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 tri-color 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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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:

$$M^I_2CO_3 + M^{II}CO_3 + 4HCl = M^I_2M^{II}Cl_4 + 2H_2O + 2CO_2$$
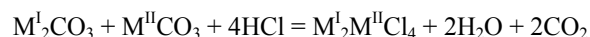
Excess acid was then boiled off and the solutions were evaporated to dryness. The resulting mass was dried at 475K for 2h in air, crushed to fine powders (<72mm) and then annealed for 1h at 925K in a reducing atmosphere provided by burning charcoal so as to reduce the activator to divalent state. The 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

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ion. The $4f^6 5d$ levels experience much more crystal field splitting than the levels of $4f^7$ configuration due to the increased spatial extent of the 5d orbitals and often are the metastable state, or the lowest excited state, when the Eu^{2+} ion is incorporated in a crystalline host. The effect of the crystal field of octahedral symmetry on the 5d electron is to split the 5d orbitals into two components t_{2g} and e_g. For lesser symmetries, the splitting can be as much as five fold. The isotropic part of the exchange interaction between 5d and 4f electrons results in an exchange splitting into states with total spins of S=7/2 and 5/2. Thus for the absorption spectra of Eu^{2+} in the solids, the lowest energy band arises from the state described by the notation $|4f^6(^7F_J)e_g, S=7/2>$ [26]. The lowest energy configuration corresponds to the situation where $^7F_J(4f^6)$ state couples to the 5d e_g orbital such that all spins are parallel. Spectral positions of these bands vary a great deal from lattice to lattice. The most commonly observed emission is the dipole and spin allowed d-f-emission starting from the relaxed $4f^6(^7F_0)5d^1$ level (Fig. 1 (b)). Due to allowed nature of the transition, d-f emission is intense. In some cases especially in certain fluorides, position of the band corresponding to f-d transition lies above f-f levels (Fig. 1 (a)). Line emission corresponding to $^6P_{j\rightarrow}, ^8S_{7/2}$ transitions of $4f^7$ configuration is then observed [27,28]. A third type of emission involving the Eu^{2+} ions is often characterized by a very large Stokes (5000 – 10000 cm^{-1}) shift, very broad (>4000 cm^{-1}) emission bands, and deviating temperature behavior. This "anomalous" emission has been attributed to auto-ionization of the 5d electron to conduction band level (Fig. 1 (c)). The electron is localized on the cations around the hole that stays behind on Eu^{2+}; and an impurity trapped exciton state is created. The "anomalous" emission is the radiative transfer of the electron back to the ground state of Eu^{2+}. Auto-ionization can also be a cause for absence of Eu^{2+} luminescence.

Depending on the strength of the crystal field, the absorption or the excitation spectrum of Eu^{2+} ion is characterized by several broad bands associated with the transition from $4f^7[^8S_{7/2}]$ to the levels of $4f^6 5d^1$ configuration. The low energy excitation band exhibits the characteristic ''staircase'' spectrum, which retain the character of the seven (Eu^{3+}) $4f^6$ levels ($^7F_{0-6}$) [29], [30]. The staircase spectrum is due to the transition from the Eu^{2+} $^8S_{7/2}$ ground state to the seven ^7F_J (J = 0–6) multiplets of the excited $4f^6[^7F_J(J=0-6)]5d^1$ electronic configuration.

PL data on Eu^{2+} activated K_2BaCl_4 are included in Fig. 2 (curve a and b). Maximum intensity was observed for the sample containing 1.0 mol% Eu^{2+} and quenched from 900 K. For 330nm excitation intense emission is observed with a maximum around 420nm. The excitation curve contains prominent band around 330nm and shoulder at 292nm.

Fig. 3 shows comparison of XRD pattern of as prepared $K_2Ba_{0.99}Cl_4Eu_{0.01}$ powder with the ICDD data file 46-1005. An excellent match is seen.
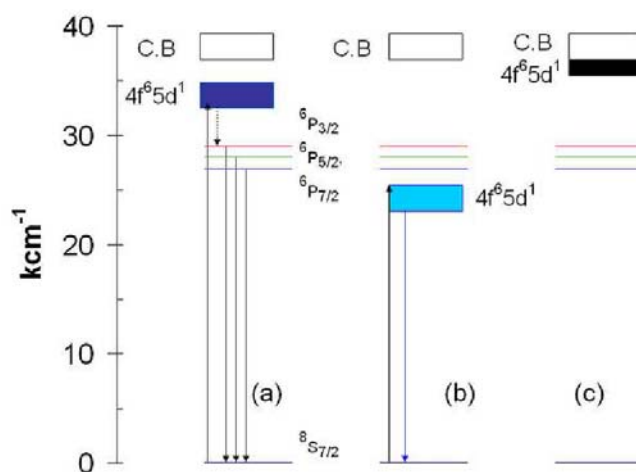

Fig. 1 Energy level diagram for Eu^{2+}. First few levels of $4f^6 5d^1$ configuration and the lowest band of the $4f^6 5d^1$ configuration are shown. Position of the conduction band (C.B.) and the lowest band of the $4f^6 5d^1$ configuration will depend upon the host. Depending on the position of the lowest band of the $4f^6 5d^1$ configuration line emission (a) band emission (b) anomalous emission/autoionization (c) may be observed
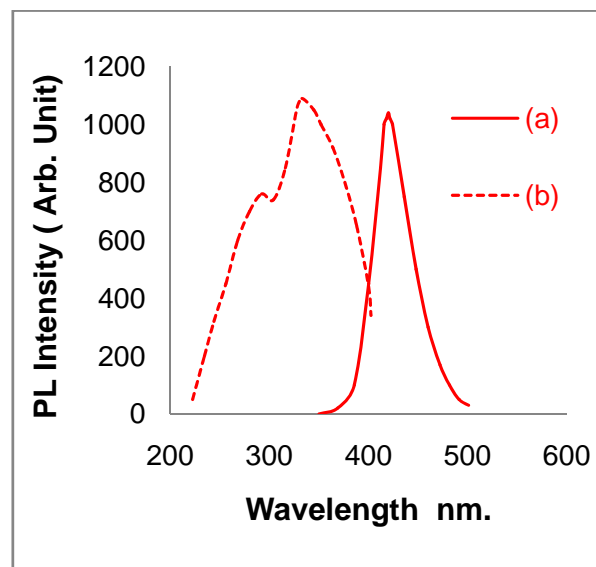

Fig. 2 PL *spectra* for K_2BaCl_4 (a)K_2BaCl_4 Emission for 330nm excitation (b) K_2BaCl_4 excitation for 420nm emission

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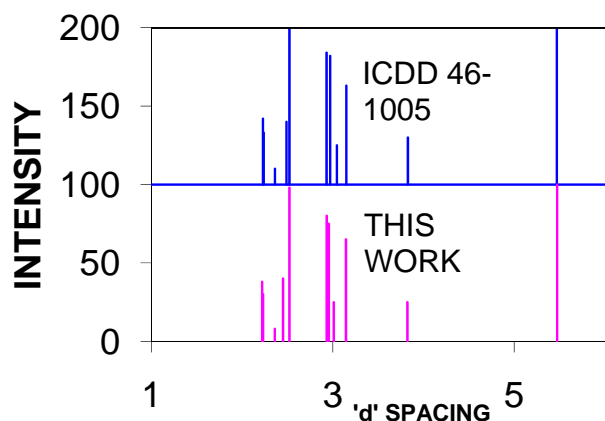Vol:7, No:7, 2013

Fig. 3 XRD pattern for $K_2Ba_{0.9}Eu_{.1}Cl_4$ Stick pattern obtained from XRD pattern obtained with this work is compared with the ICDD data for $CsSrCl_3$
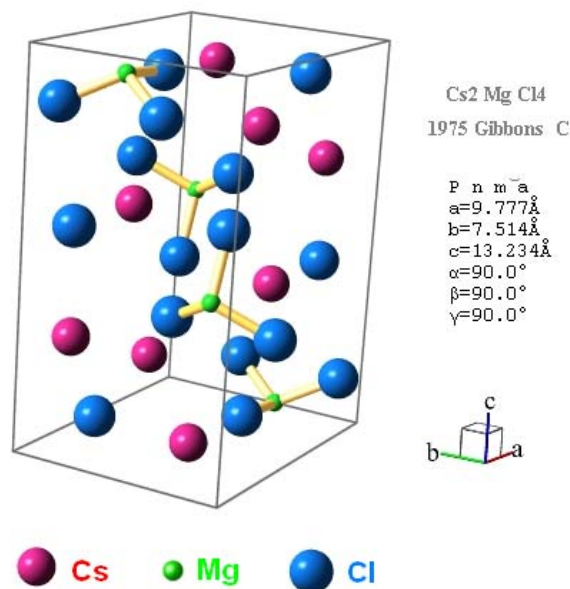
K_2SrCl_4 crystallizes to hexagonal structure with space group -3m with unit cell parameters a = b 12.981A°, c = 8.044A° (Fig. 4).

Fig. 4 Unit cell of K_2SrCl_4

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.
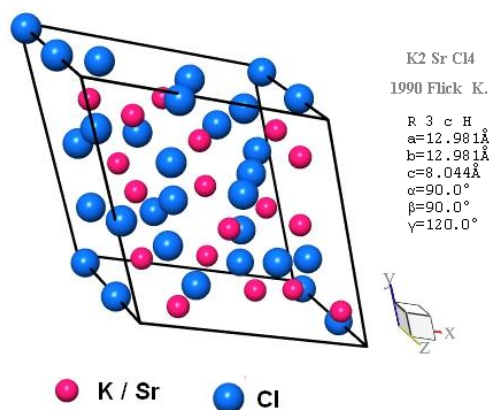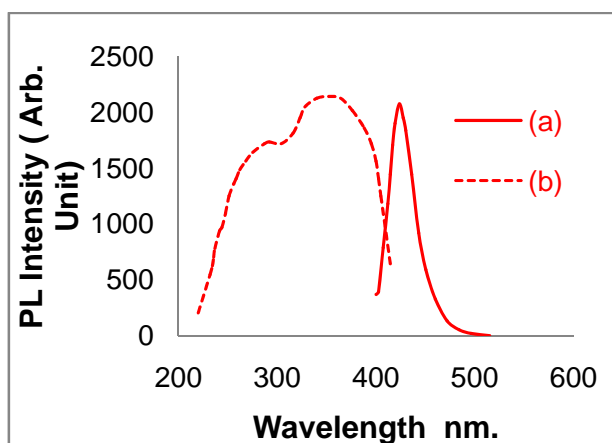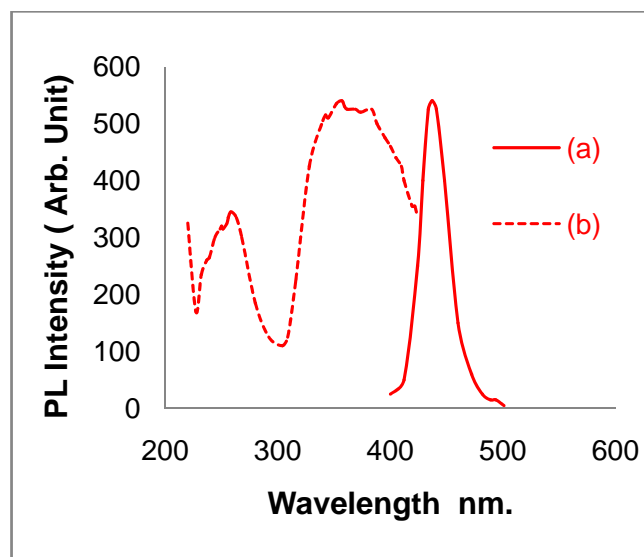

Fig. 5 PL *spectra* for K_2SrCl_4 (a) K_2SrCl_4 Emission for 365nm excitation (b) K_2SrCl_4 excitation for 424nm emission

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

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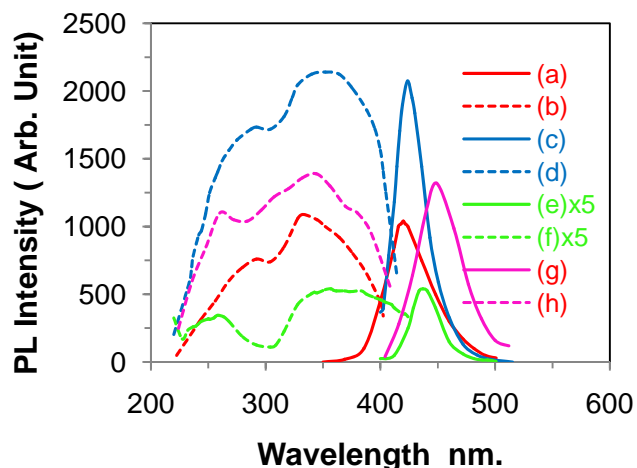International Journal of Physical and Mathematical Sciences
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Fig. 8 PL *spectra* for K_2BaCl_4, K_2SrCl_4 and Cs_2MgCl_4 (a) K_2BaCl_4 Emission for 330nm excitation (b) K_2BaCl_4 excitation for 420nm emission (c) K_2SrCl_4 Emission for 365nm excitation (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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