Investigation of Nanostructured CaO-ZnO Solid Solutions by X-ray Diffraction

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Nanostructured zinc oxide (ZnO) is a versatile material with a wide range of applications ranging from nutrition to light-emitting devices, and doping of ZnO with calcium (Ca) may improve its performance. However, there is only a limited understanding of the crystalline properties of nanostructured CaO-ZnO systems. Here, nanostructured Ca-doped ZnO was produced by flame spray pyrolysis and characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). No Ca-Zn oxide phase with specific stoichiometry was formed, but an increase in the ZnO unit cell parameters was observed with increased Ca content. Using Vegard’s law, approximately 2.8 at% Ca was incorporated substitutionally for Zn in nano-ZnO, in agreement with solubility limits reported for bulk ZnO. These results indicate that there is no specific particle size effect for the formation of CaO-ZnO solid solutions. This Ca incorporation inside the ZnO wurtzite structure resulted in a transformation from slightly elongated to more spherical crystals, as indicated by the ZnO aspect ratio and TEM images.

Key Words
Nanoparticles, Zinc oxide, Calcium, Solid solution, Doping

1. Introduction
Nanostructured zinc oxide (ZnO) is a versatile material with a wide range of applications in, e.g., electronics, photocatalysis and nutrition 1) ~ 3). Doped ZnO has received increased research interest since it can greatly improve material performance. One of such dopants is calcium (Ca), which may improve ZnO material properties in a number of applications 4) ~ 6) such as nutrition 7), catalysis 8) ~ 10), and bactericides 11) ~ 12). The CaO-ZnO system is particularly studied for the development of wide bandgap materials 6) ~ 13). Despite its wide range of potential applications and number of experimental investigations, the phase behavior of CaO-ZnO remains complex. Phase diagrams containing CaO and ZnO present no mixed Ca-Zn oxide phases 14) ~ 15), and according to theoretical calculations these two oxides do not form stable solid solutions 16) ~ 19); at room temperature such solid solutions made from nonisostructural components (wurtzite ZnO and rocksalt CaO 6) 16) are predicted to be unstable 18). The structural differences between the wurtzite ZnO and rocksalt CaO crystal structures are too large, which results in phase separation 19). Low amounts of Ca, however, can be incorporated into ZnO: experimentally, Xia et al. 20) found a solubility limit of 4.81 at% Ca in ZnO at 1535 °C, and Hayashi et al. 21) measured a substitution of 1.5 at% Ca in ZnO at 1200 °C. At elevated temperatures (>500-1650 °C, depending on composition), density functional theory (DFT) calculations predict a stable, homogeneous CaO-ZnO solid solution at any composition 10). For some systems, the formation of solid solutions depends on the particle size. For example, the solubility of Co, Ni, and Mn in ZnO increases with decreasing size 17) ~ 19). Whether such effects occur with Ca has, to the best of the author’s knowledge, not yet been investigated.

Flame spray pyrolysis (FSP) is a one-step, scalable process for the size-controlled synthesis of high-purity nanomaterials without any liquid by-products 22). The high reaction temperature in FSP followed by rapid quenching to ambient conditions has resulted in the formation of unique metastable phases 22) ~ 23). In this work, nanostructured Ca-doped ZnO powders are produced by FSP and the incorporation of Ca into the nano-ZnO crystal structure is investigated by X-ray diffraction.
2. Materials and methods

The Ca-doped ZnO nanopowders were produced by FSP. Mixtures of Ca(NO$_3$)$_2$·4H$_2$O (≥99%, Fluka) and Zn(NO$_3$)$_2$·6H$_2$O (≥99%, Fluka) were dissolved in a 1:1 (vol:vol) mixture of ethanol (abs. denat. 2% 2-butanone, Alcosuisse) and 2-ethylhexanoic acid (>99%, Riedel-de-Haën). The precursor solution with a total metal (Ca+Zn) concentration of 0.5 M was fed into the FSP reactor at 5 mL/min and dispersed by 5 L/min oxygen, and the spray was ignited by a ring-shaped premixed flame consisting of 1 L/min methane and 2 L/min oxygen. The composition of the powders is indicated by the nominal Ca content (at% Ca) calculated by \( \frac{c_{\text{Ca}}}{c_{\text{Ca}} + c_{\text{Zn}}} \), where \( c_{\text{Ca}} \) and \( c_{\text{Zn}} \) are the Ca and Zn concentrations in the precursor (mol/L).

The produced particles were collected on a water-cooled glass fiber filter placed above the FSP reactor. The nanopowders were characterized by X-ray diffraction (XRD, Bruker AXS D8 Advance diffractometer) directly after production to prevent conversion of CaO into Ca(OH)$_2$ or CaCO$_3$. For each composition at least three independent samples were measured. Peak shifts resulting from sample preparation were eliminated by mixing product powder with metallic Cu (dendritic, 3 µm, 99.7%, Sigma-Aldrich) with known peak positions. Rietveld refinement of the XRD patterns was done using TOPAS 4 software (Bruker). The cell constants \( a \) and \( c \) for ZnO were determined at the (110) plane at \( 2\theta = 56.6^\circ \) and the (103) plane at \( 2\theta = 629^\circ \). The unit cell volume was calculated by \( V_{\text{ZnO}} = a^2 c \sin(\pi/3) \). The ZnO aspect ratio was obtained from the ratio \( d_{\text{ZnO}}(100)/d_{\text{ZnO}}(002) \). Particles were deposited on a carbon foil supported on a copper grid for analysis by transmission electron microscopy (TEM, FEI Tecnai F30, field emission, 300 kV).

3. Results and Discussion

The XRD patterns of the Ca-doped ZnO nanopowders are shown in Fig. 1. The ZnO nanoparticles were formed in the zincite (wurtzite) crystal structure of hexagonal space group P6$_3$mc (ICDD Card No. 79-2205) while CaO crystallizes in the rocksalt structure of cubic space group Fm3m (ICDD Card No. 82-1690). As reported in a previous study, the nanostructured nature of the ZnO produced under similar conditions is demonstrated by its crystallite size of 5-20 nm and specific surface area of 70-94 m$^2$/g. The three characteristic peaks of ZnO at \( 2\theta = 31.7^\circ, 34.4^\circ, \) and \( 36.2^\circ \) are clearly visible in all patterns, as well as peaks at \( 2\theta = 47.5^\circ, 56.6^\circ, 62.8^\circ, 66.4^\circ, 67.9^\circ, \) and \( 69.0^\circ \). Crystalline CaO is not visible at 1.6 at% Ca, but the main CaO peak appears at \( 2\theta = 37.4^\circ \) for the sample containing 7.5 at% Ca, which increases in intensity for higher Ca contents. Additional CaO peaks are visible at \( 2\theta = 32.3^\circ, 53.9^\circ, 64.2^\circ, \) and \( 67.5^\circ \). No separate peaks for any mixed oxides are visible in all XRD patterns, indicating that CaO and ZnO primarily crystallize as separate structures, in agreement with the CaO-ZnO phase diagram.

The unit cell parameters of ZnO change as function of Ca-content in the precursor (Fig. 2). Each of these data points was reproducible as indicated by the small error bars (triplicate measurements). The lattice constant \( a \) for pure ZnO was 3.250 Å, which increased linearly to a value of

![Fig. 1 XRD patterns (normalized to the largest peak intensity) of ZnO nanoparticles containing different amounts of Ca indicated by the nominal Ca content (at% Ca). The XRD patterns (except 1.6 and 14.0 at% Ca) in the range 2θ = 20-40° are discussed in Knippenburg et al.]

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of 3.262 Å at 14 at% Ca (a relative increase of 0.34%) after which it stabilizes with a potential decrease (Fig. 2 (a)). The \(c\) parameter for pure ZnO was 5.209 Å and increases as well, up to 5.216 Å at the same Ca content, but the relative increase is only 0.13%. So there is a preferential expansion of the ZnO unit cell in the \(a\) direction, similar to Cd-doped ZnO. Both trends of \(a\) and \(c\) parameters are in good qualitative agreement with Hayashi et al. (Fig. 2 (a), triangles) who sintered mixtures of ZnO and CaO powders for 5 hours at 1200 °C. The absolute values in this study are slightly higher, quite likely due to different preparation methods and particle sizes. Hayashi et al. did not report a particle size, but due to their long treatment at high temperature their crystals were likely not nanosized.

The ZnO unit cell volume \(V_{\text{ZnO}}\) shows a distinct increase from 47.65 to 48.05 Å\(^3\) at 14 at% Ca after which it remains constant (Fig. 2 (b)). The expanded \(V_{\text{ZnO}}\) is in good agreement with previous work, and is found at approximately the same composition as Hayashi et al. and Yamamoto et al., who prepared such mixed oxides by heat treatment of ZnO and CaO powders for several hours. Karthikeyan et al. also observed a comparable increase in unit cell volume for nano-ZnO doped with 6 at% Ca prepared by a wet chemical method, although their absolute values were slightly lower.

The increase in \(V_{\text{ZnO}}\) by Ca-doping was also estimated using Vegard’s law (gray dashed line), which predicts a linear relation with composition between the end points of the crystal lattice constants \(a\) and \(c\). Even though wurtzite CaO is unstable at room temperature, its lattice parameters were calculated to be \(a = 3.8939\) Å and \(c = 4.6755\) Å\(^3\), corresponding to a wurtzite CaO unit cell volume of 61.39 Å\(^3\). The predicted increase in unit cell volume portrayed in Fig. 2 (b) demonstrates that not all of the Ca is substitutionally present for Zn in ZnO; at the maximum \(V_{\text{ZnO}}\) at 14 at% Ca it was estimated (using Vegard’s law) that only 2.8 at% Ca is truly incorporated in the ZnO, while the majority of CaO forms segregated crystals. This is in agreement with the XRD patterns where even at 7.5 at% Ca a fraction of crystalline CaO was observed.

The difference between the nominal Ca composition in the precursor and the Ca substitutionally incorporated inside the ZnO lattice is likely because the FSP reactor that was used to produce the Ca-doped ZnO operates far from thermodynamic equilibrium. During FSP, particle synthesis at high temperature followed by rapid quenching typically takes in the order of milliseconds. In addition, the difference in melting point (MP) and boiling point (BP) between CaO and ZnO may also explain why some CaO has segregated. CaO has a MP of ~ 2860 K and a BP of 3773 K, while ZnO has a MP of 2248 K (and no BP because ZnO decomposes). Because of its higher MP and BP, CaO particles form earlier in the flame at higher temperatures, where Zn is still in the gas phase. The ZnO particles solidify downstream where the temperatures are cooler. These differences in MP and BP may result in partial phase segregation. Similar observations were previously made in the flame synthesis of ZrO\(_2\)-Al\(_2\)O\(_3\) nanopowders.

Compared to 2.8 at% found in the present study, the lower solubility limit of 1.5 at% by Hayashi et al. could be due to the difference in particle size, as it was reported that...
Co, Ni, and Mn solubility in ZnO increases with decreasing size \cite{17}~\cite{19}. On the other hand, Xia et al. \cite{15} present a higher solubility limit of 4.81 at% Ca, which was reached after more than 40 hours equilibrium time, much longer than the comparably very short (in the order of milliseconds) equilibrium time in the current study. It should also be noted that Vegard’s law assumes complete intermiscibility of the two crystal structures, which (according to calculations \cite{6}) is not the case for wurtzite CaO and wurtzite ZnO. Due to the instability of wurtzite CaO crystals, the behavior of the CaO-ZnO solid solution may deviate from Vegard’s law \cite{6} even at low Ca concentrations.

The increase in unit cell parameters clearly demonstrates that some of the Ca is incorporated in the ZnO crystal structure. Substitution \cite{5} of Zn\textsuperscript{2+} (ionic radius 0.74 Å) by the larger Ca\textsuperscript{2+} (1.00 Å) in the ZnO structure deforms the wurtzite unit cell and thus increases the unit cell parameters, changing from an elongated towards a more isotropic wurtzite unit cell \cite{6}. The CaO-ZnO solid solutions observed here are unlikely to be size-dependent (as for TiO\textsubscript{2}/SnO\textsubscript{2} \cite{34}) since these were also formed for 0.5 µm particles \cite{11} and as thermodynamically stable phase \cite{15}. The high temperature during flame synthesis followed by rapid cooling by ambient air enabled the rapid formation of Ca-doped ZnO, which otherwise could only be formed after several hours of thermal treatment \cite{11,15}.

Variation of the XRD lattice aspect ratio by Ca-doping is shown in Fig. 3 (a). The aspect ratio of pure ZnO is 0.68, in agreement with flame-made ZnO \cite{24} and increases to 1.1 for 7.5 at% Ca after which it remains constant. So there is a transition from elongated towards more spherical crystals. This is also seen in the TEM images in Fig. 3 (b) and Fig. 3 (c) pure ZnO consists of elongated crystals while 24.6 at% Ca-containing ZnO such elongated crystals are absent.

This increase in aspect ratio is likely a result of incorporation of Ca\textsuperscript{2+} in the ZnO structure, as it follows the same trend as the increase in unit cell parameters (Fig. 2). Substitution of Zn\textsuperscript{2+} in flame-made ZnO with higher valency ions (e.g., In\textsuperscript{3+} or Sn\textsuperscript{4+}) strongly increases the aspect ratio (around 3 for 10 at% dopant) thus promoting the formation of rodlike crystals, while lower valency ions (such as Li\textsuperscript{+}) showed no effect as dopant \cite{26}. Here, the effect of Ca\textsuperscript{2+} doping is not as strong as for In\textsuperscript{3+} or Sn\textsuperscript{4+} and slightly stronger than Li\textsuperscript{+}. Since Ca\textsuperscript{2+} and Zn\textsuperscript{2+} have the same valency, Ca-doping thus causes only limited growth inhibition and does not promote nanorod formation.

4. Conclusions

Nanostructured Ca-doped ZnO was produced by flame spray pyrolysis. For all compositions (0-44.9 at% Ca), no Ca-Zn oxide with specific composition was observed in agreement with the binary phase diagram. The ZnO unit cell parameters increased up to 14 at% Ca by substitutionally replacing Zn\textsuperscript{2+} with Ca\textsuperscript{2+} in ZnO, demonstrating that CaO-ZnO solid solutions were formed. Using Vegard’s law it is estimated that approximately 2.8 at% Ca is dissolved in nano-ZnO, which is similar to the solubility limits reported for bulk ZnO. These results indicate that there is no specific particle size effect for the

![Fig. 3](image-url) (a) XRD lattice aspect ratio of ZnO as function of Ca-content in the precursor, compared to literature data for flame-made ZnO containing other dopants \cite{24}. While pure ZnO is slightly elongated, incorporation of Ca results in more isotropic crystals as indicated by the aspect ratio around 1.0. This is also visualized in the typical TEM images of (b) ZnO and (c) 24.6 at% Ca-containing ZnO.
formation of CaO-ZnO solid solutions. Calculation of the aspect ratio showed that the ZnO nanocrystals transformed from elongated to more spherical particles by Ca-doping, as confirmed by TEM analysis.

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References
1) Ozgur, U.; Alivov, Y. I.; Liu, C.; Teke, A.; Reschchikov, M. A.; Dogan, S.; Avrutin, V.; Cho, S. J.; Morkoc, H., J. Appl. Phys., 98, 041301 (2005)
2) Ryu, Y. R.; Lee, T. S.; Lubguban, J. A.; White, H. W.; Kim, B. J.; Park, Y. S.; Youn, C. J., Appl. Phys. Lett., 88, 241108 (2006)
3) Hilty, F. M.; Arnold, M.; Hilbe, M.; Teleki, A.; Knijnenburg, J. T. N.; Ehrensperger, F.; Hurrell, R. F.; Pratsinis, S. E.; Langhans, W.; Zimmermann, M. B., Nat. Nanotechnol., 5, 374-380 (2010)
4) Misra, K. P.; Shukla, R. K.; Srivastava, A., Appl. Phys. Lett., 95, 031901 (2009)
5) Bai, L. N.; Lian, J. S.; Zheng, W. T.; Jiang, Q., Cent. Eur. J. Phys., 10, 1144-1149 (2012)
6) Fan, X. F.; Sun, H. D.; Shen, Z. X.; Kuo, J. L.; Lu, Y. M., J. Phys.-Condens. Matter, 20, 235221 (2008)
7) Knijnenburg, J. T. N.; Hilty, F. M.; Krumkefe, F.; Zimmermann, M. B.; Pratsinis, S. E., J. Mater. Res., 28, 1129-1138 (2013)
8) Taufiq-Yap, Y. H.; Lee, H. V.; Hussein, M. Z.; Yunus, R., Biomass Bioenergy, 35, 827-834 (2011)
9) Ngamcharussrivichai, C.; Totarat, P.; Bunyakiat, K., Appl. Catal. A-Gen., 341, 77-85 (2008)
10) Mloua, R.; Kebab, Z.; Mloua, F.; Benramdane, N., Phys. Lett. A, 372, 1910-1914 (2008)
11) Yamamoto, O.; Shimura, T.; Sawai, J.; Kojima, H.; Sasamoto, T., J. Ceram. Soc. Jpn., 108, 156-160 (2000)
12) Hameed, A. S. H.; Karthikeyan, C.; Sasikumar, S.; Kumar, V. S.; Kumaresan, S.; Ravi, G., J. Mater. Chem. B, 1, 5950-5962 (2013)
13) Sha, X.; Tian, F.; Li, D.; Duan, D.; Chu, B.; Liu, Y.; Liu, B.; Cui, T., Sci. Rep., 5, (2015)
14) Shevchenko, M.; Jak, E., CALPHAD: Comput. Coupling Phase Diagrams Thermochem., 70, (2020)
15) Xia, L.; Liu, Z.; Taskinen, P., J. Am. Ceram. Soc., 99, 3809-3815 (2016)
16) Hayashi, F.; Uematsu, T.; Hashimoto, H., J. Mater. Sci., 16, 3227-3229 (1981)
17) Straumal, B. B.; Mazilkin, A. A.; Protasova, S. G.; Myatiev, A. A.; Straumal, P. B.; Baretzky, B., Acta Mater., 56, 6246-6256 (2008)
18) Straumal, B.; Baretzky, B.; Mazilkin, A.; Protasova, S.; Myatiev, A.; Straumal, P., J. Eur. Ceram. Soc., 29, 1963-1970 (2009)
19) Straumal, B. B.; Mazilkin, A. A.; Protasova, S. G.; Stakhanova, S. V.; Straumal, P. B.; Bulatov, M. F.; Schutz, G.; Tietze, T.; Goering, E.; Baretzky, B., Rev. Adv. Mater. Sci., 41, 61-71 (2015)
20) Strobel, R.; Pratsinis, S. E., J. Mater. Chem., 17, 4743-4756 (2007)
21) Righettoni, M.; Tricoli, A.; Pratsinis, S. E., Chem. Mater., 22, 3152-3157 (2010)
22) Teoh, W. Y.; Amal, R.; Madler, L., Nanoscale, 2, 1324-1347 (2010)
23) Hilty, F. M.; Knijnenburg, J. T. N.; Teleki, A.; Krumkefe, F.; Hurrell, R. F.; Pratsinis, S. E.; Zimmermann, M. B., J. Food Sci., 76, N2-N10 (2011)
24) Height, M. J.; Madler, L.; Pratsinis, S. E.; Krumkefe, F., Chem. Mater., 18, 572-578 (2006)
25) Tani, T.; Madler, L.; Pratsinis, S. E., J. Nanopart. Res., 4, 337-343 (2002)
26) Karthikeyan, B.; Pandiyarajan, T.; Mangaiyarkarasi, K., Spectrochim. Acta Part A, 82, 97-101 (2011)
27) Ghosh, M.; Raychaudhuri, A. K., Nanotechnology, 18, 115618 (2007)
28) Ewsuk, K. G.; Ellerby, D. T.; DiAntonio, C. B., J. Am. Ceram. Soc., 89, 2003-2009 (2006)
29) Denton, A. R.; Ashcroft, N. W., Phys. Rev. A, 43, 3161-3164 (1991)
30) Gröhn, A. J.; Pratsinis, S. E.; Sánchez-Ferrer, A.; Mezzenga, R.; Wegner, K., Ind. Eng. Chem. Res., 53, 10734-10742 (2014)
31) Samsonov, G., The Oxide Handbook, IFI/Plenum, 1973
32) Kim, M.; Laine, R. M., J. Nanopart. Res., 8, 129-136 (2007)
33) Shannon, R. D., Acta Crystallogr. Sect. A, 32, 751-767 (1976)
34) Tricoli, A.; Righettoni, M.; Pratsinis, S. E., Nanotechnology, 20, 315502 (2009)