# Effect of stabilizer on optical and structural properties of MgO thin films prepared by sol–gel method

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**Abstract.** The effects of monoethanolamine (MEA) and acetylacetone (ACAC) addition as stabilizer on the crystallization behaviour, morphology and optical properties of magnesium oxide were investigated using thermogravimetry (TG/DTG), X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Visible, photoluminescence (PL) and Fourier transform infrared (FTIR) spectroscopy. Stabilizer addition reduces transparency of the films. MgO films prepared at 500 °C showed weak orientation of (200). However, the films prepared by addition of stabilizer are amorphous. MgO powders were prepared for exhibiting the structural properties. The patterns of MgO powders showed a preferred orientation of (200). The addition of stabilizer causes a reduction in grain size. SEM micrographs show that a homogenous and crack-free film can be prepared at 500 °C and addition of stabilizer causes an increase in packing density.

**Keywords.** MgO; thin film; sol–gel; stabilizer.

## 1. Introduction

MgO is a very important scientific and commercial material. It is a highly ionic insulating crystalline which is stable at high temperature. Magnesium oxide thin films have received much attention due to its various applications. They are widely used as a protective layer for AC-plasma display panels because of their high durability, good protection characteristics against ion bombardment, high secondary electron emission coefficient and high transparency (Choi *et al* 1998). MgO thin films have been used as buffer layers for superconducting and ferroelectric thin films (Fujii *et al* 1994). MgO has added advantages of a wide bandgap, low optical loss and a relatively low refractive index (∼1·7) which can permit confined optical modes in many ferroelectric materials. Also MgO powder has been utilized as a catalyst (Utamapanya *et al* 1991). MgO was prepared by conventional methods such as pulsed laser deposition (Ishiguro *et al* 1996) chemical vapour deposition (Kamata *et al* 1984), rf magnetron sputtering (Shih *et al* 1991), e-beam evaporation (Hsu and Raj 1992) and spray pyrolysis (Yi *et al* 1996). But these methods often yield a relatively small surface area and hence, show low reaction activity. It is believed that the materials prepared by sol–gel technique show much better surface or bulk properties than those obtained by the conventional methods. High purity, controllable thickness, easy control of composition, good homogeneity, large area coating capability, low process temperature and low cost are other advantages of sol–gel method. MgO thin films preparation by sol–gel method

involve the use of alkoxide as precursors (Jung *et al* 2003a, b; Menon and Bullard 1999). These alkoxides are expensive and are not easy to handle due to high moisture sensitivity. Metal salts include chlorides, acetates, nitrates and sulfides which are very useful, cheaper and very easy to handle than metal alkoxides. There are only a few reports on preparation of MgO thin film from Mg acetate precursor (Chakrabarti *et al* 2002). Acetate ions can stabilize the metal ions in solutions through coordination by C=O groups. Also in order to prepare reproducible films via sol–gel process, maintaining the stability of sol is critical and usually alkanoamines have been introduced to increase the stability of sols (Nishio and Tsuchiya 2005). In the present work, we prepared MgO thin films and powders using Mg-acetate tetrahydrate by sol–gel method by dip-coating technique. The influences of stabilizer addition on optical, structural and morphological properties of MgO films and nanopowders were investigated.

## 2. Experimental

The sols were prepared by dissolution of Mg-acetate tetrahydrate (($CH_3COO)_2Mg \cdot 4H_2O$) 99%) in methanol. Acid nitric was added in the solution under stirring as catalysis. The stirring was continued for 1 h at room temperature to yield a clear and homogeneous solution. We tested four different kinds of stabilizers: monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA) and acetylacetone (ACAC). By adding TEA we could not get a clear solution. The sol containing TEA was not stable for more than one day. So we chose three different kinds of sols for our investigation as shown in figure 1. Glass substrates were cleaned by putting them in a mixture of acetone and

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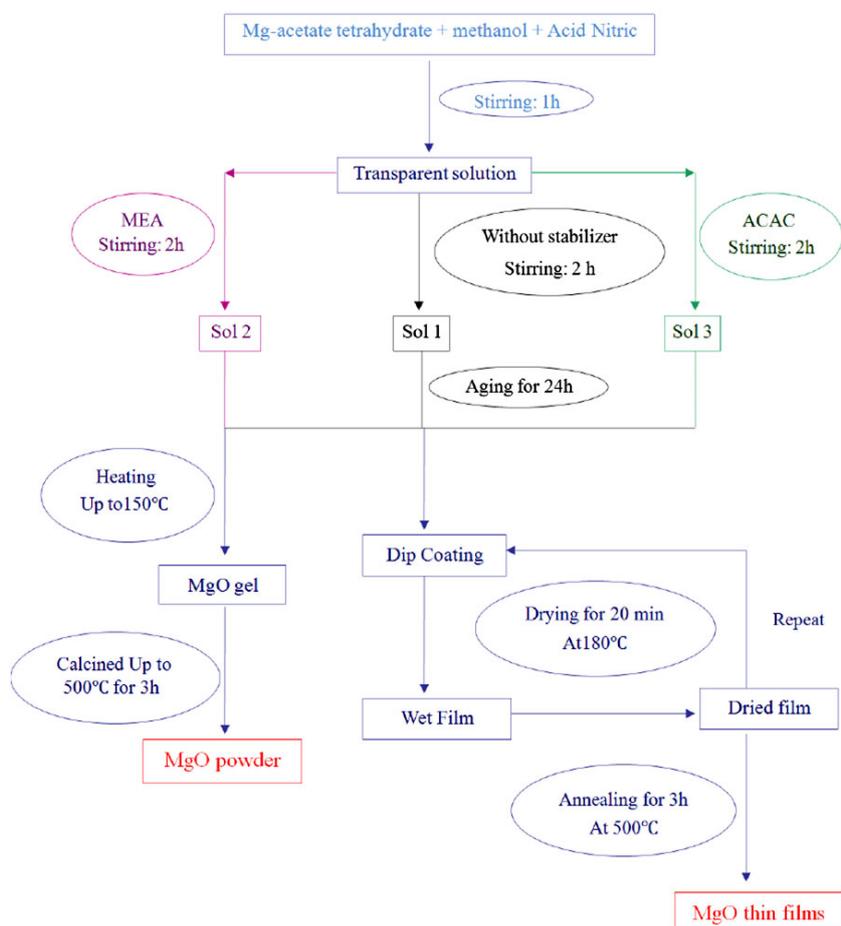
**Figure 1.** Diagram for preparation of MgO thin films and powders using different sol routes.

ethanol in ultrasonic cleaner. The films were deposited on cleaned glass substrates by the multiple dipping with intermediate drying at 180 °C. The multilayer films were annealed at 500 °C for 3 h. Magnesium oxide powders were prepared by heating the sols up to 150 °C for evaporating solvent and post heating at 500 °C for 3 h. The flowchart for depositing MgO thin films using sol–gel dip-coating process is shown in figure 1.

## 3. Characterization

Thermogravimetric analysis was performed in the temperature range of 30–1000 °C using Perkin Elmer Pyris Diamond. Optical properties of films were investigated using UV visible spectrophotometer (Varian Carry 100) and photoluminescence (PL) spectrophotometer (Perkin Elmer LS-55). FTIR spectra were taken using a FTIR spectrometer (8900, Shimatzu model). The structural properties of films and powders were characterized by X-ray diffraction (XRD) analysis (Unisantis model xmd300). The surface morphology of films was characterized using scanning electron microscope (Leo1430vp model).

## 4. Results and discussion

### 4.1 *Thermogravimetry and differential thermal analysis*

The thermogravimetric and derivative thermogravimetric analysis of dried gels prepared at 100 °C for three different sols are shown in figure 2. In all the cases, the primary weight loss occurred roughly at 170 °C. The primary weight loss originates from desorption of residual methanol or physically adsorbed water (Shukla *et al* 2004).

Secondary weight loss for sols 1, 2 and 3 occurs in the temperature ranges of 290–331, 235–262 and 291–327 °C, respectively. This exothermic transition could be attributed to phase transition of $Mg(OOCCH_3)_2$ (Menon and Bullard 1999; Shukla *et al* 2004). Strong exothermic signals between 331 and 370 °C for sols 1 and 2 and between 416 and 462 °C for sol 3 could be due to conversion of $Mg(OOCCH_3)_2$ to MgO (Menon and Bullard 1999; Shukla *et al* 2004) and it shows that powders start to decompose at higher temperature by the addition of acetylacetone as stabilizer. The difference in the decomposition temperature, in turn, influenced crystallization of the resultant powders.
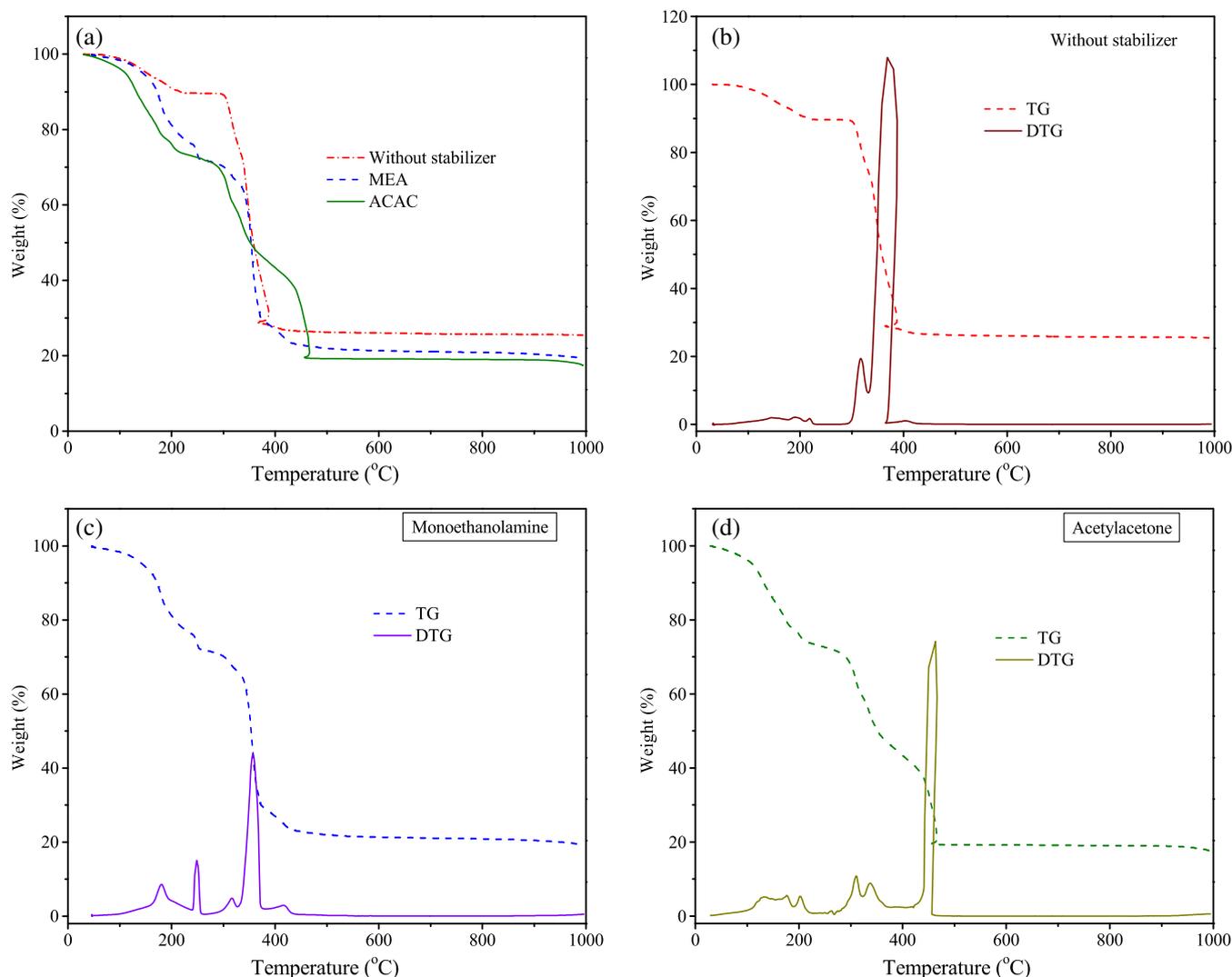
**Figure 2.** TG and DTG curves of precursor gel powders.

FTIR spectra of MgO films annealed at 500 °C are shown in figure 3. The O–H stretching appearing at about 3701 cm$^{-1}$ is assigned to the adsorbed water from air (Jung *et al* 2003a, b) and it can be seen just in the sample prepared by sol 1. The broad peak around 3400 could be assigned to O–H or N–H stretching absorption which is observed at all the three spectra and noticeably increased by the addition of stabilizer (Jung 2003a, b; Han *et al* 2009). The absorption in 2370 cm$^{-1}$ is because of the existence of $CO_2$ molecule in air (Wu *et al* 2006).

The peaks around 1704 cm$^{-1}$ are assigned to C=O bond. The C–O stretching mode observed around 1430 cm$^{-1}$ corresponds to the carbonate ion and it can be seen in all the samples and the addition of stabilizer increases the intensity of peaks (Jung *et al* 2003a, b). The Mg–O absorption peaks are expected in the 400–600 cm$^{-1}$ region (Moses *et al* 2007). The sharp peaks seen at MgO thin film spectra at this region are associated with Mg–O bond vibrations.

### 4.2 *Optical properties*

Figure 4 shows transmission spectra of MgO thin films prepared by three different sols. The results indicate that the transparency of films will decrease by the addition of stabilizer. The monoethanolamine has one nitrogen atom and one oxygen atom and acetylacetone has two oxygen atoms. In general, the coordination power of the oxygen atom is stronger than that of the nitrogen atom (Nishio and Tsuchiya 2005). Specially, ring type chelates with acetylacetone may form two Mg–O bonds. Therefore, density of films increases with the addition of stabilizer, especially with acetylacetone due to reduction of pores. The transmittance of films increases when porosity increases (Helsch *et al* 2000; Gross *et al* 2007; Tachibana *et al* 2007). This is because of the reduction of specular reflectance due to light scattering on voids. Also, the presence of organic residual group like C–O which is due to the addition of stabilizer and revealed by FTIR spectroscopy can be the other reason for lower transparency of films.
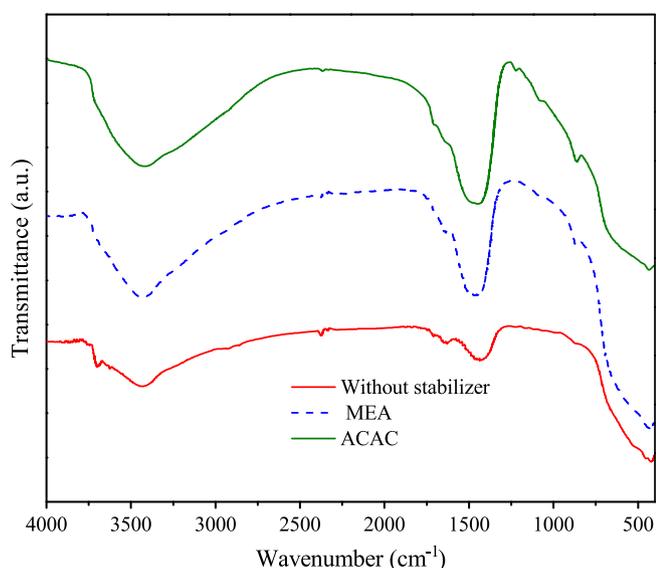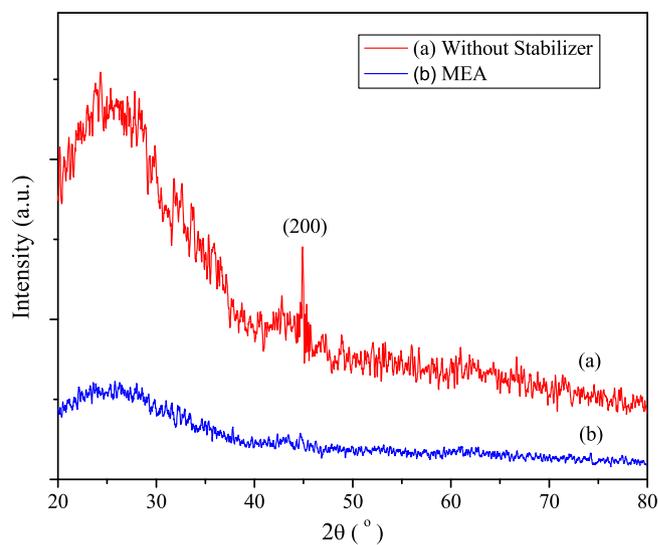
**Figure 3.** FTIR spectra of initial sol and MgO thin film annealed at 500 °C.
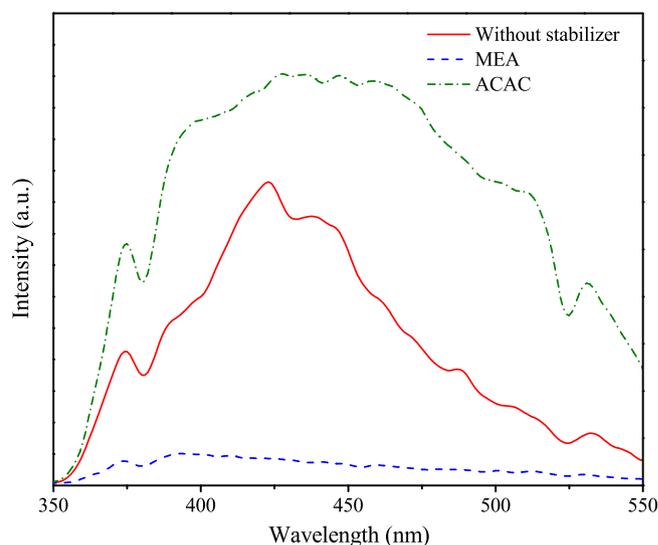


**Figure 5.** PL spectra of MgO thin films prepared by three different sols.
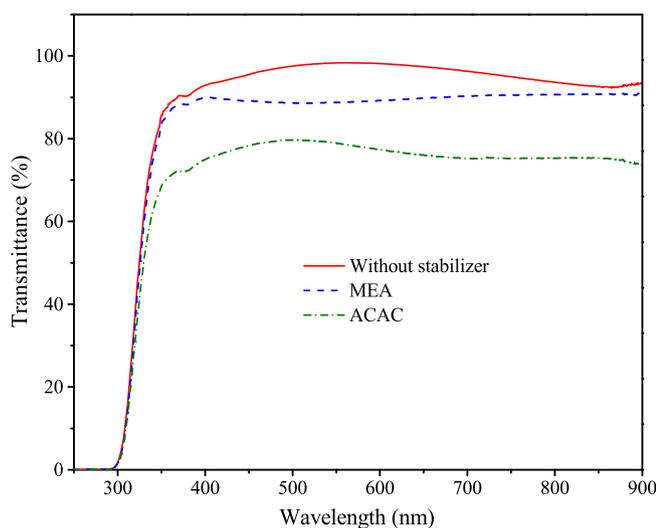


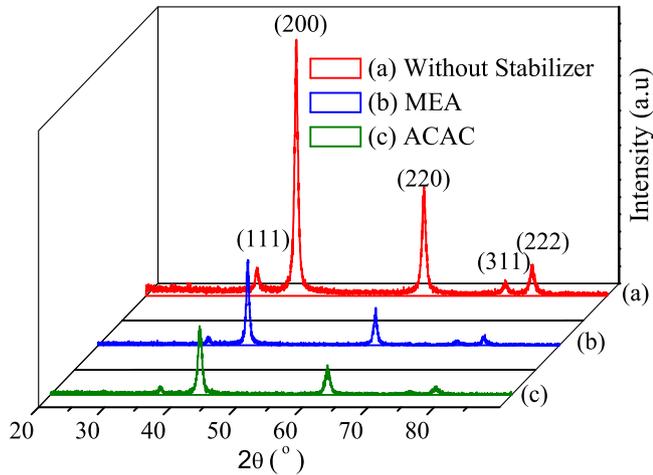**Figure 4.** Transmission spectra of MgO thin films prepared by three different sols.



**Figure 6.** XRD patterns of MgO thin films prepared by two different sols.

Figure 5 shows photoluminescence spectra of MgO thin films prepared by different sols at 500 °C. There are four peaks in PL spectra of MgO thin films, a peak about 375 nm which is related to ultra-light emission, peak at 393 nm in violet region, peak at 454 nm in blue region and 531 nm in green region which is close to other reports (Kim *et al* 2008). UV, blue and green light emissions originate from the defects in MgO, such as oxygen and Mg vacancies. The violet emission in MgO is attributed to defect centres, such as $F^+$ centres (Kim *et al* 2007).

It is clearly seen that the intensity of peaks enhanced with the addition of acetylacetone. But addition of MEA strongly decreases the intensity of peaks in comparison with the sample without stabilizer. Acetylacetone can make complex in prepared sols and heating can help it to produce denser films and it causes an increase in photoluminescence property of films. Presence of non-radiation recombination centre which may be due to the presence of N-group results in a noticeable decrease in photoluminescence property of the samples containing MEA.

## 4.3 *Structural studies*

XRD patterns of MgO thin films and powders prepared by sol–gel method are shown in figures 6 and 7, respectively.



**Figure 7.** XRD patterns of MgO powders prepared by three different sols.
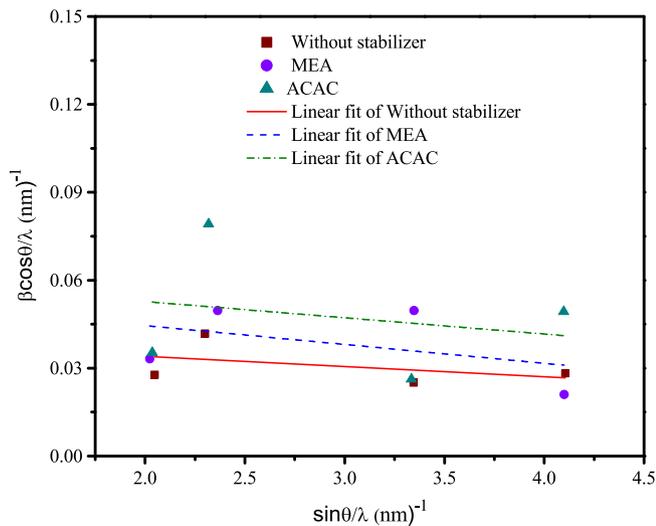


**Figure 8.** Plot to determine strain and particle size of MgO powders prepared by three different sols.

MgO thin film with very weak (200) peak was obtained by sol 1. The film prepared by sol 2 shows amorphous structure. It has been reported that MgO thin films prepared at low annealing temperature show amorphous structure (Chakrabarti *et al* 2002). Also, it has been reported that the surface structure of substrate has effect on preferential orientation of the sol–gel derived MgO film and the crystalline structure of MgO films can improve by using (100) Si substrate (Ho *et al* 1997).

MgO powders showed crystalline structure with preferred orientation of (200). These patterns correspond to periclase phase of MgO having *fcc* structure (Kumar and Kumar 2008). The average grain size was calculated by the Scherrer's formula (Patterson 1939):

$$D = \frac{K\lambda}{\beta \cos\theta},  \tag{1}$$

where $K$ is Scherrer constant, $\lambda_{\text{CuK}\alpha} = 1 \cdot 54$ the wavelength of X-ray and $\beta$ the full width at half maximum.

The information on strain and particle size is obtained from the full width at half maximum (FWHM) of the diffraction peaks by using the Williamson and Hall theorem (Williamson and Hall 1953):

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{D} + \eta \frac{\sin\theta}{\lambda},  \tag{2}$$

where $\beta$ is the full width at half-maximum (FWHM), $\theta$ the diffraction angle, $\lambda$ the X-ray wavelength, $D$ the effective particle size and $\eta$ the effective strain. Figure 8 represents the plot of $\beta \cos\theta / \lambda$ against $\sin\theta / \lambda$. The strain is measured from the slope and the crystallite size, $D$, is measured from the intercept of plot. The results are compiled in table 1. The slope is negative for all the samples which indicates compressive strain. $d$ is the spacing between planes for (200) orientation.

For investigating morphology of MgO thin films, we used SEM analysis. Figure 9 shows SEM micrographs of MgO films prepared by three different sols. SEM micrographs of MgO thin films confirm difference between porosity of three samples and show that porosity of films decreased with addition of stabilizer. In sol–gel films, cracks are common because of strain which could have resulted from fragile nature of gels. Film prepared by sol without stabilizer had

**Table 1.** Structural values of MgO powders calculated for preferred orientation of (200).

| Sample | $2\theta$ | FWHM | $d$ | $D_{\text{Scherrer}}$ | $D_{\text{effective}}$ | $\eta$ |
|--------|-----------|---------|--------|-----------------------|------------------------|------------|
| Sol 1  | 41·50014  | 0·39438 | 0·217  | 23                    | 24                     | −0·00349   |
| Sol 2  | 42·72383  | 0·47041 | 0·211  | 19                    | 17                     | −0·00643   |
| Sol 3  | 42·59195  | 0·52005 | 0·212  | 17                    | 15                     | −0·00555   |
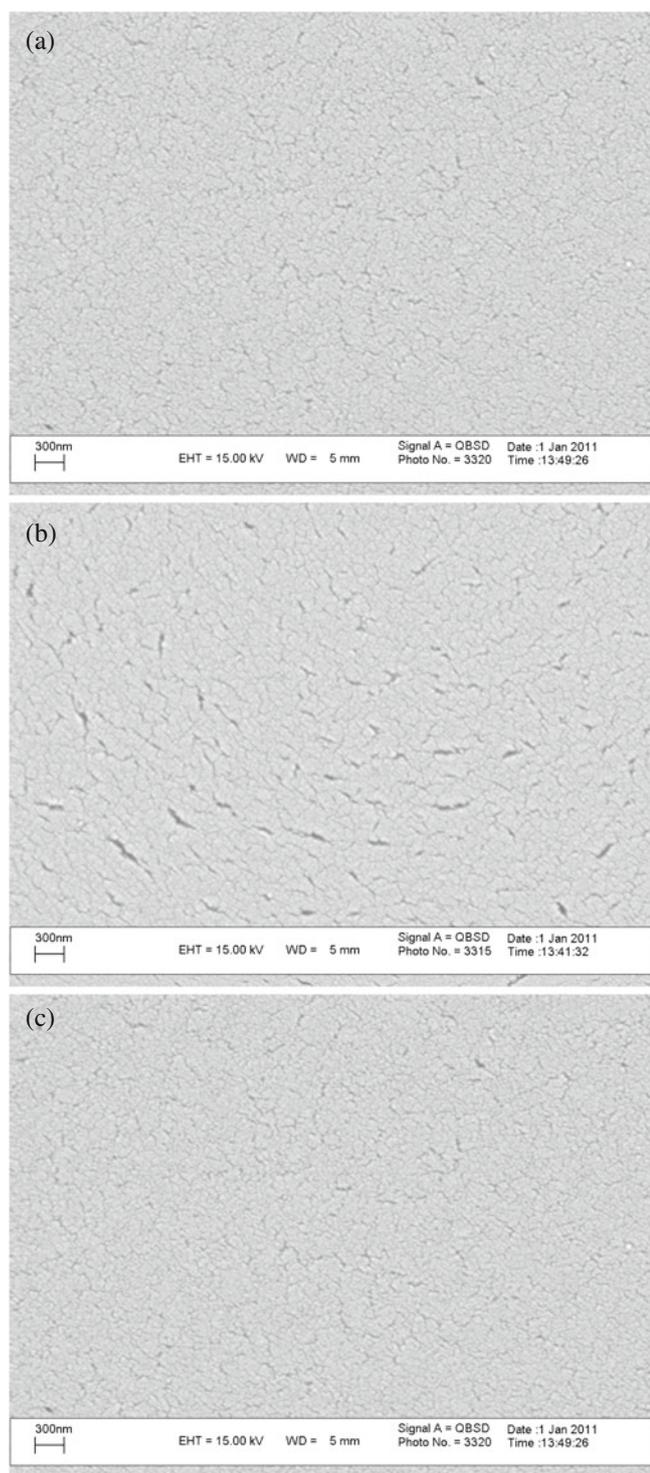
**Figure 9.** SEM micrographs of MgO thin film prepared by (**a**) without stabilizer, (**b**) addition of MEA and (**c**) addition of acetylacetone.

a lot of cracks on its surface (figure 9(a)). Addition of stabilizer helps to produce dense uniform and crack-free films (figure 9(b,c)) Most close packed and crack-free structure is obtained for films prepared by the addition of acetylacetone (figure 9(c)).

## 5. Conclusions

MgO thin films and stable periclase MgO powders with (200) orientation were fabricated successfully by sol–gel method. Thermal analysis shows that conversion of Mg(OOCCH$_3$)$_2$ acetate to MgO happens between 331 and 370 °C even by the addition of MEA. But gels start decomposition at higher temperature by adding acetylacetone as stabilizer. In MgO thin film FTIR spectra, there is a sharp peak at 400–600 cm$^{-1}$ region which is related to Mg–O bond vibrations. Transparency of prepared films by sol 1 is about 95%. Addition of stabilizer and specially acetylacetone strongly decreases transparency of films. Photoluminescence property of MgO films is enhanced by the addition of acetylacetone. The film prepared by sol 1 shows very weak orientation of (200). But the film prepared by sol 2 shows amorphous structure. Low annealing temperature or unsuitable substrate can be mentioned as main reasons for having amorphous structure. The lattice strain of MgO nano powders varies by the addition of stabilizer. SEM images show that crack free films can be prepared at 500 °C and by adding stabilizer we can decrease porosity of films.

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