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Molten Salt Oxidation as a Route for the Synthesis of Nano-sized Powders of Zinc and Magnesium Oxides.

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ABSTRACT

The use of molten salts as a medium for the production of inorganic nano compounds has been but little explored. Here we describe an alternative molten salt procedure for the production of finely dispersed zinc and magnesium oxides, compounds that are used in the electronic and pharmaceutical industries, and also for the production of adsorbents, catalysts, sensors, abrasives, and ceramics requiring excellent operating characteristics. Bubbling air or oxygen through zinc and magnesium chloride melts at 600°C produced nano-sized (ZnO) and coarse-crystalline nano-structured (MgO) oxides and gaseous chlorine. A mixed magnesium and zinc oxide powder was obtained using a melt containing MgCl₂ and ZnCl₂ at a molar ratio of 1:5. The oxides formed were obtained by dissolving the cooled reaction mixture in a hot water-ethanol solution followed by centrifuging. The oxide powders were dried at 100–130°C and calcined at 650°C for five hours. Chlorine formation and its liberation obeyed the zeroth-order rate equation. The mixed zinc and magnesium oxides formed were analyzed using optical and atomic force microscopy, and X-ray diffraction analysis. Particle size, chemical composition, and surface area for some samples were determined.

Keywords: Molten chlorides oxidation, nano-sized metal (II) oxides.

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INTRODUCTION

The first report of the precipitation of nano compounds in a molten salt, of which we are aware, was of lanthanide phosphates in chloride melts by Griffiths et al. in 2002 [1]. Other reports using high temperature molten salts did not appear until 2005. Currently magnesium and zinc oxides are important functional materials widely used in science and engineering [2] and a straightforward alternative preparative method thus has merit. Zinc oxide is well known as an optically transparent wide-gap semiconductor for the production of electronics, gas sensors, UV-filters, and solar batteries, etc. Magnesium oxide is used in the manufacture of cement and fireproof materials, in oil refining processes, and as a filler in rubber production. Fine magnesia powder is also an effective abrasive material.

Nano-sized metal oxides have been studied for several years and nano-sized materials can be produced by various methods, including hydrothermal synthesis, gas-phase deposition, plasma-chemical synthesis, and thermal decomposition of precipitates produced in water solutions [3–7]. The use of molten salts has more recently been shown to be a promising technique for the synthesis of fine dispersed metal oxides [8, 9].

Molten salts have been widely used to synthesize single and binary metal oxides [10–13]. The high temperature reaction of metal chlorides with gaseous oxygen is of interest for obtaining of complex metal oxides including sodium and potassium vanadates, the synthesis of the fine powder metal oxides and mono-crystalline films (single and mixed) [14–18]. A method of obtaining metal oxides and oxychlorides from spent nuclear fuel in molten carbonates and chlorides has been described [19].

The results of Zn and mixed Zn-Mg oxides synthesis via oxidation in their corresponding chlorides melts are here presented.

EXPERIMENTAL

All chemicals (magnesium and zinc chlorides, potassium iodide) were of “chemically pure” grade. Reagent pre-treatment consisted of removal of traces of water from Mg and Zn chlorides by holding them in muffle furnace at 250°C until constant weight: they were subsequently ground in a porcelain mortar. Completely anhydrous ZnCl₂ cannot be obtained this way: Zn metal and HCl gas would be required but, for our purposes here, any traces of oxide or hydroxide remaining cannot affect the formation of nano-ZnO. The melting point of ZnCl₂ is only 275°C, indicating its somewhat covalent character. In general, 30g of zinc chloride or a MgCl₂–ZnCl₂ mixture with molar ratio MgCl₂:ZnCl₂ 1:5 were loaded in a corundum crucible (h = 80mm, i.d. = 35mm), which was then placed in a quartz vessel (h = 300mm, i.d. = 40mm) and heated in the tube furnace up to 600°C. The experimental facility is shown in Figure 7. Oxidation was carried out by bubbling air or oxygen through the melt. To remove water from the oxidizing gas it was passed through cylinder filled with CaA zeolite prior to feeding into the reaction vessel: oxidizing gas velocity 2.5 L·h⁻¹. Any water remaining would be in the low ppm level.

When the temperature reached its targeted value and the reaction mixture was fully molten, the quartz vessel was sealed with a cap fitted with gas inlet and outlet tubes. The lower end of the inlet tube was 2mm above the crucible bottom.

Outlet gas was bubbled through an aqueous KI solution (20g of KI per 250mL of H₂O). To quantify chlorine formed during the reaction the KI solution was titrated (using 5mL taken every 30 min) with 0.01n. Na₂S₂O₃.

After 360–420 min, the bubbling of oxygen (or air) was stopped, and the heating switched off. Extraction of Zn and Mg oxides from the reaction mixture was based on the different solubility of chlorides and oxides in water. If an aqueous solution of MgCl₂ is mixed with MgO it forms a cement-like composition MgCl₂·mMg(OH)₂·nH₂O [20]. To prevent such formation a water-ethanol solution (50:50 vol.) was used.

The reaction mixture, after cooling to room temperature, was dissolved in a water-ethanol solution with slight heating; the zinc oxide was characteristically slightly yellow before cooling, due to various lattice defects resulting from slight oxygen loss. Zinc and magnesium oxides were separated from solution by

centrifuging, and then rinsed several times with a fresh water-ethanol mixture. Rinsing and centrifuging operations were repeated until no chloride ions remained in the washing solution (using AgNO_3). Chloride ion residues in washing solution were detected by a high performance capillary electrophoresis unit Agilent G1600 AX with specific Agilent buffer solution for anions (pH = 7.7) 20°C, -30 kV.

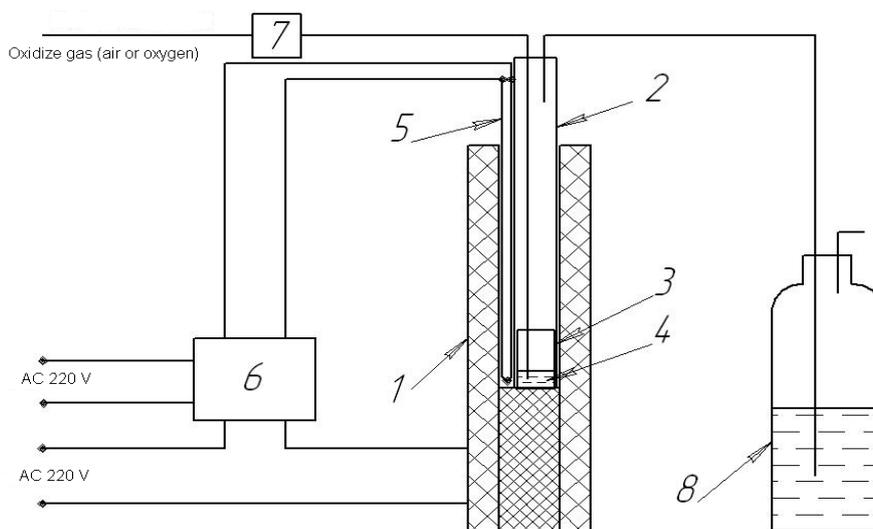


Figure 7: Design of the molten chlorides oxidation unit

1 – furnace; 2 – quartz vessel; 3 – corundum crucible; 4 – molten chlorides; 5 – thermocouple (K Type);
6 – temperature regulator; 7 – gas flow regulator; 8 – aqueous KI solution.

After extraction, the oxide powders were calcined first at 300 then at 650°C, the zinc oxide powder again turning yellow in this temperature range, the colour as normal fading upon cooling as oxygen re-entered the lattice. Particle sizes of oxide powder were determined after calcining with an optical microscope, Olympus BX51. Oxides powders with particle sizes less than 0.5 μm were analyzed with an atomic-force microscope, Solver Pro.

X-ray diffraction analysis (XRD) of reaction products was performed with a Shimadzu XRD 7000 instrument (Cu-K α , 40 kV, 30 mA). Unit cell size calculations were based on half-width of diffraction reflections. For an experimental sample (FWHM_{exp}) and for a coarse-crystalline reference sample (FWHM_{ref}) the presence of nano-sized material was identified using the Selyakov-Sherrer equation [21-23]:

$$D = K\lambda / \beta \cos \theta_{\text{HKL}}$$

where K – constant, 0.94;

λ – wavelength, for Cu anode $\lambda = 0.15406$ nm

β – physical broadening value

$$\beta = [(\text{FWHM}_{\text{exp}})^2 - (\text{FWHM}_{\text{ref}})^2]^{1/2}$$

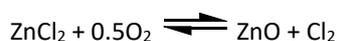
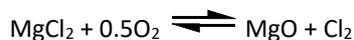
FWHM_{ref} values were determined by XRD analysis of chemically pure coarse-crystalline MgO and ZnO. BET surface area and pore volume were determined with ASAP 2020 (Micromeritics, USA) after degassing of samples at 350°C under vacuum for 3h. The surface area was calculated for P/P_0 range 0.05–0.37. Pore volume was found by the amount of the nitrogen adsorbed at $P/P_0 \approx 0.99$.

Zinc content in oxide mixtures was determined by atomic absorption spectrometry (AAS) instrument using an iCE 3500 with flame atomization. A hollow-cathode Zn lamp (wavelength 213.8 nm) was the emission source. Oxide mixtures were dissolved in nitric acid prior to analysis.

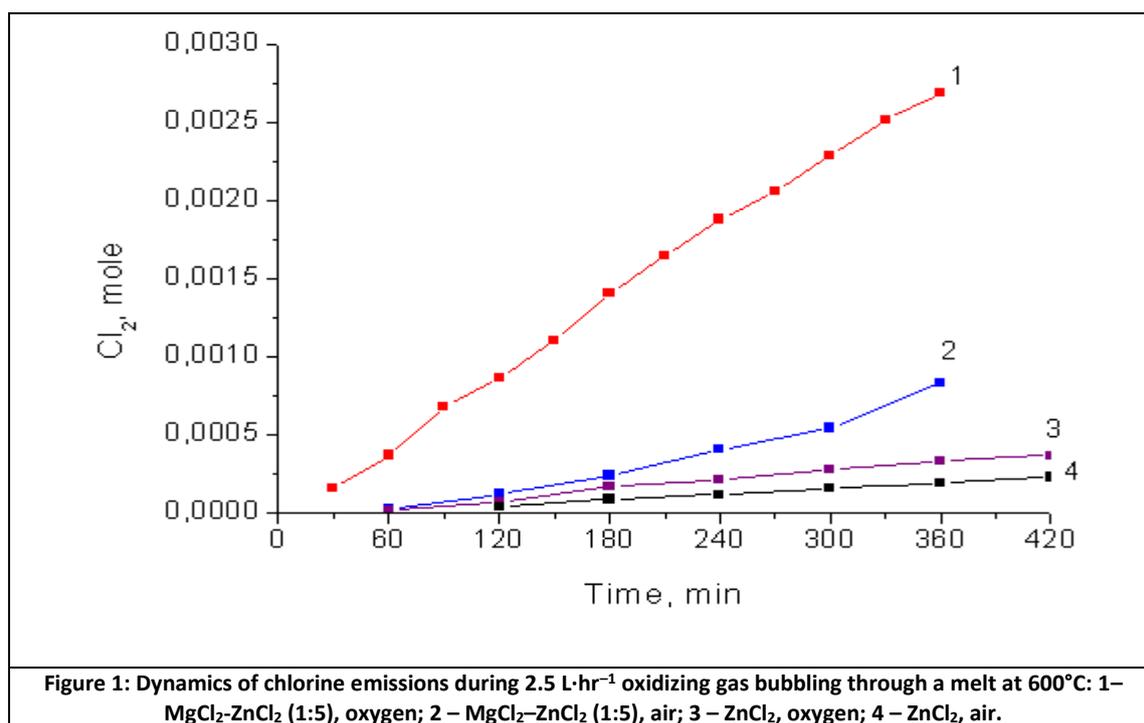
RESULTS AND DISCUSSION

Chlorides oxidation reaction

Magnesium and zinc chloride oxidation can be described by:



Average kinetic curves of chlorine emission from the melt during air or oxygen bubbling are shown in Figure 1. As expected, the reaction is more efficient using oxygen rather than air.



Molten salts in general do not dissolve large volumes of gases, mainly because the high temperature involved would eliminate any dissolved gases. However, in the case of oxygen, it dissolves *chemically*, not physically, and thereby reacts with the ions in the melt, in this case, displacing the chlorine atoms around magnesium and zinc. When chlorides are added to molten carbonates the solubility of oxygen is increased. In the molten state magnesium and zinc chlorides contain tetrahedral chloro complex ions and metal cations, for example,



Thus the chemically dissolved oxygen here reacts to replace the chloride ligands by oxygen, releasing chlorine and forming the insoluble oxides of magnesium and zinc by a zeroth order reaction. The amount of chemically dissolved oxygen is small but as it dissolves and reacts to form the magnesium and zinc oxides it is continually replaced as long as more is bubbled through the melt. A possible mechanism can be described as chemically dissolved oxygen reacting with chloride ligands and removing electrons to form a peroxide ion thereby releasing a chlorine atom: two chlorine atoms then combine to form a chlorine molecule that is released and swept out from the melt with the (unreacted) bubbled oxygen, or air, from the hot melt. The peroxide ion formed therein can now react with the metal cations to form the desired nano-sized oxides and release an oxygen atom for further reaction, for example:



The reaction is driven to the right since MgO and ZnO are insoluble and drop out of solution as a fine powder. Griffiths and Volkovich [24] have shown that bubbling oxygen into molten carbonate, with nitrate as catalyst, is an effective way to oxidize insoluble UO_2 to insoluble diuranate by the peroxide and superoxide ions generated therein and, in principle, will release fission products from spent nuclear fuel into the molten carbonate for subsequent reprocessing. They give a detailed description of their results with largely non-radioactive species.

In molten $ZnCl_2$ the reaction rate appears weakly dependent on the oxygen concentration in the gas flow but actually depends on the small amount of oxygen that dissolves in the melt: for the mixture of zinc and magnesium chlorides the oxidation rate depends strongly on gas flow composition (Figure 1, Table 1) and the overall process is limited by the kinetics and nature of oxygen dissolution.

Table 1: Reaction constants of molten $ZnCl_2$ and $MgCl_2$ - $ZnCl_2$ (1:5 mol.) oxidation

Melt composition	t, °C	$k_0 \cdot 10^8, \text{mole} \cdot \text{s}^{-1}$	
		Air	Oxygen
$ZnCl_2$	600	1.15±0.17	1.24±0.04
$MgCl_2$ - $ZnCl_2$, 1:5 mol.		5.40±0.28	12.15±0.61

Experimental results with magnesium chloride and its eutectic mixture with NaCl oxidation were reported previously [2]. It was suggested that oxidation in the $MgCl_2$ -NaCl (eutectic melt) is limited by diffusion and also with $ZnCl_2$ melts. The authors described their experimental data as showing that magnesium chloride appeared to be more active in a Cl^- oxidation reaction as compared with $ZnCl_2$, but the term Cl^- oxidation reaction is not an adequate description as we have now shown here. In our case of $MgCl_2$ - $ZnCl_2$ mixtures, as might be expected, both magnesium and zinc species are oxidized.

Khokhlov et al. [25] have recently reported on the preparation of $LiCoO_2$ nanoparticles in the chloride melts, involving oxygen but without recognizing the chemical dissolution of oxygen and thus have not described the mechanism involved that we find here.

Greenwood and Earnshaw [26] indicate that zinc chloride is a surprisingly difficult material to obtain absolutely dry and absolutely pure: treating the metal with HCl gas is the best recommended method. Watson et al. [27] have noted that zinc chloride does not become completely anhydrous using the traditional methods of removing trace amounts of water from inorganic salts by strong heating: some oxychloride is formed and this has to be removed by bubbling chlorine gas into the molten salt. Even so, the resulting material is very hygroscopic and consequently all subsequent reactions have to be carried out in an efficient drybox. The drying procedures and handling techniques employed here (see Experimental) could probably result in traces of oxychloride in the zinc chloride used but no oxychloride was found in the oxides finally separated from the melts (Figures 2-4). We suggest that these trace oxychlorides existing in initial zinc chloride melts may have participated in the reaction with the slightly soluble oxygen gas but an unambiguous mechanism for the reaction cannot be identified at this time.

Zn and Mg oxides analysis results

The zinc oxide and the mixed Zn-Mg oxides produced were analyzed using XRD and AAS methods and the BET surface of oxide powders was measured.

The concentration of Zn^{2+} found with AAS was 107.97 mg/L. The molar ratio of Mg and Zn oxides calculated on the basis of AAS data as 1:0.99.

XRD analysis of mixtures of oxides powders, calcined at 300°C, showed the presence of zinc oxychloride, e.g., $Zn_5(OH)_8Cl_2 \cdot H_2O$ (Figure 2, 3). Garcia-Martinez *et al.* have shown that zinc oxychloride compounds can be decomposed to ZnO upon heating to 600°C [28]. No oxychloride compounds were found in the oxide nano-powders by XRD after calcination at 650°C (Figure 4).

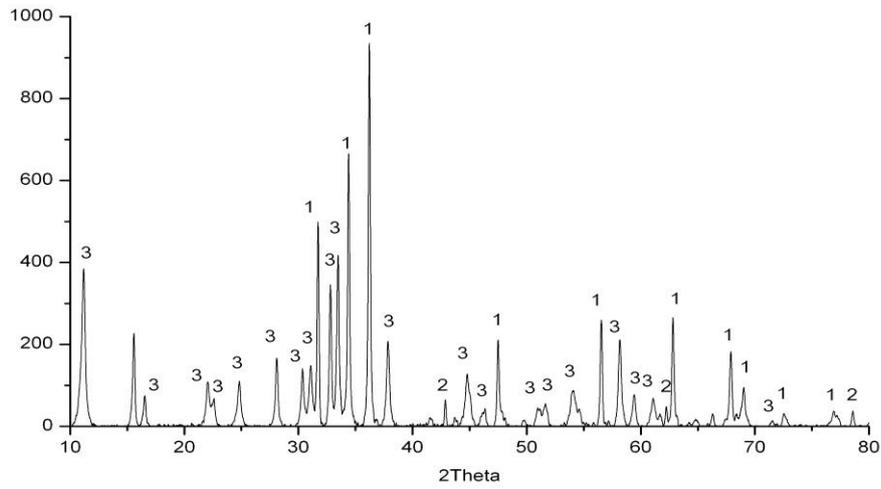


Figure 2: XRD pattern of MgO-ZnO mixture (produced in air) after calcining at 300°C for 5 hrs: 1 – ZnO; 2 – MgO; 3 – $Zn_5(OH)_8Cl_2 \cdot H_2O$.

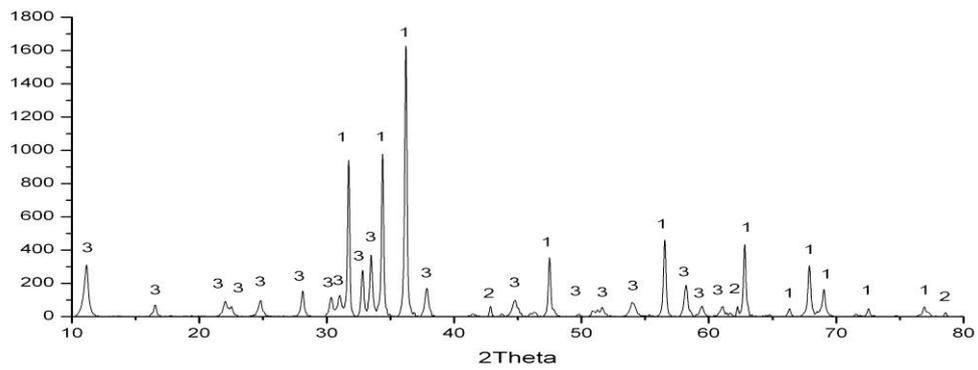


Figure 3: XRD pattern of MgO-ZnO mixture (produced in oxygen) after calcining at 300°C for 5 hrs: 1 – ZnO; 2 – MgO; 3 – $Zn_5(OH)_8Cl_2 \cdot H_2O$.

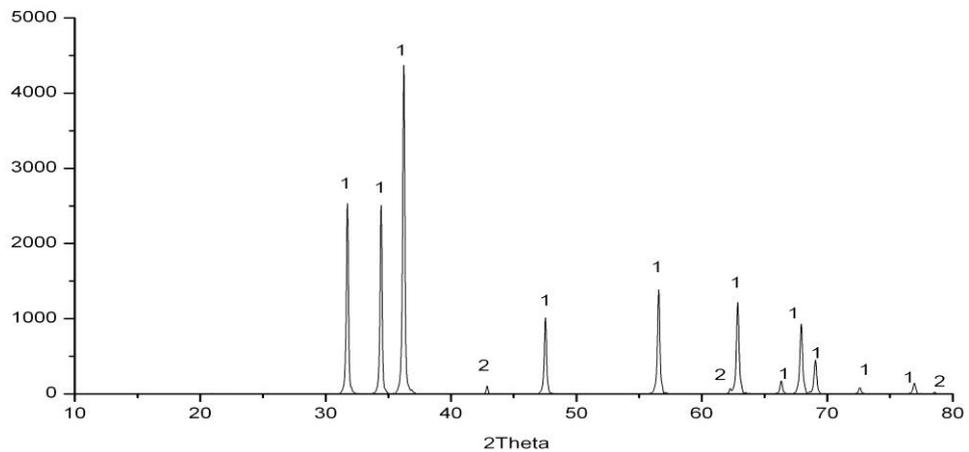


Figure 4: XRD pattern of MgO-ZnO mixture (produced in oxygen) after calcining at 650°C for 5 hrs: 1 – ZnO; 2 – MgO.

Average unit cell size (D , nm) values for Zn and Mg oxides were calculated by the Selyakov-Sherrer equation: $D_{MgO} = 62$ nm, $D_{ZnO} = 60$ nm (in mixture with MgO), $D_{ZnO} = 58$ nm (single ZnO). BET surface and pore volume were determined for oxides powders. For single ZnO the surface area was $S = 1.92$ m²/g, average pore diameter $d = 10$ nm, pore volume $V = 0.005$ ccm/g. For ZnO–MgO mix (produced in oxygen) $S = 4.73$ m²/g, $d = 18$ nm, $V = 0.02$ ccm/g. Surface and pore parameters are higher for mixed oxides powder.

Powders of ZnO and ZnO–MgO were investigated with an atomic-force microscope. Particle sizes measured with this method were in the range 30–200 nm (Figure 5, 6)

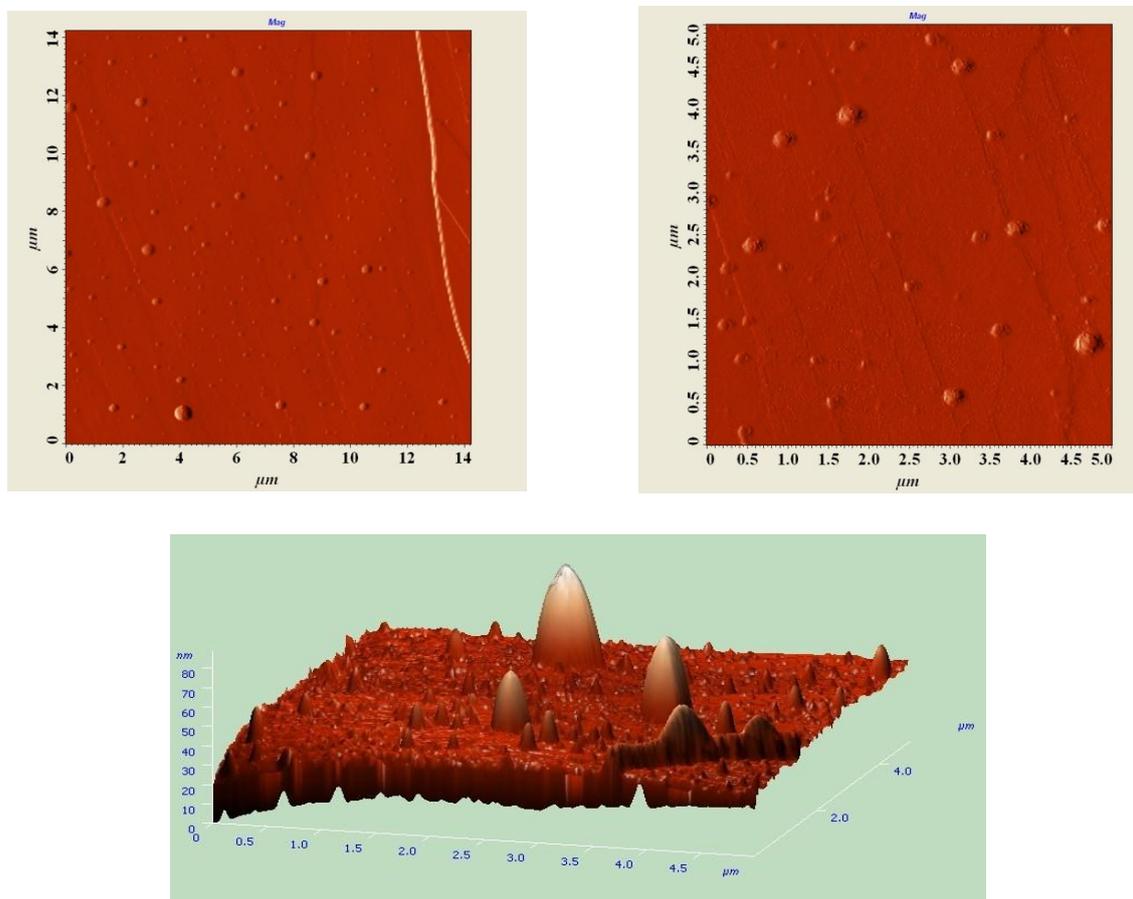


Figure 5: Particles of ZnO

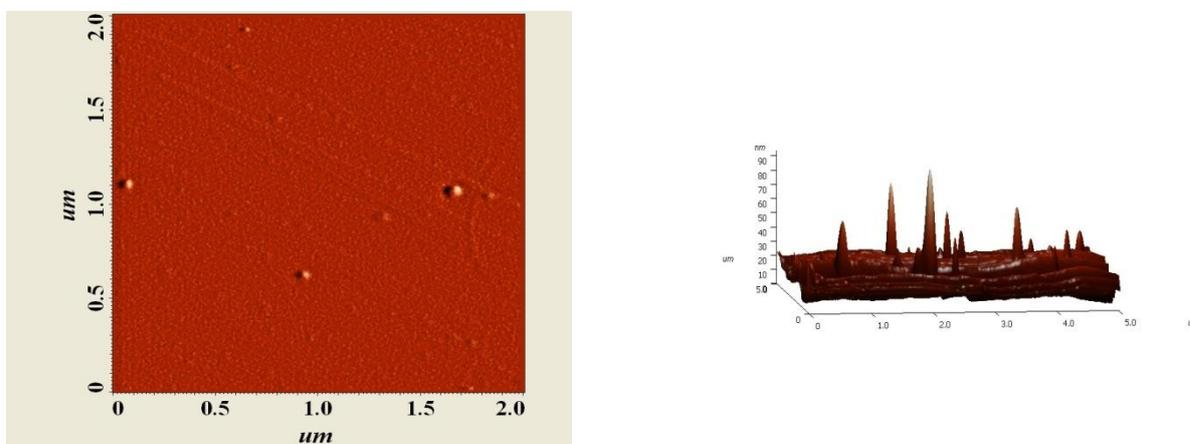


Figure 6a: Particles of MgO-ZnO (MgCl₂-ZnCl₂ (1:5), air)

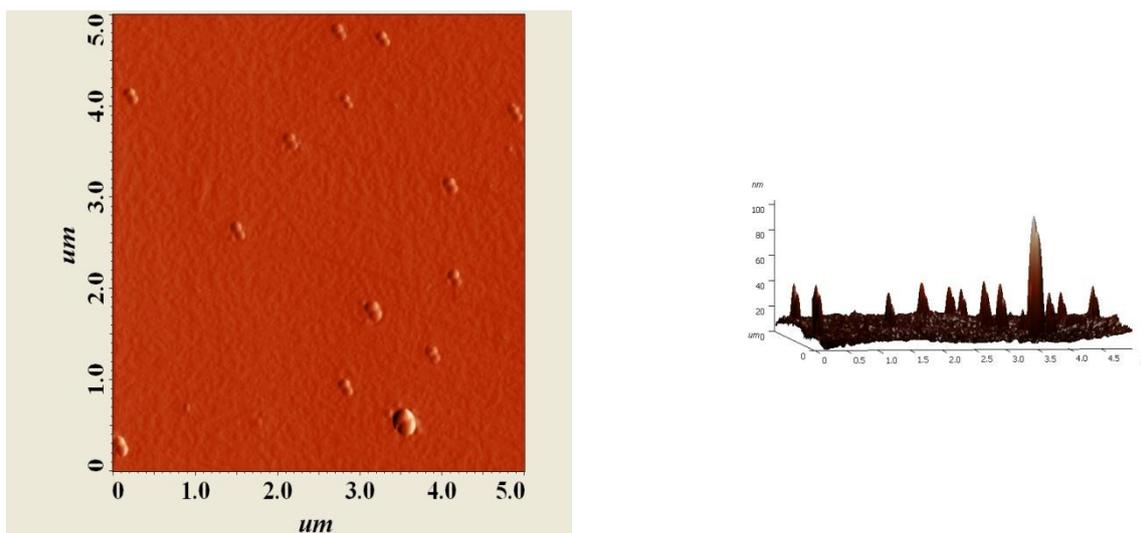


Figure 6b: Particles of MgO-ZnO ($\text{MgCl}_2\text{-ZnCl}_2$ (1:5), oxygen)

Oxides formed in the oxygen flow have larger-size particles. When using oxygen rather than the air, the growth of oxide particles in the melt is more rapid in oxygen.

CONCLUSIONS

Mg and Zn oxides can be obtained in molten salts by an oxidation reaction whereby oxygen is bubbled into their molten chlorides at above 600°C . This method allows synthesis of nano-sized and nano-structured metal oxide powders of high purity, since only two reagents are involved and the process is straightforward. No toxic or flammable solvents are needed to separate the reaction products. The mechanism involves a reaction wherein oxygen that has dissolved chemically (not physically) into the chloride melt reacts with the tetrahedral chloride ions of magnesium and of zinc now present, liberating chlorine gas and forming insoluble nano-sized oxides of these metals. The chemically dissolved oxygen reacts steadily to liberate chlorine. The reaction has a zero order rate constant because the solubility, and thus the concentration, of chemically dissolved oxygen is low but kept constant because of the continuous bubbling of oxygen (or air) into the melt. The observation that the nano zinc oxide still showed the standard reaction of turning yellow upon heating above 300°C , due to slight oxygen loss and consequent defect formation, confirms that, though small in size, these nano particles still retained the property of defect formation. The colour did not disappear completely upon cooling but became pale yellow and this property of may be related to the variation in nano-sized ZnO powder particles (Figure 5).

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