Effects of metal doping on photoinduced hydrophilicity of SnO₂ thin films

DEBARUN DHAR PURKAYASTHA^{1,*}, RAJEEB BRAHMA¹, M GHANASHYAM KRISHNA¹
and V MADHURIMA²

¹School of Physics, University of Hyderabad, Hyderabad 500046, India

²Department of Physics, Central University of Tamil Nadu, Thiruvavur 610004, India

MS received 5 March 2014; revised 20 May 2014

Abstract. The influence of metal dopants (Mn²⁺, Al³⁺ and Cu²⁺) on the wetting properties of SnO₂ thin films deposited by thermal evaporation is reported. The undoped and doped SnO₂ films crystallize into the orthorhombic structure upon annealing at 200°C for 110 h. It is shown that wettability behaviour, before and after ultraviolet (UV) irradiation, is dependent on the ionic radius of the dopant. The contact angle of un-irradiated samples increases with increase in ionic radius of the dopant and also in comparison with the undoped sample. It is 54° for pure SnO₂ and increases to 77.5°, 92.3° and 95.9° for the Al³⁺, Mn²⁺ and Cu²⁺ doped samples, respectively. After UV irradiation, the value is 5.4° for the undoped sample. This increases to 21.2° for Al doping reaching a minimum of 6.4° for the Mn-doped sample increasing thereafter to 63.3° for the Cu-doped sample. It is observed that pre-irradiation contact angle behaviour can be correlated with the change in roughness of the films with increasing ionic radius. In contrast, photoinduced hydrophilicity of the films correlates with their optical bandgap. The contact angle is lowest for the lowest bandgap material, i.e., Mn-doped SnO₂, with a bandgap of 2.48 eV. Thus, the band structure of SnO₂ that can be controlled by dopant ionic radius can in turn be employed to manipulate the wettability of these surfaces.

Keywords. Bandgap; hydrophilicity; doping; wettability.

1. Introduction

Metal oxides such as TiO₂, ZnO and SnO₂ have been widely studied owing to their potential applications in industries producing self-cleaning and antifogging surfaces.^{1–5} Driven by the thrust of fabricating self-cleaning surfaces, the above-mentioned metal oxides have received increasing attention because of their tunable wettability by external stimuli such as ultraviolet (UV) irradiation.^{6–8} The phenomenon of wettability switching by UV irradiation is used in self-cleaning windows, exterior construction materials, solar cells, car mirrors, textiles.^{9–13} Several attempts have been made to improve the photoinduced hydrophilicity of metal oxides.^{14–16} The doping of metal and non-metal in metal oxides is one of the important strategies to control wetting properties and offer an avenue to improve the photoinduced properties of metal oxides under UV irradiation.^{17–22} The effect of metal and non-metal doping on wetting properties of TiO₂ has been extensively studied.^{23,24} The advantage of doping in TiO₂ is that it narrows the bandgap and significantly inhibits recombination of photogenerated electron-hole pairs.²⁵ Thus, on the one hand, doping suppresses the charge carrier recombination and, on the other, it shifts the bandgap absorption to the visible region thus enhancing the activity.¹⁰

Recent studies demonstrated that SnO₂ thin films have a potential to act as self-cleaning material.²⁶ SnO₂ is an n-type

metal oxide semiconductor having wide bandgap of 3.6 eV and, as in the case of TiO₂, it is also possible to modulate the band structure by metal doping. Although there are reports on the use of dopants to tailor photoinduced hydrophilicity of films,^{10,27} to the best of our knowledge, systematic studies on the effect of dopants on wettability of SnO₂ thin films have not been reported. In order to explore the photoinduced hydrophilicity, three metal ions, Al³⁺, Mn²⁺ and Cu²⁺, were doped in SnO₂ films. The basis for the selection of above metals is that the ionic radius of Al³⁺ (0.53 Å) is less than Sn⁴⁺ (0.69 Å), which is almost equal to Mn²⁺ (0.67 Å), whereas the ionic radius of Cu²⁺ (0.73 Å) is greater than that of Sn⁴⁺ (0.69 Å).²⁸ This was done to understand the effect, if any, of ionic radius on the wettability of SnO₂ films. In addition to contact angle, the film morphology was characterized using scanning electron microscopy, roughness by atomic force microscopy, structure by X-ray diffraction and optical bandgap was derived from measured spectral transmission curves. The metal-dopant concentration was maintained constant at 2 at.% due to limited solubility of these metals in the host metal oxide lattice.^{29,30}

2. Experimental

Al³⁺, Mn²⁺ and Cu²⁺ doped SnO₂ and pure SnO₂ thin films are prepared by thermal evaporation. Mn, Al and Cu films are first deposited on borosilicate glass followed by deposition of SnO₂ films on top of the metal layers. The thickness of

* Author for correspondence (ddebarun@yahoo.com)

the metal layer is approximately 20 nm. The bilayer films are annealed at 200°C for 110 h to obtain crystalline phases. On annealing, metal ($\text{Al}^{3+}/\text{Mn}^{2+}/\text{Cu}^{2+}$) diffuses into the SnO_2 layer and exists as a dopant in SnO_2 host matrix. The thickness of the films is approximately 150 nm in all cases, as measured using a surface profilometer (Model XP-1, Ambios Technology, USA).

The optical transmittances of the films are recorded in a UV–VIS–NIR spectrophotometer (Model V-570 JASCO) in the wavelength range of 190–2500 nm. The crystalline structure of the samples are characterized by an X-ray diffractometer (Bruker D8) using $\text{Cu K}\alpha$ radiation of wavelength = 0.15405 nm in the 2θ range of 20°–80°. The surface topography and roughness of film is estimated by an atomic force microscope (SPA-400 of SII Inc., Japan), operating in the intermittent contact dynamic force mode. The surface morphology of the sample is analysed by field emission scanning electron microscopy (FESEM) (Model Ultra55 of Carl Zeiss). The film composition is determined by energy dispersive X-ray (EDX) analysis. The photoinduced hydrophilicity of undoped and metal-doped films are evaluated with the aid of a Rame-Hart contact angle goniometer (Model 250). Surface energy is calculated from measured contact angle by geometric mean method using water and diiodomethane as test liquid. Films are irradiated with an 8-W UV lamp of wavelength 253.7 nm, which offers the photon energy greater than the bandgap.

3. Results and discussion

The dopant concentration of metals in the SnO_2 films determined using EDX analysis is approximately 2 at% in all the cases. A typical XRD pattern for undoped and metal-doped SnO_2 films is presented in figure 1. The XRD pattern shows that both doped and undoped films are polycrystalline with the major peak position along the (113) plane of SnO_2 . All the diffraction peaks in the XRD pattern correspond to the orthorhombic phase structure of SnO_2 (JCPDS 78-1063)

Figure 1. XRD pattern of undoped and Mn^{2+} , Al^{3+} and Cu^{2+} doped SnO_2 films.

without any secondary phases. The XRD patterns of metal-doped film only show the characteristic peaks due to SnO_2 with no evidence of any peaks corresponding to the dopants (Mn^{2+} , Al^{3+} and Cu^{2+}) in the XRD pattern. This may be due to either dispersion of metal in metal oxide or low concentration of metal in the composite. The shift in (113) peak position and decrease in peak intensity for metal-doped film is due to the presence of metal dopant in the film. Thus, XRD results reveal that the metal ions are incorporated into the SnO_2 matrix. The crystallite sizes of the film are calculated from full-width at half-maxima (FWHM) of the most intense (113) X-ray diffraction peak using Scherrer's formula,

$$d = \frac{0.9\lambda}{\beta \cos \theta},$$

where d the average crystallite size, λ the wavelength of the $\text{CuK}\alpha$ line, θ the angle between the incident beam and the reflection lattice planes, and β FWHM of the diffraction peak in radian. The average crystallite sizes are approximately 14 ± 2 nm for SnO_2 , Al-SnO_2 , Cu-SnO_2 , and 22 ± 2 nm for Mn-SnO_2 , respectively. The addition of Mn^{2+} in the SnO_2 matrix leads to an increase in the grain size of SnO_2 films. However, addition of Al^{3+} and Cu^{2+} has little influence on film morphology and crystallite size.

In order to investigate the surface wettability of pure and metal-doped film, the contact angle of water over these surfaces are measured. Contact angle can be related to the three interfacial tensions *via* Young's equation³¹

$$\cos \theta = \frac{Y_{SV} - Y_{SL}}{Y_{LV}},$$

where, Y_{SV} = solid–vapour interfacial tension, Y_{SL} = solid–liquid interfacial tension and Y_{LV} = liquid–vapour interfacial tension.

Young's equation is developed for the case of an ideal solid surface which is relatively smooth. However, most thin film surfaces are not ideal and generally have finitely large surface roughness. Wenzel³² modified Young's equation by taking into account the roughness of the surface. The apparent contact angle can then be related to true contact angle by

$$\cos \theta_W = r_W \left\{ \frac{Y_{SV} - Y_{SL}}{Y_{LV}} \right\} = r_W \cos \theta_Y,$$

where, θ_W and θ_Y are Wenzel's and Young's contact angles and r_W is Wenzel's roughness factor and may be defined as the ratio of the actual area of a rough surface to the geometric projected area.

The measured contact angle and surface energies are presented in table 1. To obtain quantitative information about wetting properties and corresponding surface roughness, AFM images were taken. AFM images of SnO_2 and metal-doped SnO_2 thin films are presented in figure 2. In order to estimate the influence of film roughness on measured initial contact angle, RMS roughnesses are calculated from AFM images. The RMS roughness of SnO_2 , Al-SnO_2 , Cu-SnO_2 and Mn-SnO_2 films is 2, 4, 10 and 10 nm, respectively. The

Table 1. Contact angle and surface energy of undoped and metal-doped SnO₂ film.

Sample	Contact angle (Water)	Surface energy (mJ m ⁻²)		
		Polar	Dispersive	Total
SnO ₂	54.5°	24.52	22.48	46.99
Al-SnO ₂	77.5°	7.41	28.33	35.74
Mn-SnO ₂	92.3°	1.02	35.17	36.19
Cu-SnO ₂	95.9°	2.15	22.49	24.64

Figure 2. AFM images of (a) SnO₂, (b) Mn-SnO₂, (c) Al-SnO₂ and (d) Cu-SnO₂.

AFM study revealed that the morphology of the undoped film is dense with smooth surface, but the RMS roughness of doped SnO₂ film increased in comparison with pure SnO₂ film. It is observed that hydrophobicity of the film increases with increase in roughness of the film. The correlation between ionic radius of the metal dopant, roughness of the film and contact angles is shown in figure 3. It is evident that there is a decrease in surface energy, increase in surface roughness and increase in contact angle with increase in dopant ionic radius. A change in slope of both the roughness as well as contact angle beyond an ionic radius of 0.67 Å is also observed. It can, thus, be inferred that contact angle of SnO₂ increases due to doping and further increases with increase in dopant ionic radius. This apparently contradicts Wenzel equation for hydrophilic surfaces, which predicts that increase in surface roughness decreases the contact angle. However, it is important to note that wettability of the surface is governed by both surface roughness and surface energy. From table 1 and figure 3, it is evident that surface energy is high for pure SnO₂ film and there is a decrease in surface energy in the presence of metal dopant. This result is in agreement with our previous report on metal buffer layer

Figure 3. Variation of contact angle, surface energy and RMS roughness with ionic radius of metal dopant.

TiO₂ film.¹⁶ So in the present case, the difference in initial contact angles of doped film is attributed to a synergetic effect between surface roughness and surface energy of the thin film due to metal doping. Significantly, it demonstrates that ionic radius of a dopant can be used to control the wettability of a SnO₂ thin film surface. A hydrophilic undoped SnO₂ surface can be tailored to become hydrophobic by simply doping with a metal of appropriate ionic radius.

FESEM images of pure and metal-doped SnO₂ thin film are shown in figure 4. FESEM images confirm the formation of homogeneous nanostructured thin films of smooth morphology. The pure SnO₂, Cu-SnO₂ and Al-SnO₂ exhibit almost similar microstructure. Thus, Al³⁺ and Cu²⁺ dopants do not affect the microstructure of SnO₂ film; but Mn²⁺ doping has large influence on the morphology of SnO₂ thin films. The doping of Mn²⁺ in SnO₂ host material gives rise to the formation of cluster of grains.

The variation in the photoinduced hydrophilicity of metal-doped films under UV irradiation is evaluated and shown in figure 5. Under UV irradiation, the contact angle of water decreases gradually on all doped and undoped SnO₂ films. However, it is observed that the contact angle of water decreases more quickly on Mn-SnO₂ film than on Al-SnO₂ and Cu-SnO₂ films. The contact angle values, along with images of water droplet before and after UV irradiation on undoped and metal-doped SnO₂ films are presented in table 2. The Mn-SnO₂ films are hydrophobic but convert into a superhydrophilic surface on being subjected to UV irradiation. There is marked improvement in photoinduced hydrophilicity when Mn²⁺ is doped in SnO₂ thin film. The enhanced hydrophilicity of the Mn²⁺ doped film is attributed to the formation of associated oxygen vacancy states between valence and conduction bands in the SnO₂ lattice. Therefore, with doping, higher concentration of oxygen vacancy is created by replacing of Sn⁴⁺ by a lower valency Mn²⁺, which is beneficial for enhancing hydrophilicity. The formation of oxygen ion vacancies makes the surface suitable for hydroxyl

Figure 4. FESEM images of (a) SnO₂, (b) Mn-SnO₂, (c) Al-SnO₂ and (d) Cu-SnO₂.

Figure 5. Variation of contact angle of water under UV irradiation time.

adsorption on the defective sites and as a result surfaces become hydrophilic after UV irradiation. The decrease in oxygen can be explained by the fact that Sn⁴⁺ ions got attached to two O²⁻ ions while, in contrast, Mn²⁺ ions got attached to only one O²⁻ ion.

No such enhancement of hydrophilicity is observed for SnO₂ films doped with Cu²⁺. Doping of Cu²⁺ makes the surface less hydrophilic in contrast to undoped SnO₂ thin film. In case of Al-SnO₂ film, the photoinduced hydrophilicity under UV irradiation considerably deteriorated in contrast to pure SnO₂. The wettability of pure and doped SnO₂ thin film can be reverted to their original state by keeping the samples in the dark for 1 h.

To understand the relation between wettability and corresponding bandgap, UV-VIS transmission spectra of the pure and doped SnO₂ thin film are presented in figure 6. It is observed that the optical transparency of the pure SnO₂ film decreases on doping of metal in SnO₂ film. The decrease in transmittances of metal-doped SnO₂ film compared to pure SnO₂ film is attributed to increase in reflectance due to the presence of metal dopants in the film. A red shift in absorption edges of metal-doped SnO₂ films are observed with respect to pure SnO₂ film, which indicates a decrease in bandgap of SnO₂ film on doping. The observed red shift in absorption edge in case of metal-doped film is due to creation of dopant energy level inside the bandgap of SnO₂ film. The bandgap values are estimated from the measured transmission spectra. The optical bandgap of the films are determined by plotting a curve between $(\alpha h\nu)^2$ and $(h\nu)$ using Tauc relation by considering direct transition between valence and conduction band.³³ Here α is the absorption coefficient of the film at a frequency ν . The linear portion of the curve is extrapolated to the $h\nu$ axis to calculate the bandgap. The direct bandgap is ~ 3.75 eV for the pure SnO₂ and is in agreement with the literature.³³ In case of doped film, it is ~ 2.48 eV for Mn-SnO₂, ~ 3.72 eV for Al-SnO₂ and ~ 3.67 eV for Cu-SnO₂ thin films. The decrease in bandgap with Mn²⁺ incorporation can be attributed to the influence of Mn²⁺ ions on the electronic states of SnO₂ film and increase in grain size. The bandgap of Cu-SnO₂ is almost the same as that of pure SnO₂ and it is consistent with the values in the literature.³³ The variation in contact angle, after UV correlates directly with the ionic radius of the dopant, is shown in figure 7. The contact angle reaches a minimum of 5.4° on the sample with the lowest bandgap (2.48 eV)

Table 2. Water contact angle before and after UV irradiation of undoped and metal-doped SnO₂ film.

Sample	Drop profile (Before UV irradiation)	Drop profile (After UV irradiation)
SnO ₂	(CA=54.0°)	(CA=5.4°)
Al-SnO ₂	(CA=77.5°)	(CA=21.2°)
Mn-SnO ₂	(CA=92.3°)	(CA=6.4°)
Cu-SnO ₂	(CA=95.9°)	(CA=63.3°)

Figure 6. Optical transmission spectra of pure SnO₂ and metal-doped SnO₂. **Figure 7.** Variation of bandgap and contact angle after UV irradiation with ionic radius of metal dopant.

and as the bandgap increases again, the contact angle also increases.

The ability to undergo photoinduced superhydrophilicity is related to surface structural changes of SnO₂ film. Based on ionic radii, the doping of metal in SnO₂ can be done in substitutional or interstitial positions. As ionic radius of Mn²⁺ ($r = 0.67 \text{ \AA}$) is nearly equal to Sn⁴⁺ ($r = 0.69 \text{ \AA}$), Mn²⁺ may replace Sn⁴⁺ and exist mainly as substitutional impurity. As a result, there is an appreciable change in the bandgap of Mn-SnO₂ thin film. The substitution of Sn⁴⁺ ions by lower valence Mn²⁺ ions create more oxygen vacancies in the SnO₂ lattice and the presence of surface oxygen vacancy favours the adsorption of water molecule on the surface. In the case of Cu-SnO₂ film, ionic radius of Cu²⁺ ($r = 0.73 \text{ \AA}$) is greater than that of Sn⁴⁺ and hence cannot be incorporated at Sn⁴⁺ sites in SnO₂ lattice. Thus, in the case of Cu-doped film, Cu²⁺ ions do not enter the lattice of SnO₂; rather they segregate on the SnO₂ surface.³⁴ The addition of metal dopant may either be beneficial or detrimental to wetting, depending on whether such metal inhibits the electron-hole recombination or acts as electron-hole recombination centres. The reduced rate of photoinduced hydrophilicity in Cu-SnO₂ film is probably due to the fast recombination of photoinduced electron-hole pairs and thus diminishing hydrophilicity of SnO₂ film. As Al³⁺ ($r = 0.53 \text{ \AA}$) has smaller ionic radius compared to Sn⁴⁺, it is incorporated in the SnO₂ matrix interstitially. Moreover, interstitial Al³⁺ incorporation in SnO₂ does not produce any oxygen vacancy and, as a consequence, it has detrimental effect on photoinduced hydrophilicity of SnO₂ thin film. Thus, the photoinduced hydrophilicity in the case of Al-SnO₂ is not as pronounced as in the case of Mn-SnO₂ film. As creation of oxygen ion vacancy is a natural consequence of substitutional doping, it can be concluded that the enhancement of hydrophilicity in Mn²⁺ doped film, in contrast to Al³⁺ and Cu²⁺ doped film, is due to replacement of Mn²⁺ by Sn⁴⁺ ion.

Photoinduced hydrophilicity is ascribed to the structural changes at the surface due to UV irradiation. Under UV irradiation, having energy greater than bandgap of metal oxide, electron-hole pairs are generated in the conduction and valence band. Owing to narrower bandgap of Mn-SnO₂, the number of photogenerated electron-hole pairs is higher than in pure SnO₂ thin films that usually have oxygen vacancies in the lattice. In the case of Mn-SnO₂ films, the number of photoactive defect sites increases and inhibits charge carrier recombination which, in turn, leads to improvement in hydrophilicity. Based on contact angle result, it can be concluded that the enhanced photoinduced hydrophilicity of Mn-SnO₂ film, among metal doped films, is due to the smaller bandgap of this material.

4. Conclusions

This research shows that the contact angle of water to undoped and doped SnO₂ thin films, prior to UV irradiation, depends upon surface roughness, surface energy and ionic radius of the metal dopant. The incorporation of ions of different radii in the SnO₂ lattice introduces significant

morphological changes without affecting crystal structure, despite the fact that the concentration of metal in all films is the same. This research also indicates the presence of a threshold dopant ionic radius, above and below which there is a large deviation in properties. The threshold value corresponds to the ionic radius of dopant (Mn^{2+} in the present case) being equal to that of the host ion (Sn^{4+}). In the current case, it has been demonstrated that a small amount of Mn^{2+} insertion in SnO_2 thin film enhances the hydrophobic-hydrophilic switching of nanostructured SnO_2 thin film under UV irradiation. The contact angle results indicate that incorporation of Mn^{2+} in SnO_2 facilitates the photoinduced hydrophilicity of SnO_2 thin film under UV irradiation, whereas Al^{3+} and Cu^{2+} dopants are detrimental. The incorporation of Mn^{2+} ions in SnO_2 further results in a red shift in the optical bandgap which, in turn, leads to superhydrophilicity in the film. It is, thus, concluded that ionic radius of a metal dopant can be used to control the wettability of given undoped metal oxide thin film surface.

Acknowledgements

We gratefully acknowledge the facilities provided by the School of Physics, University of Hyderabad. DD Purkayastha thanks the Council of Scientific and Industrial Research (CSIR), Government of India, for the Fellowship granted to him.

References

1. Krishna M G, Madhurima V and Purkayastha D D 2013 *Eur. Phys. J. Appl. Phys.* **62** 30001
2. Lai Y, Tang Y, Gong J, Gong D, Lin L C C and Chen Z 2012 *J. Mater. Chem.* **22** 7420
3. Karuppachamy S and Ito S 2008 *Vacuum* **82** 547
4. Kenanakis G, Vernardou D and Katsarakis N 2012 *Appl. Catal. A* **411–412** 7
5. Xin B and Hao J 2010 *Chem. Soc. Rev.* **39** 769
6. Miyauchi M, Nakajima A, Watanabe T and Hashimoto K 2002 *Chem. Mater.* **14** 2812
7. Shaik U P, Kshirsagar S, Krishna M G, Tewari S P, Purkayastha D D and Madhurima V 2012 *Mater. Lett.* **75** 51
8. Zhu W, Feng X, Feng L and Jiang L 2006 *Chem. Commun.* 2753
9. Eiamchai P, Chindaudom P, Horprathum M, Patthanasettakul V and Limsuwan P 2009 *Mater. Design* **30** 3428
10. Weng K W and Huang Y P 2013 *Surf. Coat. Technol.* **231** 201
11. Valtierra J M, Reyes C F, Ortiz J R and Martinez G C 2009 *Ind. Eng. Chem. Res.* **48** 598
12. Hadnadjev M, Ranogajec J, Petrovic S, Markov S, Ducman V and Neducin R M 2010 *Philos. Magazine* **90** 2989
13. Sayilkan H 2007 *Appl. Catal. A* **319** 230
14. Tonooka K and Kikuchi N 2013 *Thin Solid Films* **532** 147
15. Xiong J, Das S N, Kim S, Lim J, Choi H and Myoung J M 2010 *Surf. Coat. Technol.* **204** 3436
16. Purkayastha D D, Pandeewari R, Madhurima V and Krishna M G 2013 *Mater. Lett.* **92** 151
17. Kumar P S, Sundaramurthy J, Mangalaraj D, Nataraj D, Rajarathnam D and Srinivasan M P 2011 *J. Colloid Interf. Sci.* **363** 51
18. Eshaghi A and Eshaghi A 2011 *Thin Solid Films* **520** 1053
19. Jiang H and Gao L 2002 *Mater. Chem. Phys.* **77** 878
20. Chekini M, Mohammadizadeh M R and Allaei S M V 2011 *Appl. Surf. Sci.* **257** 7179
21. Xu Q C, Wellia D V, Sk M A, Lim K H, Loo J S C, Liao D W, Amal R and Tan T T Y 2010 *J. Photochem. Photobiol. A* **210** 181
22. Lu J, Huang K, Chen X, Zhu J, Meng F, Song X and Sun Z 2011 *Appl. Surf. Sci.* **257** 2086
23. Fujishima A, Zhang X and Tryk D A 2008 *Surf. Sci. Rep.* **63** 515
24. Borrás A, López C, Rico V, Gracia F, Gonzalez-Elipe A R, Richter E, Battiston G, Gerbasi R, McSporran N, Sauthier G, Gyorgy E and Figueras A J 2007 *Phys. Chem. C* **111** 1801
25. Qi K, Fei B and Xin J H 2011 *Thin Solid Films* **519** 2438
26. Andre R, Natalio F, Tahir M N, Bergerb R and Tremel W 2013 *Nanoscale* **5** 3447
27. Zaleska A 2008 *Recent Patents Eng.* **2** 157
28. Shannon R D 1976 *Acta Cryst. A* **32** 751
29. Serpone N and Lawless D 1994 *Langmuir* **10** 643
30. Gopinadhan K, Kashyap S C, Pandya D K and Chaudhary S 2007 *J. Appl. Phys.* **102** 113513
31. Young T 1805 *Philos. Trans. R. Soc. London* **95** 65
32. Wenzel R N 1936 *Ind. Eng. Chem.* **28** 988
33. Ao D and Ichimura M 2012 *J. Non-Cryst. Solids* **358** 2470
34. Rumyantseva M, Labeau M, Delabouglise G, Ryabova L, Kutsenoka I and Gaskov A 1997 *J. Mater. Chem.* **7** 1785