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Preparation, sintering and electrical behaviour of cobalt, nickel and zinc germanate

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Cobalt, nickel and zinc germanate were prepared by solid state reactions between the relevant oxides in air. Ceramics with monophase structures could be obtained by adopting the optimum temperature and time. The as-fired ceramics exhibited insulating properties; however, by an additional heat treatment under reducing conditions, variable electrical conductivity could be induced in the ceramic bodies. Temperature/resistivity characteristics of these materials showed typical semiconducting behaviour. X-ray studies showed that despite the changes in electrical behaviour, and apparent changes in colour after annealing, the structures remained unaltered. Microstructural studies using scanning electron microscopy also showed that there were no substantial changes due to the reductive annealing processes.

1. Introduction

Ternary compounds with the general formula M_x–M′–O_y, where M and M′ represent two different metal ions, and normally $x = 1$ or 2, $y = 2$–4, are of scientific and technological interest. The germanates of cobalt, nickel and zinc are examples of such ternary compounds for which limited numbers of individual studies have been performed. For example, the optical properties of a number of ceramics including zinc germanate have been studied using infrared spectroscopy [1]. The post-spinel phases of a number of silicates and germanates under high-pressure phase transitions have been observed showing that zinc germanate in a distorted spinel form yields an unidentified orthorhombic phase of $ZnGeO_3$ [2]. The behaviour of germanium in roasting, purification and electrowinning stages of electrolytic production of zinc have also been studied. In this, germanium dioxide and zinc sulphide were roasted at 900 °C to form Zn_2GeO_4 [3]. In the patent literature, zinc germanate has been mentioned in the production of solid-state batteries and solid electrolyte thin films [4, 5].

There is even less research reported in the literature concerning cobalt germanate, and most studies seem to have been carried out in conjunction with other germanates [6]. With reference to Co_2GeO_4, structural studies by X-ray diffraction (XRD) and visible light reflectance were carried out on the spinel solid solutions containing cobalt germanate and were found to be of the inverse-type spinel.

The crystallographic and electrical properties of nickel germanate (Ni_2GeO_4) have been studied with respect to other nickel germanium oxides [7]. Monophasic samples were found to possess a structure similar to that of the NaCl-type unit cell and it was found that Ge^{4+} ions were accommodated in the NiO lattice by substitution, thereby, increasing the nickel vacancy concentration and simultaneously decreasing the number of charge carriers (holes). Further, the mechanism of electron transport in the above material is explained by reinvoking the "hopping" model [7].

In a systematic study of ternary ceramic compounds, the preparation, physical properties and potential applications of many members of this family have already been investigated. In particular, cadmium germanate, Cd_2GeO_4, zinc stannate, Zn_2SnO_4, copper germanate, $CuGeO_3$, and lead stannate, Pb_2SnO_4, have been the subject of recent reports [8–11].

2. Experimental procedure

Cobalt, nickel and zinc germanates (Co_2GeO_4, Ni_2GeO_4 and Zn_2GeO_4) have been prepared in the present study, using conventional ceramic-processing routes, to investigate their sintering characteristics. Samples were then partially reduced, and the electrical behaviour compared with that of the as-fired samples.

Cobalt germanate was prepared by ball milling Co_3O_4 and GeO_2 in a molar ratio of 2:3, using high-purity commercially available powders. The powder was calcined at 800–900 °C for 6–12 h, followed by crushing and regrinding to a fine powder. It is commonly believed that Co_3O_4 decomposes to CoO at temperatures above 800 °C in air [12]. Therefore, it is reasonable to assume the solid-state reaction takes place between GeO_2 and CoO to produce Co_2GeO_4.

In both zinc and nickel germanates, the starting materials were analar grade oxides. The ball milling,

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calcination and sintering processes were identical to the cobalt germanate case, as described above.

Pellets, 13 mm diameter, were pressed and sintered in air at temperatures around 1200 °C for 12 h. As-fired samples which were generally electrically insulating and had a dark blue colour (cobalt germanate), white (zinc germanate), and light blue (nickel germanate), were ground to a powder and examined using XRD. Microstructural studies of sintered samples together with the microanalysis of grain boundaries and grains were performed using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. A series of the as-fired samples were annealed in a stream of H_2/N_2 gas at temperatures in the range 300–450 °C for a further 12 h in order to establish the optimum annealing temperature for improved electrical conductivity. The same sequence of investigations, i.e. XRD, SEM and EDX, were performed in order to determine any compositional and microstructural changes to the material upon secondary heat treatment. Two-point resistivity measurements were performed between room temperature and ~ 100 K, using a microprocessor-controlled cryostat system, to study the electrical behaviour of samples before and after the heat treatment.

3. Results and discussion

Fig. 1 shows XRD patterns of cobalt, nickel and zinc germanate samples at three stages of preparation. The XRD patterns of the precursor powders prior to any heat treatment are shown in Figs 1a, 2a and 3a for Co_3O_4/GeO_2, NiO/GeO_2 and ZnO/GeO_2, respectively.

Calcined powders that were pressed and sintered at 1200 °C for 12 h exhibited XRD patterns of Co_2GeO_4, Ni_2GeO_4 and Zn_2GeO_4, as shown in Figs 1b, 2b and 3b, respectively. It is evident that the choice of a suitable regime of heat-treatment can lead to the production of almost monophase materials having no residual precursor material. Also, there is evidently a striking resemblence between the XRD patterns of cobalt and nickel germanates, suggesting that despite slight differences, the two structures are basically similar.

It is worth noting that the obvious choice of original oxide for production of cobalt germanate is cobaltous oxide (CoO); however, the use of cobaltic oxide (Co_3O_4) was justified as it produced a single-phase Co_2GeO_4, at a far lower cost.

As in many other ternary compounds, the as-fired bodies were found to be electrically insulating materials [8–11]. A subsequent heat treatment in a reducing atmosphere, however, produced ceramic bodies with variable degrees of conduction. Figs 1c, 2c and 3c show typical XRD patterns for germanates reduced at 350 °C for 12 h, which can be seen to be identical to those of the as-fired materials. A dramatic change in colour was also observed on reduction, from pale colours in as-fired nickel and zinc germanates, to dark grey or black.

The similarity for the XRD patterns of the two differently treated materials suggests that no phase changes have taken place during the reduction treatments, despite the colour changes. This implies that the processes of reduction are not associated with the formation of any metallic species. This behaviour has also been observed in some other members of the

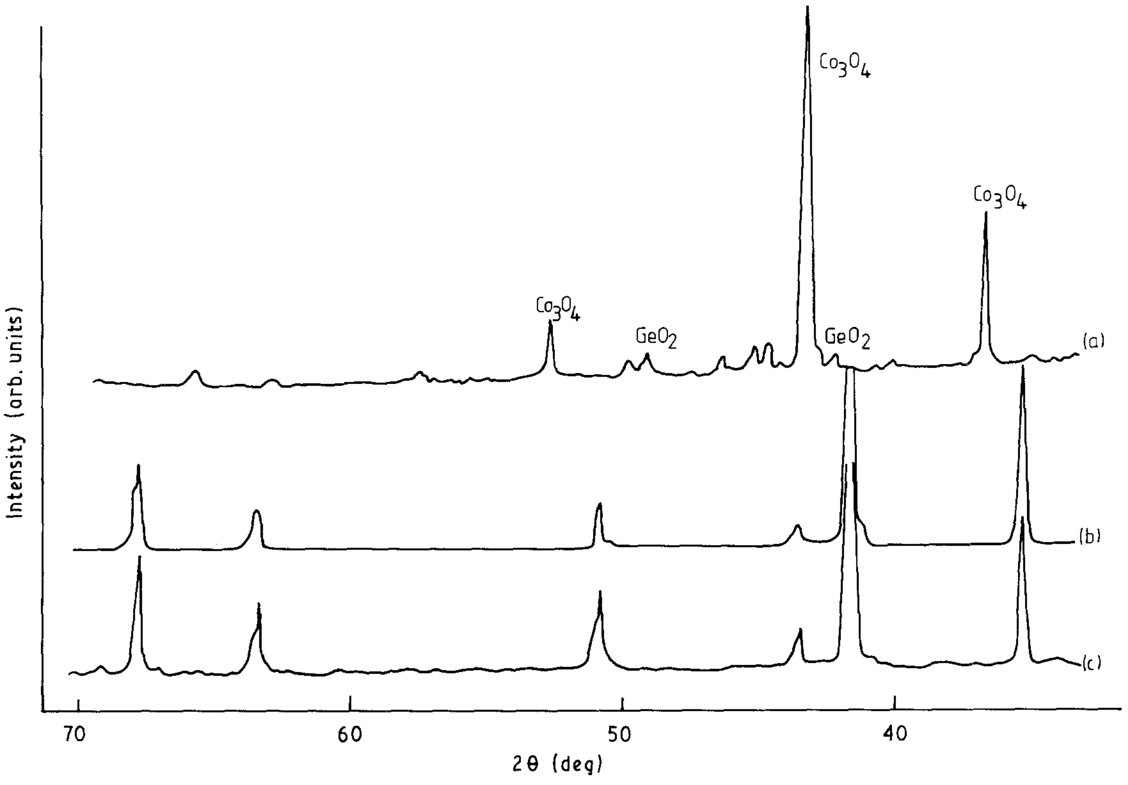

Figure 1 X-ray diffraction patterns of the (a) precursor powder, (b) as-fired, and (c) reductively annealed cobalt germanate.

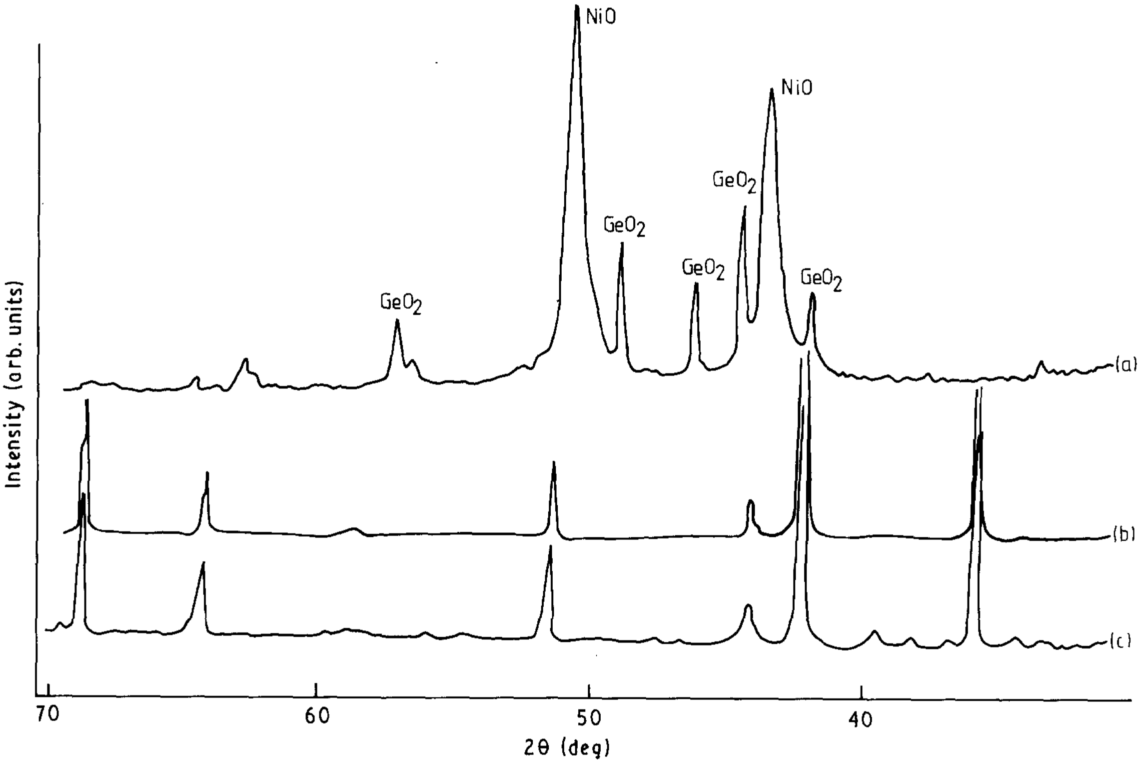

Figure 2 X-ray diffraction patterns of the (a) precursor powder, (b) as-fired, and (c) reductively annealed nickel germanate.

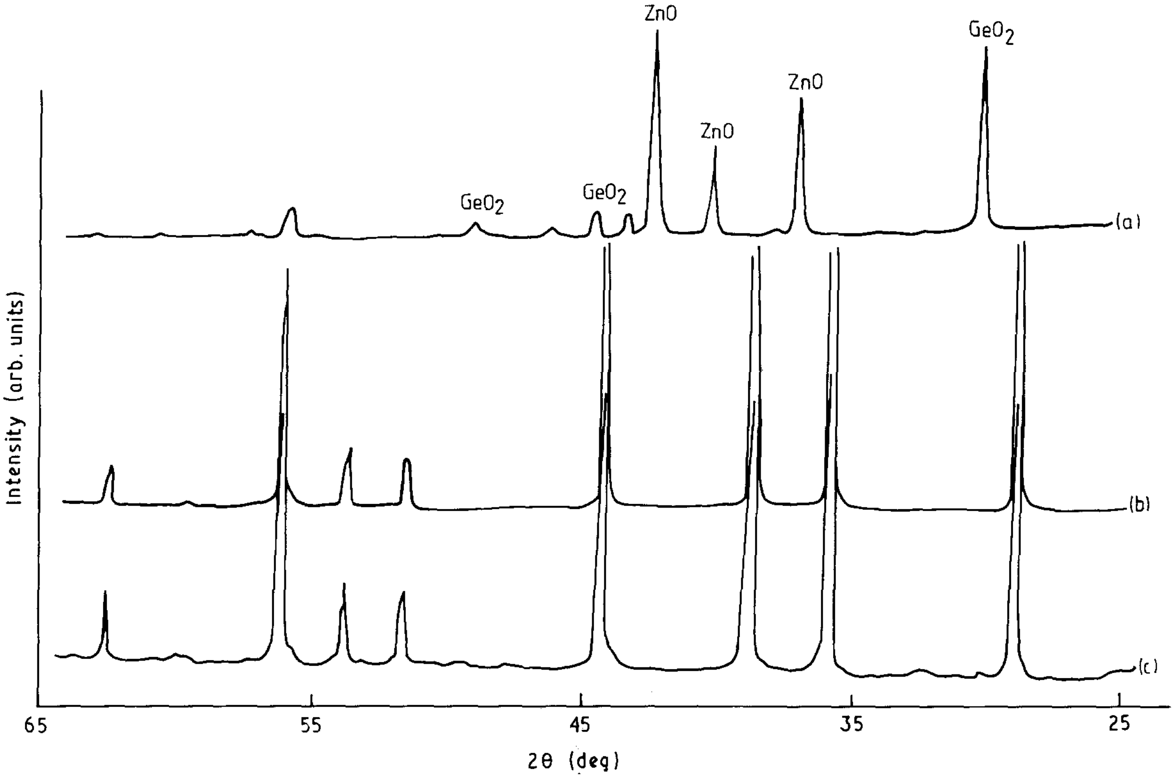

Figure 3 X-ray diffraction patterns of the (a) precursor powder, (b) as-fired, and (c) reductively annealed zinc germanate.

ternary compounds [8–11], and has important consequences.

Firstly, as was mentioned earlier, there is a large increase in electrical conductivity on annealing in a reducing atmosphere, giving these materials potential applications as sensors for reducing or oxidizing atmospheres. Secondly, because the reduction processes were not associated with any phase changes, the oxidation/reduction cycles may, in principle, be repeated for an infinite number of cycles, without the danger of the build-up of any internal stress.

The typical microstructure of an as-fired sample is shown in Fig. 4a–c which in the cases of zinc and cobalt germanates indicates lamellar structures.

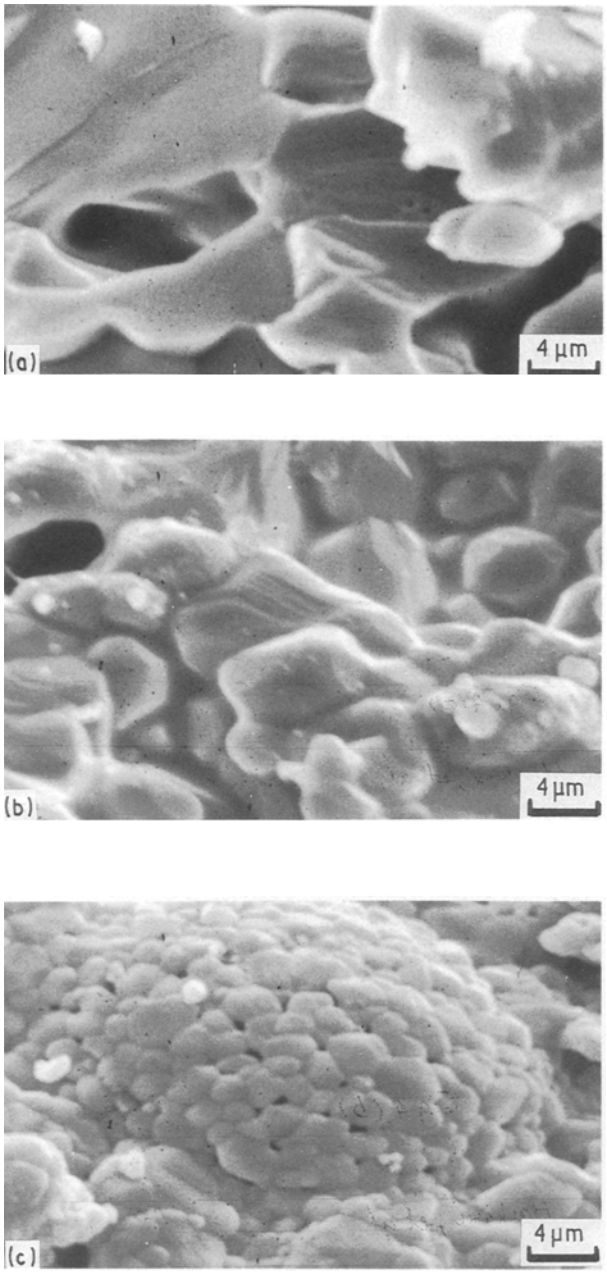

Figure 4 Scanning electron micrographs of as-fired surfaces of (a) cobalt, (b) nickel, and (c) zinc germanates.

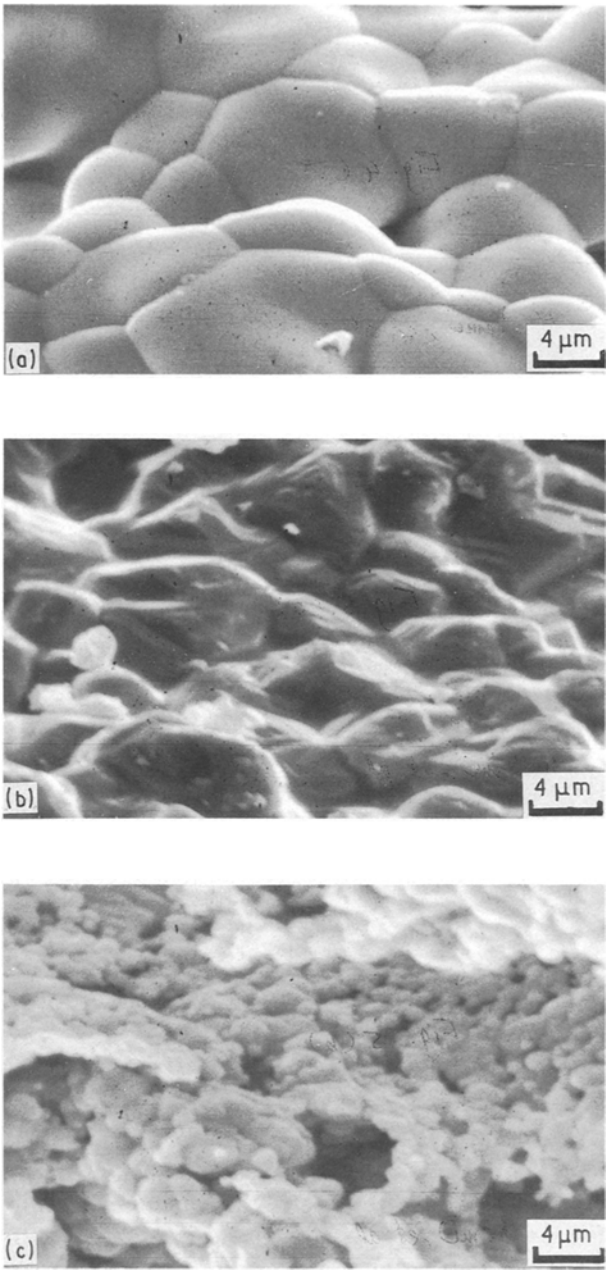

Figure 5 Scanning electron micrograph of reductively annealed samples of (a) cobalt, (b) nickel, and (c) zinc germanates.

Fig. 5a–c show the typical microstructures of reduced samples. The little differences in microstructures of the annealed samples compared with those of the as-fired body, are due to small but finite rearrangements of the grains at the annealing temperature.

EDX analysis of grains and grain boundaries of as-fired samples of both cobalt and nickel revealed a slight but reproducible increase in the germanium peak compared to that of the other metallic constituent occurring in the grain boundaries. This suggests that the mechanism of the solid-state reaction leading to grain growth and sintering in both cases is through the germanium-rich liquid-phase formation. This mechanism of sintering is similar to that of other closely related compounds such as cadmium germanate in which a germanium-rich second phase proved to be responsible for sintering and grain growth [9], and a germanium-rich grain-boundary phase could be readily identified.

On the other hand, in the case of zinc germanate, the ratio of zinc to germanium peaks in EDX spectra increased within the pores, with no indication of liquid-phase formation. This behaviour is quite similar to the closely related ternary compound zinc stannate in which an evaporation–condensation mechanism for sintering was found [8], where like the zinc germanate case, the EDX analysis showed an increase in Zn/Sn ratio between grains and pores.

Measurement of the shrinkage of the green bodies during the sintering also supports the suggested sintering mechanisms. In both cobalt and nickel germanates, the samples suffered shrinkages of 4% and 7%, respectively, whereas in the case of zinc germanate there was an *expansion* of about 5%, which is consistent with an evaporation–condensation model.

Two-point resistivity measurements revealed the light-coloured air-sintered samples to be electrically insulating. The reduced (black) samples, on the other

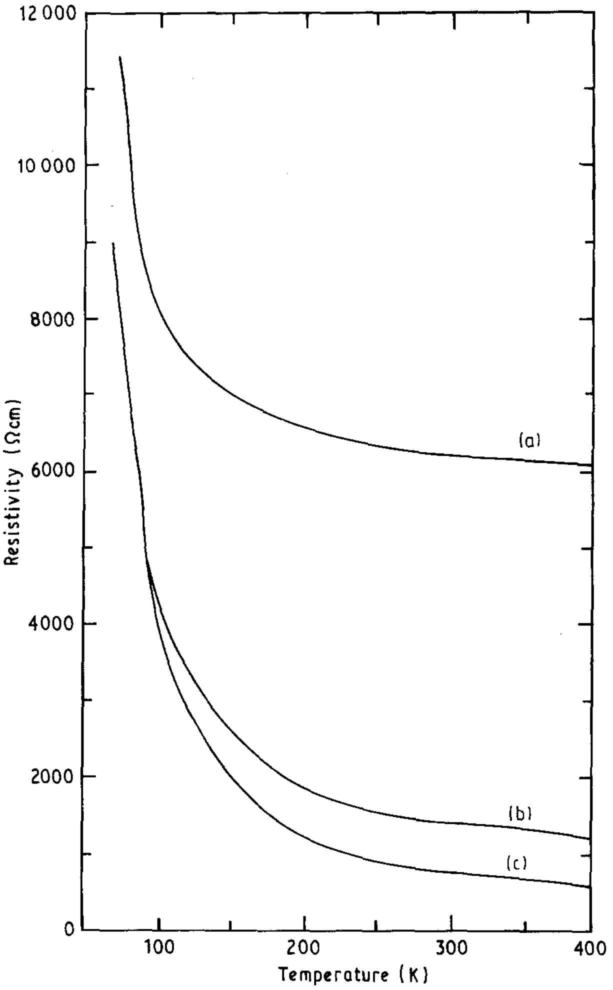

Figure 6 Resistivity–temperature characteristics of samples sintered in air and subsequently annealed in a stream of H_2/N_2 gas at 350 °C for 12 h: (a) Zn_2GeO_4, (b) Ni_2GeO_4, and (c) Co_2GeO_4.

hand, exhibited greatly improved electrical resistivity, of a few kilo-ohm centimetres at room temperature. Fig. 6 is a plot of resistivity versus absolute temperature for samples annealed at 350 °C, showing behaviour typical of semiconductors. It was possible to induce much higher conductivity in these samples by annealing them at higher temperatures. On the other hand, if the black coloured, reduced samples were heated in air at 600 °C for a few minutes, they returned to their original light colours and exhibited insulating properties.

4. Conclusion

Monophase germanates of cobalt (Co_2GeO_4), nickel (Ni_2GeO_4), and zinc (Zn_2GeO_4), can be prepared by solid-state reactions between the two relevant oxides at a temperature around 1200 °C in air. The resulting electrically insulating bodies can then be reductively annealed at 300–400 °C to produce an identical phase with variable electrical conductivities, orders of magnitude higher than in the unreduced cases. Although the solid-state reaction is thought to involve the interdiffusion of the two metallic species, this would not necessarily lead to sintering on its own. Consequently, the degree of densification observed in the cobalt and nickel germanates would suggest that a liquid-phase mechanism, rich in germanium, is responsible. On the other hand, in the case of zinc germanate, a germanium-rich liquid phase proved to be absent and the mechanism responsible for sintering is thought to be one of evaporation–condensation. The reductively annealed samples appeared to behave as typical semiconductors, with identical structures and microstructures to those of the as-fired samples.

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References

1. S. MUSIKANT and W. F. SAVAGE, *Proc. Soc. Photo-opt. Instrum. Engng* **256** (1980) 27.
2. L. LIU, in "High-Pressure Research: Applied Geophysical", edited by M. H. Manghani and S. Akimoto (Academic Press, New York, 1977) p. 245.
3. Y. UMETSU and K. TOZAWA, *Nippon Kogyo Kaishi* **102** (1986) 423.
4. H. OTSUKA, T. OKADA and A. YAMAJI, Jpn Kokai Tokkyo Koho Jp 61 128 468 (1986).
5. Jpn Kokai Tokyo Koho Jp 59 12 503 (1984).
6. K. HIROTA, M. OHTANI, N. MOCHIDA and A. OHTSUKA, *Nippon Seramikkusa Kyokai Gakujutsu Ronbunshi* **97** (1989) 8.
7. A. L. SHASHIMOHAN, H. N. SHRIVASTAVA and A. B. BISWASS, *Indian J. Pure Appl. Phys.* **14** (1976) 947.
8. T. HASHEMI, H. M. Al-ALLAK, J. ILLINGSWORTH, A. W. BRINKMAN and J. WOODS, *J. Mater. Sci. Lett.* **9** (1990) 776.
9. T. HASHEMI, J. ILLINGSWORTH and A. W. BRINKMAN, *ibid.* **8** (1990) 1176.
10. *Idem., ibid.* **11** (1992) 255.
11. *Idem., ibid.* **11** (1992) 666.
12. A. NAVROTSKY, in "Inorganic Chemistry Series", Vol. 5(1), edited by D. W. A. Sharp (Butterworths, London, 1974) 43.

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