7 GPa. The first feature is that  $T_c$  rises rapidly with pressure. This is again unlike  $\text{KH}_2\text{PO}_4$ , in which the hydrogen bonds go from double-minimum to single-minimum with increasing pressure and eliminate the possibility of an order-disorder transition, thereby driving  $T_c$  to 0 K at 1.5 GPa pressure.<sup>20</sup> Apparently, pressure increases the barrier for sarcosine reorientation and raises  $T_c$ . This PE-FE transition is second-order, though there is some indication of a triple point near 0.4 GPa where it may become first-order. Other studies of this transition have been made over a narrower pressure range.<sup>21-24</sup> Recently, Roth, Schaack, and Hochheimer<sup>25</sup> made Raman measurements to 0.5 GPa to study this transition in the 100 to 180 K range, and fit their results to a soft mode model.

The other feature of interest is the transition from the PE phase to an antiferroelectric (AFE) phase which only exists at high pressure.<sup>19</sup> From dielectric measurements this transition is strongly first-order. One evidence of the first-order nature was that with decreasing temperature the dielectric constant first rose according to the Curie-Weiss law which should be obeyed if there were a FE transition at the extension of the PE-FE transition line across the AFE transition line in Figure 1. Then at  $T_N$  the dielectric constant fell immediately to a low level and stayed there as temperature was further reduced. The other evidence was that the crystal developed cracks in going repeatedly through this transition. This transition is assumed to be the same one seen at considerably higher pressure and temperature (room temperature) in the present work.

In this work, we have determined the capacitance-pressure ( $C-p$ ) relationship for TSCC up to 14 GPa at room temperature, well above the highest pressure of 0.7 GPa reached in earlier work.<sup>19</sup> This work was accomplished using a diamond anvil cell (DAC),<sup>26</sup> and the capacitance measurement method established by us recently.<sup>27</sup>

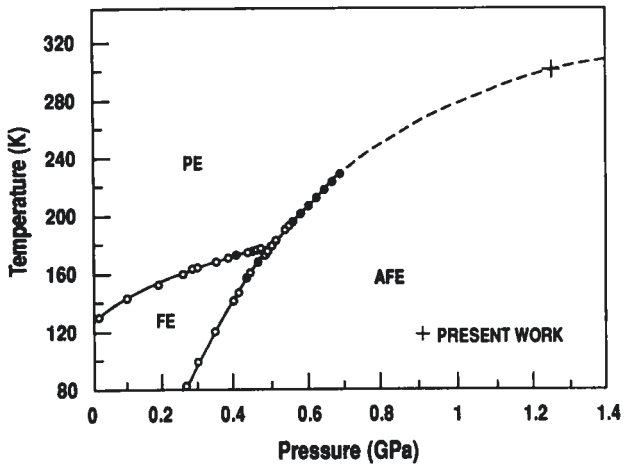


FIGURE 1 First phase transition from the present work shown on the phase diagram of TSCC due to Schmidt.<sup>19</sup>

## II. EXPERIMENTAL

The experiment consists of measuring the capacitance of the sample while the pressure is controlled by a DAC. Details of the experimental technique are described in our recent work.<sup>27</sup> Samples of TSCC were obtained by grinding to a fine powder crystals which were grown from water solution. Fourteen samples were studied. Nine of these were dried in a desiccator for a minimum of three weeks, and dry argon was passed over the sample cell during the measurement. We made no provision for drying the other five samples. All of the samples studied were compressed prior to the measurement compression. Most of the samples were subjected to a second measurement compression, after allowing the DAC with sample in place to relax at 1 atm for 24 hours. The dry samples in the DAC were retained in an argon atmosphere during the relaxation period. Capacitance measurements were made with a General Radio model 1621 Capacitance Measurement System at 500 Hz.

The effect of the adsorption of water is less evident in our study of TSCC than was the case with  $\text{KH}_2\text{PO}_4$  or  $\text{RbH}_2\text{PO}_4$ .<sup>27</sup> Nevertheless, we found that maintaining the samples free from adsorbed water and precompression of the samples are important components of the measurement method.

## III. RESULTS AND DISCUSSION

Room temperature  $C$ - $p$  relationships were obtained for the fourteen TSCC samples at pressures up to 14 GPa. Figure 2 shows the result obtained for one of the dry samples which had been prepressed to 4.7 GPa. This figure illustrates anomalous changes in capacitance with pressure near 1.3 GPa and 4.1 GPa which were observed repeatedly in samples which were dry as well as those which had not been dried.

Consistent with the phase diagram due to Schmidt,<sup>19</sup> the anomaly near 1.3 GPa is attributed to a phase transition from the PE phase to a probable AFE phase (Figure 1). The capacitance drop shown in Figure 2 at the 1.3 GPa transition is about 0.2 fF, which is typical of our six runs in which the drop ranged from 0.1 to 0.5 fF. We estimate the geometrical capacitance between the anvils at 0.1 to 0.4 fF, so the capacitance drop corresponds to a change of about 1 in the permittivity of the powder sample. This corresponds to a larger change, of about 3, in the ferroelectric direction if no change is assumed for the other two directions. Given the Curie-Weiss constant of  $C = 31$  K measured<sup>19</sup> at 1 bar, and assuming a Curie-Weiss  $T_0$  of 210 K found by making a (long) extrapolation of the PE-FE transition line in Figure 2 up to the 1.3 GPa, 300 K transition point found in this measurement, the Curie-Weiss law gives  $\Delta\epsilon = C/(T - T_0) = 31/(300 - 210)$  which is only about 0.35. This is somewhat outside the range expected, based on the range of measured capacitance change and estimated geometrical capacitance. The discrepancy cannot be attributed to a larger Curie-Weiss constant  $C$  at high pressure, because  $C$  was found<sup>19,21</sup> to be independent of pressure. It could be attributed to a comparable drop in permittivity in the other directions also, because a drop of such magnitude (0.35) perpendicular to the FE axis is not uncommon. Accordingly we conclude

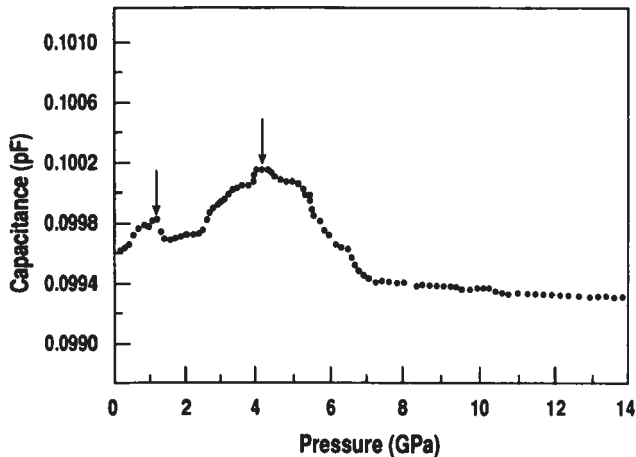


FIGURE 2  $C$ - $p$  relationship for a dry TSCC sample from the first compression to 14 GPa. The sample was precompressed to 4.7 GPa.

that the capacitance drop at 1.3 GPa can reasonably be attributed to the PE-AFE transition observed<sup>19</sup> at lower pressures.

The anomaly at 4.1 GPa, which appears much broader, may correspond to a transition from the probably AFE phase to another high pressure phase which has not been reported previously.

#### ACKNOWLEDGEMENTS

This work was supported in part by National Science Foundation Grants DMR-8714487 and DMR-9017429. The authors express sincere thanks to Profs. J. R. Anderson, G. J. Lapeyre, R. J. Swenson, J. C. Hermanson, G. F. Tuthill, M. Lu, N. Pinto, N. Williams, and E. Andersen, for their support and help. We also thank the University of North Dakota Energy and Mineral Research Center for the loan of the Capacitance Measurement System employed in this study.

#### REFERENCES

1. R. Pepinsky and Y. Makita, *Bull. Am. Phys. Soc.*, **7**, 241 (1962).
2. T. Ashida, S. Bando and M. Kakudo, *Acta Cryst. B*, **28**, 1560 (1972).
3. C. Pawlaczyk, H. G. Unruh and J. Petzelt, *Phys. Stat. Sol. B*, **136**, 435 (1986).
4. S. D. Prokhorova, G. A. Smolensky, A. K. Tagantsev, I. G. Siny, V. D. Mikvabia and W. Windsch, *Ferroelectrics*, **63**, 115 (1985).
5. J. T. Wang and V. H. Schmidt, *Phys. Rev. B*, **34**, 416 (1986).
6. R. Laiho, T. Levola, S. D. Prokhorova, I. G. Siny, A. K. Tagantsev and W. Windsch, *Ferroelectrics*, **80**, 181 (1988).
7. D. Michel, M. K. Gergs, H. Schlemmbach, W. Windsch, J. Fruwert, R. Salzer, H. Rosenberger and G. Scheler, *Chem. Phys. Lett.*, **124**, 349 (1986).
8. T. Erge, F. Engelke, D. Michel, W. Windsch and J. Petersson, *Ferroelectrics*, **108**, 331 (1990).
9. M. Fujimoto, S. Jerzak and W. Windsch, *Phys. Rev. B*, **34**, 1668 (1986).
10. M. Fujimoto, *J. Chem. Phys.*, **90**, 522 (1980).
11. J. Bornarel and V. H. Schmidt, *J. Phys. C*, **14**, 2017 (1981).
12. S. Fujimoto, N. Yasuda and H. Kashiki, *J. Phys. D: Appl. Phys.*, **15**, 487 (1982).
13. S. Fujimoto, N. Yasuda and S. Funado, *J. Phys. D: Appl. Phys.*, **15**, 1469 (1982).
14. S. Fujimoto, N. Yasuda, A. Kawamura and T. Hachiga, *J. Phys. D: Appl. Phys.*, **17**, 1019 (1984).
15. M. K. Gergs, D. Michel, H. Schlemmbach and W. Windsch, *J. Phys. D*, **19**, 2431 (1986).

16. F. Engelke, D. Michel, W. Windsch and J. Petersson, *Phys. Stat. Sol. B*, **139**, 609 (1987).
17. H. Metz, R. Böttcher and W. Windsch, *Chem. Phys. Lett.*, **127**, 278 (1986).
18. R. Roth and G. Schaack, *Ferroelectrics*, **80**, 165 (1988).
19. V. H. Schmidt, *Solid State Commun.*, **35**, 649 (1980).
20. G. A. Samara, *Phys. Rev. Lett.*, **27**, 165 (1988).
21. W. W. Windsch and V. H. Schmidt, *Ferroelectrics*, **29**, 229 (1980).
22. E. Hegenbarth and B. Schmidt, *Ferroelectrics*, **25**, 359 (1980).
23. S. Fujimoto, N. Yasuda, K. Takagi, P. S. Narayanan and H. L. Bhat, *J. Phys. D: Appl. Phys.*, **13**, L107 (1980).
24. S. Fujimoto, N. Yasuda and K. Takagi, *Jpn. J. Appl. Phys.*, **20**, 1449 (1981).
25. R. Roth, G. Schaack and H. D. Hochheimer, *Jpn. J. Appl. Phys.*, **24**, Suppl. 24-2, 497 (1985).
26. Z. X. Bao, Z. T. Zhang and T. N. Yu, *Chin. Sci. Bull.*, **30**, 1019 (1985).
27. Z. X. Bao, V. H. Schmidt and F. L. Howell, *J. Appl. Phys.*, **70**, 6804 (1991).