Optical, mechanical and TEM assessment of titania-doped $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ bismuth vanadate oxides

GURBINDER KAUR^{a,*}, GARY PICKRELL^a, VISHAL KUMAR^{a,b}, OM PRAKASH PANDEY^c, KULVIR SINGH^c and DANIEL HOMA^a

^aDepartment of Material Science and Engineering, Holden Hall, Virginia Tech, Blacksburg, Virginia 24060, USA

^bSri Guru Granth Sahib World University, Fategarh Sahib 140 406, India

^cSchool of Physics and Materials Science, Thapar University, Patiala 147 004, India

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Abstract. Optical, mechanical and structural behaviors have been studied for titania-doped $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ which are used as electrolytes for intermediate temperature fuel cells. Parameters like band gap (E_g), Urbach energy (E_u), refractive index, hardness (H) and fracture strength (K) have been calculated as a function of dopant concentration, i.e. $0.05 \leq x \leq 0.2$. Furthermore, analysis of transmission electron microscopy (TEM) images for all the oxides was conducted along with line spectra of planes. Results are discussed in light of correlation of these optical and mechanical parameters to their structural properties. Band gap has also been correlated to the conductivity of these oxides. Good correlation has been obtained between them.

Keywords. Transmission electron microscopy; optical properties; ceramics; mechanical properties.

1. Introduction

Doped bismuth vanadates (BIMEVOXs) belong to the aurivillius family and exhibit high oxide ion conductivity at an intermediate temperature range of 600–800 °C. BIMEVOX is doped bismuth vanadate compounds having the general formula $\text{Bi}_2(\text{V}_{1-x}\text{ME}_x)\text{O}_{5.5-\delta}$ where ME is a dopant metal ion, x is the dopant concentration and δ is the deviation of oxygen content from the original stoichiometry (Lee *et al* 1994; Simner *et al* 1997; Culea 1998; Watanable 2001; Abrahmas and Krok 2002, 2003; Cho *et al* 2005; Zhen *et al* 2005). BIMEVOXs are favourable oxide ion electrolyte conductors for intermediate temperature solid oxide fuel cells (IT-SOFCs) (Abraham *et al* 1990; Boivin and Mairesse 1998; Taninouchi *et al* 2010). Moreover, BIMEVOXs are promising materials for oxygen sensors and oxygen separation devices (Abraham *et al* 1990; Boivin and Mairesse 1998; Taninouchi *et al* 2010).

The parent compound $\text{Bi}_2\text{VO}_{5.5-\delta}$ consists of alternate bismuth–oxygen (Bi–O) and vanadium–oxygen (V–O) layers. Bi–O layer in $[\text{Bi}_2\text{O}_2]^{2+}$ exhibits a square pyramidal co-ordination for bismuth. Stereochemical activity of non-bonding $6s^2$ lone pairs of Bi contributes for its asymmetric coordination geometry. The Electroneutrality of the system is preserved by VO_6 octahedrons present in V–O layer $[\text{VO}_{3.5}\text{K}_{0.5}]$ (Dygas *et al* 1994; Yan and Greenblatt 1995). $\text{Bi}_2\text{VO}_{5.5-\delta}$ exhibits three main polymorphs i.e. α (below 450 °C), β (from 450 to 570 °C) and γ (above 570 °C) (Abraham *et al* 1990). Disordered β and γ phases show high

oxide ion conductivities above 500 °C. Among these three primary phases, the γ phase exhibits the highest conductivity where the V–O layer is made up of corner-sharing oxygen octahedrons that contain oxygen vacancies. Cu, Ni, Ti, Pb, Zn, Fe, Al, Sb, Nb and others are used as dopants which occupy some of the vanadium sites to increase the ionic conductivity by stabilizing the γ phase at room temperatures (Lee *et al* 1994; Simner *et al* 1997; Culea 1998; Watanable 2001; Abrahmas and Krok 2002, 2003; Cho *et al* 2005; Zhen *et al* 2005; Lofberg *et al* 2006; Kumar *et al* 2010).

The $\text{Bi}_2\text{VO}_{5.5-\delta}$ compound contains bismuth, which is susceptible to reduction at moderate oxygen partial pressures ($<10^{-13}$ atm) (Qiu *et al* 1997a, b). This characteristic property makes it suitable to be used as an electrolyte for intermediate temperature fuel cells as it exhibits high ionic conductivity in addition to structural integrity. In addition to these applications, Bi^{3+} containing mixed metal oxides have been viewed as a potential visible light active photocatalyst (Park and Woodward 2000). V_2O_5 has an advantage because vanadium ions make the material exhibit semiconducting behavior within the electrical conductivity range $>10^{-3}$ – 10^{-5} ($\Omega \text{ cm}$)^{−1}. This behavior is due to electron hopping between V^{4+} and V^{5+} ions. It is known that doping at the vanadium site changes the phase transformation behavior as well as the electrical conductivity of BIMEVOX (Abraham *et al* 1990; Dygas *et al* 1994; Lee *et al* 1994; Yan and Greenblatt 1995; Simner *et al* 1997; Boivin and Mairesse 1998; Lofberg *et al* 2006; Kumar *et al* 2010; Taninouchi *et al* 2010). With doping, the rate of hopping increases which ultimately leads to the enhancement of conductivity (Nicula *et al* 1986). Moreover, the doping may also cause variation in their optical

*Author for correspondence (gkaur82@vt.edu)

properties as reported by our group in the previous work (Kaur et al 2012a, b, c, 2014).

Most of the research till now has been carried out to understand structural behavior of doped/undoped bismuth vanadate and its effect particularly on electrical properties. However, to the best of our knowledge, their optical behavior in correlation to doping as well as morphological parameters obtained from electron microscopy has not been reported. In this present work, we have investigated the optical and mechanical properties of $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.2$) oxides as a function of doping concentration. The selected area diffraction (SAED) patterns for the different grains of the same material have been analyzed to determine the lattice structure. In addition, these properties have been correlated to the conductivity of above-mentioned compounds, which has already been reported by our group (Kant et al 2008, 2009, 2010; Kaur et al 2012a, b, c, 2014). The as prepared samples are characterized using UV-Visible spectroscopy, Vicker's microhardness test and transmission electron microscopy (TEM). The results are discussed in light of the TEM and optical parameters.

2. Experimental

$\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{11-\delta}$ ($0.05 \leq x \leq 0.2$ in the steps of 0.05) powders were prepared by solid-state reaction from stoichiometric amounts of the following oxides: Bi_2O_3 (99%), V_2O_5 (99%) and Ti_2O_3 (99.995%). The starting oxide powders were weighed in defined proportion and ground in acetone medium for 2 h (using an agate mortar and pestle) to achieve homogeneous mixtures. The resulting mixtures were dried, ground, and then calcined at 750 °C in an alumina crucible for 12 h in air. Calcined powders were again ground and pellets of this mixture were made by compacting these powders in a hydraulic press at a load of 12 kN cm⁻². The 10 × 10 × 3 mm pellets so prepared were sintered at 800 °C for 12 h. The pellets were broken and ball-milled again to obtain fine powder. The details are given elsewhere (Kaur et al 2012c, 2014). The sample composition along with sample designation is listed in table 1.

The optical transmission spectra of the prepared samples were recorded at room temperature using a doublebeam, three-detector UV-3600 UV-VIS-NIR Spectrophotometer (Model: Shimadzu) in the wavelength range of 200–650 nm. A sample of concentration 0.1 g l⁻¹ was prepared using

methanol as a reference solution. The spectrum of each sample was normalized to the spectrum of blank methanol. A LECO LM247AT Microhardness Tester and Control Software are used for measuring micro hardness of the samples. The morphology study and microanalysis of the samples were done using a Philips EM420 TEM, mainly focusing on Bright field (BF)/dark field (DF) imaging and electron diffraction with an acceleration voltage of 120 kV. The point to point resolution is 0.34 nm and line to line is 0.2 nm. The samples were ground in an agate mortar and then sieved. The sieved powders were then flocculated by ultrasonication in an ethanol medium for 1 h. The dispersed liquid is allowed to stand for 12 h so that the finest particles are present in suspension and heavy ones are settled. The TEM samples have been prepared using Wick's procedure. A drop of liquid is placed on a carbon film supported over copper grid. After the film is dried, the grid is introduced to TEM.

3. Results and discussion

3.1 Absorption studies

The optical properties of materials are always governed by the interaction between the solid and the electromagnetic radiation. Optical absorption (α) is related to transmittance (T) by the following relation (Baki et al 2007):

$$\alpha = (2.303/d) \log(1/T), \quad (1)$$

where d is the sample thickness. Figure 1 gives plots for absorption (α) vs wavelength (λ) for all samples in the UV-Visible optical absorption region.

The absorption edges are sharply defined, indicating the crystalline nature of samples. The absorption follows the trend $T_4 > T_3 > T_2 > T_1$. The transmission spectra follow the reverse order for samples as depicted by figure 2.

According to Bouguer's law or Lambert's law of absorption, when the velocity of light in vacuum is c , the attenuation coefficient (η) as a function of absorption coefficient and thickness d of the sample is given by the following relation (Rajesh and Menon 2002; Baki et al 2007):

$$\eta = P/P_0 = \exp(-\alpha(\lambda)d). \quad (2)$$

Hence, the radiation is absorbed to an extent that depends on wavelength of radiation and thickness of medium. In other words, the intensity of incident radiation is attenuated to $1/e$

Table 1. Sample name, composition, band gap (E_{opt}), Urbach energy (E_u), Vickers hardness (H) and fracture toughness (K) for all the samples.

Sample name	Composition	E_{opt} (eV) $\pm$ 0.001		E_u (eV) $\pm$ 0.001	Vickers hardness (H) GPa	Fracture toughness (K) MPa m ^{1/2}
		Direct	Indirect			
T1	$\text{Bi}_2\text{V}_{0.95}\text{Ti}_{0.05}\text{O}_{5.5-\delta}$	2.391	3.814	0.678	5.661	2.823
T2	$\text{Bi}_2\text{V}_{0.90}\text{Ti}_{0.10}\text{O}_{5.5-\delta}$	2.312	3.752	0.702	6.129	3.191
T3	$\text{Bi}_2\text{V}_{0.85}\text{Ti}_{0.15}\text{O}_{5.5-\delta}$	2.263	3.426	0.739	6.783	3.814
T4	$\text{Bi}_2\text{V}_{0.80}\text{Ti}_{0.20}\text{O}_{5.5-\delta}$	2.194	2.731	0.795	7.354	4.303

Figure 1. Absorbance spectra for all the samples.

Figure 3. Refractive index for all the samples.

Figure 2. Transmittance spectra for all the samples.

of its initial value at a distance of $1/\alpha$ from the surface. The absorption coefficient is also related to the extinction coefficient as follows:

$$\alpha = 4\pi k/\lambda, \quad (3)$$

α is generally related to decay or damping of the oscillation amplitude of the incident electric field. According to the theory of reflectivity of light the refractive index n , as a function of the transmission measurements, is determined by the Fresnel equation

$$R = (n - 1)^2 / (n + 1)^2. \quad (4)$$

The extinction coefficient is neglected because k is almost of the range of 10^{-7} – 10^{-6} when wavelength is taken in cm. It is clear from figure 3 that the refractive index decreases with an increase in the wavelength of the incident photon.

Refractive index increases with doping concentration in the present samples and follows the trend $T4 > T3 > T2 > T1$.

3.2 UV-Visible and band gap

Optical measurements are very productive tools for indepth analysis of band structure. UV-Visible studies allow investigation of mechanisms like quenching color centers absorbing in edge region, reducing structure disorder and controlling band gap (Abdel-Baki *et al* 2006; Kaur *et al* 2012a, b, c, 2014). Band gap is a region where a particle or quasiparticle is forbidden from propagating (Kaur *et al* 2012a, b, c, 2014). Near the absorption edge of UV-Visible spectra, two types of transitions take place namely direct and indirect (Mott and Davis 1979). Direct band gap means direct combination of electrons at conduction band minimum with holes at valence band maximum while conserving momentum. Indirect band gap means recombination of an electron and hole with the mediation of third body such as phonon or a crystallographic defect, which allows conservation of momentum.

Tauc divided absorption edge into three regions, i.e. interband absorption, Urbach tails and weak tails, which are residual below gap absorption (Tauc 1974). The first region, also known as 'Tauc region', is associated with interband transitions, i.e. it may correspond to transition of an electron belonging to an ion in an excited state. It corresponds to high absorption and optical energy gap can be calculated from it. In this region, absorption varies directly as photon energy. The more weakly the electrons of material are bound, the more easily absorption occurs in UV-Visible region. For Tauc's region, absorption coefficient is given in a quadratic form, which is discussed by Mott and Davis (1979) in the more general form

$$\alpha h\nu = B \left[\frac{(h\nu - E_{\text{opt}})^n}{h\nu} \right], \quad (5)$$

where B is a constant which depends upon transition probability, $h\nu$ is the photon energy and E_{opt} is the optical band gap related to energy gap between valence band and conduction band. Here n is an index, which characterizes the optical absorption process. Exponent n can have four values: 2, $1/2$, 3 and $3/2$ representing, respectively, indirect allowed, direct allowed, indirect forbidden and direct forbidden (Qasrawi 2005). Plots of $(\alpha h\nu)^{1/n}$ vs incident photon energy $h\nu$ are used in determining the type of optical transition. The plots for $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs $h\nu$ are shown in figure 4(a–d) for all the four samples under investigation.

From the coefficient of correlation, it is difficult to decide whether the material has direct band gap or indirect band gap. The plots that satisfy the widest linearity of data determine the dominant transitions. According to this criterion, indirect allowed transitions dominate in the present case. E_{opt} values are determined by extrapolating linear region of the plots to $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2} = 0$. The values of direct and indirect E_{opt} are listed in table 1. Indirect band gaps are larger than direct band gaps for all the samples. But as the doping concentration increases, both the direct and indirect E_{opt} values decrease. Variation in optical band gap is also attributed to different structural cations present in the network. For the present samples, it is attributed to the network structural differences introduced due to titanium atom. Decrease of average bond energy of the system also decreases the energy of the conduction band edge (Abdel-Baki et al 2006). These

materials have narrow band gaps, which can be due to formation of excitons i.e. electron–hole pairs due to absorption of photon (Vaish and Verma 2011). The reverse trend has been observed in conductivity behavior as reported earlier (Kaur et al 2012a, b, c, 2014). The band gap depends inversely on the conductivity i.e. a material with smaller band gap possesses higher conductivity. As the band gap is the lowest for T4 sample, conductivity would be the highest at this concentration. These results are consistent with earlier reported results for conductivity. Moreover, at $x = 0.2$, there can be an increase in the concentration of vacancies located on equatorial lines of the perovskite layers $(\text{VO}_{3.5})^{2-}$ available for the oxide ion migration. Hence for $x = 0.2$, the concentration of vacancies and pathways for O^{2-} motion are optimized. The high oxide ion conductivity mainly depends on the presence of oxide ion vacancies.

When the energy of the photon is less than the band gap of materials, the increase in absorption coefficient is followed by exponential decay of the density of states (Abay et al 1999). Here the absorption edge is the Urbach edge, which is a exponential region due to the structural disorientations and randomness of the system. For small absorption coefficients ($\alpha < 10^{-4} \text{ cm}^{-1}$), there is usually an Urbach tail where $\alpha(\nu)$ depends exponentially on the photon energy $h\nu$ as follows:

$$\alpha(\nu) = \alpha_0 \exp(h\nu/E_u), \quad (6)$$

Figure 4. Direct and indirect band gap of all the samples.

where α_0 is a constant and E_u the Urbach energy indicating the width of the band tails of localized states representing the degree of disorder. E_u values are calculated from the slopes of the linear portion of the curve of $\ln(\alpha)$ against $h\nu$ and are tabulated in table 1.

Urbach energy (E_u) characterizes the extent of the exponential tail of absorption edge and it depends on temperature, thermal vibrations in lattices, strong ionic bonds, static disorder, average photon energies and induced disorders (Saito and Ikushima 2000). Hence the Urbach energy measures the degree of disorder for amorphous/crystalline materials (Redfield 1963; Dexter 1967). For crystalline materials, the disorder can be dynamic or static. Generally, crystalline materials possess dynamic disorders because of electron phonon coupling (Sumalatha *et al* 2011). In all the samples the Urbach energy increases, suggesting the formation of more defect pairs leading to an increase in the disorder of the states. The third region is the weak absorption tail produced from defects and impurities in the UV spectra.

3.3 Mechanical properties

Since the sintered pellets exhibit uniform and homogenous structure, the hardness and strength may vary with variation in doping type and its concentration. Hardness and indentation fracture toughness of all the mixed ion conductors are measured and summarized in table 1. Hardness of the specimen has been obtained using the following equation (Nilihara *et al* 1982):

$$H = F/A \approx 1.8544F/d^2, \quad (7)$$

where F is the load (kgf) and d is the diagonal length of indentation. The fracture toughness (K) is measured using the relevant solution for the Anstis equation (Anstis *et al* 1981):

$$K = 0.016 (E/H)^{1/2} (F/c^{3/2}), \quad (8)$$

where F is the indentation load and c is the half-length of the resultant indentation cracks; E and H are Young's modulus and the hardness of the test materials, respectively. An elastic modulus (E) of 200 GPa is generally used as standard for brittle ceramics (Adams *et al* 1997). An increasing trend of hardness as well as fracture toughness has been observed with increasing dopant concentration, i.e. $x = 0.05$ – 0.2 . The toughness value depends upon many parameters like starting powder, sintering parameter, microstructure variables and testing techniques (Basu 2005). Fracture strength of a brittle material is not a characteristic material property as it depends upon size of flaws and their distribution in the specimen. Fracture strength is generally lowered by defects such as flaws, cracks or inclusions existing in the sintered sample. However, grain size strongly influences the toughness of ceramics (Adams *et al* 1997; Basu 2005). In the present study, T4 oxides have the smallest grain sizes, indicating the finest microstructure (Kaur *et al* 2012a, b, c, 2014). The results obtained indeed suggest that the finer microstructure

substantially yields higher hardness and fracture toughness. The samples have hardness in the range 5.66–7.35 GPa and fracture toughness variation between 2.8 and 4.3 $\text{MPa m}^{1/2}$. The variation of fracture toughness and hardness for all samples is shown in figure 5. Hence, the fracture toughness and hardness improve with increase in dopant concentration, which ultimately results in decrease of grain size.

3.4 Transmission electron microscopy

The morphological photographs are taken using TEM. The bright and dark spots are superimposed on a background of speckle, which results due to random scattering due to the carbon substrate. For the crystal structure determination, selected area diffraction pattern (SAED) of prepared samples is used. The diameter of the aperture has been kept below $20 \mu\text{m}$. Before doing SAED, the area is selected carefully to yield the most prominent diffraction pattern. For every sample, four SAED patterns were observed from different grains. The crystal structure for sample T1 is shown in figure 6(a–d). Highly symmetrical aligned bright spots are observed, indicating crystalline structure. Figure 6(c) indicates some superlattice peaks also along both sides of the basal planes. Figure 6(e) gives the line spectra of a single plane in figure 6(c). The line spectra indicate three superlattice peaks between primary Bragg diffraction spots. The distance between adjacent superlattice peaks is 1.1198 nm whereas diffraction spots are 0.2740 nm apart. The distance between Bragg spot and superlattice peak is 1.091 nm. The superlattice peaks may arise from cation ordering rather than oxygen vacancies (Qiu *et al* 1997a, b; Williams and Carter 2009). The diffuse streaking between Bragg spots also indicates superlattice peaks. Patterns with a sharp superlattice are of two types. The first type includes bright superlattice reflections at $n/3$ along a^* and b^* . The second pattern has superlattice reflections at $n/2$ positions along a^* and b^* . Sometimes the pattern does not have very sharp superlattice

Figure 5. Variation of hardness (H) and fracture strength (K) with concentration of dopants.

Figure 7. (a–d) SAED patterns for sample T2 for different grains and (e) line profile of atoms along the plane shown in (c).

the atoms or vacancies in different structures essentially arrange themselves in order to increase the lattice parameters and hence give rise to superlattice reflections. The superlattice peaks in sample T2 are separated by 1.754 nm and Bragg's diffraction spots are 0.2763 nm apart. The distance between Bragg spot and superlattice peak is 0.8319 nm. Figure 8(a–d) indicates the SAED pattern for T3 sample. In

sample T3, no superlattice has been observed as is evident from the line profile analysis in figure 8(e). The distance between the diffraction spots is 0.4923 nm. The diffraction pattern of sample T4 also does not reveal any superlattice peaks as indicated in figure 9(a–e). The line spectra for sample T4 indicate the separation of diffraction peaks to be 0.4069 nm.

Figure 8. (a–d) SAED patterns for sample T3 for different grains and (e) line profile of atoms along the plane shown in (c).

4. Conclusions

The optical, mechanical and structural properties of $\text{Bi}_2\text{V}_{1-x}\text{Ti}_x\text{O}_{5.5-\delta}$ ($0.05 \leq x \leq 0.2$) oxides as a function of

doping concentration have been investigated. The absorption coefficient and refractive index increase with doping concentration of titanium whereas transmission and dielectric constants follow the reverse trend. Band gap is observed to

Figure 9. (a–d) SAED patterns for sample T4 for different grains and (e) line profile of atoms along the plane shown in (c).

decrease with dopant concentration, which is in complete agreement with conductivity results. Urbach energy is the highest for the T4 sample, indicating its disordered structure due to higher doping concentration. The band gap is in the semiconducting range for all the samples. The fracture

toughness and hardness are also increased by the dopant concentration. The electron microscopy indicates the presence of superlattice peaks in T1 and T2 samples. The results have been further supported by line spectra of plane of atoms.

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References

- Abay B, Guder H S and Yogurtchu Y K 1999 *Solid State Commun.* **112** 489
- Abdel-Baki M, Abdel Wahab F A and El-Diasty F 2006 *Mater. Chem. Phys.* **96** 201
- Abraham F, Boivin J C, Mairesse G and Nowogrocki G 1990 *Solid State Ion.* **40** 934
- Abrahmas I and Krok F 2002 *J. Mater. Chem.* **12** 3351
- Abrahmas I and Krok F 2003 *Solid State Ion.* **157** 139
- Adams J W, Ruh R and Mazdiyasni K S 1997 *J. Am. Ceram. Soc.* **80** 903
- Anstis G R, Chantikul P, Lawn B R and Marshall D B 1981 *J. Am. Ceram. Soc.* **64** 533
- Baki M A, Wahab F A A, Radi A and Diasty F E 2007 *J. Phys. Chem. Solids* **68** 1457
- Basu B 2005 *Int. Mater. Rev.* **50** 239
- Boivin J C and Mairesse G 1998 *Chem Mater.* **10** 2870
- Cho H S, Sakai G, Shimanoe K and Yamazoe N 2005 *Sens. Actuators B* **109** 307
- Culea E 1998 *J. Non-Cryst. Solids* **223** 147
- Dexter D L 1967 *Phys. Rev. Lett.* **19** 1383
- Dygas J R, Krok F, Bogusz W, Kurek P, Reiselhuber K and Breiter M W 1994 *Solid State Ion.* **70** 239
- Kant R, Pandey O P and Singh K 2008 *Int. J. Hydrogen Energy* **33** 455
- Kant R, Pandey O P and Singh K 2009 *Mater. Sci. Eng. B* **158** 63
- Kant R, Pandey O P and Singh K 2010 *Ionics* **16** 277
- Kaur G, Pandey O P and Singh K 2012a *Phys. Status Solidi A* **209** 1231
- Kaur G, Pandey O P and Singh K 2012b *J. Non-Cryst. Solids* **358** 2589
- Kaur G 2012c *Investigations on interfacial interaction of glass sealants with electrolytes and interconnect for SOFC applications*, Ph.D thesis (Patiala (India): Thapar University)
- Kaur G, Pandey O P and Singh K 2014 *Ind. J. Pure Appl. Phys.* **52** 262
- Kumar V, Sharma S, Pandey O P and Singh K 2010 *Solid State Ion.* **181** 79
- Lee C K, Lim G S and West A R 1994 *J. Mater. Chem.* **4** 1441
- Lofberg A, Bodet H, Pirovano C, Steil M C, Vannier R N and Bordes-Richard E 2006 *Catal. Today* **118** 223
- Mott N F and Davis E A 1979 *Electronic processes in non-crystalline materials* (Clarendon: Oxford)
- Nicula A, Culea E and Lupsa I 1986 *J. Non-Cryst. Solids* **79** 325
- Nilihara K, Morena R and Hasselman D P H 1982 *J. Mater. Sci. Lett.* **1** 13
- Park H and Woodward P M 2000 *Int. J. Inorg. Mater.* **2** 153
- Qasrawi A F 2005 *Cryst. Res. Technol.* **40** 610
- Qiu L, Yang Y L and Jacobson A J 1997a *J. Mater. Chem.* **7** 243
- Qiu L, Yang Y L and Jacobson A J 1997b *J. Mater. Chem.* **7** 249
- Rajesh K R and Menon C S 2002 *Mater. Lett.* **53** 329
- Redfield D 1963 *Phys. Rev.* **130** 916
- Saito K and Ikushima A J 2000 *Phys. Rev. B* **62** 8584
- Simner S P, Sandoval D S, Mackenzie J D and Dunn B 1997 *J. Am. Ceram. Soc.* **80** 2563
- Sumalatha B, Omkaram I, Rao T R and Raju Ch L 2011 *J. Non-Cryst. Solids* **357** 3143
- Taninouchi Y K, Uda T and Ichitsubo T 2010 *Solid State Ion.* **181** 719
- Tauc J 1974 *Amorphous and liquid semiconductors* (London: Plenum)
- Vaish R and Verma K B R 2011 *J. Non-Cryst. Solids* **357** 1485
- Watanabe A 2001 *J. Solid State Chem.* **161** 410
- Williams D B and Carter C B 2009 *Transmission electron microscopy* (New York: Springer) 2nd edn
- Yan J and Greenblatt M 1995 *Solid State Ion.* **81** 225
- Zhen Q, Kale G M, Shi G, Li R, He W and Liu J 2005 *Solid State Ion.* **176** 2727