

# Optical Properties of Some $A_2BCl_4$ Type Chlorides

D. H. Gahane, B. M. Bahirwar, and S. V. Moharil

**Abstract**—Efficient luminescence is reported for the first time in  $Eu^{2+}$  activated double Chlorides  $A_2BCl_4$  (A=Alkali metal, B=Alkaline earth element). A simple wet-chemical preparation is described. Emission intensities are comparable to that of the commercial phosphor. Excitation covers near UV region. These phosphors may be useful for applications like solid state lighting, scintillation detectors and X-ray storage using photo-stimulable phosphors.

**Keywords**—Alkaline Earth, Chloride, Luminescence.

## I. INTRODUCTION

$Eu^{2+}$  activated phosphors find use in many applications. e.g.  $BaMgAl_{10}O_{17}:Eu$  and  $Sr_5(PO_4)_3Cl:Eu$  are efficient tricolor lamp phosphors [1].  $BaFBr:Eu$  is used as intensifier for X-ray imaging films [2], [3] as well as for x-ray imaging using photo-stimulated luminescence (PSL) [4].  $CaSO_4:Eu$  is near UV emitting phosphor for photoluminescent liquid crystal displays (PLLCD) [5].  $SrB_4O_7:Eu$  is an efficient phosphor for tanning lamps [6]. Use of  $SrMgAl_{10}O_{17}:Eu$  [7] and  $CaMgSi_2O_6:Eu$  [8] has been advocated as blue emitting component of a phosphor blend for plasma display panels (PDP).  $CaMgSi_2O_6:Eu$  coactivated with  $Mn^{2+}$  has also been proposed for solid state lighting [9]. Nitrides such as  $Sr_2Si_5N_8:Eu^{2+}$  [10], [11] have shown high potential as red-emitting conversion phosphors for two phosphor white light emitting diodes (WLED).  $SrGa_2S_4:Eu^{2+}$  [12] and  $SrSi_2O_2N_2:Eu^{2+}$  [13] are used as green emitting phosphors for similar application.  $Ca$ -alfa-Sialon: $Eu^{2+}$  [14] finds use as a yellow emitting phosphor in single chip phosphor (SCP) converted LED lamp.  $CaS:Eu^{2+}$  has been proposed as a red-emitting phosphor for white UVLED [15]. Calcium sulfides codoped with europium and  $Sm/Pr^{3+}$  are well-known infrared converting phosphors [16], [17]. Intense thermoluminescence was found in  $Eu^{2+}$  activated phosphors like  $LiCaAlF_6:Eu$  [18] and  $K_2Ca_2(SO_4)_3:Eu$  [19] which can be useful in dosimetry of ionizing radiations and related applications.

Efficient emission of  $Eu^{2+}$  luminescence has been observed in alkaline earth chlorides [20]. Recently, use of  $CaCl_2:Eu^{2+}$  phosphor for phototherapy lamps has been proposed [21]. Several solid solutions of alkaline earth halides are known [22]-[25]. There is no information on  $Eu^{2+}$  luminescence in these compounds.

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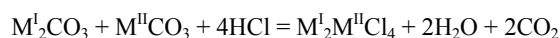
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Several tetrachlorides of the type  $A_2BCl_4$  are known. Where A=Alkali Metal and B=Alkaline earth element. Amongst such chlorides included in the present investigations are  $K_2BaCl_4$ ,  $K_2SrCl_4$ , and  $Cs_2MgCl_4$ . We observed very intense  $Eu^{2+}$  luminescence in these compounds. These results are reported in this paper.

## II. EXPERIMENTAL

Samples were prepared by dissolving desired quantities of metal carbonates and  $Eu_2O_3$  in HCl. The reactions proceed as:



Excess acid was then boiled off and the solutions were evaporated to dryness. The resulting mass was dried at 475K for 2h in air, crushed to fine powders (<72mm) and then annealed for 1h at 925K in a reducing atmosphere provided by burning charcoal so as to reduce the activator to divalent state. The annealed powders were quickly sandwiched between quartz plates and transferred to photoluminescence (PL) cell. Of about 300mg powder was used every time. Photoluminescence spectra were recorded at the room temperature in the spectral range 220–700nm on Hitachi F-4000 spectro-fluorimeter with spectral slit widths of 1.5nm. Precision of the method was adequate. The variations in PL intensities for several trials for the same phosphor were within 5%. X-ray diffraction patterns were recorded on Philips PANalytical X'pert Pro diffractometer.

## III. RESULTS AND DISCUSSION

As all the results are related to PL of  $Eu^{2+}$ , general features of the emission are first briefly mentioned.  $Eu^{3+}$  or  $Eu^{2+}$  can be identified from the characteristic photoluminescence they exhibit. f-f transitions of  $Eu^{3+}$  are forbidden and  $Eu^{3+}$  PL is in general weak, unless there is excitation by charge transfer or energy transfer from a sensitizer. In general, narrow emission bands may be observed at about 570, 590, 610, 650 and 700nm corresponding to transitions  $^5D_0 \rightarrow ^7F_0, ^7F_1, ^7F_2, ^7F_3, ^7F_4$ , respectively. Exact positions, fine structure and relative intensities of these bands depend on the local environment of  $Eu^{3+}$  ion.

$Eu^{2+}$  emission arises from the lowest band of  $4f^65d^1$  configuration to  $^8S_{7/2}$  state of  $4f^7$  configuration. The excitation arises from the transition from  $^8S_{7/2}$  state of  $4f^7$  configuration to the states belonging to  $4f^65d^1$  configuration. The ground state electronic configuration of  $Eu^{2+}$  is  $4f^7$ . This results in a  $^8S_{7/2}$  level for the ground state. The next  $f^7$  manifold ( $^6P_j$ ) lies approximately  $28000cm^{-1}$  higher. The lowest lying  $4f^65d$  levels begin near  $34000cm^{-1}$  and are labeled  $^8H_j$  for the free



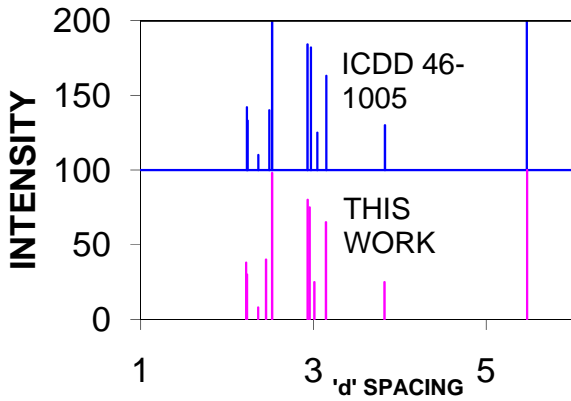


Fig. 3 XRD pattern for  $K_2Ba_{0.9}Eu_1Cl_4$  Stick pattern obtained from XRD pattern obtained with this work is compared with the ICDD data for  $CsSrCl_3$

$K_2SrCl_4$  crystallizes to hexagonal structure with space group  $-3m$  with unit cell parameters  $a = b = 12.981\text{\AA}$ ,  $c = 8.044\text{\AA}$  (Fig. 4).

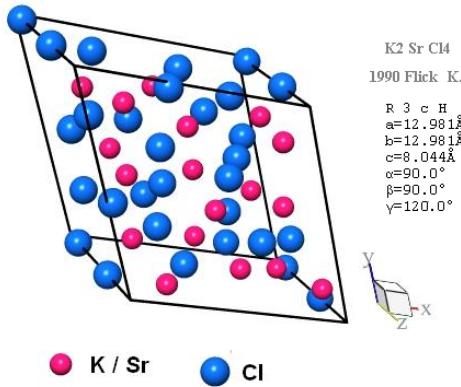


Fig. 4 Unit cell of  $K_2SrCl_4$

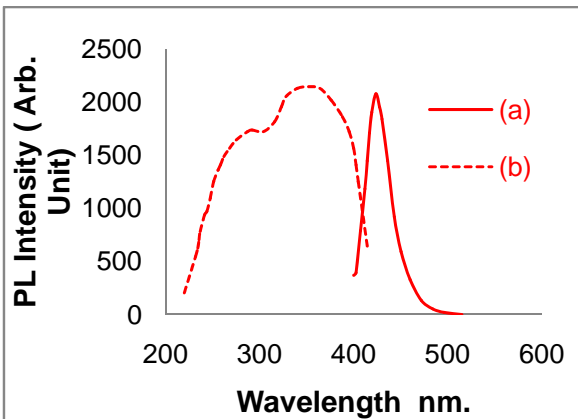


Fig. 5 PL spectra for  $K_2SrCl_4$  (a)  $K_2SrCl_4$  Emission for 365nm excitation (b)  $K_2SrCl_4$  excitation for 424nm emission

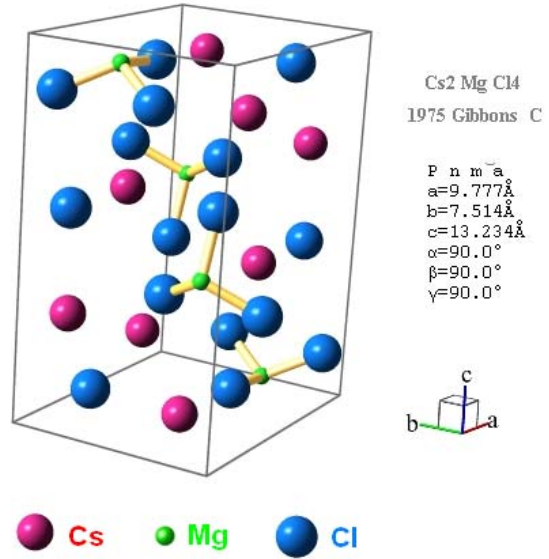


Fig. 6 Unit cell of  $Cs_2MgCl_4$

PL spectra for  $K_2SrCl_4$  are quite similar to that for  $K_2BaCl_4$ , but shifted to longer wavelengths. Emission corresponding to 365nm excitation (Fig. 5 (a)) is in violet region with maximum around 424nm. Excitation spectra consists of several overlapping bands around 241, 287, 340, 364 and 395nm (Fig. 5 (b)). Compared to  $K_2BaCl_4$  the excitation in near UV region is much more prominent. Emission intensity is also highest for  $K_2SrCl_4$ .

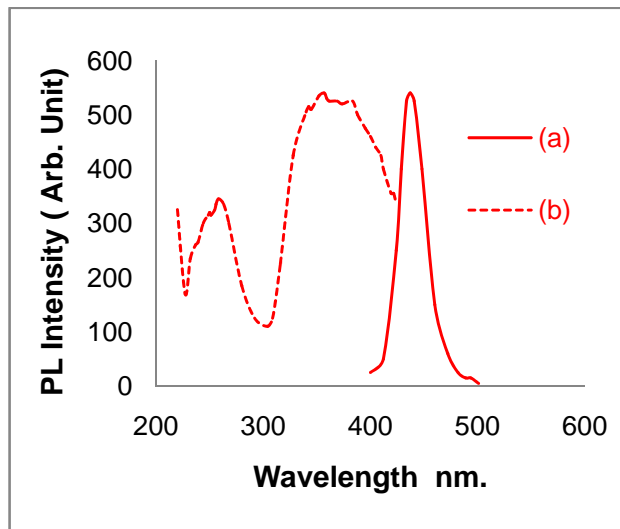


Fig. 7 PL spectra for  $Cs_2MgCl_4$  (a)  $Cs_2MgCl_4$  Emission for 360nm excitation (b)  $Cs_2MgCl_4$  excitation for 437nm emission

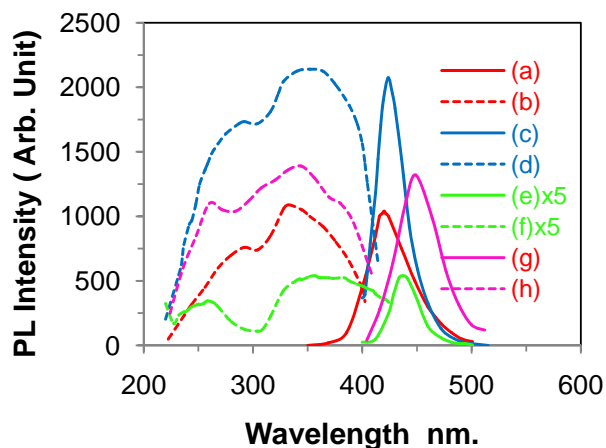


Fig. 8 PL spectra for  $K_2BaCl_4$ ,  $K_2SrCl_4$  and  $Cs_2MgCl_4$  (a)  $K_2BaCl_4$  Emission for 330nm excitation (b)  $K_2BaCl_4$  excitation for 420nm emission (c)  $K_2SrCl_4$  Emission for 365nm excitation (d)  $K_2SrCl_4$  excitation for 424nm emission (e)  $Cs_2MgCl_4$  Emission for 360nm excitation (f)  $Cs_2MgCl_4$  excitation for 437nm emission For comparison PL spectra for commercial lamp phosphor (BAM, sylvania 2466 blue) are included (g) BAM Emission for 365nm excitation (h) BAM excitation for 450nm emission

Fig. 6 shows unit cell of  $Cs_2MgCl_4$ . In contrast to  $K_2BaCl_4$  and  $K_2SrCl_4$ ,  $Cs_2MgCl_4$  shows very weak blue emission at 437nm (Fig. 7 (a)). Excitation spectra consist of several overlapping bands at 258, 356, 368, 583 and 409nm (Fig. 7 (b)).

To get an idea of PL intensity of phosphor prepared, PL spectra for the commercial BAM (Sylvania 2466) are also compared (Figs. 8 (g) and (h)). Peak height for  $K_2SrCl_4$  is more than that of BAM. Emission intensities of  $K_2BaCl_4$  are comparable to BAM.

#### IV. CONCLUSIONS

A simple procedure to prepare  $Eu^{2+}$  activated  $A_2BCl_4$  type chloride phosphors is described.  $Eu^{2+}$  emission in all these  $A_2BCl_4$  type chlorides except  $Cs_2MgCl_4$  is very intense. Emission intensity varies in order  $Cs_2MgCl_4 < K_2BaCl_4 < K_2SrCl_4$ .

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#### REFERENCES

- [1] B.M.J. Smets, Mater. Chem. Phys. 16 (1987) 283.
- [2] A.L.N. Stevels, F. Pingault, Philips Res. Rep. 30 (1975) 277.
- [3] S.V. Moharil, Bull. Mater. Sci. 17 (1994) 25.
- [4] K. Takahashi, J. Miyahara, Y. Shibahara, J. Electrochem. Soc. 132 (1985) 1492.
- [5] A. Vecht, A.C. Newport, P.A. Bayley, W.A. Crossland, J. Appl. Phys. 84 (1998) 3827.
- [6] R.P. Yavetskiy, E.F. Dolzhenkova, A.V. Tolmachev, S.V. Parkhomenko, V.N. Baumer, A.L. Prosvirnin, J. Alloys Compd. 441 (2007) 202.
- [7] D.-S. Xing, K.-W. Cheah, P.-Y. Cheng, J. Xu, J.-X. Shi, H.-B. Liang, M.-L. Gong, Solid State Commun. 134 (2005) 809.

- [8] K.Y. Jung, Jpn. J. Appl. Phys. 46 (2007) 5809.
- [9] S.H. Lee, J.H. Park, S.M. Son, J.S. Kim, H.L. Park, Appl. Phys. Lett. 89 (2006) 221916.
- [10] Y.Q. Li, J.E.J. van Steen, J.W.H. van Krevel, G. Botty, A.C.A. Delsing, F.J. DiSalvo, G. de With, H.T. Hintzen, J. Alloys Compd. 417 (2006) 273.
- [11] R. Mueller-Mach, G.O. Mueller, P.J. Schmidt, D.U. Wiechert, J. Meyer, Proc. SPIE 5941 (2005) 59410Z.
- [12] R. Mueller-Mach, G.O. Mueller, T.A. Trottier, M.R. Krames, A. Kim, D.A. Steigerwald, Proc. SPIE 4776 (2002) 131.
- [13] Y.Q. Li, A.C.A. Delsing, G. de With, H.T. Hintzen, Chem. Mater. 17 (2005) 3242.
- [14] J.W.H. van Krevel, J.W.T. van Rutten, H. Mandal, H.T. Hintzen, R. Metselaar, J. Solid State Chem. 165 (2002) 19.
- [15] C. Guo, D. Huang, Q. Su, Mater. Sci. Eng. B 130 (2006) 189.
- [16] M. Weidner, A. Osvet, G. Schiering, M. Batentschuka, A. Winnacker, J. Appl. Phys. 100 (2006) 073701.
- [17] Y. Kojima, T. Toyama, J. Alloys Compd. 475 (2009) 524.
- [18] G.A. Aghalte, S.K. Omanwar, S.V. Moharil, Phys. Stat. Solidi A 204 (2007) 1561.
- [19] P.D. Sahare, S.V. Moharil, J. Phys. D: Appl. Phys. 23 (1990) 1990.
- [20] T. Kobayashi, S. Mroczkowski, J.F. Owen, L.H. Brixner, J. Lumin. 21 (1980) 247.
- [21] Zhendong Hao, Jiahua Zhang, Xia Zhang, Xinguang Ren, Yongshi Luo, Shaozhe Lu, Xiaojun Wang, J. Phys. D: Appl. Phys. 41 (2008) 182001.
- [22] C. Brauer, G. Mueller, Z. Anorg. Allg. Chem. 295 (1958) 218.
- [23] T. Monika, Olejak-Chodan, H.A. Eick, J. Solid State Chem. 69 (1987) 274.
- [24] W. Lasocha, H.A. Eick, J. Solid State Chem. 75 (1988) 175.
- [25] B. Frit, C.R. Seances Acad. Sci., Ser. C 267 (1968) 1046.
- [26] J.K. Lawson and S.A. Payne Phys. Rev. B 47 (1993) 14003.
- [27] Mary V. Hoffman J. Electrochem. Soc. 118 (1971) 0933.
- [28] Mary V. Hoffman J. Electrochem. Soc. 119 (1972) 0905.
- [29] M.J. Freiser, S. Methfesskl and F. Holtzberg J. Appl. Phys. 39 (1968) 900.
- [30] F.M. Ryan, W. Lehmann, D.W. Feldman and J. Murphy, J. Electrochem. Soc. 121 (1974) 1475.