

ALUMINIUM-SUBSTITUTED ZINC OXIDE FOR THERMOELECTRIC ENERGY CONVERSION

Schaeuble N., Aguirre M. H., Robert R., Weidenkaff A., Trottmann M., Haemmerli A., Bocher L., Hug P.

Solid State Chemistry, EMPA, Ueberlandstrasse 129, CH-8600 Duebendorf
Contact author: anke.weidenkaff@empa.ch

Abstract

Polycrystalline $Zn_{1-x}Al_xO$ ($x = 0, 0.01$) phases were prepared by different soft chemistry (SC) synthesis routes. SC leads to particle sizes one order of magnitude smaller compared to solid state reaction (SSR) products. The particle size has an important impact on reducing the thermal conductivity κ , e. g. SC samples exhibit κ values which are three to five times lower than the ones from SSR at room temperature.

The Seebeck coefficient values of the n-type thermoelectric materials lie in the range of -80 to -250 $\mu V/K$ for $Zn_{1-x}Al_xO$, ($x = 0.01$) and -800 to -450 $\mu V/K$ for ZnO from room temperature to 1273 K. The electrical resistivity decreases from 250 Ωcm at room temperature to 0.1 Ωcm at 1273 K for ZnO. 1 % Al-substitution decreases the resistivity to a value of 0.5 Ωcm at room temperature and 0.2 Ωcm at 1273 K. These results promise a high figure of merit for Al-substituted ZnO combined with a thermal stability over a large temperature range.

Introduction

Thermoelectricity (TE) allows the direct transformation of heat into electricity. In TE modules, there is no need for mechanical parts that cause noise and abrasion and there are neither emissions nor waste products. Suitable TE materials are those with a high figure of merit $ZT = S^2T / \rho\kappa$ (with the temperature T , the Seebeck coefficient S , the resistivity ρ and the thermal conductivity κ). State-of-the-art Bi_2Te_3 materials display good TE properties in a low temperature range however they are toxic and unstable at high temperatures. Materials with a high thermal stability open the field to high temperature applications.

Zinc oxide is one of these materials with a high stability in air up to temperatures higher than 800 K. It has already been pointed out to be a promising TE material by Tsubota et al in 1997 [1] due to its high Seebeck coefficient, low-cost production and non-toxicity. But zinc oxide exhibits high electrical resistivity and high thermal conductivity. Substituting 1 mol% zinc by aluminium improves the thermoelectrical properties. The electrical resistivity decreases without a strong effect on the Seebeck coefficient. However, the thermal conductivity is still a drawback of either doped and undoped zinc oxide in comparison to the state-of-

the-art TE materials. One way to reduce the thermal conductivity is structuring the morphology on the nano-scale range. The increase of boundary scattering for phonons could be highly beneficial to lower the lattice thermal conductivity in oxides without deteriorating the electron mobility.

Nano-scaled materials were prepared in order to reduce the thermal conductivity. Aluminium-substituted zinc oxide (with 1 mol% Al-content) was synthesised by different SC methods:

1) by mixing zinc and aluminium nitrates with citric acid (CA) and ethylene glycol (EG) and 2) by using a tri-block copolymer as the organic supermolecular template. The results were compared to state-of-the-art solid state reaction synthesised material.

The aim of this work is to analyse the effect of the morphology of the samples prepared by the different synthesis methods on the thermoelectric properties.

Experimental

The first method to produce fine particles of $Zn_{1-x}Al_xO$, ($x = 0.01$) was by thermal decomposition of the corresponding polymeric citrate precursors [2]. The required amount of $Zn(NO_3)_2 \cdot 6 H_2O$ (Sigma Aldrich, 98 %) and $Al(NO_3)_3 \cdot 9 H_2O$ (Merck, ≥ 98.5 %) was dissolved in water. Citric acid (anhydrous, Riedel-de Haën) was added as chelating ligand to complex the different cations. Two batches were prepared with the following ratios: a) cations/CA molar ratio of 1:4 and b) cations/CA/EG molar ratio of 1:4:10.4. The solutions were homogenized at 373 K for 4h under continuous stirring and reflux. The precursor solutions were dried by removing the reflux to promote the formation of colourless viscous gels. The precursors were heated up to 573 K with a heating rate of 20 K/min and decomposed at 573 K for 2 to 10h.

The second synthesis method was based on copolymerisation using a poly(alkyl oxide) copolymer as a structure-giving agent. The polymer $HO(CH_2CH_2O)_{20}-(CH_2CH(CH_3)O)_{70}-(CH_2CH_2O)_{20}H$ ($EO_{20}PO_{70}EO_{20}$, Aldrich) was solved in ethanol (EtOH). 1 M HCl was added and the mixture was stirred for 10 min. The required amount of $Zn(NO_3)_2 \cdot 6 H_2O$ (Sigma Aldrich, 98 %) was added and after stirring the solution for 1h it was gelled at 313 K for 7 days to build the metal oxide network. The gel was then dried at 353 K for another 7 days.

Few mg of the SC precursors were collected to determine the thermal decomposition mechanism and the lowest synthesis temperature of the phase formation. The phases were obtained by milling and calcination of the amorphous xerogel at 1073 K.

For comparison $Zn_{1-x}Al_xO$ ($x = 0.01$) was synthesised by solid state reaction (SSR). The required amount of ZnO (Aldrich, nanopowder < 100 nm) and Al_2O_3 (Sigma Aldrich, 99.7 %) was mixed in a agate mortar with acetone and pressed into round pellets. The pellets were sintered at 1673 K for 10h.

The thermal decomposition of the citrate and the copolymer precursor was studied by thermogravimetric analysis (TGA) using a Netzsch STA 409 CD thermobalance coupled to a mass spectrometer (MS). Simultaneously recorded thermogravimetric (TG) and differential thermal analysis (DTA) was carried out in synthetic air (80% helium and 20% oxygen) up to 1273 K with a heating rate of 10 K/min. The Netzsch QMS 403 C Aëlos mass spectrometer allows to identify gaseous reaction products released during the decomposition. Phase purity of the products was confirmed by X-Ray Diffraction (XRD) with a PANanalytical X'pert diffractometer using $Cu-K\alpha$ radiation. The morphology of the calcined powders was studied using a Scanning Electron Microscope (SEM) LEO JSM-6300F and a Hitachi S-4800. The structure of the samples was studied by Transmission Electron Microscopy (TEM) using a Philips CM 30. The cationic composition was investigated by EDS (Energy Dispersive Spectroscopy) *in situ* in conventional TEM in the range of 30 nanometers.

Powder calcined at 1073 K was pressed into pellets and sintered in air at 1273 K and 1673 K in order to determine transport and thermal properties. The circular pellets of 10mm diameter were used for thermal conductivity measurements. The thermal conductivity k was calculated by the following equation: $\kappa = \rho \alpha C_p$, where ρ is the bulk density determined by geometrical method. The thermal diffusivity α was measured by the laser flash method using a Netzsch LFA-457 apparatus from 300 K to 1273 K in argon atmosphere. The heat capacity C_p was measured by differential scanning calorimetry using a Netzsch DSC 404C Pegasus. The transport properties measurements were done on bar-shaped pellets cut from the circular pellets with general dimensions of 1.70 mm \times 1.60 mm \times 3.50 mm. The electrical conductivity and Seebeck coefficient were measured in air simultaneously as a function of temperature from 313 K to 1273 K using the RZ2001i measurement system from Ozawa Science, Japan. The electrical conductivity was determined using a four-point probe method. Two electrical contacts were positioned at both ends of the sample and the two other contacts were on the sample body. The contacts at both ends were fixed mechanically

with Pt layers. The contacts on the sample are made by surrounding the bar-shaped sample with Pt wires.

Results and discussions

Polycrystalline $Zn_{1-x}Al_xO$ ($x = 0, 0.01$) phases were synthesized by different SC synthesis routes. During the cation complexation process in polymerisation, a network is formed between citric acid (CA) and the different cations. When ethylene glycol (EG) is added, this forms an even stronger network by polyesterification with CA. The thermogravimetric analysis of the AlZn-citrate precursor reveals a stepwise decomposition mechanism leading to $Zn_{1-x}Al_xO$ phase formation. Fig. 1 shows the TGA and DTA curves for the decomposition and phase formation of $Zn_{1-x}Al_xO$ with CA (polymerisation route a). The TGA/DTA curves of polymerisation with EG (route b) and copolymerisation look similar (not shown).

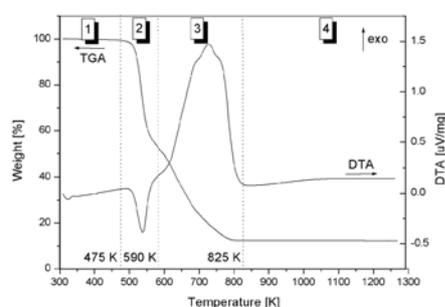


Fig. 1: TGA/DTA of the thermal decomposition and phase formation of the $Zn_{0.99}Al_{0.01}O$ precursor with CA

At 475 K the decomposition of the organic material and the phase formation start and proceed up to 825 K. There is a weight loss of 87.2 % accompanied by the emissions of CO_2 (m/z 44), H_2O (m/z 18) and CO (m/z 28) and the consumption of oxygen (m/z 32) detected by the mass spectrometer (Fig. 2). In the synthesis with CA and EG there are emissions of citric acid fragments like $C_3H_3O^+$ (m/z 39) which were not measured in the synthesis with CA only (not shown). The endothermic peak at 540 K and the exothermic peak at 730 K show both the gas emissions confirming the combustion process. The first peak might be endothermic due to the heavy emission of H_2O .

The DTA curve above 825 K does not show any thermal event which confirms the thermal stability of the phase up to 1273 K.

From thermogravimetric analysis the temperature for calcination was chosen at 1073 K. XRD pattern after calcination show that all $Zn_{1-x}Al_xO$ ($x = 0, 0.1$) samples from SC crystallise in wurtzite ZnO crystal structure (Fig. 3). No secondary phases can be detected.

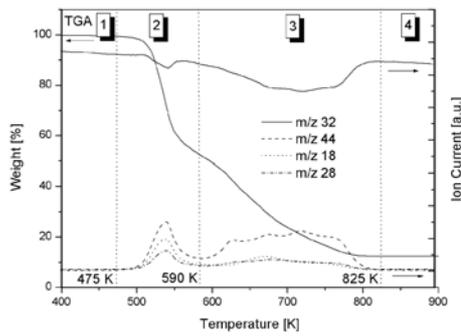


Fig. 2: TGA/MS of the thermal decomposition and phase formation of the $Zn_{0.99}Al_{0.01}O$ precursor with CA (MS plots: m/z 32: O_2 , m/z 44: CO_2 , m/z 18: H_2O , m/z 28: CO)

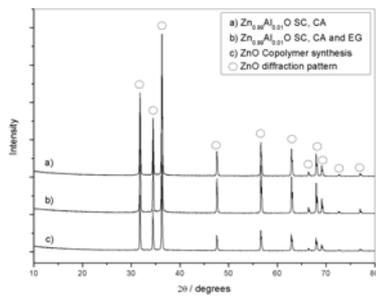


Fig. 3: XRD pattern of $Zn_{1-x}Al_xO$ ($x = 0, 0.01$) after calcinations at 1073 K

The TEM micrographs of $Zn_{1-x}Al_xO$ ($x = 0.01$) show three different morphologies for the synthesis variations with CA (route a) (Fig. 4) and CA/EG (route b, not shown). Large particles, needles and small particles were found. EDS and electron diffraction (ED) patterns in TEM reveal that the large particles consist of ZnO (diffraction pattern in Fig. 5 a) with aluminium substitution in the range of 1 %. The needles show typical ZnO ED pattern as well (Fig. 5 b) but no aluminium content in the EDS. In the small particles there is a aluminium to zinc ratio of about 2:1 and the ED pattern (Fig. 5 c) match with the spinel phase $ZnAl_2O_4$. The $ZnAl_2O_4$ is present in the material in such a low amount that it is not seen in XRD.

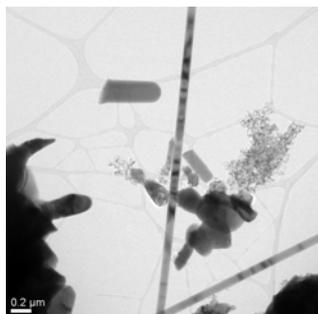
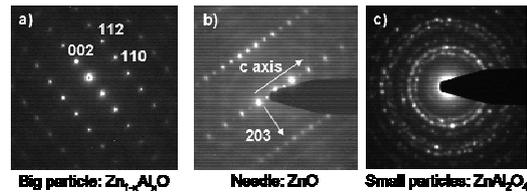


Fig. 4: TEM micrograph picture of $Zn_{0.99}Al_{0.01}O$ synthesised with CA calcined at 1073 K



Big particle: $Zn_{1-x}Al_xO$ Needle: ZnO Small particles: $ZnAl_2O_4$

Fig. 5: ED patterns from TEM analysis: a) large particle, b) needle, c) ring pattern from small particles (measured from particles in Fig. 4)

The large $Zn_{1-x}Al_xO$ particles from SC with CA (route a) have dimensions from 100 nm to 1.4 μm after calcination at 1073 K. The addition of EG (route b) leads to smaller particles from 300 to 800 nm. This difference can still be seen after sintering the pressed pellets at 1273 K. The CA synthesis leads to particles from 500 nm to 3 μm diameter (Fig. 6 a). Particles from the EG synthesis are smaller ranging from 300 nm to 2 μm diameter (Fig. 6 b).

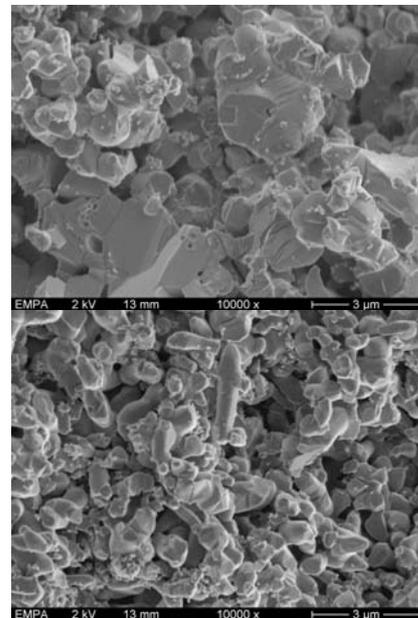


Fig. 6: SEM micrograph pictures of $Zn_{0.99}Al_{0.01}O$ sintered at 1273 K: a) with CA, b) with CA/EG

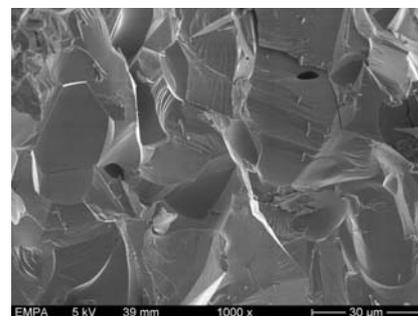


Fig. 7: SEM micrograph picture of $Zn_{0.99}Al_{0.01}O$ from SSR sintered at 1673 K

The particle and crystallite size influence the thermal conductivity of the sintered pellets. The smaller the particles, the smaller is the thermal

conductivity. As the temperature for the soft chemistry synthesis is much lower than for solid state reaction, the particles grow much less. SSR with sintering at 1673 K leads to particle sizes from 40 to 70 μm (Fig. 7), which is much bigger than for SC. Accordingly, the thermal conductivity values are higher for SSR $\text{Zn}_{1-x}\text{Al}_x\text{O}$ ($x = 0.01$) than for SC (Fig. 9). There is even a difference between the SC variations. The smaller particles obtained by CA/EG synthesis (route b) show lower thermal conductivity than the particles from CA synthesis (route a). The copolymer synthesis of ZnO leads to a particle size similar to $\text{Zn}_{1-x}\text{Al}_x\text{O}$ ($x = 0.01$) prepared by routes a and b. To that effect the thermal conductivity is similar (Fig. 8).

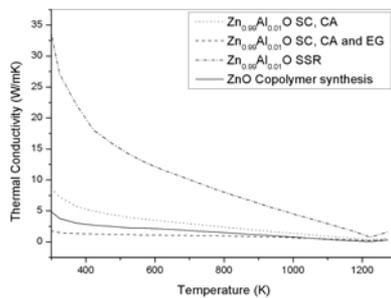


Fig. 8: Thermal conductivity for $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$ from SC and SSR and for ZnO from copolymer synthesis

$\text{Zn}_{1-x}\text{Al}_x\text{O}$ ($x = 0.01$) sintered at 1273 K showed very high electrical resistivity values up to 2000 Ωcm at room temperature (RT) (not shown). The high resistivity arises from the low density of only about 60 % of the theoretical density. Sintering the pellet at 1673 K improves dramatically the resistivity to values of 0.05 Ωcm at RT decreasing to 0.02 Ωcm at 1273 K for $\text{Zn}_{1-x}\text{Al}_x\text{O}$ ($x = 0.01$) prepared by SC with CA (route a) (Fig. 9). The Seebeck coefficient of this sample is $-80 \mu\text{V/K}$ at RT and $-250 \mu\text{V/K}$ at 1273 K (Fig. 10). ZnO from copolymer synthesis gave resistivity values (Fig. 9) and Seebeck coefficient values (Fig. 10) of 250 Ωcm and $-400 \mu\text{V/K}$ at RT and 0.1 Ωcm and $-300 \mu\text{V/K}$ at 1273K.

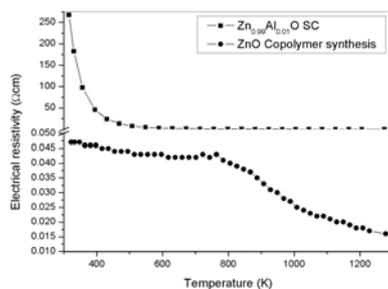


Fig. 9: Resistivity for $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$ from SC with CA and for ZnO from copolymer synthesis sintered at 1673 K.

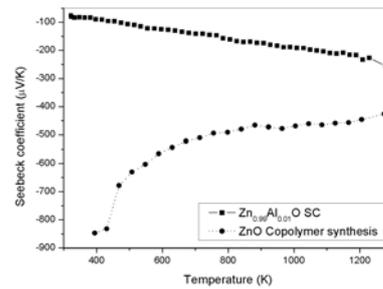


Fig. 10: Seebeck coefficient for $\text{Zn}_{0.99}\text{Al}_{0.01}\text{O}$ from SC and SSR and for ZnO from copolymer synthesis sintered at 1673 K

Conclusions

Soft chemistry is an appropriate method to prepare zinc oxide with a low level aluminium substitution. This synthesis method leads to smaller particles compared to solid state reaction. It is shown that the particle size strongly affects the thermal conductivity κ , e. g. SC samples exhibit κ values which are one third to one 20th of the ones from SSR at room temperature.

However, the sintering the samples at 1273 K results in a low density which has an effect on the resistivity. There is a demand for a pressing and sintering method where high density can be reached at low temperature without losing the advantage of getting small particle size.

Copolymer synthesis leads to zinc oxide with small particle size and low thermal conductivity.

The results for the thermoelectric properties promise a high figure of merit for the materials prepared by the described methods.

Acknowledgments

Empa and SNF MANEP are highly acknowledged for the financial support.

References

1. Tsubota, T. *et al*, J. Mater. Chem., 7 (1) (1997), pp. 85-90.
2. Robert, R., Romer, S., Reller, A., and Weidenkaff, A., Adv. Eng. Mat., Vol. 7 (2005), pp. 303-308.