



## Synthesis and characterization of some binuclear alkylene dithiophosphate complexes of bis(acetylacetonato)aluminium(III)-di-( $\mu$ -isopropoxo)di-isopropoxoaluminium(III) and sol-gel synthesis of nanosized $\theta$ -alumina

Vinita Sharma<sup>a</sup>, Anita Raj Sanwaria<sup>b</sup> & Nikita Sharma<sup>c,\*</sup>

<sup>a</sup>Department of Chemistry, BBD Govt. College, Chimanpura, Shahpura, Jaipur, Rajasthan, India

<sup>b</sup>Department of Chemistry, University of Rajasthan, Jaipur, Rajasthan, India

<sup>c</sup>Department of Chemistry, SPNKS Government PG College, Dausa, Rajasthan, India

\*E-mail: drnikitasharma21@gmail.com

Received 30 April 2021; revised and accepted 13 September 2021

Reactions of bis(acetylacetonato)aluminium(III)-di-( $\mu$ -isopropoxo)-di-isopropoxoaluminium(III) (**A**) with a variety of alkylenedithiophosphoric acids in different molar ratio yield products of the type  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{O-G-O})_n(\text{OPr}^i)_{2-n}\}]$  (**1-9**) {where G = C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>, n=1[**1**], n=2[**2**]; -CH<sub>2</sub>CH(C<sub>2</sub>H<sub>5</sub>), n=1[**3**], n=2[**4**]; CH<sub>2</sub>CH(CH<sub>3</sub>), n=1[**5**], n=2[**6**]; C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>), n=1[**7**]; CH(CH<sub>3</sub>)CH(CH<sub>3</sub>), n=1[**8**], n=2[**9**]}. Progress of the reaction is monitored by estimating liberated 2-propanol in benzene-2-propanol azeotrope by oxidimetric method. All pale coloured viscous products were soluble in common organic solvents and are characterized by elemental analyses, FT-IR and NMR (<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR) spectral studies. Molecular weight measurements in refluxing anhydrous benzene indicated binuclear nature of the complexes. <sup>27</sup>Al NMR spectra of two of the derivatives, (**1**) and (**2**), suggested the presence of aluminium(III) atoms in different coordination states. <sup>31</sup>P NMR spectra of the representative derivatives (**1**) and (**2**) exhibited only a single peak at 95.71 and 90.59 ppm, respectively, suggesting tetra-coordination around phosphorus atom and a bidentate mode of chelation of the dithio ligand. Sol-gel transformation of Al(OPr<sup>i</sup>)<sub>3</sub> and  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}(\text{OPr}^i)_2]$  (**A**) followed by sintering at ~850 °C yield alumina (**a**) and (**b**), respectively. The powder X-ray diffraction patterns, SEM images and FT-IR spectral studies of (**a**) and (**b**) has indicated formation of nano-crystallites of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> [PDF # 110517] in both the cases. The energy band gaps of 4.78 eV and 5.01 eV for (a) and (b), respectively are obtained from the absorption spectra.

**Keywords:** Bis(acetylacetonato)aluminium(III)-di-( $\mu$ -isopropoxo)-di-isopropoxoaluminium(III), alkylenedithiophosphoric acid, sol-gel transformation, nano-sized  $\theta$ -Al<sub>2</sub>O<sub>3</sub>

The role of metal-alkoxides as precursors for pure materials by sol-gel technique is very well established, but to get targeted materials having suitable shape, size and porous structure, a good control over the rate of hydrolysis of the alkoxide appears to be essential<sup>1-3</sup>. This could be achieved by partial substitution of some of the alkoxy groups in metal alkoxides by chelating/sterically demanding ligands, such as oximes<sup>4,5</sup>, glycols<sup>6,7</sup>, Schiff bases<sup>8,9</sup> etc. The chemical modifications help in modifying the solubility and reactivity of the resulting alkoxide derivatives to make them better precursors for their applications in high-purity metal-oxide based ceramic materials<sup>10,11</sup>. Aluminium being a hard acid, is expected to bond strongly to hard bases<sup>12-14</sup> as compared to soft bases like sulphur containing ligands<sup>15,16</sup>. The dithiophosphate ligand system gained a great deal of attention due to their ability to stabilize metals in higher oxidation state<sup>17-19</sup>. The

dithiophosphate derivatives of metals are found to be biologically active<sup>20-21</sup> and hence find extensive potential applications in agriculture, medicine and also in chemical industries<sup>22,23</sup>, yet corresponding aluminium(III) derivatives are comparatively less known.

Alumina, which is an important material due to its high thermal and mechanical stability, its chemical inertness with non-toxic nature<sup>24</sup> exist in a variety of structural polymorph such as  $\eta$ -,  $\gamma$ -,  $\delta$ -,  $\theta$ - and  $\alpha$ -alumina. Aluminium hydroxide converts into the most stable form  $\alpha$ -alumina (corundum, sapphire) via different transition phases as  $\gamma$ ,  $\delta$  and  $\theta$  with increase of temperature upto 1100 °C<sup>25</sup>. Although the atomic structures of transition alumina are still matter of discussion, it has been found that the structure  $\gamma$ ,  $\delta$  and  $\eta$  phases possess a defected spinel structure<sup>26</sup>. It is interesting to mention here that sol-gel transformation of Al(OPr<sup>i</sup>)<sub>3</sub> as well as its chemically modified

derivatives as precursors for transition alumina, at different sintering temperatures, have been done successfully<sup>10, 13,14</sup>. Transition alumina are versatile ceramic oxides known for exhibiting a wide variety of applications in engineering, biochemical areas, as building and refractory materials, electric and heat insulators etc.<sup>27-29</sup>. Among various transition aluminas, the  $\theta$ -alumina phase is very important due to its specific structure and is widely used as catalyst and adsorbent<sup>30-32</sup>.

In this article we report synthesis and characterization of some binuclear alkylenedithiophosphate complexes of bis(acetylacetonato)aluminium(III)-di-( $\mu$ -isopropoxo)di-isopropoxoaluminium(III) (**A**) along with the sol-gel transformation of aluminium isopropoxide and its acetylacetonate modified precursor (**A**) into nano-sized  $\theta$ -alumina.

## Materials and Methods

All the experiments (except hydrolysis reaction) were carried out under strictly anhydrous conditions. The solvent and reagents were purified and dried according to the standard procedures<sup>33</sup>. Due precautions were taken while handling hazardous chemicals and solvents such as benzene. Aluminium was estimated gravimetrically as the oxinate<sup>34</sup>, sulphur and isopropanol were estimated as reported in the literature<sup>33</sup>. Aluminium (III) isopropoxide was synthesized and purified as reported in the literature<sup>35</sup>. The precursor material [(acac)<sub>2</sub>Al( $\mu$ -OPr<sup>i</sup>)<sub>2</sub>Al(OPr<sup>i</sup>)<sub>2</sub>] (**A**) was prepared by the reported method<sup>36</sup>. IR spectra were obtained as Nujol mulls on a Nicolet Magna 550 spectrophotometer in the range 4000 – 400 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a JEOL FX 90Q spectrometer using TMS as an internal reference in CDCl<sub>3</sub> and CHCl<sub>3</sub>, respectively. The <sup>27</sup>Al NMR studies were carried out in toluene using aluminum nitrate as an external reference in aqueous solution and <sup>31</sup>P NMR spectra were recorded in CDCl<sub>3</sub>. The molecular weight measurements were carried out by the elevation in boiling point method using a Beckmann thermometer fitted in a glass assembly (supplied by JSGW, India) in anhydrous benzene. The XRD patterns were recorded on Panalytical make X'Pert PRO MPD diffractometer (model 3040). SEM was performed on Carl -Zeiss (30keV) make and model EVO. The optical absorption spectra of samples have been recorded over wavelength 200 to 800 nm in solution using spectrophotometer JASCO Corp., UV-530, Rev.1.00 at room temperature.

## Preparation of [(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>Al( $\mu$ -OPr<sup>i</sup>)<sub>2</sub>Al(OPr<sup>i</sup>)<sub>2</sub>]{S(S)P(O(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CO)}

Benzene solutions of [(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>Al( $\mu$ -OPr<sup>i</sup>)<sub>2</sub>Al(OPr<sup>i</sup>)<sub>2</sub>] (**A**) (2.52 g; 5.15 mmol in 40 mL) and [(OC(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>O)P(S)SH] (1.09 g; 5.14 mmol in 20 mL) were refluxed for 4 h. The liberated 2-propanol was continuously fractionated out azeotropically with benzene. The progress as well as the completion of the reaction was checked by the estimation of the 2-propanol in the azeotrope by oxidimetric titration<sup>33</sup>. After stripping off the excess solvent under reduced pressure, a pale viscous compound was obtained. The purification as well as the formation of good quality crystals of the compound from a mixture of dichloromethane and *n*-hexane (1:1) could not be achieved. The other derivatives were prepared using similar procedure. Their analytical data are summarized in Table 1.

## Hydrolysis of (**A**) using sol-gel technique

To the clear 2-propanolic solution of (**A**) (2 g in ~30 mL 2-propanol) a drop of distilled water- 2-propanol mixture (1 mL water and 4 mL anhydrous 2-propanol) was added and stirred on a magnetic stirrer. Sol formation occurred immediately. Excess amount of water was added in small lots with continuous stirring for 4-5 h to ensure complete hydrolysis. The yellow gel formed during this process was dried in a preheated oven (at ~120 °C). The powder obtained was washed with acetone and *n*-hexane (1:1) mixture to remove any organic impurity. The resulting yellow powder was sintered at ~ 850 °C for 3 h in a muffle furnace to give a white powder, which was characterized as  $\theta$ -alumina by powder XRD [PDF # 110517]. Hydrolysis of the other precursor Al(OPr<sup>i</sup>)<sub>3</sub> was also carried out separately by similar route.

## Results and Discussion

### Synthesis and characterization of alkylene dithiophosphate complexes of bis(acetylacetonato)aluminium(III)di( $\mu$ -isopropoxo)di(isopropoxo)aluminium(III)

Reaction of the precursor, (**A**) with [(O-G-O)P(S)SH] in 1:1 and 1:2 molar ratio in refluxing anhydrous benzene yield products of the following type [(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>Al( $\mu$ -OPr<sup>i</sup>)<sub>2</sub>Al{S(S)P(O-G-O)}(OPr<sup>i</sup>)] and [(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>Al( $\mu$ -OPr<sup>i</sup>)<sub>2</sub>Al{S(S)P(O-G-O)}<sub>2</sub>], respectively:

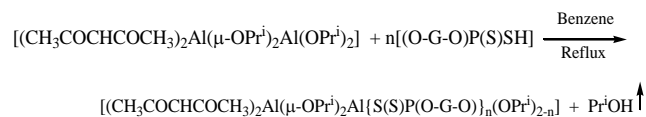


Table 1 — Analytical data for  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{O-G-O})_n(\text{OPr}^i)_{2-n}\}]$  ( $n = 1$  or  $2$ )

*Complex	Pr <sup>i</sup> OH(g) Found (Calcd.)	Yield %	Analysis %					Mol. wt. Found (Calcd.)
			Al	OPr <sub>ii</sub>	C	H	S	
(1)	0.43 (0.43)	99	8.4 (8.4)	27.01 (27.60)	46.72 (46.87)	7.21 (7.34)	9.5 (9.9)	659 (640)
(2)	0.49 (0.51)	99.9	6.29 (6.81)	14.43 (14.89)	42.22 (42.42)	6.61 (6.56)	16.13 (16.15)	725 (792)
(3)	0.40 (0.43)	98	8.1 (8.8)	28.21 (28.85)	45.14 (45.02)	7.07 (7.01)	10.21 (10.43)	628 (613)
(4)	0.50 (0.51)	98.5	7.3 (7.3)	15.59 (15.96)	45.38 (45.12)	6.02 (6.89)	17.28 (17.33)	654 (638)
(5)	0.27 (0.27)	99.6	9.7 (9.8)	28.99 (29.63)	44.14 (44.12)	6.90 (6.86)	10.74 (10.75)	590 (597)
(6)	0.60 (0.69)	99.5	7.59 (7.64)	16.01 (16.71)	37.28 (37.34)	5.69 (5.65)	17.92 (18.12)	684 (707)
(7)	0.31 (8.32)	96.2	8.25 (8.43)	27.02 (27.63)	46.07 (46.87)	7.39 (7.34)	9.7 (9.9)	638 (640)
(8)	0.61 (0.62)	99	8.6 (8.8)	28.1 (28.9)	45.32 (45.09)	7.09 (7.03)	10.41 (10.43)	630 (612)
(9)	0.49 (0.50)	99	7.2 (7.3)	16.2 (16.02)	39.17 (39.13)	6.01 (5.97)	17.03 (17.30)	718 (736)

\* $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})\}(\text{OPr}^i)]$  (1),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OC}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{O})\}_2]$  (2),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O})\}(\text{OPr}^i)]$  (3),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{O})\}_2]$  (4),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OCH}_2\text{CH}(\text{CH}_3)\text{O})\}(\text{OPr}^i)]$  (5),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OCH}_2\text{CH}(\text{CH}_3)\text{O})\}_2]$  (6),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OC}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)\text{O})\}(\text{OPr}^i)]$  (7),  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OCH}(\text{CH}_3)_2\text{CH}(\text{CH}_3)\text{O})\}(\text{OPr}^i)]$  (8) and  $[(\text{CH}_3\text{COCHCOCH}_3)_2\text{Al}(\mu\text{-OPr}^i)_2\text{Al}\{\text{S}(\text{S})\text{P}(\text{OC}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{O})_2\}]$  (9)

[where G = C(CH<sub>3</sub>)<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>, -CH<sub>2</sub>CH(C<sub>2</sub>H<sub>5</sub>), CH<sub>2</sub>CH(CH<sub>3</sub>), C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>) and CH(CH<sub>3</sub>)CH(CH<sub>3</sub>); n = 1 or 2]

These reactions are quite facile and can be pushed to completion by fractionating the liberated 2-propanol azeotropically with benzene. The progress of the reactions was monitored by estimating the liberated 2-propanol present in the azeotrope oxidimetrically. All these derivatives are pale viscous solids and are soluble in common organic solvents. Molecular weight measurements in refluxing anhydrous benzene indicated their binuclear nature (Table 1).

#### IR spectra

The tentative assignments of some of the important bands have been made and are summarized in Table 2. Medium intensity band at 2500 cm<sup>-1</sup> in the free ligand due to  $\nu_{(\text{SH})}$  is absent in the IR spectra of these complexes, indicating deprotonation of -SH group and formation of Al-S bond<sup>34</sup>. Medium intensity band in the region 975-998 cm<sup>-1</sup> due to  $\nu_{(\text{P-O-C})}$ , in the alkylendithiophosphoric acid, do not show any significant shift in the aluminium(III) complexes.

Band due to  $\nu_{(\text{P-S})}$  present<sup>35</sup> at 660-685 cm<sup>-1</sup> show shifting to lower frequencies in the aluminium (III) complexes indicating the bidentate nature of the ligand<sup>16</sup>.

The presence of strong bands in the region 1600-1610 and 1510-1545 cm<sup>-1</sup> due to  $\nu(\text{C=O})$  and  $\nu(\text{C=C})$  stretching vibrations, respectively, suggest the bidentate quasi-aromatic nature of the acetylacetonate moiety<sup>36</sup>. The medium intensity band observed in the region 1000-1020 cm<sup>-1</sup> have been assigned  $\nu(\text{C-O})$  of isopropoxy group<sup>36</sup>. A band at 515-575 cm<sup>-1</sup> may be assigned to be  $\nu(\text{Al-S})$ <sup>16</sup>. The Al-O-Al vibrations have been observed<sup>36</sup> in the region 760-790 cm<sup>-1</sup>.

#### <sup>1</sup>H NMR spectra

The important signals in the <sup>1</sup>H NMR spectra of these derivatives are summarized in Table 3. A comparison of the spectra of the free ligand (alkylendithiophosphoric acid) with the spectra of the corresponding derivatives show the absence of -SH signals, again indicating deprotonation of the -SH group of the ligand and formation of Al-S bond<sup>16,37</sup>. The methine protons of the bridging and







Fig. 5 — SEM images of alumina samples (a,c) obtained from  $\text{Al}(\text{OPr}^i)_3$  and (b,d) from complex (A)

Fig. 6 — Absorption spectra (a) & (b) and corresponding *Tauc*-Plots, (c) & (d) of alumina obtained from  $\text{Al}(\text{OPr}^i)_3$  & (A), respectively

### Conclusions

The above studies suggest the formation of unsymmetrical binuclear complexes containing aluminium(III) atoms in different coordination environment. Spectroscopic studies suggest chelating mode of attachment of dialkylenedithio ligands. Sol-

gel hydrolysis in organic media of aluminium isopropoxide as well as its chemically modified precursors exhibit interesting structural variations around aluminum(III) atoms. These appear to be potential precursors for the preparation of nanosized alumina by sol-gel technique.

### Acknowledgement

We are highly thankful to late Prof. Rakesh Bohra, Emeritus Scientist (DST), Department of Chemistry, UOR, Jaipur for his valuable suggestions and help in the preparation of the manuscript. We are thankful to the Department of Physics, University of Rajasthan, Jaipur for carrying out XRD and SEM analyses.

### References

- 1 Dhayal V, Sharma N, Sharma V, Bohra R, Drake J E & McDonald C L B, *Polyhedron*, 26 (2007) 3168.
- 2 Mishra S & Daniele S, *Chem Rev*, 115 (2015) 8379.
- 3 Mishra S & Daniele S, *Chem-Eur J*, 26 (2020) 9292.
- 4 Choudhary A, Sharma N, Nagar M, Bohra R, Mobin S M & Mathur P, *J Sol-Gel Sci Technol*, 70 (2014) 464.
- 5 Jain J & Nagar M, *J Sol-Gel Sci Technol*, 71 (2014) 447.
- 6 Atal M K, Dhayal V, Nagar M, Bohra R, Rathore K S & Saxena N S, *J Sol-Gel Sci Technol*, 53 (2010) 67.
- 7 Sanwaria A R, Gopal R, Jain J, Nagar M & Chaudhary A, *J Inorg Organomet Polym Mater*, 30 (2020) 1393.
- 8 Sharma N, Sharma V, Bohra R & Raju V S, *Appl Organomet Chem*, 21 (2007) 763.
- 9 Sharma N, Sanwaria A R, Nagar M & Bohra R, *Main Group Met Chem*, 36 (2013) 109.
- 10 Sanwaria A R, Nagar M, Bohra R, Chaudhary A, Mobin M S, Mathur P & Choudhary B L, *RSC Adv*, 4 (2014) 30081.
- 11 Sharma V, *J Sol-gel Sci Technol*, 84 (2017) 231.
- 12 Mehrotra R C & Rai A K, *Polyhedron*, 10 (1991) 1967.
- 13 Sharma N, Sharma R K, Bohra R, Drake J E, Hursthouse M B & Light M E, *J Chem Soc Dalton Trans*, (2002) 1631.
- 14 Gopal R, Sharma N, Nagar M, Chaudhary A, Mobin S M & Bohra R, *Main Group Met Chem*, 41 (2018) 43.
- 15 Badiei Y M, Jiang Y, Widger L R, Siegler M A & Goldberg D P, *Inorg Chim Acta*, 382 (2012) 19.
- 16 George K, Jura M, Levason W, Light M E & Reid G, *Dalton Trans*, 43 (2014), 3637.
- 17 Garcia-Garcia P, Martinez-Salasb P, Hernandez-Ortega S, Roman-Bravo P, Lopez-Cardoso M, Perez-Redondo M C, Vargas-Pineda G, Coterio-Villegas A M & Cea-Olivares R, *Polyhedron*, 37 (2012) 48.
- 18 Bhasin C P, Patel M B & Prajapati C G, *Int J Adv Res Chem Sci*, 1 (2014) 13.
- 19 El khaldy A A S, Janen A, Abushanab A & Stallworth E, *Main Group Met Chem*, 39 (2016) 167.
- 20 Khajuria R, Syed A, Kumar S & Pandey S K, *Bioinorg Chem Appl*, (2013) Article ID 261731.
- 21 El-Khaldy A A S, Okafor F & Shanab M A, *Int J Org Chem*, 4 (2014) 339.
- 22 Drill V A & DiPalma J R, *Drill's pharmacol med*, 4th edn, (McGraw Hill Book Co., New York) 1971.
- 23 Demkowicz S, Rachon J, Dasko M & Kozak W, *RSC Adv*, 6 (2016) 7101.
- 24 Cava S, Tebcherani S M, Souza I A, Pianaro S A, Paskocimas C A, Longo E & Varelo J A, *Mater Chem Phys*, 103 (2007) 394.
- 25 Levin I & Brandon D, *J Am Ceram Soc*, 81 (1998) 1995.
- 26 Wolverton C & Hass K C, *Phys Rev B*, 63 (2001) 024102.
- 27 Lukic I, Krstic J, Jovanovic D & Skala D, *Bio-Resource Tech*, 100 (2009) 4690.
- 28 Rozita Y, Brydson R & Scott A J, *J Phys Conf Ser*, 241 (2010) 012096.
- 29 Keyvani A, Saremi M & Sohi M H, *J Alloy Compd*, 506 (2010) 103.
- 30 Ramesh G, Mangalaraja R V, Ananthakumar S & Manohar P, *J Mater Sci*, 44 (2009) 1016.
- 31 Repo P, Talvitie H, Li S, Skarp S & Savin H, *Energy Procedia*, 8 (2011) 681.
- 32 Rogoan R, Andronescu E, Ghitulica C & Vasile B S, *UPB Sci Bul Series B*, 73 (2011) 67.
- 33 Vogel A I, *Text Book of Quantitative Chemical Analysis*, 5<sup>th</sup> edn, (Longmans, London) 1989.
- 34 Hossein-Zadeh M, Razavi M, Mirzaee O & Ghaderi R, *J King Saud Uni Eng Sci*, 25 (2013) 75.
- 35 Bradley D C, Mehrotra R C, Rothwell I P & Singh A, *Alkoxo and Aryloxo Derivatives of Metals*, (Academic Press, London) 2001.
- 36 Bradley D C, Halim F M A & Wardlaw W, *J Chem Soc*, (1950) 3450.
- 37 Sharma N, Sharma R K, Bohra R, *Main Group Met Chem*, 24 (2001) 781.
- 38 Dhammani A, Bohra R & Mehrotra R C, *Polyhedron*, 15 (1996) 1097.
- 39 Glidewell C, *Inorg Chim Acta*, 25 (1977) 159.
- 40 Lodziana Z & Parlinski K, *Phys Rev B Condensed Matter*, 67 (2003) 174106.
- 41 Warren B E, *X-ray diffraction*, (Dover publication, New York) 1990.
- 42 Tauc J, *Amorphous & Liquid Semiconductors*, (Plenum Press, New York) 1974.