

9. A. J. Bosman and C. Crevecoeur, Phys. Rev. 144 (1966) 763.  
 10. E. H. Putley, The Hall effect and related phenomena, (Butterworths, London, 1960).  
 11. M. O'Keeffe and W. J. Moore, J. Chem. Phys. 36 (1962) 3009.  
 12. F. L. Weichman, Phys. Rev. 177 (1960) 998.

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## THE THERMAL CONDUCTIVITY OF $\text{BaTiO}_3$ IN THE NEIGHBOURHOOD OF ITS FERROELECTRIC TRANSITION TEMPERATURES

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The thermal conductivity of single crystalline  $\text{BaTiO}_3$  has been measured in the temperature range of 100 - 500°K. In the neighbourhood of the transition temperature a reduction of the thermal conductivity is observed. This result can be explained in view of a current theory on ferroelectricity which introduces the concept of low frequency ferroelectric modes of lattice vibration.

Optical phonon effects in thermal conductivity studies have been reported before [1-3].

In this note we report measurements on  $\text{BaTiO}_3$  near its transition temperatures that differ from previous measurements [4-6]. We believe to see the influence of low lying transverse optical phonon branches. Our way of reasoning can also be applied to measurements on other single crystalline ferroelectric materials near their Curie temperature [7,8].

Thermal conductivity measurements have been performed by a steady state heat flow method [9] in a temperature range of 100 - 500°K. Differential thermocouples of copper-constantan were used. A Leeds and Northrup K3 potentiometer together with a Hewlett and Packard 419-A d.c. null detector were used for the thermocouple measurements. The temperature difference was of the order of one to four degrees centigrades. The sample of roughly three millimeter diameter and one millimeter thickness, was grown by floating zone process [10] with a Sr dope of 1.5%. At room temperature under a polarizing microscope it showed a multidomain structure. The heater and the thermocouples of 0.05 mm diameter were glued to the sample and the sample to the heat sink by a high temperature-setting epoxy resin.

The result of the measurements is shown in fig. 1. The curve shows dips in the neighbourhood of the transition temperatures. At the high temperature side it is rising. We expect it to merge to a higher lying curve that has a  $T^{-1}$  dependence at these temperatures.

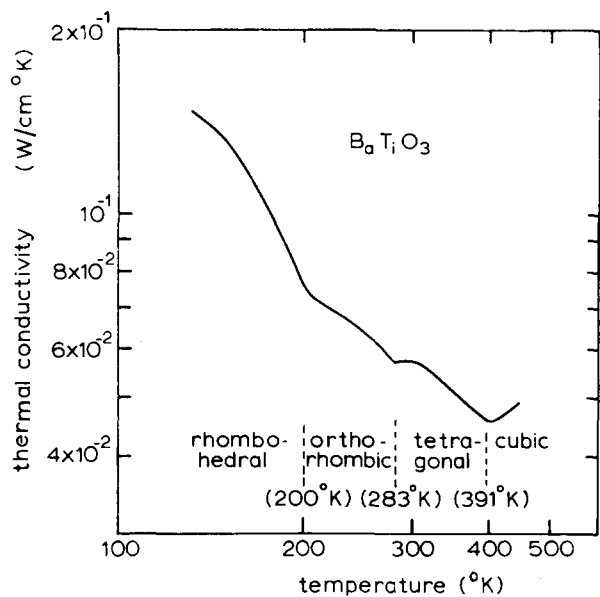


Fig. 1. The thermal conductivity of a  $\text{BaTiO}_3$  single crystal. Vertical lines indicate the values of the transition temperatures as taken from literature on specific heat measurements.

Due to the smallness of the sample the absolute accuracy of our measurements is not so good, thirty percent is a realistic estimate.

Anderson [11] and Cochran [12] have suggested

that the anomalous temperature behaviour of the dielectric constant of ferroelectrics can be related to the temperature dependence of a transverse optic mode of lattice vibration.

Low lying optical phonon branches have been observed in several ferroelectric material by infrared spectroscopy [13-15] in strontium titanate and tin telluride by neutron spectroscopy [16,17] and in barium titanate by electron diffraction [18].

Apparently these low lying temperature dependent optical phonon branches can get zero energy at zero wave vector which causes the permanent polarization of the crystal. Near the transition temperature the optical branches have energies comparable to the energies of the acoustic branches which usually transport the heat. Quite clearly this will influence the number of scattering processes in which optical phonons participate, resulting in a reduction of the conductivity due to the acoustic branches. In case the transverse optical phonon branch shows enough dispersion and is not scattered too much itself, one might expect some additional conductivity which might compensate for the effect of the decreased conduction by the acoustic phonons.

Infrared spectroscopy data reveal [15] that the transverse acoustic phonon branch in barium titanate is strongly damped near the ferroelectric Curie temperature, reason to believe that it will not contribute heavily to the conductivity so that a reduced conductivity in the neighbourhood of the ferroelectric Curie temperature may be expected.

Electron diffraction data [18] below the Curie temperature show that in the ferroelectric state (with the polarization vector along  $\langle 001 \rangle$ ) there are still low lying transverse optical phonon branches near  $k = 0$  with polarization vectors pointing in the  $\langle 100 \rangle$  and  $\langle 010 \rangle$  directions. On decreasing the temperature below  $-5^\circ\text{C}$  the tetragonal barium titanate goes over into an orthorhombic phase. At this transition the polarization turns from being along a  $\langle 001 \rangle$  axis to being a face diagonal. At about  $-90^\circ\text{C}$  another phase transition to a rhombohedral phase occurs. Here the polarization turns into the  $\langle 111 \rangle$  direction.

Both these phase transitions are accompanied by peaks in the dielectric constant, like at the Curie temperature. This seems to indicate that, like at the Curie transition, low lying transverse optical branches in other crystallographic directions get zero energy which results in a turning of the direction of the spontaneous polarization. Clearly one may again expect an anomaly in the thermal conductivity at these temperatures, as has been found.

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#### References

1. E. D. Deviatkova and I. A. Smirnov, *Fiz. Tver. Tela* 4 (1962) 2507; *Soviet Phys. Solid State* 4 (1963) 1836.
2. E. F. Steigmeyer and I. Kudman, *Phys. Rev.* 132 (1963) 508.
3. J. M. Ziman, *Electrons and phonons* (Oxford and Clarendon Press 1960).
4. I. Yoshida, S. Nomura and S. Sawada, *J. Phys. Soc. Japan* 13 (1958) 1550.
5. F. F. Kodzhespirov, *Fiz. Tver. Tela* 3 (1961) 781; *Soviet Phys. Solid State* 3 (1961) 567.
6. Y. Suemune, *J. Phys. Soc. Japan* 20 (1965) 174.
7. I. Yoshida and S. Sawada, *J. Phys. Soc. Japan* 16 (1961) 2467.
8. Y. Suemune, *J. Phys. Soc. Japan* 21 (1966) 802.
9. W. R. Thurber and A. J. H. Mante, *Phys. Rev.* 139 (1965) A1655.
10. F. Brown and W. H. Todt, *J. Appl. Phys.* 35 (1964) 1595.
11. P. W. Anderson, *Fizika dielektrikov*, ed. G. I. Skanavi, Akad. Nauk. SSSR (Moscow 1960).
12. W. Cochran, *Adv. Phys.* 6 (1960) 387.
13. A. S. Barber and M. Tinkham, *Phys. Rev.* 125 (1962) 1527.
14. W. G. Spitzer, R. C. Miller, D. A. Kleinman and L. E. Howarth, *Phys. Rev.* 126 (1962) 1710.
15. A. S. Barker Jr., *Phys. Rev.* 145 (1966) A391.
16. R. A. Cowley, *Phys. Rev.* 134 (1964) A981.
17. G. S. Pawley, W. Cochran, R. A. Cowley and G. Dolling, *Phys. Rev. Letters* 17 (1966) 753.
18. J. Harada, M. Tanaka and G. Honjo, *J. Phys. Soc. Japan* 21 (1966) 968.

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