

# D.C. conduction mechanisms of certain perovskite ceramics

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A series of a complex perovskite  $\text{Ca}_x\text{Sr}_{(1-x)}\text{TiO}_3$  (CST) where ( $0 \leq x \leq 1$ ) has been prepared by mechanical mixing of their oxides ( $\text{CaTiO}_3$  and  $\text{SrTiO}_3$ ). X-ray diffraction showed that no traces of other compounds and the line widths indicated that the products were homogeneous. The d.c. conductivity of the sample were measured over the range of temperature between 303–800 K. Temperature dependent of d.c. measurement revealed that the conductivity is thermally activated. Over the low temperature range between (333–573 K) for  $\text{CaTiO}_3$ , (353–483 K) for  $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  and (373–423 K) for  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  a semiconductor—metal behavior was observed. From the relationship between activation energy  $E_a$  and the compositions, it has been found that  $E_a$  goes through a minimum around 50% Sr—fraction. The field lowering coefficient  $\beta$  is evaluated experimentally.

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## 1. Introduction

Perovskite type oxides of general formula  $\text{ABO}_3$  [1] are important in material sciences, physics and earth sciences, e.g., for their electric properties [2], the ability to immobilize high-level radioactive waste [3] and as the dominant mineral in the Earth's lower mantle. They are also well-known for their phase transitions, which may strongly affect their physical and chemical properties. Especially the ternary system formed by the compounds barium, strontium and calcium titanate is of great interest in the field of dielectrics. The perovskite structure is ideally suited for the study of  $180^\circ$  cation-anion-cation interaction of octahedral site cations. Cation-cation interaction is remote because of the large interaction distance along the cube-face diagonal. Perovskite oxides exhibit a variety of electronic properties. Goodenough and Longo [4] and Nomura [5] have compiled the properties of known perovskites. Several perovskite oxides exhibits metallic conductivity, typical examples being  $\text{ReO}_3$ ,  $\text{A}_x\text{WO}_3$ ,  $\text{LaTiO}_3$ ,  $\text{AMoO}_3$  ( $A = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ )  $\text{SrVO}_3$  and  $\text{LaNiO}_3$ . Metallic conductivity in perovskite oxides is exclusively due to strong cation-anion-cation interaction. Following Goodenough [6, 7], we have seen important perovskite oxides;  $\text{SrTiO}_3$  and  $\text{CaTiO}_3$  containing B-Site transition-metal atoms oxides having the same d-electron configuration are grouped together in the columns.

It is known that strontium titanate, which has an ideal cubic structure of the perovskite type, and calcium titanate, which crystallizes in an orthorhombically distorted structure of the perovskite type, form continuous series of solid solutions with each other El-Mallah [8]. It would be natural to expect that at fixed temperature the orthorhombic distortions would decrease in the solid

solutions with increasing strontium titanate concentration, and at a certain concentration of strontium titanate the solid solution would have a cubic structure. However, the optical, X-ray, and electrical investigations of Granicher and Jakits [9] and McQuarrie [10] have shown that the phase transition diagram for the system  $\text{Ca}_x\text{Sr}_{(1-x)}\text{TiO}_3$  where ( $0 \leq x \leq 1$ ) is of more complex form (CST), It belongs to the complex perovskite family of compounds with general formula  $(A'A'')\text{BX}$ . In fact the  $A'$ ,  $A''$ , B and X atoms contact each other according to the very definition of ionic radii. It is called a complex perovskite because they have more than one type of ion on a particular crystallographic site with site sharing ions, it is possible to occupy those sites in an order fashion. Ordering is generally related to the critical percentage difference in ionic radii for the atoms concerned. Some of the complex perovskite have been studied by Galasso and Darby [11] determined this to lie between 7 and 17%, a difference larger than 17% gives an ordered structure, and smaller than 7% gives disordered structure (percentage differences in ionic radii of the  $A'$ ,  $A''$  ions).

A continuous series of solid solutions is found only between elements of the same crystal structure and only when the size of the solute and solvent atoms are not too different. Rothery *et al.* [12] found that the atomic diameters of solvent and solute differ by more than 14 or 15%, the size factor is unfavorable, otherwise it is favorable. In other words when the ratio of the diameter of the smaller element to that of the longer is greater than 0.85, the size factor is favorable. Ca and Sr are in the same electron group in the periodic table, the ionic radii are  $\text{Ca} = 0.99 \text{ \AA}$  and  $\text{Sr} = 1.13 \text{ \AA}$  so that the size factor for Ca and Sr is roughly 0.88 [13].

The presence of superlattice lines in the X-ray patterns, the absence of dielectric hysteresis, and the linear relationship between total polarization of the solid solutions and field potential, lead to that these solid solutions may be antiferroelectric materials [8–10]. It is true that Gränicher and Jakits [9] also state that the transitions in the solid solutions in the (CST) system may possibly be crystallographic, i.e., transitions which do not give rise to an electric moment in a unit cell of the perovskite type. These phase transitions are apparently caused by short range forces, in contrast to ferroelectric and antiferroelectric transitions, in which long range forces play the determining role.

Smolenskii *et al.* [14] studied the dielectric constant as a function of  $T$  for the solid solution of (CST) with range 423–473 K, the crystallographic transition temperature decreases as the smaller calcium ion is replaced by the larger strontium ion.

Bednorz and Muller [15] have showed that the transition appears to be due to random electronic fields introduced by  $\text{Ca}^{2+}$  doping in  $\text{SrTiO}_3$ . The  $\text{Ca}^{2+}$  has the same charge as  $\text{Sr}^{2+}$  and will mainly occupy this site. Some of the  $\text{Ca}^{2+}$  may be located at  $\text{Ti}^{4+}$  sites. To balance the charge misfit, a next-neighbor oxygen can be vacant  $V_o$  forming a  $\text{Ca}^{2+}\text{-}V_o$  neutral center. Such  $\text{Ca}^{2+}\text{-}V_o$  centers form dipoles and thus set up local electric fields.

Francombe *et al.* [16] have called the transitions in  $\text{CaTiO}_3$ ,  $(\text{Ca,Sr})\text{TiO}_3$  is puckering. The deformed structures arising in these transitions are considered to be paraelectric. In fact,  $(\text{Ca,Sr})\text{TiO}_3$  solid solutions containing much  $\text{CaTiO}_3$  have a high temperature  $\theta$  with a low  $\epsilon$  (dielectric constant), which does not change at puckering transition  $\theta'$ . Solution containing much  $\text{SrTiO}_3$  have low values of  $\theta'$  (ones near to  $\theta$ ) and large values of  $\epsilon$ , which therefore, shows a large discontinuity of  $\theta'$ .

The present work concerned with d.c. electrical properties of  $\text{Ca}_x\text{Sr}_{(1-x)}\text{TiO}_3$  where  $(0 \leq x \leq 1)$  as a function of temperature through the range 300–800 K, to study the electrical conductivity through this range and to determine different electrical parameters.

## 2. Experimental details

### 2.1. Sample preparation

CST ceramics have been prepared by using the following techniques:

(a) The oxides were mechanically mixed, (b) Cold pressed and (c) Sintered (Mitsui and Westphal [17]).

For production of  $\text{Ca}_x\text{Sr}_{(1-x)}\text{TiO}_3$  where  $(x = 1.0, 0.7, 0.5, 0.4, 0.3, 0.1, 0)$ ,  $\text{CaTiO}_3$  and  $\text{SrTiO}_3$  powder (purity > 99.9%) were weighted out in appropriate proportions. The powders were thoroughly mixed together in acetone using a pascall ceramic Ball mill. The mixed powders were dried, then fired at 1300°C for 24 h, reground and pressed under  $1.1 \times 10^4$  kg/cm<sup>2</sup> into small discs of diameter 1.3 cm using a hydraulic press. These discs were then put in alumina crucible provided with a lid and fired at temperature of 1350°C for 24 h. They were cooled, crushed, ground, repressed and fired in the same conditions. The room temperature study of the samples in the investigated system

was accomplished using X-ray powder diffraction in a Philips diffractometer with  $\text{Cu K}_{\alpha 1,2}$  radiation. Data were recorded between 10° and 80°  $2\theta$  with steps of 0.02°.

### 2.2. D.C. electrical measurements

Bulk samples of the considered system were obtained in the form of discs (1.3 cm in diameter) with uniform thickness were used for measuring electrical conductivity using specially constructed sample holder provided with two copper electrodes. The sample covered with silver paste film on the opposite surfaces to obtain a good contact was inserted between the two electrodes. Then the sample holder was inserted in a small furnace and the temperature was measured to better than 1°C with calibrated Ni/NiCr thermocouple which was set close to one of the electrodes.

A programmable Keithly electrometer (617) was used to measure the electrical resistance of the samples under study using the constant current method. This electrometer can resolve resistance as low as 0.1 K $\Omega$  and as high as 200 G $\Omega$ , with accuracy of 0.2%.

## 3. Results and discussion

X-ray diffraction analysis has been elaborated for the compositions of  $\text{Ca}_x\text{Sr}_{(1-x)}\text{TiO}_3$  where  $(0 \leq x \leq 1)$  in the form of bulk material. The obtained X-ray diffraction patterns for the investigated system shows that no traces of other compounds and the line widths indicated that the products were homogeneous, thus all the compositions are in good quality with the perovskite structure.

### 3.1. Electrical properties

The variation of d.c. specific conductivity  $\ln \sigma$  as a function of temperature  $T^{-1}$  for the  $(x = 1, 0.7$  and  $0.5)$  and  $(x = 0.4, 0.3, 0.1$  and  $0)$  are shown in Fig. 1a and b respectively. The plots suggest that there are two types of conduction channels contributing to the conductivity. The d.c. conductivity  $\sigma(T)$  exhibits an activated temperature dependence, in accordance with the relation:

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (1)$$

where  $\sigma_0$  is the pre-exponential factor and includes the charge carrier mobility and density of states,  $k$  the Boltzmann constant,  $T$  the absolute temperature and  $E_a$  is the corresponding activation energy which is a function of the electronic energy levels of the chemically interacting atoms in the samples and hence of the energy band gap.

Values of  $\sigma_{\text{RT}}$  (the electrical conductivity at room temperature  $\sim 305$  K),  $\sigma_0$  and  $E_a$  which are estimated from Equation 1 for all compositions under test, are given in Table I and Fig. 2. It is seen that  $\sigma_{\text{RT}}$ ,  $\sigma_0$  and  $E_a$  quantities change remarkably with increasing Sr content for CST. This is because the increase of Sr content leads to change in the structure of the system [8–10, 18–21].

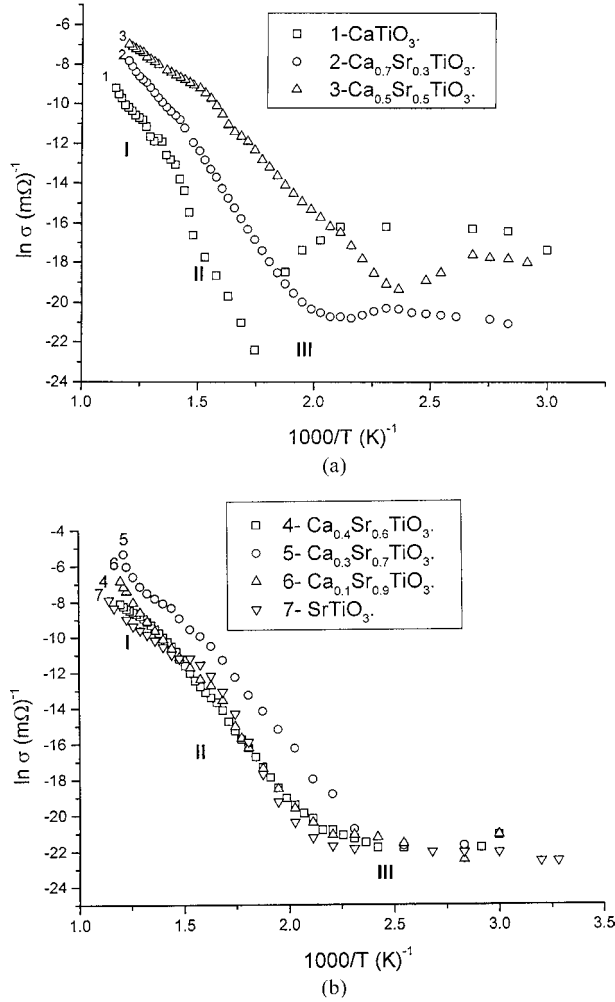


Figure 1 The relation between  $\ln$  of the electrical conductivity as a function of  $T^{-1}$  for each composition.

Data given in Table I, Table II and Fig. 2 indicate that the conductivity confirm the thermally assisted tunneling of the charge carriers in the extended states over the high temperature range for all compositions, but over the low temperature range (333–573 K) for  $\text{CaTiO}_3$ , (353–483 K) for  $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$  and (373–423 K) for  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ , the conduction occurs via variable range hopping of the charge carriers in the localized states near the Fermi-level [22]. The contribution from the different process is very much dependent upon the composition of  $\text{Ca}_x\text{Sr}_{(1-x)}\text{TiO}_3$  where ( $x = 1, 0.7, 0.5, 0.4, 0.3, 0.1$  and 0), as shown in Fig. 1a and b.

Over the high temperature range the dependence of the conductivity exhibited the normal behavior of semiconductor till a critical transition temperature  $T_C$  which are reported in Table I. This may be due to a change

TABLE II The values of  $\sigma_0$  and  $E_a$  in the low temperature range (region III)

Composition	$\sigma_0$ ( $\text{m}^{-1}$ )	$E_a$ (eV)
$\text{CaTiO}_3$	$3.262 \times 10^{-6}$	0.125
$\text{Ca}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$	$3.096 \times 10^{-8}$	0.113
$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$	$1.480 \times 10^{-6}$	0.135
$\text{Ca}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$	$1.615 \times 10^{-5}$	0.382
$\text{Ca}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$	$5.726 \times 10^{-8}$	0.153
$\text{Ca}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$	$1.460 \times 10^{-7}$	0.200
$\text{SrTiO}_3$	$1.209 \times 10^{-9}$	0.047

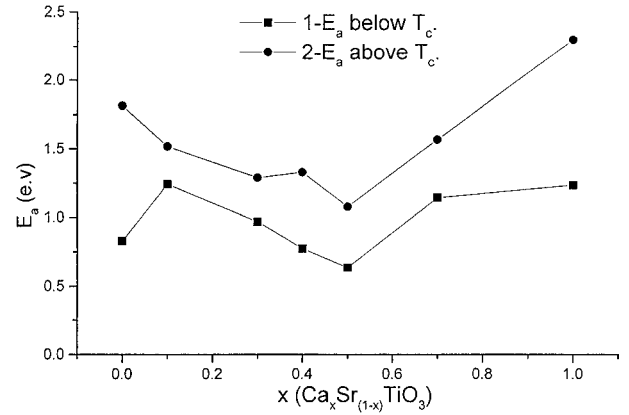


Figure 2 Dependence of activation energy on Sr-fraction in (CST) system.

in the structure of all investigated compositions. Over the low temperature range the behavior of the conductivity is that of a semiconductor obeying the relation (1), yielding a small value of the activation energy, as reported in Table II. Following a well defined constant values in conduction, the conductivity decreases with temperature, in a manner analogous to that of a metal. This transition could thus be of the semiconductor-metal type. Semiconductor-metal transitions have been observed in many oxides materials (Rao and Rao [23] and Groves [24]). There are two models that can be conceived for these transitions, one involving overlap of the filled valence and empty conduction bands. As the temperature is increased, it is assumed that the energy gap of the intrinsic semiconductor decreases and finally vanishes at a finite temperature thus leading to metallic conductivity. The other is accompanied either by displacive phase transition involving a change of crystal symmetry or by equally anomalous behavior of the lattice constant.

Fig. 1b showed that the Semiconductor-metal type over a limits temperature range disappear, while the

TABLE I Effect of the composition on the values  $\sigma_{RT}$ ,  $\sigma_0$  and  $E_a$  for CST system

Composition	$\sigma_{RT}$ (305 K) ( $\text{m} \Omega$ ) <sup>-1</sup>	$\sigma_0$ ( $\text{m} \Omega$ ) <sup>-1</sup> (region II)	$\sigma_0$ ( $\text{m} \Omega$ ) <sup>-1</sup> (region I)	$E_a$ (eV) (region II)	$E_a$ (eV) (region I)	$T_C$ (K)
$\text{CaTiO}_3$	$2.242 \times 10^{-8}$	$2.046 \times 10^{10}$	$1.203 \times 10^3$	2.2965	1.235	783
$\text{Ca}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$	$1.383 \times 10^{-8}$	$3.168 \times 10^6$	$3.009 \times 10^3$	1.5666	1.145	723
$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$	$1.68 \times 10^{-6}$	$1.469 \times 10^4$	$6.44 \times$	1.08	0.637	653
$\text{Ca}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$	$8.53 \times 10^{-9}$	$5.539 \times 10^{11}$	$1.546 \times 10^1$	1.33	0.775	713
$\text{Ca}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$	$9.26 \times 10^{-10}$	$1.183 \times 10^6$	$5.57 \times 10^7$	1.29	0.97	613
$\text{Ca}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$	$9.5 \times 10^{-9}$	$7.4196 \times 10^6$	$2.762 \times 10^4$	1.517	1.243	633
$\text{SrTiO}_3$	$6.04 \times 10^{-10}$	$3.874 \times 10^9$	$1.885 \times 10^1$	1.813	0.8297	653

TABLE III The experimental values of the coefficient  $\beta$  and the calculated value of  $\beta_{SC}$  and  $\beta_{PF}$  for CST system

Composition $x$	Dielectric const. $\epsilon$ (RT) El-Mallah [8]	$B_{SC} (\times 10^{-6})$	$\beta_{PF} (\times 10^{-6})$	$\beta$ (exp.) $(\times 10^{-4})$
CaTiO <sub>3</sub>	166.14	2.94	5.89	9.1
Ca <sub>0.7</sub> Sr <sub>0.3</sub> TiO <sub>3</sub>	177.73	2.85	5.69	4.705
Ca <sub>0.5</sub> Sr <sub>0.5</sub> TiO <sub>3</sub>	220.03	2.56	5.11	9.71
Ca <sub>0.4</sub> Sr <sub>0.6</sub> TiO <sub>3</sub>	219.3	2.56	5.12	8.19
Ca <sub>0.3</sub> Sr <sub>0.7</sub> TiO <sub>3</sub>	228.8	2.51	5.02	9.59
Ca <sub>0.1</sub> Sr <sub>0.9</sub> TiO <sub>3</sub>	259.0	2.357	4.71	8.41
SrTiO <sub>3</sub>	249.6	2.401	4.802	5.91

normal temperature dependent of the conductivities is observed over the low and high temperature ranges. The critical transition temperature  $T_C$  is composition-dependent, as reported in Table I. We have noticed agreement between the  $T_C$  obtained by d.c. measurement in this work and those obtained before by a.c. [8]. Another noteworthy characteristic, the composition for CST system seems to play a major role in guiding the activation energy. In Fig. 2, we have plotted the value of  $E_{aI}$  and  $E_{aII}$  versus the composition  $x$  for  $(Ca_xSr_{1-x})TiO_3$  and have found that  $E_a$  goes through a minimum around 50% Sr-fraction. These results do indicate the dominant role of Sr in estimating the activation energy of the system.

### 3.2. The conduction mechanism in CST system

The field lowering coefficient  $\beta$  is an essential factor that determines the conduction mechanism [25, 26] and comparing it by either Schottky (SC) or Poole–Frenkel (PF) type are discussed by the following.

#### (i) Schottky effect.

The Schottky effect is thermionic emission over a field lowered (due to of the image force ) barrier and the expression for current density is given in the form

$$J = AT^2 \exp\{e(\beta_{SC}F^{1/2} - \varphi)/kT\} \quad (2)$$

#### (ii) Poole–Frenkel effect.

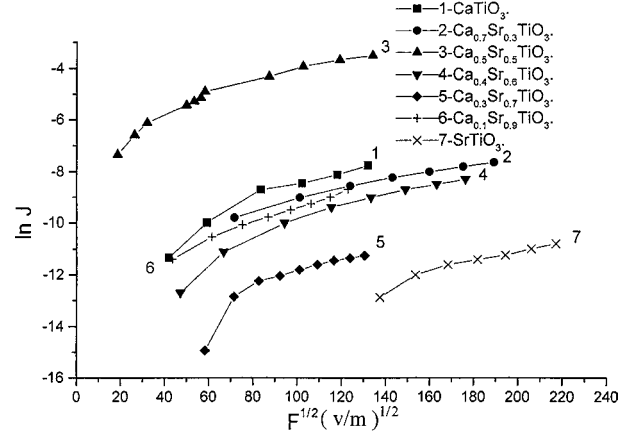
The Poole–Frenkel effect is the lowering of coulombic potential barrier when it interacts with an electric field, i.e., when the electric field  $F$  interacts with the coulombic potential barrier of a donor center or trap, the height of the barrier ( $\varphi$ ) is lowered. The equation for the current density can be given as:

$$J = J_0 \exp\{e(\beta_{SC}F^{1/2} - \varphi)/kT\} \quad (3)$$

where the Schottky and Poole–Frenkel field lowering coefficient are given by

$$2\beta_{PF} = \beta_{SC} = (e/4\pi\epsilon_0\epsilon_r)^{1/2} \quad (4)$$

where  $\epsilon_0$  is the permittivity of the free space and  $\epsilon_r$  the dielectric constant. But at high fields in excess of some  $10^6$  v/m many dielectric samples exhibits current


 Figure 3 The relation between  $\ln$  of the current density and the square root of the electric field at R.T.

density-voltage characteristics of the form.

$$J \propto \exp(e\beta F^{1/2}/kT) \quad (5)$$

To calculate the experimental value of the coefficient  $\beta$ , we determine the slope of each composition from Fig. 3. Using the Equation 5 we can calculate the coefficient  $\beta$ . While  $\beta_{SC}$  and  $\beta_{PF}$  values are calculated from Equation 4 by taking low frequency (1.5915 Hz) dielectric constant  $\epsilon$ , obtained before [8].

The coefficient  $\beta$ ,  $\beta_{SC}$  and  $\beta_{PF}$  were reported in Table III. Data given in this table indicate that the experimental values of  $\beta$  do not agree neither with the calculated values of  $\beta_{SC}$  nor that of  $\beta_{PF}$ . This may be due to that the dielectric constant was measured at low frequency or due to the low electric field which is used or the nature of the sample itself or all these factors together.

## 4. Conclusions

The effect of the composition for  $Ca_xSr_{1-x}TiO_3$  where  $(x = 1, 0.7, 0.5, 0.4, 0.3, 0.1$  and  $0)$  of ceramic appears clearly on d.c. conductivities values at room temperature.  $Ca_{0.5}Sr_{0.5}TiO_3$  composition has the value  $1.68 \times 10^{-6} (m \cdot \Omega)^{-1}$  see Table I. Temperature dependent of d.c. measurements revealed that the conductivity is thermally activated. There are two types of conduction channels contributing to the conductivity. Over the low temperature range the conduction occurs via variable range hopping of the charge carrier in the localized states near Fermi level. Over the high temperature

range the conductivity confirm the thermally assisted tunneling of the charge carriers in the extended states. The composition for (CST) systems play major role in guiding the activation energy.  $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$  has a minimum value of  $E_a$  indicating the dominant role of Sr in estimating the activation energy of the system. The experimental value of the field lowering coefficient do not agree neither with the Schottky nor Poole Frenkel types.

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