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Materials Today: Proceedings XX (2016) XXX–XXX

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PMME 2016

Radiative Properties of Er^{3+} Doped Borosilicate Glasses for Fibre Optics Applications

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Abstract

In this paper Er^{3+} doped borosilicate glasses with compositions (50-x) B_2O_3 - (10+x) SiO_2 – 10 Na_2O – 20PbO – 10 ZnO – 0.3 Er_2O_3 (where x= 0, 5, 10, 15, 20, 25, 30, 35, 40) have been prepared by conventional melt quenching technique and their spectral and physical properties were investigated. Prepared glass specimens were characterized by XRD, FTIR, EDAX, SEM and TEM. Absorption and Fluorescence spectra were recorded in UV/VIS – NIR region at room temperature. Experimental oscillator strength was used to calculate the Judd-Ofelt parameters. These JO parameters were further used in the calculation of radiative properties. These laser parameters are useful for fibre optics applications.

Selection and Peer-review under responsibility of International Conference on Processing of Materials, Minerals and Energy (July 29th – 30th) 2016, Ongole, Andhra Pradesh, India.

Keywords: Borosilicate glasses; Physical Properties ; Absorption and Fluorescence spectra.

1. Introduction

Glasses doped with lanthanides are important due to their wide applications in various fields such as optical amplifiers, optical materials, temperature sensors and solar concentrators [1]. In Lanthanides doped glasses, in-homogeneously broadened emission profiles are common due to the dopant ion location in a variety of chemical environments [2]. Also in general glass host is more preferable then crystalline host because the glasses are produced in large volumes with high optical homogeneity and it is free of absorbing particle [1]. Also its has non-linear refractive indices and it acts like a good elastic matrix by taking the large amount of rare earth ions. Crystalline host doesn't possess such properties, this makes the glass a good optical medium. Recently,

2214-7853
Selection and Peer-review under responsibility of International Conference on Processing of Materials, Minerals and Energy (July 29th – 30th) 2016, Ongole, Andhra Pradesh, India.

borate based glasses like (55–x) H_3BO_3 + $20Li_2CO_3$ + 20ZnO + 5LiF+ xEr_2O_3 [1], (25 − x)Bi2O3:20Li2O:20ZnO:35B2O3:Nd2O3 [3], (50-x) PbO + (0+x) CaO + 12ZnO + 33B2O3 + 4Al2O3 + 1 Pr6 O11 [4], $60Li_2O–10Y_2O_3–(30−x)B_2O_3–xSm_2O_3$ [5], $70.28SiO_2 – 10.06Na_2O – 1.82CaO – 2.43K_2O – 15.21B_2O_3 – xPr_6O_{11}$ [6], have applications in the field of thin amorphous film for battery applications, bioactive glasses for tissue engineering, photonic applications, optic fibre amplifiers, short pulse lasers and fibre lasers etc. [7, 8].

As host matrix plays an important role in the properties of glasses, the combination of borate and silicate is important due to their melting point, thermal stability, chemically durable and good optical transparency towards the excitation and lasing wavelengths. Also alkali ions are thermally activated so that this can moves from one side to the other within the glass. Thus it is helpful in the easy replacement of other ions of the same valance and addition of alkali ion in borate network decrases the thermal expansion coefficient and increases T_g [9]. Addition of ZnO, a transition metal ion, in glassy system results in the different dopant sites by generating strong interaction that enhances the optical and spectral studies [10]. The properties of ZnO like optical, electrical and magnetic along with its non-toxicity and non- hygroscopic nature, makes ZnO doped glasses are useful in the development of opto electronic devices, solar converters, gas sensors and ultraviolet emitting lasers [11].

For the present work we have chosen (50-x) B_2O_3 – (10 + x) SiO_2 – $10Na_2O$ - 20 PbO – 10 ZnO doped with Er^{3+} which is prepared by melt quenching technique with varying concentration of SiO_2 and B_2O_3. In the present study we have to evaluate, (i) the different vibrational levels of borate network, (ii) Physical and optical properties of the glass samples, (iii) with the help of oscillator strength Judd-Ofelt parameters, (iv) study of luminescence spectra and (v) calculation of radiative properties of desired levels.

2. Experimental Details

The Er^{3+} doped borosilicate glasses were prepared by mixing the high purity A R grade reagents silicon dioxide (SiO_2), Borax ($Na_2B_4O_7.10H_2O$), Lead carbonate ($PbCO_3$) and Zinc carbonate $\{ZnCO_3\}_2$ $\{Zn(OH)_2\}_3$. The final chemical composition for present glass materials is (50-x) B_2O_3 - (10+x) SiO_2 – 10 Na_2O – 20PbO – 10 ZnO – 0.3 Er_2O_3 (where x= 0, 5, 10, 15, 20, 25, 30, 35, 40).

The chemical composition are of 10 g batches, were taken in agate mortar for proper grinding of the samples and then it was preheated in an electric furnace at 300^0 C for 1 hour. After that the temperature of the furnace was increased slowly up to the working temperature i.e. 1000^0 C and the samples were heated for 3 hours at this temperature. The melt was poured on to a preheated brass moulds at room temperature. The prepared samples were then annealed for 6 hours. The glass samples were cut and polished for optical measurements.

The Characterization of the borosilicate glass specimens was done to ensure the glass formation by X-ray diffraction. Composition and functional groups are justified by the EDX and FTIR respectively. Optical absorption spectra were recorded at room temperature using UV-VIS/NIR spectrophotometer model Varian carry with a resolution of 0.5 nm. The density of the glass specimens were calculated using Archimedes principle with toluene as immersion liquid. Optical path lengths of the glass materials were measured using digital Vernier callipers. SEM and TEM images were recorded by using FEI Quanta 200F and Tecnai G2 20 repectively.

3. Results and Discussion

XRD spectrum of the borosilicate glasses doped with Er^{3+} ions is shown in fig. 1. From figure 1 it is clear that Bragg's peak are absence, only a broad diffuse hump is around at lower region. This indicates the amorphous nature of the prepared samples, which is due to the low resolution limit of the XRD instrument.

EDX spectra of the present glass specimens have been shown in fig. 2. From this spectrum it is seen that all the elements are available in the final compositions. Figure 3 represents the FTIR spectrum of the title glass samples doped with Er^{3+} ions in the spectral range 400-4000 cm^{-1}. Different vibrations of the borate network are present in the spectral range 500 – 1500 cm^{-1} and their band assignments are given in table 1. From fig. 3 it can be seen that ZnO tetrahedral bond is present at ~474 (cm^{-1}). Different networking of borate groups are in the region 500-1500cm^{-1}. Tetrahedral υ_4 vibrations of BO_4 unit is nearby 510 cm^{-1}. B-O-B bending of the borate network is ~706cm^{-1} and penta borate groups are present at ~980 cm^{-1}. Position around 1077 cm^{-1} is due to the vibrational structure of pentaborate group along with BO^-_4 tetrahedral. Stretching and vibrations of B-O bond have the positions ~1224 and ~1305 cm^{-1} respectively. Band around the 1390 cm^{-1} shows the presence of the anti symmetric stretching vibrations with three non bridging oxygens of B – O – B groups. A broad band nearby 3410 cm^{-1} is due the the presence of OH group.

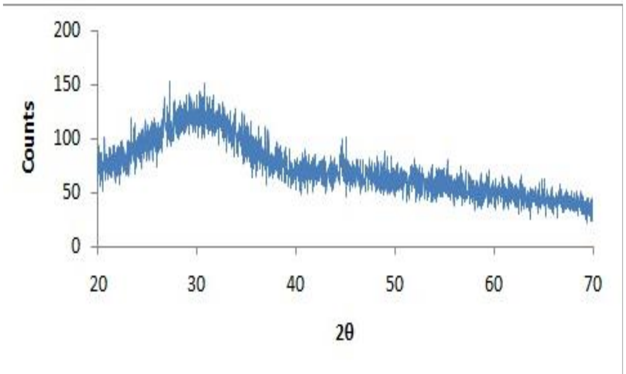

Figure 1: XRD spectrum of Er^{3+} doped borosilicate glass of E specimen.

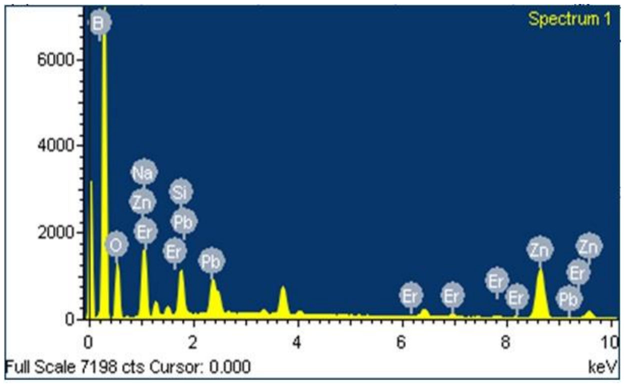

Figure 2: EDX spectrum of Er^{3+} doped borosilicate glass of E specimen.

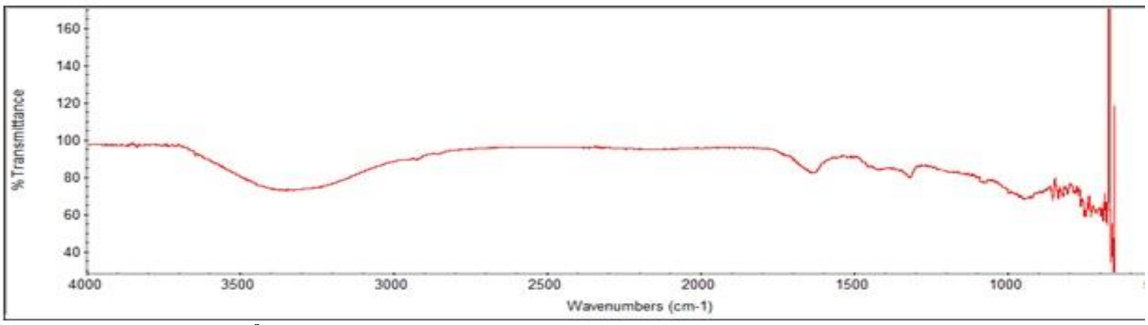

Figure 3: FTIR spectrum of Er^{3+} doped borosilicate glass of E specimen.

Table 1: Band positions in FTIR spectra of Er^{3+} doped borosilicate glass.

S. No.	Band Position (cm^{-1})	Structural vibrations
1)	~474	Presence of ZnO tetrahedral bond
2)	~ 510	υ_4 vibration of BO_4 tetrahedral
3)	~706	B-O-B bending
4)	~980	Penta borate groups
5)	~1077	Vibrations of pentaborate along with BO^-_4 tetrahedral
6)	~1224	Stretching of B – O bonds
7)	~1305	B – O vibrations of borate group
8)	~1390	Anti symmetric stretching vibrations with three non bridging oxygens of B – O – B groups
9)	~3410	Presence of OH group

Physical and optical properties of the present glass samples were computed and collected in table 2. For the present study we have calculated density, refractive index, average molecular weight, refractive index, dielectric constant, optical dielectric constant, molar volume, rare earth ion concentration, polaron radius, field strength, reflection losses, molar refractivity, metallization, electronic polarizability, molar polarizability, inter ionic separation, optical energy band gap and Urbach energy by using their respective formulae which are reported in literature [12]. From table 2 it is clear that some properties like density, average molecular weight, rare earth ion concentration, OPD, polaron radius, refractive index, dielectric constant, optical dielectric constant, reflection losses decreases by varying concentration of SiO_2 while some increases with it. On the other hand inter ionic separation, molar volume, metallization, field strength and electronic polarizability increases with increasing concentration of SiO_2.

Table 2: Physical and Optical parameters of Er^{3+} doped borosilicate glasses.

Parameters	Glass Name								
Physical parameters	A	B	C	D	E	F	G	H	I
Density(ρ) (gm/cm^3)	6.73	6.67	6.59	6.52	6.45	6.38	6.3	6.23	6.15
Thickness (cm)	0.15	0.2	0.11	0.2	0.2	0.2	0.21	0.19	0.21
Average molecular weight (M_{AV})(gm)	100.944	100.467	99.990	99.513	99.036	98.560	98.083	97.606	97.129
Rare earth ion concentration N (*10^{22})	1.606	1.599	1.587	1.578	1.569	1.559	1.547	1.537	1.525
Oxygen Packing Density (OPD)	140.609	136.697	132.406	128.351	124.328	120.337	116.195	112.274	108.210
Polaron radius r_p	7.265	7.256	7.237	7.224	7.210	7.195	7.176	7.161	7.155
Inter ionic separation r_i	8.539	8.551	8.572	8.589	8.606	8.623	8.646	8.664	8.687
Field strength (F) (10^{16})	3.169	3.177	3.193	3.205	3.218	3.231	3.247	3.261	3.267
Optical parameters									
Refractive index n_d	1.613	1.609	1.607	1.605	1.599	1.594	1.589	1.584	1.583
Dielectric constant (Є)	2.602	2.590	2.582	2.577	2.558	2.541	2.528	2.508	2.507
Optical dielectric constant	1.602	1.590	1.582	1.577	1.558	1.541	1.528	1.508	1.507
Molar volume V_m	14.999	15.062	15.173	15.263	15.354	15.448	15.569	15.667	15.793
Reflection Losses R	5.504	5.456	5.420	5.398	5.315	5.245	5.187	5.105	5.101
Molar Refractivity R_m	5.222	5.219	5.239	5.259	5.248	5.243	5.253	5.243	5.282
Metallization (M)	0.652	0.653	0.654	0.655	0.658	0.661	0.662	0.665	0.666
Molar polarizability (α_m)	2.072	2.071	2.079	2.087	2.082	2.080	2.084	2.080	2.095
Electronic polarazability (α_e) (10^{-24})	0.05177	0.05175	0.05195	0.05214	0.05204	0.05198	0.05209	0.05197	0.05237
Optical Energy band gap (E_o)	0.948	0.939	0.943	0.944	0.945	0.941	0.937	0.939	0.943

Urbach Energy	1.055	1.053	1.057	1.087	1.064	1.065	1.086	1.076	1.067

Absorption spectrum of the Er^{3+} doped borosilicate glass specimen was shown in fig. 8 in the wavelength region 300-2300nm. In this absorption spectrum nine absorption levels were observed in which one peak is in the NIR region and remaining eight peaks are in the UV/VIS region. These peaks are observed at 1531 nm ($^4I_{13/2}$), 1006 nm($^4I_{11/2}$), 827nm ($^4I_{9/2}$), 681 nm ($^4F_{9/2}$), 573nm ($^4S_{3/2}$), 550nm ($^4H_{11/2}$), 518nm ($^4F_{7/2}$), 481nm ($^4F_{5/2}$, $^4F_{3/2}$) and 407nm ($^2G_{9/2}$). The positions of the peaks observed are similar to the reported data in literature [1]. This indicates that Er^{3+} ions is homogeneous through the glass network without any changes and clusters. From this absorption spectra JO parameters were determined by using partial regression method. The calculated values of these parameters were collected in table 3. The trend of JO intensity parameters is $\Omega_2 > \Omega_4 > \Omega_6$ for glass samples A, B, C, D, E and I, $\Omega_4 > \Omega_2 > \Omega_6$ for F, G and H.

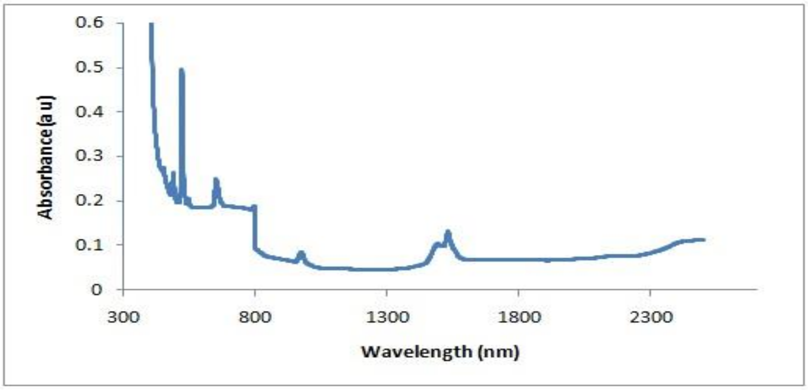

Figure 4: Absorption spectrum of Er^{3+} doped borosilicate glass of E specimen.

Table 3: Judd-Ofelt intensity parameters for Er^{3+} doped Borosilicate glasses.

Omega parameter	GLASS A	GLASS B	GLASS C	GLASS D	GLASS E	GLASSF	GLASSG	GLASS H	GLASS I
$\Omega_2(10^{-20})$	1.9698	1.7493	2.6668	2.1697	1.4678	1.3178	1.7316	1.776099	1.5169
$\Omega_4(10^{-20})$	1.4645	1.4346	1.7079	1.4569	1.3617	1.5196	2.0434	1.799279	1.3531
$\Omega_6(10^{-20})$	0.9401	1.2254	1.3804	0.6545	0.8297	0.7102	0.2394	0.4768	0.2998
Trend in omega parameters	$\Omega_2 > \Omega_4 > \Omega_6$	$\Omega_2 > \Omega_4 > \Omega_6$	$\Omega_2 > \Omega_4 > \Omega_6$	$\Omega_2 > \Omega_4 > \Omega_6$	$\Omega_2 > \Omega_4 > \Omega_6$	$\Omega_4 > \Omega_2 > \Omega_6$	$\Omega_4 > \Omega_2 > \Omega_6$	$\Omega_4 > \Omega_2 > \Omega_6$	$\Omega_2 > \Omega_4 > \Omega_6$

The fluorescence spectra have been recorded in visible region and collected in fig. 5. Radiative properties like transition probability (A), branching ratio (β) and radiative lifetimes were calculated by using the Judd-Ofelt parameters following the expressions given in literature [13]. For finding the application in fibre optics amplifier, gain band width and gain line width is also computed. Gain band width is detremined by multiplying effective band width ($\Delta\lambda_{eff}$) and stimulated emission cross-section (σ_p) and gain line width (FOM) is the product of radiative lifetime and stimulated emission cross-section (σ_p). Calculated values of all these parameters were collected in table 4. High values of these parameters show that borosilicate glass doped with Er^{3+} is suitable for fibre optic amplifier. The transition $^4\mathbf{S}_{3/2} \rightarrow {}^4\mathbf{I}_{15/2}$ is the suitable laser transition for preparing fibre optic amplifiers. Similar results were also reported in literature [1].

For measuring the colour of visible emission that the human eye perceives the Commission Internationale de l' Eclairage, (CIE) coordinates were calculated. It is a standard method for defining the colours and obtained by considering the sensitivity of human to human eye for different colours (wavelengths) [5]. The CIE chromaticity diagram is shown in figure 6. The CIE coordinates for this diagram is (x,y) = (0.3608,0.6287).

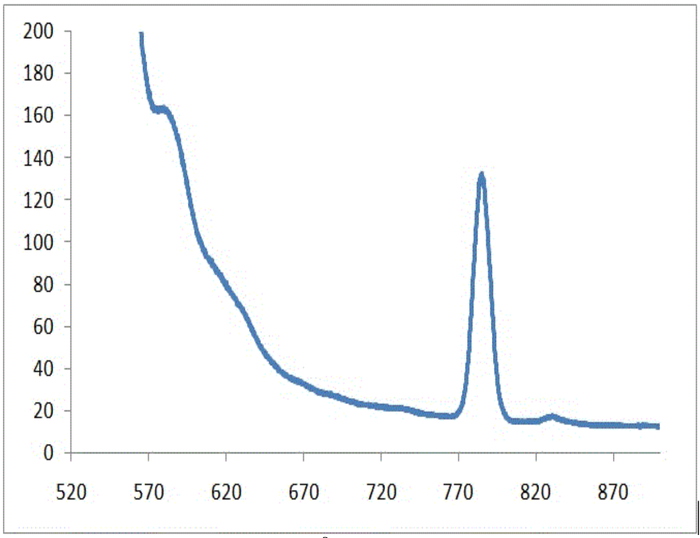

Figure 5: Fluorescence spectrum of Er^{3+} doped borosilicate glass of E specimen.

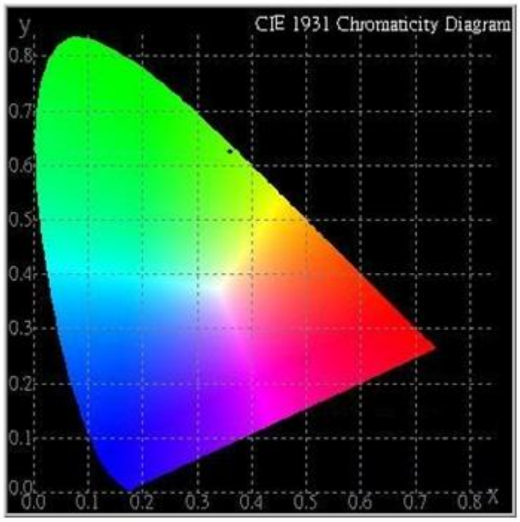

Figure 6: CIE Chromaticity diagram of Er^{3+} doped borosilicate glass of E specimen

.

Table 4: Radiative properties of Er3+ doped borosilicate glass of E specimen.

Parameters	$^4S_{3/2}\rightarrow{}^4I_{15/2}$	$^4F_{9/2}\rightarrow{}^4I_{15/2}$
(λ) nm	581	785
A(sec^{-1})	70.07919	166.2404
β	0.296544	0.703456
τ (μ sec)	1426.957	601.5384
$\Delta\lambda_{eff}$(nm)	16	14
σ_p (10^{-20}) (cm^2)	27.24	10.38
Gain Band Width	43.584	14.532
Gain Line width	388.7031	62.43968

The SEM and TEM image were also given in this paper and given in fig.7 and fig. 8. From SEM image it is seen that there are no grains in this image which confirms the amo rphous nature of the glass samples. TEM image shows the structure of the glass samples and confirms the results of FTIR.

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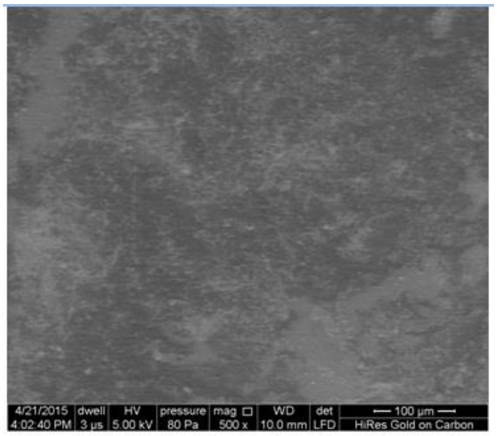

Figure 7: SEM image of Er^{3+} doped borosilicate glass of E specimen.

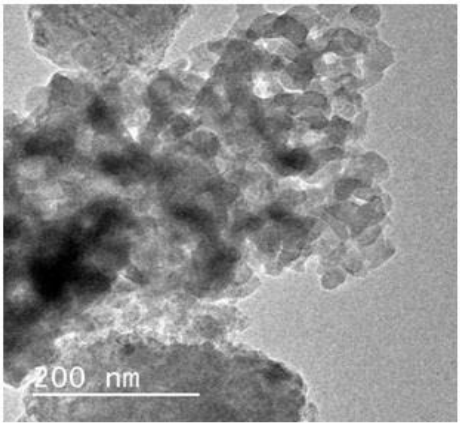

Figure 8: TEM image of Er^{3+} doped borosilicate glass of E specimen.

Conclusion

Present glass were prepared by melt quenching technique. Glass samples were characterized by XRD, EDX and FTIR. FTIR shows the various stretching and vibrational bonds of the present glasses. Physical and optical parameters of the glass samples were measuserd and calculated by using their respective formulas. Absorption spectra of the present glass samples were recorded in the UV/VIS-NIR region. Judd – Ofelt parameters were calculated with this absorption spectra. Fluorescence spectrum is recorded and radiative properties of the glass samples were calculated by using Judd- Ofelt parameters. . The transition $^4S_{3/2}\rightarrow{}^4I_{15/2}$ is the suitable laser transition for fibre optic amplifiers. CIE chromaticity coordinates were given for measuring the sensitivity of human eye towards emission wavelength. SEM and TEM images were recorded and given in this paper for defining nature of the glass samples.

Acknowledgements:

The authors would like to thanks to Dr. Jagdish Prasad, Principal, S. B. S. Govt. College, Rudrapur for lab facilities and Dr. R. K. Dutta, Nanoscience and Nanotechnology, IIT Roorkee for characterization of the present glass specimens. One of the author's are thankful to the UGC grant commission for financial support.

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Selection and Peer-review under responsibility of International Conference on Processing of Materials, Minerals and Energy (July 29th – 30th) 2016, Ongole, Andhra Pradesh, India.

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