Growth Of Zinc Oxide Crystals By Accelerated Evoporation Technique From Supersaturated Solutions

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Abstract: Low-temperature solution growth (LTSG) is one such simplest but efficient method for production of good optical quality crystals. It was probably the first and the most widely used technique to produce artificial crystals for many useful applications. However, it is used at large for the growth of large and commercially important single crystals like ADP, KDP, Rochelle Salt and Alums. An indigenous LTSG workstation capable of room temperature and at various elevated temperatures is fabricated using locally available components. The starting materials are taken in adequate quantities and then dissolved in double distilled water in order to attain super saturation. The supersaturated solution is left to crystallize by accelerated evaporation process. Another supersaturated solution is prepared and filtered and loaded into 1000ml beakers and kept in a constant temperature water bath under rapid crystallization process. Each of the crystals will appear spontaneously nucleated after a prescribed amount of time which is unique and proportional to the growth rate of the said crystal. The crystals will be analysed for their physical, scientific and spectroscopic properties.

Keywords: Low Temperature Solution growth, ZnO, LTSG, NLO, piezoelectric, ferroelectric.

Introduction

Synthetic ZnO is primarily used as a white powder that is insoluble in water, or naturally as the mineral zincite [1]. The powder is widely used as an additive in numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g., car tyres), lubricants[2], paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, and first aid tapes.

In materials science, ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group (since oxygen was classed as an element of VIA group and the 6th main group, now referred to as 16th) of the periodic table and zinc, a transition metal, as a member of the IIB (2nd B), now 12th, group). The native doping of

the semiconductor (due to oxygen vacancies) is n-type. This semiconductor has several favorable properties, including good transparency, high electron mobility, wide bandgap, and strong room-temperature luminescence. Those properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes [3].

Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zincblende. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral,

the most characteristic geometry for Zn(II). ZnO is a relatively soft material with approximate hardness of 4.5 on the Mohs scale. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial [4] for ceramics. ZnO's most stable phase being wurtzite, ZnO exhibits a very long lived optical phonon E2 (low) with a lifetime as high as 133 ps at 10 K.

Materials And Methods

The starting materials viz., Analar Grade chemicals of Zinc Nitrate are taken in equal quantities and mixed with de-ionised, double distilled water and made into a saturated solution using a hot plate with magnetic stirrer. Then an additional quantity of the solute is mixed with the solvent which maintained at a slightly elevated temperature of 40°C so that an additional amount of Zinc Nitrate is miscible with the saturated solution making it supersaturated. The supersaturated solution is filtered using 0.5 micron filter paper and left for crystallization in the modified constant temperature bath with accelerated evaporation with rapid crystallization technique.

Solubility And Induction Time

The solubility (Fig.1) of Zinc Oxide by taking Zinc Nitrate in the pure state and dissolved in double distilled de-ionised water was studied. Solubility of KDP in its undoped state was found to be 36 grams per 100ml of the solvent (double distilled water). The induction time (Fig.2) was calculated using the standard procedures advised and available. The metastable zone width is the measure of stability of a solution in its supersaturated region where the largest width implies the substance having higher stability. 100 ml of the saturated solution was kept in the cryostat and the temperature reduced at 5°C per hour while the solution was stirred continuously. The temperature of formation of the first speck was found which corresponds to the width of the metastable zone [5]. The metastable zone width of KDP was found to be the maximum in the lower temperature gradients than the higher gradients (Fig.2). Induction period i.e., the formation of the first speck of nuclei of pure KDP and with different dopants were studied. It was found that the induction period corresponding to concentration 1.1 was 325 sec and 1.5 was 50 sec respectively. All five trials showed minimal to very minimal deviation and was seen to meander an identical common slope.
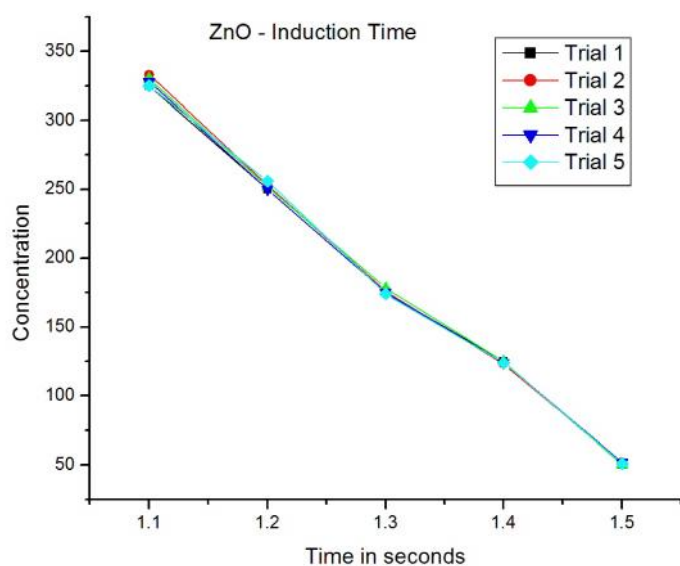
Fig. 1: Zinc Oxide – Induction Time
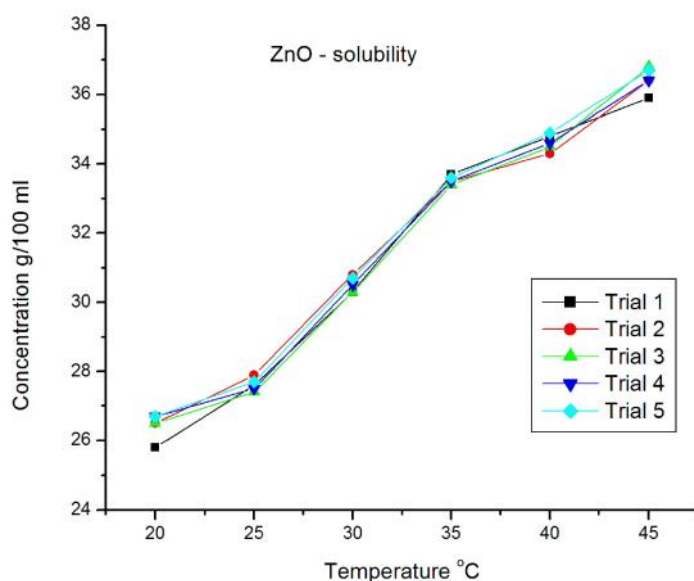
Fig.2: Zinc Oxide – solubility graph

Crystal Growth Of Zinc Oxide

Zinc Oxide crystals are grown from Solution Growth process where the precursors are Analar Grade Zinc Nitrate in the form of white crystalline powders dissolved in double distilled de-ionised water. The saturated solution is then made supersaturated by way of elevating the temperature and dissolving more of the solute in the solvent. This homogenous mixture is made to settle for a prescribed period of twenty four hours. Then the solution is filtered using filter paper of 0.5 micron thickness using a peristaltic pump. The crystal to be grown is then placed inside a constant temperature bath and kept for crystallization for an optimal period of time. Micro crystals are formed out of nucleation at the first phase which gets transformed into macro crystals and then form a crystal of bigger size and shape. At the outset, a large crystal is formed in the beaker where almost 100% of the solvent is evaporated and the crystallization is complete. The time taken for the crystallization is observed and then similar runs are engaged with rapid evaporation of the solution. The beaker with the water bath is placed inside a solar concentrator when the process of evaporation becomes faster [6]. The time of crystallization or complete crystallization of the solution is observed. It was noted that the first process of crystallization involved two full weeks of crystallization where complete crystallization was not achieved. But when crystal growth was carried out using accelerated evaporation and rapid crystallization technique, the same crystal growth is realized in a matter of a few days. This is an important milestone achieved in rapid crystallization where solution grown crystals can be realized in a shortest time possible and paves a way for industrial crystallization leading to mass production of crystals.

Fig. 3: Zinc Oxide crystal grown from solution (a) side view (b) top view

The grown crystals were characterized for their optical, structural and scientific properties.

Fourier Transform Infra-Red Spectroscopy

FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy [7]. The term *Fourier transform infrared spectroscopy* originates from the fact that a Fourier transform (a mathematical algorithm) is required to convert the raw data into the actual spectrum. For other uses of this kind of technique, see Fourier transform spectroscopy.

The goal of any absorption spectroscopy (FTIR, ultraviolet-visible ("UV-Vis") spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the "dispersive spectroscopy" technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength. Fourier transform spectroscopy is a less intuitive way to obtain the same information. Rather than shining a *monochromatic* beam of light at the sample, this technique shines a beam containing many different frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength.

The beam described above is generated by starting with a broadband light source—one containing the full spectrum of wavelengths to be measured. The light shines into a certain configuration of mirrors, called a Michelson interferometer, that allows some wavelengths to pass through but blocks others (due to wave interference). The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that pass through. As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram".
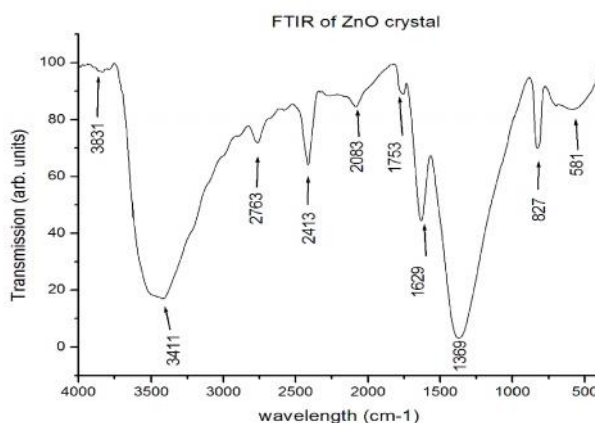
Fig. 4: FTIR of ZnO crystal

FTIR of ZnO was done (Fig. 4) on Perkin Elmer Lambda Spectrophotometer between 400-4000 cm^{-1} The OH bands observed on ZnO crystals are assigned to the OH species on the (3831 cm^{-1}), the isolated (3411 cm^{-1}) and with H_2O co-adsorbed OH species (2763 cm^{-1}) on mixed-terminated ZnO surfaces, respectively. The hydroxyl species on ZnO are formed via dissociative adsorption of water on oxygen vacancy sites, while the interaction of water with the perfect ZnO surface results in partial dissociation, yielding both H_2O and OH species [8]. The molecularly adsorbed H_2O on ZnO is clearly identified by the characteristic scissoring mode at 1629 cm^{-1} as well as the low-lying O-H stretching mode due to the unexpected strong hydrogen-bonding interactions with both neighboring H_2O molecules and surface oxygen atoms. Two additional broadbands at 2413 cm^{-1} and 2083 cm^{-1} are tentatively attributed to hydroxyl groups (or OH$\cdots$O species), formed via water adsorption on defect sites. Based on these assignments, D_2O adsorption has been further investigated by means of spectroscopy method [9]. The dissociation of D_2O at 323 K on ZnO is proved by the formation of isolated OD bands. The bands at 3687, 3672, 3657, 3639, 3620, 3564, and 3449 cm^{-1} shift, after the adsorption of D_2O towards the expected lower wavenumbers at 2716, 2707, 2698, 2683, 2669, 2626, and 2551 cm^{-1}, assigned to the different O-H and O-D stretching vibrations on ZnO, respectively. These features give rise to an excellent assignment of O-H species on ZnO in relation to those on single crystal surfaces.
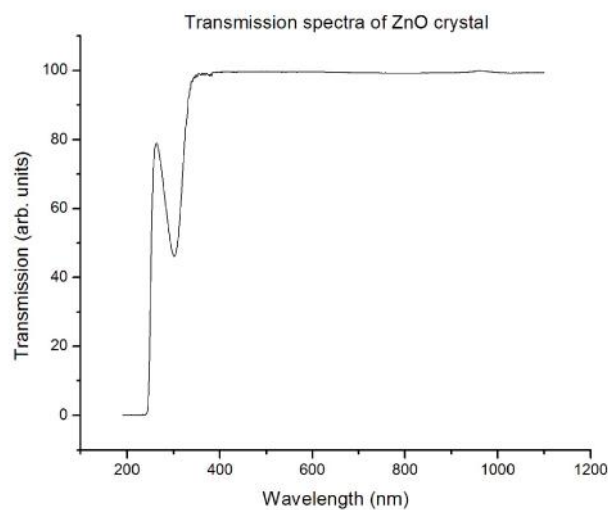
Absorption Spectroscopy

Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance is directly proportional to the path length, *b*, and the concentration, *c*, of the absorbing species. *Beer's Law* states that $A = ebc$, where **e** is a constant of proportionality, called the *absorbtivity*. Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. For example, the absorption that is observed in the UV region [10] for the carbonyl group in acetone is of the same wavelength as the absorption from the carbonyl group in diethyl ketone. Absorption may be presented as **transmittance** ($T = I/I_0$) or **absorbance** ($A = \log I_0/I$). If no absorption has occurred, T = 1.0 and A= 0. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance). The wavelength of maximum absorbance is a characteristic value, designated as $_{max}$. Different compounds may have very different absorption maxima and absorbances. Intensely absorbing compounds must be examined in dilute solution, so that significant light energy is received by the detector, and this requires the use of completely transparent (non-absorbing) solvents. The most commonly used solvents are water, ethanol, hexane and cyclohexane. Solvents having double or triple bonds, or heavy atoms (e.g. S, Br & I) are generally avoided. Because the absorbance of a sample will be proportional to its molar concentration in the sample cuvette, a corrected absorption value known as the **molar absorptivity** is used when comparing the spectra of different compounds [11]. Absorption o=spectra of Zinc Oxide was taken between 200-1200nm. It has near to near total transmission from 300nm. Almost 90% transmission was observed in the Absorption Spectra and Transmission spectra of ZnO. It is very much evident from both the spectra since they were complimentary to each other.
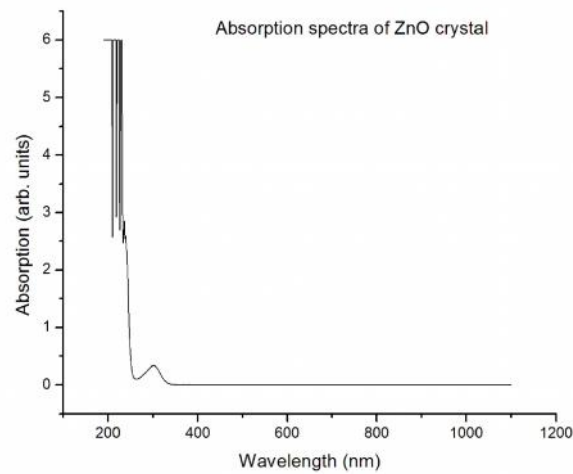
Fig. 5: Absorption Spectra of ZnO

Fig. 6: Transmission spectra of ZnO

Conclusion

Crystals of Zinc Oxide are grown using Low Temperature Solution Growth Technique, The grown crystals are characterized by structural, optical and spectroscopic studies [12]. The absorption and transmission spectra proves that the Zinc Oxide Crystal has good order of transparency. FTIR spectra are conveniently divided into sections according to the type of vibration in the structure. Thus bands were assigned to hydroxyl stretching, hydroxyl deformation, CuO stretching modes. Combination bands are present in some cases. The observation of CuO bands is significant as they are often hidden beneath vibrations arising from oxy-anions in other basic copper minerals [13]. The FTIR spectra elaborates the essential assignments for the bonds which are identified as symmetric, anti-symmetric or bending modes.

Acknowledgement

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