PREPARATION OF SODIUM BETA-ALUMINA USING COMBUSTION SYNTHESIS

By

M. A. KALE * S. A. KALE ** C. P. JOSHI *** S. V. MOHARIL ****

* Department of Applied Physics, Dr. Babasaheb Ambedkar College of Engineering & Research, Nagpur, Maharashtra, India.
** Department of Electrical Engineering, Dr. Babasaheb Ambedkar College of Engineering & Research, Nagpur, Maharashtra, India.
*** Department of Physics, Ramdeobaba College of Engineering & Management, Nagpur, Maharashtra, India.
**** Department of Physics, RTM Nagpur University, Nagpur, Maharashtra, India.

Date Received: 05/02/2019 Date Revised: 24/05/2019 Date Accepted: 16/10/2019

ABSTRACT

The present work is on the study of Na β-Al_2O_3, a ceramic that belongs to a family of oxides exhibiting fast-ionic conductivity. Na β-Al_2O_3 has the best solid electrolyte properties. This material is appropriate for use in electronic devices. $NaA_{l7}O_{11}$, $NaAl_{11}O_{17}$, and $Na_2MgAl_{10}O_{17}$ are well known three compounds in the system of Sodium beta-alumina ceramics. NaAl7O11, $Na_2MgAl_{10}O_{17}$, and $NaAl_{11}O_{17}$ compounds were prepare by combustion method in a single step. Attempts to synthesize $NaAl_{11}O_{17}$ by combustion synthesis failed. Metal nitrates as oxidizer and urea as a fuel are the starting material for preparation of these compounds. The method used is combustion synthesis, which is feasible, low cost, and a time saving method. Among the three compounds used in this study, NaA_{l7} O_{11} and $Na_2MgAl_{10}O_{17}$ show better results. $NaAl_{11}O_{17}$ doped with rare earth ions like Cerium and Europium could be achieved.

Keywords: Aluminate, Combustion Synthesis, Photoluminescence, Phosphor, Spinel.

INTRODUCTION

Sodium beta alumina is a non-stoichiometric sodium aluminate known for its rapid transport of Na+ ions. The material was first introduced by Rankin and Merwin (1916). Initially it was found that beta alumina is a modification of Al_2O_3. But planes between the spinel blocks were filled by the alkali ions. Spacing between the spinel blocks is about 11.2 A°, and successive blocks are related by a two-fold screw axis.

A rhombohedral variant of β-alumina was reported in (Yamaguchi & Suzuki, 1968), which was denoted as β”-alumina because another compound, in the same work, was designated as β'-alumina. β''-Alumina is an isomorphic form of aluminium oxide (Al_2O_3), a hard polycrystalline ceramic. Beta-alumina is a good conductor of its mobile ion yet allows no non-ionic (i.e., electronic) conductivity. After a long study, researchers (Bettman & Terner, 1971) have recommended that b''-Alumina “compound” was only a high sodium b-alumina, but the unlucky nomenclature persists. Both the crystal has spinel block geometry, but the only difference in after the, X-ray diffraction studies (Bragg et al., 1931) sodium beta alumina was formulated by $Na_2O.11Al_2O_3$. This established the structure of crystal, position of the sodium ions in crystal and crystalline phase. Crystal structure of sodium beta alumina consists of “spinel blocks” of aluminum and oxygen which are placed apart by columns of aluminum-oxygen-aluminum parallel to the c, axis. It belongs to the space group P6, /mmc. The partially vacant structure of β”-alumina as three 11.2 A° spinel blocks related by a threefold screw axis was described by Yamaguchi and Suzuki. Thery and Briancon (1964) in their work also reported this phase, and given the idealized formula as $Na_2O.5A1_2O_3$. The first single-crystal determination of this structure with an MgO - containing crystal was performed and described the idealized formula of the ternary compound as $Na_2O.MgO.5Al_2O_3$. It was found that the binary compound is an omission solid solution having no ideal formula. They suggested that the structure to be rhombohedral which belongs to the space group R3m (Bettman & Peters, 1969).

Charge transport is determined by the structure of Na^+ beta-alumina in which two-dimensional conduction planes partially filled by Na^+ ions are separated by crystalline Al_2O_3 spinel blocks (Imai & Harata, 1972). The reported activation energy values for ion transport in the conduction plane are small that lies between 0.12 and 0.27 eV (Takahashi & Kuwabara, 1980).

A variety of techniques i.e., starting from simple mechanical mixing of oxides to sol-gel method, have been developed for formation of beta alumina ceramics (Hodge, 1983; Yoldas et al., 1980; Chowdhry & Cannon, 1978; Beckers et al., 2000). The samples which were obtained were found to be single crystal or polycrystalline ceramics carrying different electrical properties. Because of two-dimensional structure, a single crystals beta-alumina are anisotropic in nature. But in case of polycrystalline, it shows isotropic property as it depends on grain-sizes, and the conduction in sintered polycrystalline samples is restricted by the contribution of the grain boundary and is generally isotropic and lower than in the single crystal (Imai & Harata, 1972).

1. Experimental Method

All the samples were prepared by a well known combustion synthesis. All the ingredients used, viz. sodium nitrate, aluminium nitrate, magnesium nitrate, and urea were of AR grade. The concentration and stoichiometric weights of the ingredients are shown in Table 1. All the starting chemicals were transferred into mortar and mixed them for one or one and a half hour to form a thick paste. The paste is then poured into a china dish. The china dish containing a thick paste was kept in a preheated furnace to 500 °C. Initially the paste starts to boil and fumes come out from the furnace. After few minutes, the mixture gets swelled, foamed, and ignited. The process of combustion was completed within 5 minutes. The dish was removed from the frurnace and the foam was crushed to get white fluffy fine powder. This fine powder was used to prepared phosphor by doping various activators. Care was taken while doping of activators. Proper amount of dopant is added in metal nitrate.

S.No.	Compound	Molar Ratios of the Constituents
1	$NaAl_7O_{11}$	$NaNO_3$: $Al(NO_3)_3.9H_2O$: Urea ; 1:7:18.33
2	$NaAl_{11}O_{17}$	$NaNO_3$: $Al(NO_3)_3.9H_2O$: Urea ;1:11:28.33
3	$Na_2MgA_{11}0O_{17}$	$NaNO_3$: $Al(NO_3)_3.9H_2O$: $Mg(NO_3)_2$: Urea 2:1:10:28.33

Table 1. Data for Molar Ratios of Constituents used to Prepare Various Aluminates

For confirmation of formation of single crystal of the compound, X-ray diffraction patterns were recorded using Philips PANalytical X'pert Pro diffractometer. Photoluminescence characteristics were studied using Hitachi F-4000 spectro- fluorimeter with spectral slit widths of 1.5 nm.

2. Result

The crystallization and phase purity of the prepared host compound is confirmed by taking XRD of the sample. Figure 1 gives the X ray diffraction graph for $NaAl_7O_{11}$ compound. The patterns of the prepared compound are verified by comparing it with file 21-1095 of JCDPS data. The work is seen to match with the standard value.

Attempts to synthesize $NaAl_{11}O_{17}$ by combustion synthesis failed.

Figure 2 shows the stick pattern deduced from X-ray diffraction data for $Na_2MgAl_{10}O_{17}$ sample. Thus to verify the formation of the compound, the work is compared with ICDD data file 35-0439 and it is found to be an excellent match.

2.1 Rare-Earth Activators

2.1.1 Ce^{3+}

The 4f-5d transitions corresponding to optical absorption and fluorescence of Ce^{3+} in crystals are parity-and spin-

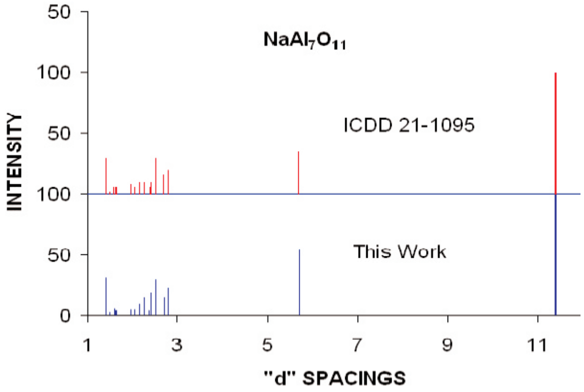

Figure 1. XRD Pattern of $NaAl_7O_{11}$ Matched with ICDD 21-1095

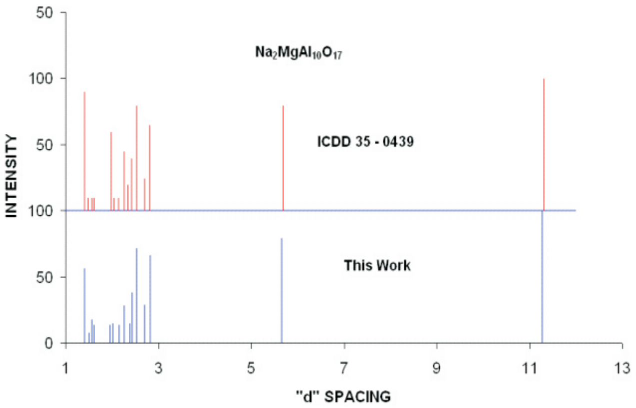

Figure 2. XRD Pattern of Na$_2$MgAl$_{10}$O$_{11}$ matched with ICDD 35-0439

allowed so that lifetimes of the fluorescence are in the range of 10-60 ns. The spatially diffused 5d electron orbital extends outward from the ion to overlap the neighboring ligand ions, and is more strongly influenced by their motion. In consequence, the optical properties depend strongly on structure of host crystals. Both absorption and emission have a usually broad band character, showing splitting characteristic of 2Fj states. As the position of 5d band itself depends on the host, not only the stoke's shift, but also the spectral positions of both the excitation and emission bands are host dependent. Energy level diagram of Ce3+ is shown in Figure 3.

The photoluminescence spectra of phosphor NaAl$_7$O$_{11}$:Ce^{3+} (1mol%) are shown in Figure 4. PL emission spectrum of Ce^{3+} in NaAl$_7$O$_{11}$ shows a broadband in the range of 300-420 nm with maximum peak near at 348 nm (curve a). In case of Ce^{3+} ion, the transition is taking place from 5d level to the ground level. In the spectra, the excitation band is most prominent around 271 nm as shown in Figure 3 (curve b).

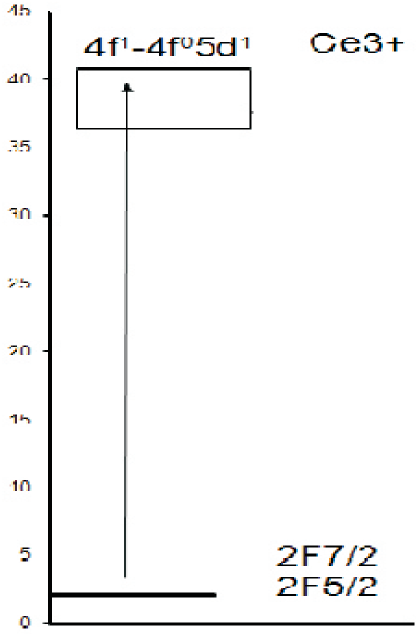

Figure 3. Energy Level diagram of Ce^{3+}

2.1.2 Eu^{3+}

The luminescence of Eu^{2+} ions in different hosts has recently attracted much attention due to its peculiar properties. Its excitation and emission spectra are usually broadband due to transitions between the 4f^7 (^{8}S$_{7/2}$) ground state and the crystal field components of the 4f^{6}5d^1 excited state configuration Eu^{2+} emission results from two types of transitions. The most common is that due to 4f^{6}5d^1 → 4f^6 (^{8}S$_{7/2}$). As the position of the band corresponding to 4f65d1 configuration is strongly influenced by the host, the emission can be anywhere from 365 nm to 650 nm.

Since the 4f → 5d transition is an allowed electrostatic dipole transition, the absorption and emission of Eu^{2+} is very efficient in many hosts, which makes the Eu^{2+} doped phosphors of practical importance. Though both the excitation and emission originate in allowed transitions, the decay time is not very short as in Ce^{3+}, but of the order of fraction of ms; the reason being that, the transitions are not of purely f → d type, but some admixture of other states. When 4f^{6}5d^1 band is higher than ^{6}P$_j$ states and the f → f

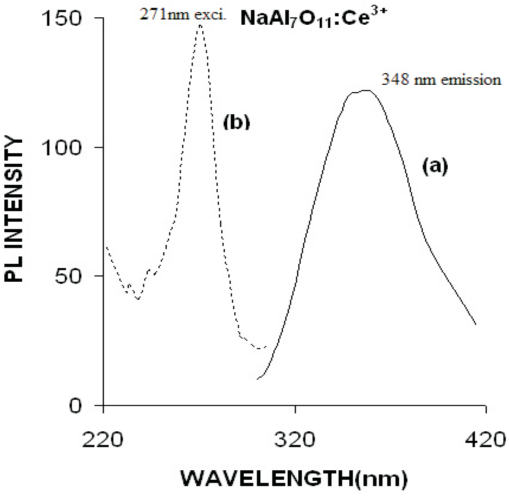

Figure 4. Photoluminescence of NaAl$_7$O$_{11}$:Ce^{3+}

transitions become parity-allowed, sharp lines corresponding to $^6P_j \rightarrow {}^8S_{7/2}$ transitions are observed. These transitions have longer decay time; of the order of several microsecond. In many compounds d → f emission is observed at room temperature, while at low enough temperatures sharp line e → f emission becomes dominant. Energy level diagram of Eu^{3+} is shown in Figure 5.

The photoluminescence study of Europium doped $NaAl_7O_{11}$ phosphor is shown in Figure 6. In this phosphor we found both Eu^{2+} and Eu^{3+} emission. In this phosphor the band of excitation for Eu^{2+} emission is located at 320 nm (curve b) and exhibits emission at around 413 nm (curve a). The emission of Eu^{3+} arises due to transition from $^5D_0N^7F_J$ transition. Emission in $NaAl_7O_{11}:Eu^{3+}$ is observed in the form of prominent line around 613 nm (curve c). The excitation band corresponding to CT state is around 254 nm (curved).

Attempts were made to synthesize $NaAl_7O_{11}$ doped with Cu^+ by combustion synthesis. After getting the result of photoluminescence for $NaAl_7O_{11}$ it is found that no emission was found in this compound. So it is concluded that $NaAl_7O_{11}$ doped with Cu^+ is not formed by combustion synthesis.

We also tried to study the PL characteristics of $Na_2MgAl_{10}O_{17}$ by using Mn^{2+} activator, but found no emission.

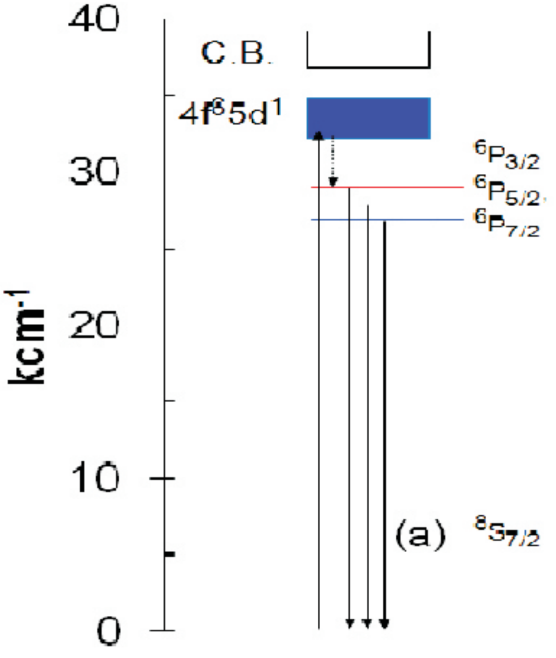

Figure 5. Energy Level diagram of Eu^{3+}

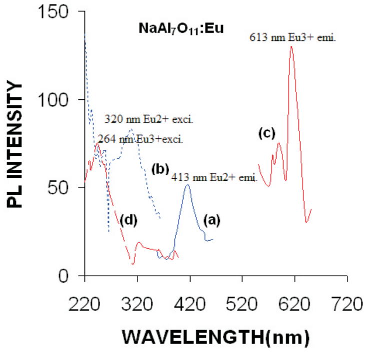

Figure 6. Photoluminescence of $NaAl_7O_{11}:Eu^{3+}$

Conclusion

It is thus seen that the compounds $NaAl_7O_{11}$ and $Na_2MgAl_{10}O_{17}$ are successfully prepared in one step by combustion synthesis. The compounds are confirmed by X-ray diffraction. $NaAl_{11}O_{17}$ is not formed by combustion synthesis. In compound $NaAl_7O_{11}$, appreciable luminescence has been found when this compound was doped with various activators. The emission of 348 nm at excitation of 271 nm is found in $NaAl_7O_{11}$ when doped with Ce^{3+}. Similarly in $NaAl_7O_{11}:Eu^{2+}$ emission is 413 nm for excitation at 320 nm and for $NaAl_7O_{11}:Eu^{3+}$ emission is 613 nm at excitation of 254 nm.

References

[1]. **Beckers, J. V. L., Van Der Bent, K. J., & De Leeuw, S. W. (2000).** Ionic conduction in Na+-b-alumina studied by molecular dynamics simulation. *Solid State Ionics*, 133(3-4), 217-231. https://doi.org/10.1016/S0167-2738(00)00685-8

[2]. **Beevers, C. A., & Ross, A. (1937).** The crystal structure of "beta alumina" $Na_2O11Al_2O_3$. *Zeitschrift für Kristallographie-Crystalline Materials,* 97(1-6), 59-66. https://doi.org/10.1524/zkri.1937.97.1.59

[3]. **Bettman, M., & Peters, C. R. (1969).** Crystal structure of Na_2O. MgO. $5Al_2O_3$ [sodium oxide-magnesia-alumina] with reference to Na_2O. $5Al_2O_3$ and other isotypal compounds. *The Journal of Physical Chemistry,* 73(6), 1774-1780. https://doi.org/10.1021/j100726a024

[4]. **Bettman, M., & Terner, L. L. (1971).** Structure of sodium oxide-4 magnesium oxide-15 aluminum oxide, a variant

of beta.-alumina. *Inorganic Chemistry*, 10(7), 1442-1446. https://doi.org/10.1021/ic50101a025

[5]. Bragg, W. L., Gottfried, C., & West, J. (1931). The structure of β - alumina. *Zeitschrift für Kristallographie-Crystalline Materials,* 77(1-6), 255-274. https://doi.org/10.1524/zkri.1931.77.1.255

[6]. Chowdhry, U., & Cannon, R. M. (1978). Microstructural evolution during the processing of sodium β-alumina. In Processing of Crystalline Ceramics (pp. 443-455). *Springer, Boston, MA.* https://doi.org/10.1007/978-1-4684-3378-4_37

[7]. Hodge, J. D. (1983). Kinetics of the b to b Transformation in the System Na$_2$oA1$_2$o$_3$. *Journal of the American Ceramic Society,* 66(3), 166-169. https://doi. org/10.1111/j.1151-2916.1983.tb10009.x

[8]. Imai, A., & Harata, M. (1972). Ionic conduction of impurity-doped β-alumina ceramics. *Japanese Journal of Applied Physics,* 11(2), 180-185.

[9]. Rankin, G. A., & Merwin, H. E. (1916). The Ternary System CaOAl2O3-MgO. *Journal of the American Chemical Society,* 38(3), 568-588. https://doi.org/10.1021/ja02260a006

[10]. Sartori, S., Martucci, A., Muffato, A., & Guglielmi, M. (2004). Sol-gel synthesis of Na+ beta-Al$_2$O$_3$ powders. *Journal of the European Ceramic Society,* 24(6), 911-914. https://doi.org/10.1016/S0955-2219(03)00513-2

[11]. Sudworth, J. L., Barrow, P., Dong, W., Dunn, B., Farrington, G. C., & Thomas, J. O. (2000). Toward commercialization of the beta-alumina family of ionic conductors. *MRS Bulletin,* 25(3), 22-26. https://doi.org/10.1557/mrs2000.14

[12]. Takahashi, T., & Kuwabara, K. (1980). ß-Al2O3 synthesis from m-Al$_2$O$_3$. *Journal of Applied Electrochemistry* , 10(3), 291-297. https://doi.org/10.1007/BF00617203

[13]. Thery, J., & Briancon, D. (1964). Structure and Properties of Sodium Aluminates. Rev. *Hautes Temp. Réfract*, 1(2), 221-227.

[14]. Yamaguchi, G., & Suzuki, K. (1968). On the structures of alkali polyaluminates. *Bulletin of the Chemical Society of Japan,* 41(1), 93-99. https://doi.org/10.1246/bcsj.41.93

[15]. Yoldas, B. E., BE, Y., & DP, P. (1980). Formation of continuous beta alumina films and coatings at low temperatures. American Ceramic Society Bulletin, 59, 640-642.

ABOUT THE AUTHORS

Dr. Minakshi A. Kale is working as an Assistant Professor and Head of the Department of Physics at Dr. Babasaheb Ambedkar College of Engineering and Research, Nagpur. She is having 20 yrs of teaching experience. She has published several research papers in International/National Journals, few of which are Scopus indexed and also presented papers in International/National conferences.

S. A. Kale in the Department of Electrical Engineering, Dr. Babasaheb Ambedkar College of Engineering & Research, Nagpur, Maharashtra, India.

C. P. Joshi in the Department of Physics, Ramdeobaba College of Engineering & Management, Nagpur, Maharashtra, India.

S. V. Moharil in the Department of Physics, RTM Nagpur University, Nagpur, Maharashtra, India.