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Characterization and Syringe Method Synthesis of MF_2: Eu (M=, Mg Ca)

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Abstract: The present report involves the syringe method synthesis of MgF_2 and CaF_2 doped with europium. The prepared materials are characterized through XRD for structural confirmation. The MgF_2 and CaF_2 are crystallized in tetragonal and cubic phase respectively. Further the prepared samples are studied for photoluminescence (PL) characteristics under UV-NUV excitation. The PL result shows the strong blue emission from Eu^{2+} transition in both MgF_2 and CaF_2.
Keywords: Simple fluorides; Syringe method; UV-NUV Excitation.

Introduction:

When fluorides are prepared by conventional solid-state diffusion (SSD) route i.e. by heating the starting materials at high temperature in air, usually unwanted impurities (OH^-, O^{2-}, etc.,) get incorporated. Such impurities are quite harmful in any application of fluorides. Especially, fluorides are highly susceptible to hydrolysis [1]. To avoid such hydrolysis use of freshly synthesized powders and inert atmosphere becomes necessary conditions. The prepared fluoride shows inefficiency in real time application possibly due to deviation from stoichiometry due to hydrolysis. The way out suggested by Belsare et al is preparing the crystals in 'reactive' atmosphere instead of the inert atmosphere. Also in SSD simple fluoride preparation is simple but at the same time preparation of complex fluorides involving several difficulties such as constituent. As it is well known the constituents may have vastly differing melting points and loss of one or more constituents during crystal growth is inevitable. This leads to non-stoichiometry as well as the presence of un-reacted constituents in the final product [2]. In Earlier years, to overcome this, excess of unstable element use in the starting material are attempted but the excess quantity has to be optimized depending on the conditions of the crystal growth. This makes the crystal growth process very tedious and time consuming. In recent, some wet chemical synthesis routes are reported for preparation of OH^- free fluorides [3, 4]. In this report syringe method is elaborated for the synthesis of fluorides. The CaF_2 and MgF_2 doped with europium are prepared and studied for its photoluminescence properties.

Experimental:

MF_2: Eu (Mg, Ca) sample was obtained using the Syringe method route. The assembly developed for the method is presented in Figure 1(a & b). During the reaction 1 Mole of $MgCl_2$/$CaCl_2$ (A.R. Grade) was dissolved in double distilled water in a Teflon beaker. To this dissolve solution, Eu_2O_3 dissolved in HNO_3 was added thoroughly by stirring for 20 min. The complete stiochometric reaction is decided by using formula $M_{1-x}F_2$: Eu_x(M=Mg, Ca) [5-6]. The thoroughly mixed solution was precipitated with drop by drop addition of hydrofluoric acid (HF) using syringe as shown in figure 1(a).

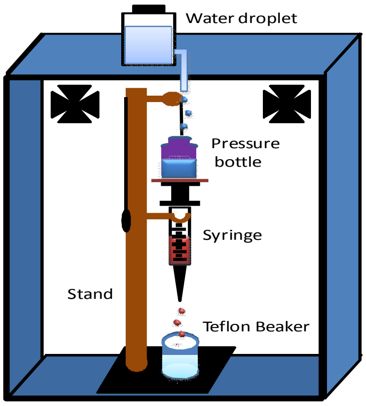

Figure 1a: Assembly used for synthesis process of MF_2: Eu^{2+}

The precipitated obtained by the reaction of HF with the dissolved precursors solution was then heated under fully black surfaced simple tungsten lamp glow box (shown in figure b). The powder obtained so washed several times with double distilled water to remove remaining impurities and dried again under tungsten glow lamp for 2 hours. The compound then sintered at 800^0C for 1 hour in a graphite crucible and quickly quenched on the graphite plate. The obtained power is the maintained in grain size between 125 um and to 200 um by using sieved and used for the further characterization.

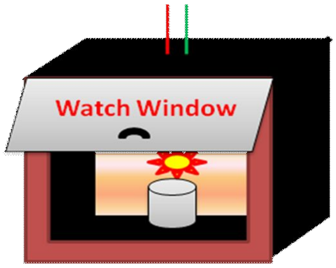

Figure 1b: Tungsten glow lamp box used for drying process

Result and Discussion:

Figure 2 and 3 represents the XRD patterns for the MgF_2 and CaF_2 synthesized by syringe method and are in good agreement with the ICDD data file 01-070-8281 and 00-004-0864 respectively. For MgF_2 important lines in ICDD pattern for the 2θ value at 28.52° for highest intensity were in exactly matching with Experimental data. In results it was found that the 2θ value for highest intensity is at 28.42°.

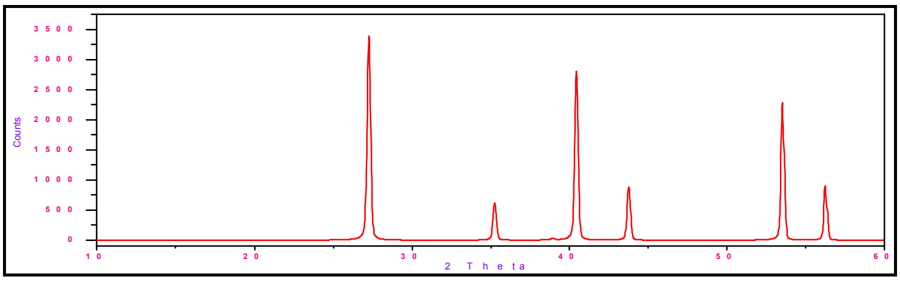

Figure 2 XRD pattern for MgF_2 (In agreement with ICDD (01-070-8281)

This agreement indicates that MgF_2 has been successfully prepared by using the syringe method. However for CaF_2 all the dominant peaks are in agreement with the ICDD pattern and reflect the high crystalline nature of prepared sample.

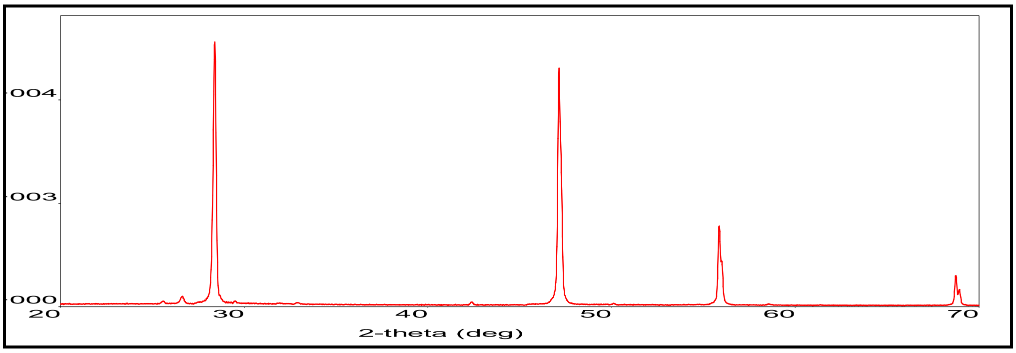

Figure 3 XRD pattern for CaF_2 (In agreement with ICDD (00-004-0864)

Excitation and emission spectra of the prepared phosphors are shown in the Figure 4. A strong emission (curve (a)) with a peak at 424 nm is observed for CaF_2: Eu phosphor. Emission consists of a single broad band with a peak at 424 nm. Emission arises due to transition from levels of $4f^65d^1$ configuration to the ground state ($^8S_{7/2}$) of $4f^7$ configuration of Eu^{2+}. The phosphor is excitable under near UV wavelengths (336-365 nm) (curve (b)). In case of MgF_2:Eu both emission (curve (c)) and excitation (curve (d)) are different and it consists of a emission band with maxima at 420 nm for an excitation at 328 nm. An excitation spectrum of MgF_2:Eu phosphors consists of band with several peaks at 327, 340 and 363 nm when scanned for emission wavelength of 420 nm. The relative intensity of CaF_2: Eu phosphor is highest among the CaF_2 and MgF_2.

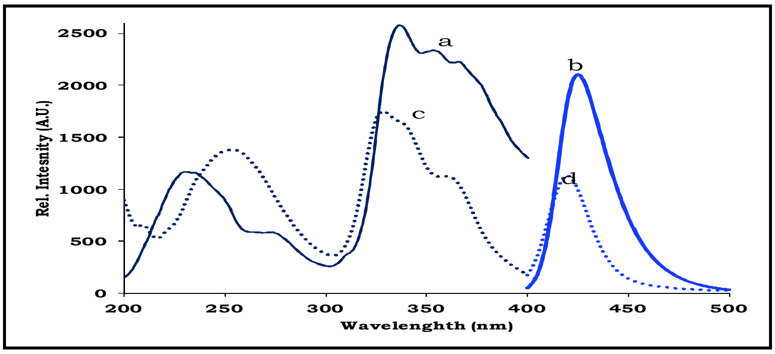

Figure 4 Photoluminescence emission and excitation spectra of a) $CaF_2:Eu^{2+}$ (curve (a) and (b)) and $MgF_2:Eu^{2+}$ (curve (c) and (d))

Conclusion:

The XRD data match excellently with the ICDD files and shows complete agreement with the 2ɵ value. This implies syringe method is successfully employed for synthesis of CaF_2 and MgF_2. The phosphors CaF_2 and MgF_2 doped with europium exhibited intense photoluminescence characteristic of Eu^{2+}, even though there was no use of reducing atmosphere utilised during the synthesis. The intensities of Eu^{2+} luminescence in both the sample is very high whereas the relative intensity of CaF_2: Eu^{2+} phosphor is highest among the CaF_2 and MgF_2.

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