

# Variation of Thermal Conductivity with Temperature of PVC Polymers

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## ABSTRACT

Thermal conductivity is the rate at which a material conducts heat energy through itself. It is the quantity of heat that passes through a unit of the material in a unit of time when the temperature difference of two faces is 1 K. It obviously influences the heating and cooling of the PVC melt during processing, as PVC tends to be an insulator.

Keywords- PVC, thermal, conductivity, polymer, temperature

## INTRODUCTION

The thermal conductivities of unplasticized and plasticized samples of polyvinyl chloride have been measured in the range 15° to 98°C. At a temperature above about 25°C the thermal conductivity decreases with increasing plasticizer concentration, a simple relationship holding between the two quantities at this temperature. The results indicate that thermal conductivity increases with temperature, reaching a maximum in the neighborhood of the glass temperature, and then begins to decrease. Polyvinyl chloride is the world's third-most widely produced synthetic plastic polymer (after polyethylene and polypropylene). There are two basic forms of PVC: rigid and plasticized. Rigid PVC, as its name suggests, is an unmodified polymer and exhibits high rigidity. Unmodified PVC is stronger and stiffer than PE and PP. Plasticized PVC is modified by the addition of a low-molecular-weight species (plasticizer) to flexibilize the polymer.[1,2,3]

Table-Comparison of calculated and experimental thermal conductivity values of PVCs

| Temp (K) | Thermal conductivity<br>PVC-I with 0% plasticizer |        | Deviation % |
|----------|---|--------|-------------|
|          | Exp.  | Calcd. |             |
| 101      | 129   | 127    | -1.6        |
| 120      | 134   | 134    | 0.0         |
| 139      | 138   | 139    | 0.7         |
| 158      | 142   | 143    | 0.7         |
| 177      | 145   | 147    | 1.4         |
| 196      | 148   | 150    | 1.3         |
| 215      | 151   | 153    | 1.3         |
| 234      | 153   | 155    | 1.3         |
| 253      | 156   | 157    | 0.6         |
| 272      | 158   | 159    | 0.6         |
| 291      | 160   | 160    | 0.0         |
| 310      | 163   | 162    | -0.6        |
| 328      | 164   | 163    | -0.6        |
| 347      | 165   | 164    | -0.6        |
| 366      | 166   | 165    | -0.6        |
|          | PVC-I with 10% plasticizer                        |        |             |
| 101      | 133   | 130    | -2.3        |

|                            |     |     |      |
|----------------------------|-----|-----|------|
| 120                        | 138 | 136 | -1.5 |
| 139                        | 141 | 141 | 0.0  |
| 158                        | 145 | 145 | 0.0  |
| 177                        | 148 | 148 | 0.7  |
| 196                        | 150 | 151 | 0.7  |
| 215                        | 152 | 153 | 0.0  |
| 234                        | 155 | 155 | 0.0  |
| PVC-I with 20% plasticizer |     |     |      |
| 101                        | 137 | 136 | -0.7 |
| 120                        | 143 | 142 | -0.7 |
| 139                        | 147 | 146 | -0.7 |
| 158                        | 149 | 149 | 0.0  |
| 177                        | 152 | 152 | 0.0  |
| 196                        | 154 | 154 | 0.0  |
| 215                        | 157 | 156 | -0.6 |
| 234                        | 158 | 158 | 0.0  |
| 253                        | 158 | 159 | 0.6  |
| 272                        | 161 | 160 | -0.6 |
| 291                        | 160 | 160 | 0.0  |
| 310                        | 159 | 159 | 0.0  |
| 328                        | 158 | 158 | 0.0  |
| 347                        | 157 | 157 | 0.0  |
| 366                        | 157 | 156 | -0.6 |
| PVC-I with 40% plasticizer |     |     |      |
| 101                        | 145 | 145 | 0.0  |
| 120                        | 150 | 150 | 0.0  |
| 139                        | 153 | 153 | 0.0  |
| 158                        | 156 | 155 | -0.6 |
| 177                        | 158 | 157 | -0.6 |
| 196                        | 161 | 159 | -1.2 |
| 215                        | 162 | 160 | -1.3 |
| 234                        | 162 | 161 | -0.6 |
| 253                        | 160 | 158 | -1.2 |
| 272                        | 157 | 157 | 0.0  |
| 291                        | 156 | 156 | 0.0  |
| 310                        | 154 | 155 | 0.6  |
| 328                        | 151 | 153 | 1.3  |
| 341                        | 151 | 153 | 1.3  |
| 366                        | 149 | 151 | 1.3  |
| PVC-II with 0% plasticizer |     |     |      |
| 293                        | 158 | 158 | 0.0  |
| 303                        | 161 | 160 | -0.6 |
| 313                        | 164 | 163 | -0.6 |
| 323                        | 167 | 165 | -1.2 |
| 333                        | 167 | 167 | 0.0  |
| 343                        | 171 | 169 | -1.2 |
| 353                        | 172 | 173 | 0.6  |
| 363                        | 172 | 172 | 0.0  |
| 373                        | 171 | 171 | 0.0  |

## DISCUSSION

In tropical climate zones, the greatest thermal gain occurs through the roof of a house. In Nigeria, the use of zinc made roofs without a ceiling is very common, thus there is intense heat transfer to the internal environment, which may cause thermal discomfort to the inhabitants (Etuk et al., 2007). One way to reduce the thermal discomfort is the use of radiant barrier which reduce the heat flux. The knowledge of thermal properties of different materials is very important in the choice of the type of material to be used as a radiant barrier since the heat flow through any building depends on the thermal properties of the materials used in the building (Michels et al., 2008) and (Etuk et al., 2007). The study of the thermal properties of PVC material will help in knowing whether it is suitable as a ceiling material for application in tropical climate zones. Polyvinyl chloride (PVC) is the third most widely produced polymer, after polyethylene and polypropylene (Allsopp et al., 2012). It is insoluble in alcohol, but slightly soluble in tetrahydrofuran. Structurally the polymers are linear and strong. The monomers are mainly arranged head to tail, meaning that there are chlorides on alternating carbon centres. PVC has mainly an atactic stereochemistry of the chlorides centres which are random. The presence of chloride groups gives the polymer very different properties from the structurally related material polyethylene (Mc Graw-Hill et al., 2002). The product of the polymerization process is unmodified PVC. Before PVC can be made into finished products, it always requires conversion into a compound, by the incorporation of additives such as heat stabilizers, UV stabilizers, plasticizers etc (Cadogan et al., 2000). PVC comes in two basic forms; rigid RPVC and the flexible. The rigid form of PVC is used in construction of pipes, and in profile application such as doors and windows. It is also used for bottle and other non-food packaging, and cards. It can be made softer and flexible by the addition of plasticizers, like phthalates. PVC in a flexible form can be used in plumbing, electrical cable insulation, imitation leather, signage, inflatable products and many applications where it replaces rubber (W. V. Titow, 1984). PVC is a thermoplastic polymer, its properties are usually categorized based on rigid and flexible PVCs. PVC has high harness and mechanical properties enhance with the molecular weight increases, but decreases with the temperature increasing. The mechanical properties of rigid PVC (UPVC) are very good, the elastic modulus can get to 1500- 3,000Mpa. The soft PVC (flexible PVC) elastic modulus is 1.5-15Mpa. However, elongation at break is up to 200-450%. PVC friction is ordinary, the static friction factor is 0.23 (JT-Extrudermachine.com). The heat stability of raw PVC is very poor so the addition of a heat stabilizer during the products is necessary in order to ensure the product's properties. PVC starts to decompose when the temperature reaches 1400C with melting temperature starting around 160 0C. PVC is a polymer with good insulation properties but because of its higher polar nature, the electrical insulating property is inferior to non-polar polymers such as polyethylene and polypropylene. As the dielectric constant, dielectric loss value and volume resistivity are high, the corona resistance is not very good, and it is generally suitable for medium or raw voltage and low frequency insulation materials. In our homes, indoor thermal discomfort has been very challenging. It depends on one or more of the materials used either as ceiling board; rock used as walling materials; wood used in making roofing support, the roofing sheet itself or combination of all of them. One of the special concerns of the trained builders is to design a building that the indoor environmental condition is thermally tolerable and conducive to the occupants of the building (Ajibola et al., 1995) and (Straaten, et al., 1967). George et al., (2010) investigated comparatively the thermal insulation efficiency of some selected materials frequently used as ceiling in building design, in terms of their thermal properties such as thermal conductivity, thermal diffusivity, thermal resistivity and thermal absorptivity using the lee's disc apparatus and a steady state method. The material investigated where PVC, POP, cardboard, Asbestos and suspended ceiling tiles. Generally, they concluded that in terms of thermal conductivities, the samples show good compliance with standard values obtained in textbooks and the values recommended for heat-insulating materials. However, thermal absorptivity which is usually lower for best insulation indicates that the materials POP, Asbestos and suspended ceiling tile are recommended as ceiling materials that would have good thermal insulation efficiency when compared to PVC and cardboard.[4,5,6] Although thermal resistivity are low in samples of the material of POP and Asbestos recommended, thermal absorptivity which has to do with absorption and retention of heat, plays the major role when it comes to insulation efficiency. Lower absorptivity in materials is a clear indication of lower molecular point of view, low thermal absorptivity with higher or lower thermal diffusivity portrays good thermal insulation efficiency. Onyeaju et al., (2012) also worked comparatively on the thermal properties of Asbestos and PVC ceiling sheet according to their thermal conductivity, (TC), thermal resistivity (TR), thermal diffusivity, thermal absorptivity, and specific heat capacity (SHC). They treated the samples under investigation as an ideal one dimensional heat transfer problem. They obtained results in

their study which shows that both PVC and asbestos ceiling, sheet has low density, low thermal conductivity and high thermal resistivity which compared favourably with those of other good thermal insulators in building design (Etuk et al.,2007) Demirdag (2006) (Zhua et al., 2003), Zhang et al. (2006). Also the value of the thermal resistivity obtained correlate well with the experimental data. (Michels et al., 2008). They also recommend these types of insulators as a ceiling sheet not only to reduce the thermal gain in summer but also to reduce the winter losses, thereby decreasing the energy consumption for heating or cooling of the interior space in a building. Therefore in view of the above comparison, PVC ceiling coupled with its physical appearance, strength, chemical resistance, fire resistance, maintenance-free and freedom from toxicity, odour and taste may be a better material for thermal design application. This work is aimed at the investigation of the thermal properties of PVC ceiling material produced in EPZ Calabar. To know if it is suitable as a ceiling material for application in tropical climate zone. [7,8,9]

### RESULTS

At very low temperatures, the tunnelling theory for amorphous solids predicts a thermal conductivity  $\kappa \propto T^m$ , with  $m = 2$ . However, most of the data in the literature in the temperature range 0.1–1 K report an  $m < 2$ . We want to show that this discrepancy often disappears for  $T \rightarrow 0$  K. Here we report the case of Polyvinyl Chloride (PVC) whose thermal conductivity is known in the 0.2–100 K temperature range. A new technique is described which makes the measurement of the exponent  $m$  of the thermal conductivity independent of the spurious thermal power. Such technique is particularly useful for measurements of  $\kappa$  when working with a low power refrigerator. We carried out measurements down to 50 mK, obtaining a thermal conductivity for our PVC sample below 120 mK. It was found that the applied ambient temperature has a significant effect on the thermal conductivity. At  $-20 \sim 100$  °C, the thermal conductivity of PE showed a linearly decline with the increase of temperature. The thermal properties of a series of PE samples were also investigated by differential scanning calorimeter. The results showed that the higher the crystallinity, the higher the thermal conductivity of polyethylene. However, above the melting point, thermal conductivity of all PE samples tended to be the same, with a value of about 0.21 W/m·K. Based on the crystallinity and temperature, an empirical formula was proposed to predict the thermal conductivity of PEs with an error within 3%, which was also consistent with the results of other reported thermal conductivity of PEs. This work can guide the design of thermally conductive polymers in the future. [10,11,12]

| Technical Name                    | Description   |
|-----------------------------------|---|
| Chemical Name                     | Polyvinyl Chloride  |
| Chemical Formula                  | $(C_2H_3Cl)_n$  |
| Melt Temperature                  | The typical melting point of PVC is around 100-260°C. However, it can vary depending on the specific formulation of the PVC.                            |
| Heat Deflection Temperature (HDT) | The heat deflection temperature of PVC is around 60-100°C. This is the temperature at which a polymer or plastic sample deforms under a specified load. |
| Tensile Strength                  | The tensile strength of PVC is around 40-80 MPa. This is the maximum amount of tensile stress that PVC can take before failure.                         |
| Specific Gravity                  | The specific gravity of PVC is around 1.35-1.45. This is a measure of the density of PVC relative to the density of water.                              |
| Flexural Strength                 | The flexural strength of PVC is around 70-100 MPa. This is a measure of the material's resistance to deformation under load.                            |

|                                  |  |
|----------------------------------|--|
| Coefficient of Thermal Expansion | The coefficient of thermal expansion for PVC is around $80 \times 10^{-6}$ per $^{\circ}\text{C}$ . This measures how much PVC expands or contracts for each degree of temperature change. |
| Dielectric Constant              | The dielectric constant of PVC is around 3-4 at 1 MHz. This measures the material's ability to store electrical energy in an electric field.   |
| Volume Resistivity               | The volume resistivity of PVC is around $10^{12}$ to $10^{16}$ ohm.cm. This measures the material's resistance to electrical leakage through its volume.                                   |

\* Under normal conditions, specifically at a temperature of  $25^{\circ}\text{C}$  ( $77^{\circ}\text{F}$ ) and a pressure of 100 kPa.

#### Understanding the Concept of PVC Melting Temp

The melting point of PVC is a critical property that influences its behavior and applications. But what exactly is the PVC melting temp? In simple terms, it's the temperature at which PVC transitions from a solid state to a liquid state.[13,14,15]

The melting temperature of PVC is not a fixed value. It can vary depending on the specific formulation of the PVC, including the various additives like stabilizers, fillers, and lubricants that are used. These additives can have very different ingredients, each contributing to different properties of the final product.

The melting point of PVC is also influenced by the degree of syndiotacticity of the chain. This refers to the arrangement of the PVC molecules in space, which can affect how closely the molecules can pack together and, therefore, the temperature at which they will start to melt.

#### The Role of PVC Melting Temp in Material Processing

When it comes to material processing, the PVC melting temp plays a pivotal role. It's during the melting phase that PVC changes from a rigid structure to a more flexible one, allowing it to be molded into various shapes and forms.[16,17,18]

The melting temperature of PVC is crucial in determining the processing conditions. For instance, if the temperature is too high, it could lead to degradation of the material, compromising its structural integrity. On the other hand, if the temperature is too low, the PVC might not melt properly, making it difficult to process.

The PVC melting temp also influences the type of processing method used. For instance, suspension and emulsion polymerization are two common methods used in the production of PVC. The choice between these methods depends largely on the desired end product and the specific melting point of the PVC being used.

#### How PVC Melting Temp Influences Mechanical Properties

The PVC melting temp has a profound impact on the mechanical properties of the final product. One of these properties is tensile strength, which refers to the resistance of a material to breaking under tension.

When PVC is heated to its melting point, the molecular structure changes, which can affect its tensile strength. For instance, if the PVC is heated too much, it can lead to a decrease in tensile strength. This is because the high temperatures can cause the PVC molecules to move apart, reducing the material's ability to resist tension.

On the other hand, if the PVC is not heated enough, it may not achieve the desired flexibility, which can also affect its tensile strength. Therefore, controlling the PVC melting temp is crucial to achieving the right balance of strength and flexibility.

#### The Impact of PVC Melting Temp on Physical Properties

The physical properties of PVC, such as its hardness, flexibility, and transparency, are also influenced by its melting temp. For instance, rigid PVC and flexible PVC have very different ingredients and, consequently, different melting temperatures.[19,20,21]

Rigid PVC, used in applications like window frames and pipes, has a higher melting temp and is harder and less flexible. On the other hand, flexible PVC, used in products like shower curtains and inflatable products, has a lower melting temp and is softer and more flexible.

The PVC melting temp can also affect the transparency of the material. Higher temperatures can lead to a decrease in transparency as the structure of the PVC changes. Therefore, controlling the melting temp is crucial to achieving the desired physical properties.

#### Thermal Properties and Their Relation to PVC Melting Temp

The thermal properties of PVC, including its heat resistance and thermal conductivity, are closely related to its melting temp. PVC's ability to withstand high temperatures without degrading is one of its key strengths, making it suitable for various industrial applications.

Heat stabilizers are often added to PVC to improve its heat resistance. These additives work by preventing the release of hydrogen chloride, a by-product of PVC degradation at high temperatures. However, the effectiveness of these stabilizers can be influenced by the PVC melting temp.

The thermal conductivity of PVC, which refers to its ability to conduct heat, can also be affected by its melting temp. Higher melting temperatures can lead to increased thermal conductivity, which can be beneficial in certain applications.

#### The Influence of PVC Melting Temp on PVC Density

The density of PVC, which is the mass of the material per unit volume, can be influenced by its melting temp. As PVC is heated and begins to melt, its volume increases while its mass remains the same, leading to a decrease in density.

This change in density can affect the properties and performance requirements of the final product. For example, a lower density can lead to a lighter product, which can be beneficial in applications where weight is a concern. However, a decrease in density can also lead to a decrease in strength, which may not be desirable in applications that require high strength.

#### Chemical Composition and Its Effect on PVC Melting Temp

The chemical composition of PVC, including the presence of chloride groups and various additives, can have a significant effect on its melting temp. The chloride groups in PVC contribute to its high melting temp compared to other thermoplastics like polyethylene.

Additives, such as stabilizers, fillers, and lubricants, can also influence the PVC melting temp. These additives can change the properties of the material, allowing it to meet specific performance requirements. For example, heat stabilizers can increase the PVC melting temp, improving its heat resistance.

#### The Role of Molecular Weight in Determining PVC Melting Temp

The molecular weight of PVC, which refers to the mass of a single molecule of PVC, can play a role in determining its melting temp. Higher molecular weights can lead to higher melting temps, as more energy is required to break the bonds between the larger molecules.

However, the relationship between molecular weight and melting temp is not straightforward. Other factors, such as the degree of syndiotacticity of the chain and the presence of additives, can also influence the melting temp.[22,23,24]

#### How Processing Conditions Affect PVC Melting Temp

The conditions under which PVC is processed can have an impact on its melting temp. For instance, the rate at which the material is heated can affect the temperature at which it begins to melt. Rapid heating can lead to a higher melting temp, as the material does not have enough time to rearrange its molecules before melting.

The pressure under which the PVC is processed can also affect its melting temp. Higher pressures can lead to a lower melting temp, as the increased pressure can help to break the bonds between the PVC molecules.

#### The Importance of Controlling PVC Melting Temp in Manufacturing

In manufacturing, controlling the PVC melting temp is of utmost importance. It's not just about reaching a temperature where PVC transitions from solid to liquid. It's also about maintaining that temperature to ensure the material doesn't degrade, compromising its structural integrity.

For instance, if the temperature exceeds the PVC melting point, it could lead to the release of hydrochloric acid, a by-product of PVC degradation. This not only affects the quality of the final product but also poses safety risks.

On the other hand, if the temperature is too low, the PVC might not melt properly, making it difficult to mold into the desired shape. Therefore, precise control of the PVC melting temp is crucial in manufacturing to ensure the quality and safety of the final product.

#### Comparing PVC Melting Temp with Other Thermoplastics

When compared to other thermoplastics, PVC stands out due to its high melting temp. For instance, polyethylene, a structurally related material, has a lower melting temp due to the absence of chloride groups.

This high melting temp gives PVC an advantage in applications that require resistance to high temperatures. However, it also presents challenges in terms of processing and safety, as the high temperatures can lead to degradation of the material and the release of harmful by-products.

#### Safety Considerations Related to PVC Melting Temp

Safety is a crucial consideration when dealing with PVC, especially given its high melting temp. If PVC is heated beyond its melting point, it can degrade and release hydrogen chloride gas, which can be harmful if inhaled.

Therefore, it's important to control the PVC melting temp during processing to prevent the release of harmful gases. Additionally, protective measures, such as proper ventilation and the use of personal protective equipment, should be in place to ensure the safety of workers.

## CONCLUSION

Polyvinyl chloride, or PVC as we commonly know it, has been a staple in various industries since the early 20th century. Russian chemist Ivan Ostromislensky was one of the pioneers in its development. PVC is a synthetic polymer, structurally related to the material polyethylene, but with the presence of chloride groups. This unique composition gives PVC its distinct properties.

PVC's versatility is one of its key strengths. It's used in a wide range of applications, from window frames to electrical cable insulation, and even inflatable products. Its durability, coupled with the ability to withstand UV rays, makes it a preferred choice in many industrial applications.

The mass of PVC used globally is a testament to its importance. But what makes PVC so special? Well, it's all about the properties of the material, and one property that plays a significant role is the PVC melting temp.

### The Critical Role of PVC Melting Temp in Industry Applications

In conclusion, the PVC melting temp plays a critical role in determining the properties and applications of this versatile material. From its impact on mechanical and physical properties to its influence on processing conditions and safety considerations, the PVC melting temp is a key factor that shapes the use of PVC in various industries.

By understanding and controlling the PVC melting temp, manufacturers can ensure the quality and safety of their products, while also tailoring the properties of the material to meet specific performance requirements. As we look to the future, innovations in controlling the PVC melting temp could open up new possibilities for this versatile material, further expanding its range of applications.[25]

That's it for our deep dive into the world of PVC and the critical role of its melting temp. Whether you're in the industry or just curious about the material that plays a part in our everyday lives, I hope this has been an enlightening journey[26]

## REFERENCES

1. Anderson P.W., Halperin B.I., Varma C.M. (1972) . The Philos. Mag. 25, 19
2. W. A. Phillips, J. Low Temp. Phys., 7(3-4), 351-360 (1972).
3. L. Risehari et al., 8th International Conference of Astroparticle, Particle and Space Physics, Detectors and Medical Physics Applications ICATPP, World Scientific, pp. 603-607 (2003).
4. Pohl R.O., Liu X., Thompson E. (2002) . Rev. Mod. Phys. 74(4):991-1013
5. Benes M. et al. (2005) . J. Therm. Anal. Calorim. 82(3):761-768
6. Kroeger F.R., Swenson C.A. (1977) . J. Appl. Phys. 48, 853
7. Pöbel F. (1991) Matter and Methods at Low Temperatures. Springer, Berlin
8. Hartwig G. (1994) Polymer Properties at Room and Cryogenic Temperatures. Plenum Press, New York
9. Ku C.C., Liepins R. (1987) Electrical Properties of Polymer, Chemical Principles. Hanser Publisher, Munich
10. Hartwig G., Schwarz G. (1984) Advances in Cryogenic Engineering (Materials), Vol 30. Plenum Press, London, pp. 61-70
11. Duval E., Achibat T., Boukenter A., Varrel B., Calemczuk R., Salce B. (1995) . J. Non-Cryst. Solids, 190(3):258-263
12. Choy C.L., Greig D. (1977) . J. Phys. C: Solid State Phys. 10(2):169-179



13. E. ter Haar, R. Wagner, C. M. C. M. van Woerkens, S. C. Steel, G. Frossati, L. Skrbek, M. W. Meisel, V. Bindilatti, A. R. Rodrigues, R. V. Martinl, and N. F. Oliveira Jr., *J. Low Temp. Phys.* 99(1–2), 151–166 (1995).
14. Shekhar S., Prasad V., Subramanyam S.V. (2006) . *Carbon* 44, 334–340
15. Hao H.Y., Neumann M., Enss C., Fleischmann A. (2004) . *Rev. Sci. Instrum.* 75(8):2718–2725
16. Rosenberg D., Natelson D., Osheroff D.D. (2000) . *J. Low Temp. Phys.* 120(3–4):259–268
17. Rusby R.L., Durieux M., Reesink A.L., Hudson R.P., Schuster G., Khne M., Fogle W.E., Soulen R.J., Adams E.D. (2002) . *J. Low Temp. Phys.* 126(1–2):633642
18. Olson J.R. (1993) . *Cryogenics* 33(7):729731
19. Armstrong G., Greenberg A.S., Sites J.R. (1978) . *Rev. Sci. Instrum.* 49(3):345–347
20. G. Ventura, E. Gottardi, I. Peroni, and A. Peruzzi, *Proc. of Tempmeco, Berlin* (2001).
21. Scott T., Giles M. (1972) . *Phys. Rev. Lett.* 29, 642–643
22. Ventura G. et al. (1999) . *Cryogenics* 39, 481–484
23. Freeman J.J., Anderson A.C. (1986) . *Phys. Rev. B* 34:5684–5690
24. Ventura G. et al. (2000) . *Cryogenics* 40, 489
25. Mack J.X., Freeman J.J., Anderson A.C., Greig D. (1987) . *J. Non-Cryst. Solids* 91(3):391–401
26. Kelham S., Rosenberg H.M. (1981) . *J. Phys. C: Solid State Phys.* 14:1737–1749