CHAPTER 1

INTRODUCTION

Metals and dielectrics are the two major groups of materials, which remained the subject of study for physicists and electric industries during last two centuries. There have been numerous advances in both materials science and materials technology that have exerted considerable impact on the development of new materials and improvement of existing materials. The main support has come from the newer technologies associated with missiles and space research, high speed flights, nuclear engineering, computer, electronics and control engineering. From these fields have come demands for new materials to withstand condition not previously experienced by manmade components and to perform functions not previously envisaged. At this juncture it was realised that a new basic and fundamental approach to materials was necessary to obtain requisite properties. The semiconductor group of materials have bridged the gulf between the two extreme groups of metals and insulators and have found diverse technical applications.

The best known semiconductor is undoubtedly silicon (Si). In addition, many minerals found in nature, such as zinc-blende (ZnS), cuprite (Cu_2O) and galena (PbS) to name a few are semiconductors. The family of semiconductors, including those synthesized in laboratory, forms one of the most versatile class of materials known to man. Si and Ge together are the prototypes of a large class of semiconductors having similar structures. Compounds formed from elements of the groups III and V of the periodic table, such as GaAs, have properties very similar to their group IV counterparts. In going from the group IV elements to the III-V compounds, the bonding becomes partly ionic due to transfer of electronic charge from the group III atom to the group V atom. The ionicity becomes even larger and more important in the II-VI compounds such as ZnS. As a result, most

TABLE 1

Current and Proposed Applications for Thermoelectric devices

REFRIGERATION

- Spot Cooling of Electronics
  - Infrared detectors
  - Computer central processing units
  - X-ray detectors
  - Fiber-optic laser packages
- Picnic Coolers (Powered by Car Battery)
- Air conditioning in Submarines and Railway Coaches
- Water Coolers
- Superconducting Electronics
- Home Regrigerators

POWER GENERATION

- Power for Deep-Space Probes (Pioneer, Viking, Voyager, Galileo)
- Remote Weather Stations
- Remote Navigational Systems
- Submarines
- Subsea Power Generation (for Petroleum Wellhead Valves)
- Conversion of Waste Heat into Useful Electrical Power
  - Large diesel trucks
  - Steel industry
  - Chemical industry

performance, is independent of the system size. This leads to fabrication of miniature low-capacity cooling devices, which are found in a variety of commercial industrial, medical and laboratory appliances. However, if we go back to the past when thermoelectric effect was first observed by Seebeck in 1822, the only devices employed until mid twentieth century were metallic thermocouples for the measurement of temperature and thermopiles for the detection of radiant energy (based on the principle of thermoelectric generation of electricity from heat). The thermoelectric refrigerator using the Peltier effect was impossible then. The lack of practical applications of thermoelectricity then had resulted from the low thermoelectric efficiency of known materials.

The thermoelectric efficiency of a material depends on the thermoelectric figure of merit (Z) defined by [4]

$$Z = \alpha^2\sigma / \kappa$$

where α is Seebeck coefficient, σ is electrical conductivity, and κ is thermal conductivity.

The basic theory of thermoelectric generators and refrigerators was first derived satisfactorily by Altenkirch in 1909 and 1911. He showed that for both the applications, materials were required with high thermoelectric coefficients and electrical conductivities to minimize Joule heating and low thermal conductivities to reduce heat transfer losses.

The Wiedeman – Franz law states that the ratio of the thermal to electrical conductivities is the same for all metals at a given temperature. The maximum values of the figure of merit for metals are therefore obtained when the Seebeck coefficient is highest. However in no metallic thermocouple can a differential Seebeck coefficient of more than 100 μV/°C be realized. Hence no real progress was made with metallic thermocouples. It is only since semiconductor thermocouples have been prepared that efficient thermoelectric generators and refrigerators have become possible. In semiconductors, absolute Seebeck coefficients of up to one or more millivolts per degree may be obtained, but it is generally found that the ratio of thermal to electrical conductivity is much higher than the value given by the Wiedemann-Franz law. It is thus not immediately obvious that semiconductors are superior to metals as thermoelectric materials. However, it has been found that higher values of Z may be obtained with some semiconductors than for any metals.

The maximum value of Z which can be achieved using metals or metallic alloys was 0.23×10^{-3} K^{-1}, viz, that of Bi-Sb couple using 91%Bi and 9% Sb instead of pure Bi as the negative thermoelement. The thermocouple having the highest figure of merit, prior to 1950 was described by Telkes. She found that the best positive thermoelectric material was ZnSb and when the compound contained small quantities of Sn and Ag, its Seebeck coefficient measured against constantan was found to be 250 $\mu V°C^{-1}$. The maximum figure of merit Z for ZnSb is about 10^{-3} $°K^{-1}$ but the overall value of Z for a ZnSb-constantan thermocouple is only 5×10^{-4} $°K^{-1}$. There has been considerable improvement in thermoelectric materials since Telkes published the results of her survey. These improvements have come about largely owing to the use of compounds composed of elements of high atomic weight.

BISMUTH TELLURIDE AND RELATED ALLOYS

The studies of Ioffe[4] showed that the most promising materials for thermoelectric applications were compound semiconductors resulting from the combination of elements from groups II_B-V_A, IV_A-VI_A, and V_A-VI_A of the periodic table. Based on the large number of possibilities suggested by early workers, an exploratory investigation on thermoelectric refrigeration was started at many laboratories in the early 1950's. The highest figure of merit has been achieved using either the compounds of lead with group VI elements or the V-VI compounds, Bi_2Te_3 and Sb_2Te_3. Lindenblad[5] of RCA Laboratories constructed a small experimental thermoelectric refrigerator in 1954 using n-type lead telluride and p-type antimony telluride; and thus opened the way for his subsequent construction of a 4-ft^3 refrigerator (using both -n and -p type bismuth telluride). This was the first demonstration of a large-scale thermoelectric refrigerator.

Among the first and perhaps the most important works that established Bi_2Te_3 as a material of great promise for Peltier cooling was the investigation by Goldsmid and Douglas published in 1954[6]. Today, this compound semiconductor remains one of the major constituents in the best thermoelectric materials for use near room temperature. Equally significant in the development of useful thermoelectric materials is the concept of solid solution alloying first proposed by Ioffe and his co-workers[7]. Their theoretical considerations suggested that solid solution alloying can improve the thermoelectric figure of merit by decreasing the lattice thermal conductivity without adversely affecting the electrical properties. This is because alloying introduces short-range distortions in the lattice, which greatly enhance scattering of phonons but are much less effective in scattering charge carriers that have longer wavelength than phonons. This concept led to considerable research in recent years on the thermoelectric properties of alloys of compound semiconductors, particularly alloys in the generalized system $(Bi, Sb)_2(Te, Se)_3$[8-11]. Important in this connection is the work of Berkholz[8], and Rosi, Abeles and Jensen[9] who showed a significant reduction in the lattice thermal conductivity of Bi_2Te_3 upon alloying with Sb_2Te_3 or Bi_2Se_3. Bismuth telluride and antimony telluride, which have the same rhombohedral structure, form a continuous series of solid solutions[12]. Undoped $Bi_2Te_3 - Sb_2Te_3$ alloys are all p-type and the hole concentration increases markedly toward the Sb_2Te_3 rich region. Because of this strong p-type characteristics, studies to optimize the figure of merit of these alloys were confined to p-type materials. Carrier concentrations can be adjusted by controlled addition of doping materials. Elements, such as those in Groups IV_A and V_A (Sn, Pb, As, Sb and Bi), as well as Cd, were all found to provide free holes in Bi_2Te_3. However, the best and most reliable results for p-type Bi_2Te_3 were obtained with additions of excess Bi[9] or Pb[13]. For p-type alloys rich in Sb_2Te_3, excess Te[10] or Se[11] (donor elements) was used to adjust the carrier concentration by compensation, since undoped Sb_2Te_3 – rich alloys exhibit p-type conductivity too high for an optimum figure of merit. Yim et al.[14] have discussed the effect of doping by excess addition of Te and Se in Sb_2Te_3.

ANTIMONY TELLURIDE

Sb_2Te_3 is a rhombohedral layer type crystal (Space group $R\bar{3}m$) with a perfect cleavage perpendicular to the c-axis like in Bi_2Te_3 and Bi_2Se_3. The structure of this compound is shown in Fig. 1. The rhombohedral lattice can be regarded as a hexagonal layered structures in which the unit cell is a sequence of three five-layer groups. The sequence of the layers is as follows:

$\bullet\ B^1 = A - B^2 - A = B^1 \bullet B^1 = A - B^2 - A = B^1 \bullet B^1 = A - B^2 - A = B^1$

where A represents elements of group V (Bi, Sb) and B represents elements of group VI (Te, Se). The superscripts 1 and 2 indicate different positions of the atoms in the crystal lattice. The atoms in any one layer are the same. Each atom is located under the center of a triangle formed by the atoms in the next layers, i.e., it has three nearest atoms in each of the two neighbouring layers. The nature of chemical binding in Sb_2Te_3 and Bi_2Se_3 is similar to the binding in $BiTe_3$. The distances between layers in Sb_2Te_3 are listed in Table 2[15]. Horak et al.[16] have presented the results of a quantum chemical calculation, which yields some data on the bonding properties in V_2VI_3 crystals and confront them with structure data. The physical properties of Sb_2Te_3 are given in Table 3[15]. A number of authors[17-25] have studied the electrical transport and optical properties of this material. Sb_2Te_3 always exhibits p-type conduction, which no dopant has been found to change to n-type. Carrier density is very high ($\sim 10^{20}cm^{-3}$)[17,18]. Electrical conductivity which decreases with increasing temperature is pretty high too: $\sim 10^3$ $ohm^{-1}cm^{-1}$ perpendicular to the c-axis and $\sim 10^2 ohm^{-1}cm^{-1}$ parallel to it at room temperature[17-20,22]. The optical band gap is quite low (0.2-0.3 eV)[24,25]. So far as the magnetic properties are concerned, studies are very sparse and have been with powdered specimens only [26-28]. De Haas-Van Alphen and de Haas-Shubnikov

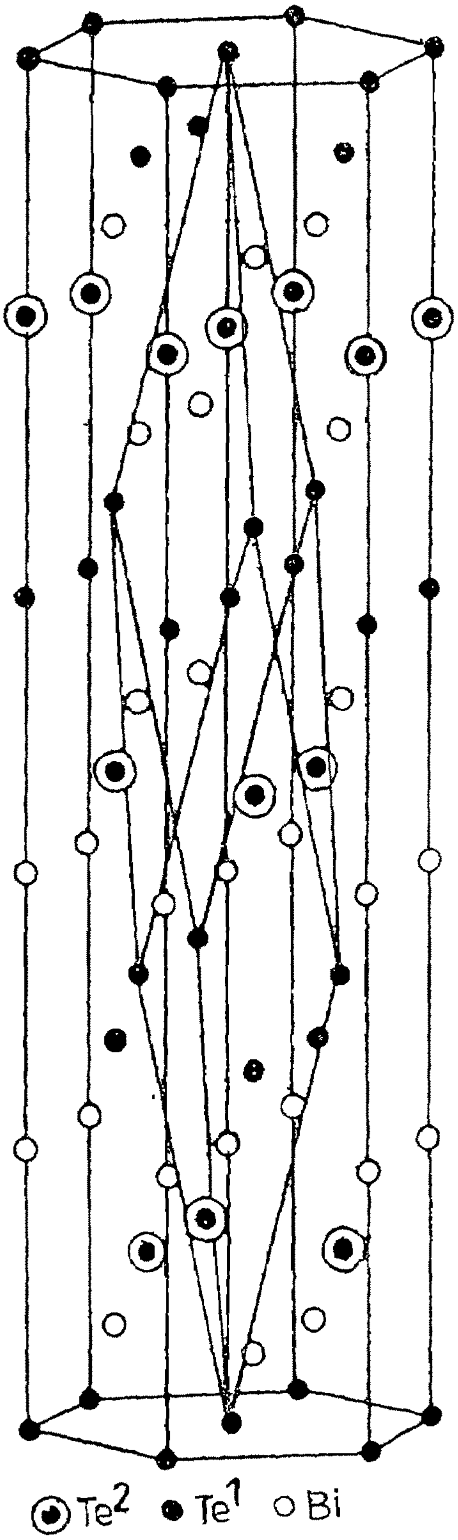

Fig. 1. Crystal Structure of the compound Bi$_2$Te$_3$

TABLE 2

Bond Lengths in Sb_2Te_3

Distance between layers, Å		
Sb-Te^1	Sb-Te^2	Te^1-Te^1
3.06	3.16	3.64

TABLE 3

Physical Properties of Sb_2Te_3

Melting point		621°C
Heat of formation (at 400°C)		-14.3 kcal.mole^{-1}
Heat of fusion		23.65 kcal.mole^{-1}
Specific heat at 80°K		4.9 cal/deg.mole
Debye temp. at 80°K		160
Density		6.57 g/cm^3
Forbidden band width	Optical	0.3eV 0.21eV
	Electrical	0.19eV
Thermal Conductivity at 300°K		0.04 W/cm.deg 0.055 W/cm.deg
Conduction type		P
Carrier density		2,3 . 10^{20} cm^{-3} 7. 10^{19}
Carrier mobility		269 cm^2/V.sec 280 cm^2/V.sec 360cm^2/V.sec
Effective mass, m^*/m_o		0.34 0.6

effects have been observed at extreme low temperatures[29,30]. A complex valence band comprising of two subbands has been suggested in both the cases, but results of one are at variance with those of others. A two valence band model has also been used by Ronnuld et al.[21] and subsequently by Smirnov et al.[22] to explain their transport data. Neither of them, however, suggests any exact mechanism involved. The electrical and optical anisotropy of Sb_2Te_3 single crystals was studied in [31] and thermoelectric and galvanomagnetic effects were investigated in [32-34]. Roy et al.[35] have done a comprehensive study of the magnetic as well as the electrical transport properties of single crystals of Sb_2Te_3 along both the principal directions over a temperature range of 100K to 600K and have proposed a mechanism of carrier excitation to explain the apparent contradiction in the electric and magnetic behavior of the substance on the basis of a two valence band model and by obtaining the values of the carrier parameters. Mzerd et al.[36] have reported the effect of heat treatment in N_2 and H_2 on the electrical properties of Sb_2Te_3 single crystals prepared by the Bridgman technique, as a function of temperature in the range from 90 to 300K and have observed that the material exhibits semiconducting behavior at low temperatures. Further, the activation energy reduces which is due to the passivation of the impurities and reduction in defect density. Banerjee and Bhattacharya[37] have studied the semiconducting behavior of semimetallic antimony telluride crystals at low temperature and showed that the impurity levels in Sb_2Te_3 are responsible for its semimetallic properties. We can find the valence band structure data of Sb_2Te_3 obtained from plasma reflectivity and transport measurements[38] and by the quantitative analysis of the dependence of galvanomagnetic and thermoelectric coefficients on temperature[35]. In [38 to 40] the nature of impurities in Sb_2Te_3 is described in connection with the doping properties. The new aspects of lattice vibrations, in [41 and 42], led to a modified concept for the chemical bonds in Bi_2Te_3 and Sb_2Te_3 single crystals. Effective masses are also given by the observation of anisotropy and dispersion of coupled plasmon-LO-phonon modes in Sb_2Te_3 [43].

The presence of antisite defects in Sb_2Te_3 and Bi_2Te_3 has been reported in several papers[44-47]. In Bi_2Te_3 crystals, their existence was confirmed by a direct method [44,45], while in Sb_2Te_3 their existence was revealed indirectly from the relations between an excess of antimony and the physical properties of the crystals [46,47]. Antisite (AS) defects Sb_{Te} have been identified to exist in p-Sb_2Te_3 crystals at concentrations of about 10^{20} cm^3; also the Bi_2Te_3 crystals have been shown to contain AS defects of Bi_{Te} at concentrations of about 10^{19} cm^{-3} [46,47]. In $A_2^VB_3^{VI}$ – type crystals the formation of antisite defects is influenced by the bond polarity. A low bond polarity is favourable for the formation of antisite defects and a change in the bond polarity of the crystals by an introduction of impurities can also change the concentration of antisite defects[48-50]. AS defects also exist in mixed crystals. Stary et al.[51] have determined the energy of formation of the antisite defects and have shown that Sb_{Te} defect concentration decreases monotonically with increasing content of Bi atoms in the whole region $0 < x < 2$ in $Bi_xSb_{2-x}Te_3$, while the Bi_{Te} defect concentration goes through a maximum at $x = 0.5$. This has been explained on the basis of changes in the bond polarity in the mixed crystals due to the variations in the concentration of Bi atoms built into the lattice of the Sb_2Te_3 crystals. Horak et al.[52] have determined the energy of formation of antisite defects in pure and doped Sb_2Te_3 and Bi_2Te_3 crystals and the changes in the energy of formation of antisite defects caused by an introduction of dopant atoms into the $A_2^VB_3^{VI}$ crystal lattice. They have shown that the incorporation of the dopant elements, In and Tl into the lattice of Sb_2Te_3 gives rise to the uncharged defects In_{Sb}^x and Tl_{Sb}^x , and the increase in the dopant elements causes the decrease of the antisite defects. This is due to the increase in the bond polarity which in turn increases the ionicity of the ternary crystals. This unfavorably affects the increase in antisite defects whose concentration decreases.

The extensive studies carried out on the single crystals of antimony telluride and its solid solutions are due to its widescope applications. The V_2VI_3 (V = Bi, Sb ; VI = Se, Te) binary compounds and their pseudobinary solid solutions are known to find applications ranging from photoconductive targets in T.V cameras to I. R. spectroscopy. Antimony telluride and its solid solutions with bismuth telluride or indium telluride, forms the current state of the art materials for applications in thermoelectric devices that act as temperature sensors, heat pumps, refrigerators, or power generators. Further, Sb_2Te_3 is also used in electromechanical devices[53], optical recording systems[54] and in infrared detectors because of its narrow band gap. In search of minimizing the dimension and cost of TE devices, thin film techniques are exploited for preparing them. Rajagopalan and Ghosh[55] reported electrical and thermoelectric properties of Sb_2Te_3 films deposited by a direct evaporation method. Patel and Patel[56] reported that Sb_2Te_3 films grown at 423 K by flash evaporation method were found to be single-phase polycrystalline, stoichiometric and to exhibit a minimum electrical resistivity. Patel and Patel[57] have investigated the feasibility and performance of p-type Sb_2Te_3 and n-type Bi_2Te_3 semiconductor thin films in the fabrication of thin film thermoelectric cooling devices. There are some results, published in recent years[58,59], about $(Bi_{0.25}Sb_{0.75})_2Te_3$ films having the same figure of merits, viz., $3.10^{-3}K^{-1}$, like single crystalline material. Thin films of these materials are also important in strain measurements. The strain-sensitivity coefficient of transducers based on bulk semiconductor elements as a rule does not exceed 100 rel unit. In reference 60 it was proposed that films of solid solutions based on bismuth telluride, in which the strain-sensitivity factor can reach values of the order 10^4 rel. units, can be used as the active elements in strain gauges.

THE PRESENT STUDY

Looking into the different perspectives of the studies that have been carried out on Sb_2Te_3 system and their widescope applications, the purpose of the present study is to explore a new aspect of this problem- namely, the interchange of atoms with the same nominal valence state between structures of different atomic symmetry. In particular, we have been concerned with the possible interchange of Bi or In with Sb between Bi_2Te_3 or In_2Te_3 and Sb_2Te_3. A systematic study on the crystal growth, compositional and structural characterization and optical and thermoelectric study of these crystals has been carried out. Further, thin film study including the effect of heat treatment on the structural, optical and electrical resistivity has been carried out on the $BiSbTe_3$ ternary system. The different techniques used and the results of the investigations are given in the chapters that follow.

REFERENCE

[1] Sales, B. C. (1998) MRS Bulletin, 23 (1), 16.

[2] Rowe, D. M. and Bhandari, C. M. (1983) Modern Thermoelectrics, Holt, Rinchart, and Winston, London, 103.

[3] "A New Generation of Cooling Devices" (1995) Photonic Spectra, 50.

[4] Ioffe. A. F. (1957) Semiconductor Thermoelements and Thermoelectric Cooling, Infosearch, London.

[5] Lindenblad, N. E. (1954) Unpublished results.

[6] Goldsmid, H. J. and Douglas, R. W. (1954) Br. J. Appl. Phys., 5, 386.

[7] Ioffe, A. F., Airapetiants, S. V., Ioffe, A. F., Kolomets, N. V. and Stil'bans, L. S. (1956) Dokl. Akad. Nauk. SSSR 106, 981.

[8] Birkholz, U. (1958) Z. Naturforsch, 13a, 780.

[9] Rosi, F. D., Abeles, B. and Jensen R. V. (1959) J. Phys. Chem. Solids 10, 191.

[10] Smirous, K. and Stourac, L. (1959) Z. Naturforsch, 14a, 848.

[11] Rosi, F. D., Hockings E. F. and Lindenblad, N. E. (1961) RCA Rev. 22, 82.

[12] Smith, M. J., Knight, R. J. and Spencer, C. W. (1962) J. Appl. Phys. 33, 2186.

[13] Rosi, F. D and Ramberg, E. G. (1960) Thermoelectricity (edited by P. H. Egli) Wiley, NewYork.

[14] Yim, W. M. and Rosi, F. D. (1972) Solid State Electronics 15, 1121.

[15] Abrikosov, N.kh., Bankina, V. F., Poretskaya, L. V., Shelimova, L. E. and Skudnova, E. V. (1969) Semiconducting II-VI, IV-VI, and V-VI Compounds, Plenum Press, New York, 178,189,197.

[16] Horak, J., Stary, Z. and Klikorka, J. (1988) Phys. Stat. Sol. (b), 147, 501.

[17] Black J., Conwell E. M., Seigle L. and Spencer C. W. (1957) J. Phys. Chem Solids 2, 240.

[18] Harman T. C., Paris B., Miller S. E. and Goering H. L. (1957) J. Phys. Chem Solids 2, 181.

[19] Jaschke R. (1965) Ann. der Physik 15, (1), 106.

[20] Liebe L. (1965) Ann. der Physik 15, (7) 179.

[21] Ronnlund B., Beckmann O. and Levy H. (1965) J. Phys. Chem Solids 26, 1281.

[22] Smirnov I. A., Andreev A. A. and Kutasov V. A. (1968) Sov. Phys. Solid State 10, (6), 1403.

[23] Alzewel K. A., Abou Sekkina M. A. and Hanafi Z. M. (1975) Z. Phys. Chem. 94, 235.

[24] Horak J., Tichy L., Vasko A. and Frumar M. (1972) Phys. Stat. Sol. (a) 14, 289.

[25] Tichy L., Horak J., Vasko A. and Frumar M. (1973) Phys. Stat. Sol. (a) 20, 725.

[26] Matyas M. (1958) Czech. J. Phys. 8, 309.

[27] Horak J., Matyas M. and Tichy L (1975) Phys. Stat. Sol. (a) 27, 621.

[28] Kutvitskii V. A., Shurygin P. M. and Kiselev V. B. (1972) Tekhnol. Mater. Elektron. Tekh. 2, 153.

[29] Schwartz H., Bjoerck G. and Beckmann O. (1967) Solid State Commun. 5, 905.

[30] Von Middendorf A., Dietrich K. and Landwehr G. (1973) Solid State Commun. 13,(4), 443.

[31] Langhammer, H. T., Stordeur, M., Sobotta, H. and Riede, V. (1982) Phys. Stat. Sol. (b) 109, 673.

[32] Simon, G. and Eichler, W. (1981) Phys. Stat. Sol. (b) 103, 289.

[33] Stordeur, M. (1984) Phys. Stat. Sol. (b) 124, 439.

[34] Stordeur, M. and Simon, G. (1984) Phys. Stat. Sol. (b) 124, 799.

[35] Roy, B., Chakraborty, B. R., Bhattacharya, R. and Dutta, A. K. (1978) Solid State Commun. 25, 617.

[36] Mzerd, A., Sayah, D., Tedenac, J. C. and Boyer, A. (1994) Phys. Stat. Sol. (a) 141, 183.

[37] Banerjee, D. and Bhattacharya, R. (1986) Indian J. Phys. 60A, 381.

[38] Horak, J., Lostak, P., Siska, L. and Stordeur, M. (1982) Phys. Stat. Sol. (b) 114, 39.

[39] Sussmann, H., Priemuth, A. and Prohl, U. (1984) Phys. Stat. Sol. (a) 82, 561.

[40] Lostak, P., Novotny, R., Horak, J. and Klikorka, J. (1985) Phys. Stat. Sol. (a) 89, K55.

[41] Kullmann, W., Geurts, J., Richter, W., Lehner, N., Rauh, H., Steigenberger, U., Eichhorn, G. and Geick, R. (1984) Phys. Stat. Sol. (b) 125, 131.

[42] Dato, P. and Kohler, H. (1984) J. Phys. C 17, 3711.

[43] Richter, W., Krost, A., Nowak, U. and Anastassakis, E. (1982) Z. Phys. B. 49, 191.

[44] Miller, G. R. and Che-Yu, Li. (1965) J. Phys. Chem. Solids 26, 173.

[45] Kutasov, V. A. and Smirnov, I. A. (1966) Phys. Stat. Sol. 18, 479.

[46] Horak, J., Tichy, L., Lostak, P. and Vasko, A. (1976) Cryst. Lattice Defects 6, 223.

[47] Brebrick, R. F. (1969) J. Phys. Chem. Solids 30, 719.

[48] Horak, J., Lostak, P. and Benes, L. (1984) Phil. Mag. B 50, 665.

[49] Lostak, P., Horak, J. and Koudelka, L. (1983) Phys. Stat. Sol. (a) 79, K71.

[50] Lostak, P., Horak, J. and Koudelka, L. (1984) Phys. Stat. Sol. (a) 84, K143.

[51] Stary, Z., Horak, J., Stordeur, M. and Stolzer, M. (1988) J. Phys. Chem. Solids 49, 29.

[52] Horak, J. Cermak, K. and Koudelka, L. (1986) J. Phys. Chem. Solids 47, 805.

[53] Sakai, N., Kajiwara, T., Takemura, K., Mimomura, S. and Fuji, Y. (1981) Solid State Commun. 40, 1045.

[54] Watanabe, K., Sato, N. and Miyaoka, S. (1983) J. Appl. Phys. 54, 1256.

[55] Rajagopalan, N. S. and Ghosh, S. K. (1963) Physica 29, 234.

[56] Patel, T. C. and Patel, P. G. (1984) Mater. Lett. 3, 46.

[57] Patel, N. G. and Patel, P. G. (1992) Solid State Electronics 35, 1269.

[58] Volklein, F., Baier, V., Dillner, U. and Kessler E. (1990) Thin Solid Films 187, 253.

[59] Stolzer, M., Stordeur, M. and Stark, I. (1996) 14th International Conference on Thermoelectrics (ICT) XIV, St. Petersburg, 445.

[60] Atakulov, Sh. B., Azimov, T. and Shamsiddinov, A. N. (1982) Sov. Phys. Semicond. 16, 1326.