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Scientific Research

Spectroscopic Studies of 50Bi_2O_3-(50 − *x*)B_2O_3-*x*Sm_2O_3 Glasses System

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ABSTRACT

Sm^{3+} doped bismuth borate glasses of the composition (50 − *x*)B_2O_3:50Bi_2O_3:*x*Sm_2O_3 (where *x* = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 mol%) have been synthesized by conventional melt quenching technique. In order to understand the role of Sm_2O_3 in bismuth borate glasses, the density, the molar volume, the refractive index and the optical absorption were investigated. The results show that density, molar volume and refractive index of glasses increased with increasing Sm_2O_3 concentration. The increase of molar volume with Sm_2O_3 concentration is due to increase of non-bridging oxygen (NBOs) in the glass matrices. The optical absorption spectra were measured in the wavelength range 300 - 1100 nm and the optical band gaps were determined. It was found that the optical band gap decreased with the increase of Sm_2O_3 concentration. Moreover, the X-rays luminescence of Sm_2O_3 glasses samples were measured and shows emission band at $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (569 nm), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (598 nm), $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (641 nm) and $^4G_{5/2}\rightarrow{}^6H_{11/2}$ (705 nm).

Keywords: Samarium; Luminescence; Optical Properties; Density

1. Introduction

Boric oxide, B_2O_3, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B_2O_3 exhibit rather high viscosity and tend to the formation of glasses. In crystalline form, on the other hand, borates with various compositions are of exceptional importance due to their interesting linear and nonlinear optical properties [1]. The boron atom usually coordinates with either three or four oxygen atoms forming $(BO_3)^{3-}$ or $(BO_4)^{5-}$ structural units. Furthermore, these two fundamental units can be arbitrarily combined to form different B_xO_y structural groups [2]. Among these borates, especially the monoclinic bismuth borate BiB_3O_6 shows up remarkably large linear and nonlinear optical coefficients [3,4]. Calculations indicate that this can be mainly attributed to the contribution of the $(BiO_4)^{5-}$ anionic group [5,6]. For the linear properties (refractive index) this anionic group should act in a similar way in an amorphous environment, *i.e.*, in glass. Combining bismuth oxide with boric oxide thus allows tuning the optical properties in a wide range depending on the composition. Consequently, the properties of glasses of the system Bi_2O_3-B_2O_3 have attracted much interest [7].

The trivalent samarium ion (Sm^{3+}) is one of the most important active ions in the RE family (cerium to lutetium) due to its convenient closely lying energy level structure [8], that has been exploited in upconversion processes mainly in low phonon crystalline hosts and rarely in glasses [9-13]. Within the Sm^{3+} ion energy scheme tricolor visible upconversion processes can take place from the $^4G_{5/2}\rightarrow{}^6H_{5/2}$ (green), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (orange) and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (red) electronic transitions. Moreover, Sm^{3+} doped bismuth-borate glass has high density and radiation hard property. Also it is easy to made, can be produced with low cost and wide range of emission band. Therefore, it is a good candidate for radiation detector and possible to apply high energy and nuclear physics, medical imaging, homeland security and radiation detection. In this work, Sm^{3+} doped bismuth borate glasses have been synthesized by conventional melt quenching technique and investigate on X-rays luminescence, optical and physical properties of glass samples.

2. Experimental

The compositions of glass are (50 − *x*) B_2O_3:50Bi_2O_3:*x*Sm_2O_3 (x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%). The batch

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was prepared from the AR grade of Bi_2O_3, H_3BO_3 and Sm_2O_3. The glasses were melted in a high alumina crucible at 1100˚C under normal atmosphere. The molten glass was cast into a stainless steel plate and properly annealed. The glass thus obtained was cut and polished for optical measurement. The density was measured by the Archimedes method using xylene as immersion liquid. Density of xylene at the experimental temperature was found to be 0.863 g/cm^3. The corresponding molar volume, V_m, was calculated using the following formula [14]:

$$V_m = M/\rho \quad (1)$$

where M is the molecular weight of the multi-component glass system.

The UV-VIS absorption spectra were obtained with a double-beam spectrophotometer (Variance, Cary-50). According to Davis and Mott, the absorption coefficient, $\alpha(\nu)$, as a function of incident photon energy ($h\nu$) for direct and indirect optical transitions is given by [15]:

$$\alpha(\nu) = \alpha_0 \left(h\nu - E_g\right)^n / h\nu \quad (2)$$

where the exponent n = 1/2 for an allowed direct transition, while n = 2 for an allowed indirect transition, α_0 is a constant related to the extent of the band tailing, and E_g is the optical band gap energy. The absorption coefficient, $\alpha(\nu)$, can be determined near the absorption edge of different photon energies for all glass sample. It is well known that for amorphous materials a reasonable fit of Equation (2) with n = 2 is achieved. Therefore, the values of optical band gap energy (E_g) can be determined from the plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) (Tauc's plot), for allowed indirect transitions.

Refractive index of these glasses has been calculated by using the relation proposed by Dimitrov *et al*. [16,17].

$$\frac{\left(n^2 - 1\right)}{\left(n^2 + 2\right)} = 1 - \sqrt{\frac{E_g}{20}} \quad (3)$$

In order to measure the X-ray luminescence of the Sm_2O_3 doped bismuth borate glass samples at room temperature, X-ray tube (DRGEM Co.) was used and faces of the glass sample were wrapped with several layers of Teflon tape excepting the one for attaching to the optical fiber. Signals from the glass sample by the induced X-ray were measured using a QE65,000 spectrometer (Ocean Optics Co.) The QE65,000 was cooled to −15˚C to reduce thermal noise in the CCD. It was used to plot the X-ray emission spectrum of the glass sample by window based-software [18,19].

3. Result and Discussion

The template is used to format your paper and style the text. All margins, column widths, line spaces, and text fonts are prescribed; please do not alter them. You may note peculiarities. For example, the head margin in this template measures proportionately more than is customary. This measurement and others are deliberate, using specifications that anticipate your paper as one part of the entire proceedings, and not as an independent document. Please do not revise any of the current designations. The measured density of Sm^{3+} doped bismuth borate glass samples for different Sm_2O_3 concentrations are shown in **Figure 1**. As seen in **Figure 1**, density increase linearly with additional content of Sm_2O_3 into the network. This indicates that replacing B_2O_3 by addition of a small amount of Sm_2O_3 results in the increase of the average molecular weight due to Sm_2O_3 has a higher relative molecular weight than that of B_2O_3. **Figure 2** shows the variation of the molar volume with Sm_2O_3 concentration. As shown in **Figure 2**, the molar volume increased with an increasing of Sm_2O_3 concentration, because of increasing of non-bridging oxygen (NBOs). The increase of NBOs in the glass structure leads to an increase in average atomic separation. The results obtained indicate that the Sm_2O_3 oxide enters the glass network as a modifier by occupying the interstitial space in the network and generating the NBOs to the structure. It can also be concluded that the addition of Sm_2O_3 may accordingly result in an extension of glass network [20].

The absorption spectra of Sm^{3+} doped bismuth borate glasses in the UV-VIS region at room temperature are shown in **Figure 3**. It is clearly observed that the absorption intensity of the absorption bands increases with the increase of Sm_2O_3 concentration. Three absorption bands peaked at 474 nm, 950 nm and 1083 nm were observed. All absorption band spectra are characteristics of Sm^{3+} doped oxide glasses [21] and the observed absorption bands were assigned to appropriate *f-f* electronic transitions of Sm^{3+} ions from the $^6H_{5/2}$ ground state to ($^4I_{13/2}$ + $^4I_{11/2}$ + $^4M_{15/2}$), $^6F_{11/2}$ and $^6F_{9/2}$ respectively.

The optical band gap were evaluated by Tauc's plot using Equation (2) and shown in **Figure 4**. When increase Sm_2O_3, bonding defect and non-bridging oxygen were increased. These leads to increase in the degree of

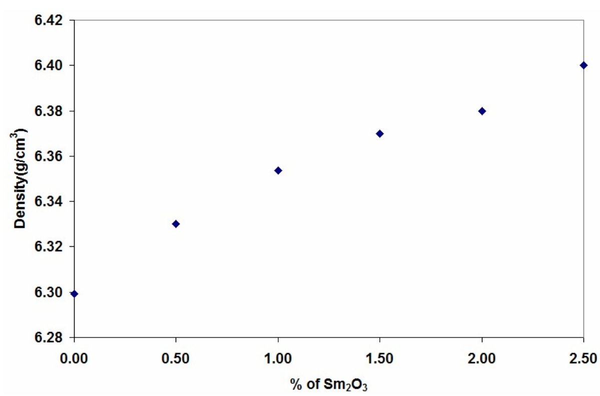

Figure 1. Densities of Sm_2O_3 doped in bismuth borate glass.

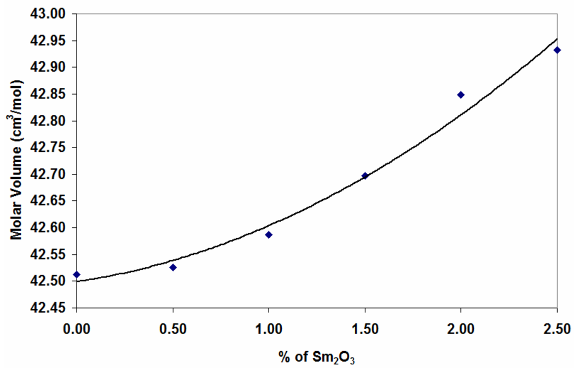

Figure 2. Molar volume of Sm_2O_3 doped in bismuth borate glass.

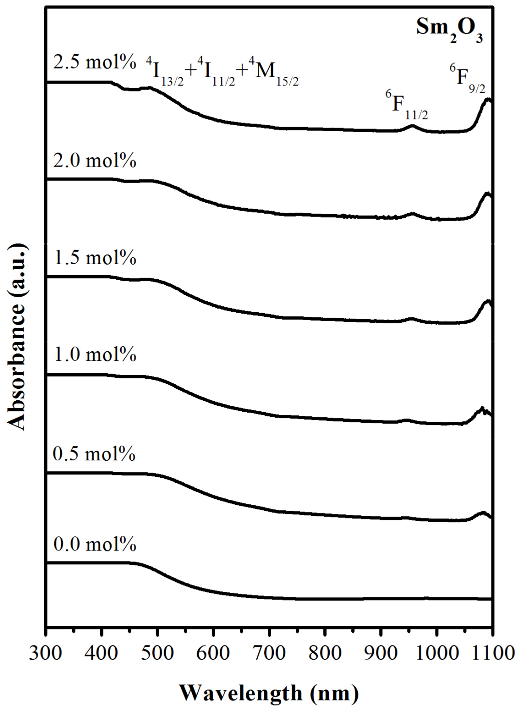

Figure 3. Absorption spectra of Sm_2O_3 doped in bismuth borate glass.

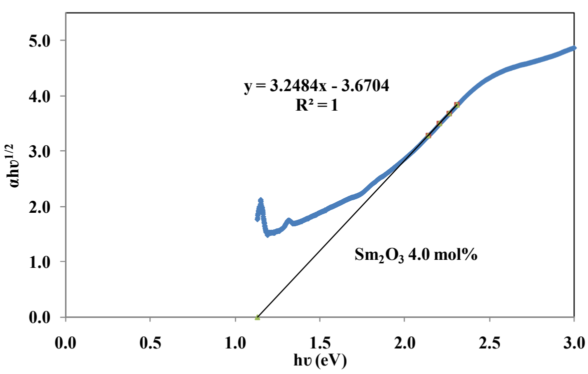

Figure 4. Typical Tauc's plot of Sm_2O_3 doped in bismuth borate glass.

localization of electrons there by increasing the donor center in the glass matrix. The increasing presence of donor center, therefore, decreases the optical band gap. As a result of this, the band gap are decreased as shown in **Figure 5**, for indirect allow transition. The refractive index of these glasses has been calculated by using Equation (3) and show in **Figure 6**. The result show the refractive index of glasses increased with increasing of Sm_2O_3 concentration.

Figure 7 showed X-rays luminescence spectra of Sm_2O_3 doped bismuth borate glasses. The emission wavelength observed at 569 nm, 598 nm, 641 nm and 705 nm The luminescence spectra of the Sm_2O_3 doped bismuth borate glass were identified as $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (569 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (598 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (641 nm) and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (705 nm) [22]. The intensity of luminescence was increase with increasing doping concentration.

4. Conclusions

In this work, properties $(50 - x)B_2O_3:50Bi_2O_3:xSm_2O_3$ (where x = 0.00, 0.50, 1.00, 1.50, 2.00 and 2.50 mol%) glasses were presented. From the entire analysis, the following observations can be made.

1) The density increase linearly with additional content

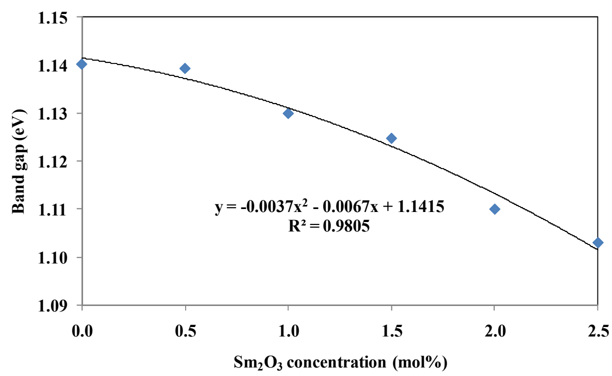

Figure 5. Variation of optical band gap (for indirect allow transition) with Sm_2O_3 concentration.

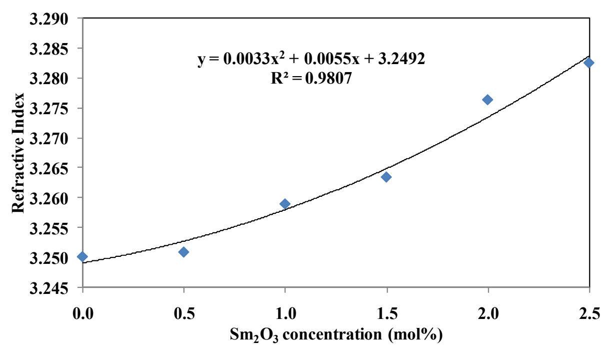

Figure 6. Refractive indices of Sm_2O_3 doped in bismuth borate glass.

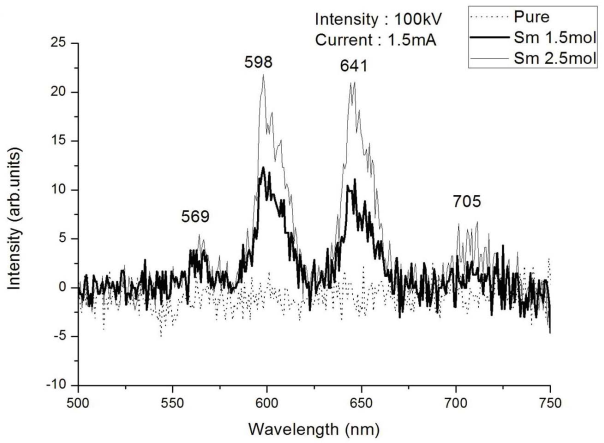

Figure 7. X-rays luminescence spectra of Sm_2O_3 doped bismuth borate glasses.

of Sm_2O_3 into the network, due to Sm_2O_3 has a higher relative molecular weight than that of B_2O_3.

2) The molar volume increases with an increase in Sm_2O_3 content, which is attributed to the increase in the number of non-bridging oxygen (NBOs).

3) Three absorption bands peaked at 474 nm, 950 nm and 1083 nm were observed, which assigned to appropriate *f-f* electronic transitions of Sm^{3+} ions from the $^6H_{5/2}$ ground state to ($^4I_{13/2}$ + $^4I_{11/2}$ + $^4M_{15/2}$), $^6F_{11/2}$ and $^6F_{9/2}$ respectively.

4) When increase Sm_2O_3, bonding defect and non-bridging oxygen were increased. These leads to increase in the degree of localization of electrons there by increasing the donor center in the glass matrix. The increasing presence of donor center, therefore, decreases the optical band gap and increases refractive index.

5) X-rays luminescence spectra of Sm_2O_3 doped bismuth borate glasses were observed at 569 nm, 598 nm, 641 nm and 705 nm, which identified from $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$, and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ respectively.

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REFERENCES

[1] P. Becker, "Borate Materials in Nonlinear Optics," *Advanced Materials*, Vol. 10, No. 13, 1998, pp. 979-992. doi:10.1002/(SICI)1521-4095(199809)10:13<979::AID-ADMA979>3.0.CO;2-N

[2] D. Xue, K. Betzler, H. Hesse and D. Lammers, "Nonlinear Optical Properties of Borate Crystals," *Solid State Communications*, Vol. 114, No. 1, 2000, pp. 21-25. doi:10.1016/S0038-1098(99)00579-7

[3] H. Hellwig, J. Liebertz and L. Bohaty, "Exceptional Large Nonlinear Optical Coefficients in the Monoclinic Bismuth Borate Bi_3O_6 (*BIBO*)," *Solid State Communications*, Vol. 109, No. 4, 1999, pp. 249-251. doi:10.1016/S0038-1098(98)00538-9

[4] H. Hellwig, J. Liebertz and L. Bohaty, "Linear Optical Properties of the Monoclinic Bismuth Borate BiB_3O_6," *Journal of Applied Physics*, Vol. 88, No. 1, 2000, pp. 240-244. doi:10.1063/1.373647

[5] D. Xue, K. Betzler, H. Hesse and D. Lammers, "Origin of the Large Nonlinear Optical Coefficients in Bismuth Borate BiB_3O_6," *Physica Status Solidi* (*A*), Vol. 176, No. 2, 1999, pp. R1-R2. doi:10.1002/(SICI)1521-396X(199912)176:2<R1::AID-PSSA99991>3.0.CO;2-H

[6] Z. Lin, Z. Wang, C. Chen and M. H. Lee, "Mechanism for Linear and Nonlinear Optical Effects in Monoclinic Bismuth Borate (BiB_3O_6) Crystal," *Journal of Applied Physics*, Vol. 90, No. 11, 2001, pp. 5585-5590. doi:10.1063/1.1413711

[7] P. Becker, "Thermal and Optical Properties of Glasses of the System Bi_2O_3-B_2O_3," *Crystal Research and Technology*, Vol. 38, No. 1, 2003, pp. 74-82. doi:10.1002/crat.200310009

[8] W. T. Carnall, P. R. Fields and K. Rajnak, "Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, and Tm^{3+}," *Journal of Chemical Physics*, Vol. 49, No. 10, 1968, pp. 4424-4442. doi:10.1063/1.1669893

[9] M. Kaczkan, Z. Frukacz and M. Malinowski, "Infra-Red-to-Visible Wavelength Upconversion in Sm^{3+}-Activated YAG Crystals," *Journal of Alloys and Compounds*, Vol. 323-324, 2001, pp. 736-739. doi:10.1016/S0925-8388(01)01066-0

[10] Y. Zhou, J. Lin and S. Wang, "Energy Transfer and Upconversion Luminescence Properties of Y_2O_3:Sm and Gd_2O_3:Sm Phosphors," *Journal of Solid State Chemistry*, Vol. 171, No. 1-2, 2003, pp. 391-395. doi:10.1016/S0022-4596(02)00219-0

[11] P. R. Biju, G. Jose, V. Thomas, V. P. N. Nampoori and N. V. Unnikrishnan, "EnergyTransfer in $Sm3^+$:$Eu3^+$ System in Zinc Sodium Phosphate Glasses," *Optical Materials*, Vol. 24, No. 4, 2004, pp. 671-677. doi:10.1016/S0925-3467(03)00183-6

[12] M. C. Farries, R. P. Morkel and J. E. Townsend, "Samarium^{3+} Doped Glass Laser Operating at 651 nm," *Electronics Letters*, Vol. 24, No. 11, 1988, pp. 709-711. doi:10.1049/el:19880479

[13] P. W. France, M. G. Drexhage, J. M. Parker, M. W. Moore, S. F. Carter and J. V. Wright, "Fluoride Glass Optical Fibers," Blackie, Boca Raton, 2000.

[14] P. Limkitjaroenporn, J. Kaewkhao, P. Limsuwan and W. Chewpraditkul, "Physical, Optical, Structural and Gamma-Ray Shielding Properties of Lead Sodium Borate

Glasses," *Journal of Physics and Chemistry of Solids*, Vol. 72, No. 4, 2011, pp. 245-251. doi:10.1016/j.jpcs.2011.01.007

[15] M. Abdel-Baki, F. El-Diasty and F. A. A. Wahab, "Optical Characterization of xTiO$_2$-(60 − x)SiO$_2$-40Na$_2$O Glasses: II. Absorption Edge, Fermi Level, Electronic Polarizabi- lity and Optical Basicity," *Optics Communications*, Vol. 261, No. 1, 2006, pp. 65-70. doi:10.1016/j.optcom.2005.11.056

[16] V. Dimitrov and T. Komatsu, "Classification of Simple Oxide: A Polarizability Approach," *Journal of Solid State Chemistry*, Vol. 163, No. 1, 2002, pp. 100-112. doi:10.1006/jssc.2001.9378

[17] B. Eraiah and S. G. Bhat, "Optical Properties of Samarium Doped Zinc-Phosphate Glasses," *Journal of Physics and Chemistry of Solids*, Vol. 68, No. 4, 2007, pp. 581-585. doi:10.1016/j.jpcs.2007.01.032

[18] M. J. Kim, H. J. Kim, H. Park, S. Kim and J. Kim, "Characterization of $BaCl_2$ Scintillation Crystal at Low Temperature," *Nuclear Instruments and Methods in Physics Research A*, Vol. 632, No. 1, 2011, pp. 47-51. doi:10.1016/j.nima.2010.12.226

[19] G. Rooh, H. Kang, H. J. Kim, H. Park and S. Kim, "The Growth and Scintillation Properties of $Cs_2NaCeCl_6$ Single Crystal," *Journal of Crystal Growth*, Vol. 311, No. 8, 2009, pp. 2470-2473. doi:10.1016/j.jcrysgro.2009.01.091

[20] S. Sindhu, S. Sanghi, A. Agarwal, V. P. Seth and N. Kishore, "Effect of Bi_2O_3 Content on the Optical Band Gap, Density and Electrical Conductivity of $MO \cdot Bi_2O_3 \cdot B_2O_3$ (M = Ba, Sr) Glasses," *Materials Chemistry and Physics*, Vol. 90, No. 1, 2005, pp. 83-89. doi:10.1016/j.matchemphys.2004.10.013

[21] T. Som and B. Karmakar, "Infrared-to-Red Upconversion Luminescence in Samarium-Doped Antimony Glasses," *Journal of Luminescence*, Vol. 128, No. 12, 2008, pp. 1989-1996. doi:10.1016/j.jlumin.2008.06.011

[22] A. B. Yusov, A. M. Fedosseev, G. B. Andreev and I. B. Shirokova, "Luminescence Properties of Solid Eu, Sm, Tb and Dy Compounds with the Molybdoaluminate Ion $Al(OH)_6Mo_6O_{18}^{3}$," *Mendeleev Communications*, Vol. 11, No. 3, 2011, pp. 86-87. doi:10.1070/mc2001v11n3ABEH001427

