Investigations on Crystal Structure and Photoluminescent Properties of Eu^{3+}/Mn^{4+} doped A_2BTeO_6 (A= Ca, Sr, B= Mg, Zn) double perovskites

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Tellurium based perovskites attracts the attention due to its structural features and technological importance in various fields such as non linear dielectrics, materials for microwave applications, Photoluminescent materials etc. The low phonon energy ($800cm^{-1}$ – $900cm^{-1}$) of tellurium based perovskites can avoid the nonradiative decay for doped rare earth activators, so the tellurates can be used as suitable host lattices for phosphor materials.

First we have investigated the crystal structure of Ba_2CdTeO_6 and the photoluminescent properties of Eu^{3+} doped Sr_2CdTeO_6 double perovskites. All the compounds were synthesized via solid state reaction route with a calcinations temperature of 900 ºC. A slow heating rate of 1.5 ºC/min is used for the oxidation of Tellurium ion from 4^+ to 6^+ states. The structure of Ba_2CdTeO_6 was reported as cubic earlier but we had noticed a possibility of different structure than cubic by analysing the tolerance factor value. The new structure for Ba_2CdTeO_6 is obtained as Tetragonal ($I4/m$) by carefully studying the Raman and FTIR spectra together with the group theoretical predictions and is confirmed by Rietveld refinement of XRD patterns. The structure of Eu^{3+} doped Sr_2CdTeO_6 is found to be monoclinic ($P21/n$) which is similar to the parent Sr_2CdTeO_6 double perovskite. The bandgap for Eu^{3+} doped Sr_2CdTeO_6 is obtained as 3.7 eV which falls in the region of absorption in the UV region and hence the sample can be used for photoluminescence studies. Photoluminescence study reveal that Eu^{3+} doped Sr_2CdTeO_6 sample shows intense red emission at 615 nm under 394 nm excitation. This red emission is due to the $^5D_0$-$^7F_2$ transition (Electric dipole transition) of Eu^{3+} ions. The critical concentration is obtained at x= 0.14 concentration ($Sr_{2-x}CdTeO_6$: xEu^{3+}). The temperature dependence of the red emission of Eu^{3+} doped sample is also studied and calculated the relative sensitivity of the material for the

non contact optical thermometric applications. This work was published in “Journal of Alloys and Compounds” [1].

Then we studied the photoluminescent properties of A_2MgTeO_6 (A=Ba,Sr) ceramics. Ba_2MgTeO_6 and Sr_2MgTeO_6 double perovskites were synthesized through solid state reaction route. The crystal structure and phase purity of the sample were analyzed by X-ray diffraction technique. The XRD patterns of both samples were well matched with the standard XRD patterns of Ba_2MgTeO_6 [ICDD- 00-016-0550] and Sr_2MgTeO_6 [ICDD 00-016-0549]. The band gap energies were calculated using UV-Visible Diffuse reflectance spectroscopy and the obtained band gap energies corresponds to a wavelength of absorption in the UV region. When the powder samples were excited with the UV radiation it shows intense cyan emission. The Ba_2MgTeO_6 sample shows cyan emission under the excitation of 268 nm radiation while the Sr_2MgTeO_6 sample shows blue emission under 237 nm excitation which indicate that these materials can be used for the applications of w-Led fabrication and other lighting purposes. Then we studied the PL properties of Ba_2MgTeO_6 material in detail. When the powder sample was excited with the UV radiation it shows intense blue emission. The un-doped Ba_2MgTeO_6 sample shows an unusual cyan emission under the excitation of 268 nm radiation. It is interestingly notice that as the excitation wavelength changes the corresponding emission changes from visible cyan to NIR region. When we excited from 225 nm to 475 nm radiation the BMTO sample shows a dominant cyan emission centred at 484 nm and a week deep red emission centred at 787 nm. There is also a very week orange red emission at 627 nm. Under 268 nm excitation, the BMTO sample shows high intense broad emission in the range 300 to 750 nm with a maximum emission at 484 nm. When the excitation wavelength changes to 340 nm, the material shows a very week orange-red emission. And when the excitation changes to 382 nm, it is observed that the obtained emission was completely shifted to deep red region. The cyan blue emission is more dominant when compared to the other emissions. The CIE coordinates of the three emissions were calculated. The CIE coordinates were obtained as (0.22, 0.33) for 484 nm emission and it correspond to cyan colour. The CIE coordinates for week 627 nm and 787 nm emissions were obtained as (0.53, 0.45) and (0.73, 0.26) which corresponds an orange-red and deep red colour respectively. So it is clear that, the CIE coordinates can be tuned from cyan to deep red region with the increase in excitation wavelength. The obtained excellent PL properties of as synthesized material can be used for phosphor applications. The temperature dependence of

cyan emission and the thermal stability of Ba_2MgTeO_6 phosphor were studied by analysing the TDPL spectra. From the TDPL spectra it is shown that the cyan emission exhibits an anti-thermal quenching behaviour in the low temperature region. Which means as the temperature increases from 80 K to 280 K the emission intensity increases. After 280 K, the emission intensity starts decreasing. The thermal stability of the material is calculated using the Arrhenius plot and the activation energy was obtained as 0.40 eV which indicates an excellent thermal stability. The life time of the cyan emission is calculated by analysing the decay curve. The decay measurement was carried out under 268 nm excitation and 484 nm emission wavelength. Then the decay curve was fitted using a bi-exponential function and the average lifetime was obtained as 0.05 ms. Then we have incorporated Eu^{3+} ions in the Ba_2MgTeO_6 system. The Eu^{3+} doped Ba_2MgTeO_6 ceramic was synthesized through solid state reaction route. The crystal structure of Eu^{3+} doped sample was analyzed from the XRD patterns of the sample and the sample was crystallizes in cubic structure with space group $Fm\bar{3}m$ which is similar to the parent Ba_2MgTeO_6 material. The Le-bail fit of XRD patterns of the Eu^{3+} doped sample indicates that the sample was phase pure and highly crystalline in nature. Again to confirm the crystal structure we have performed the Raman spectroscopy. The spectral profiles of doped samples were identical to that of parent Ba_2MgTeO_6 ceramics which again indicates similar structure for all the samples. Next we plan to study the PL properties of Eu^{3+} doped sample.

Further we have fabricated a cyan emitting LED based on the cyan emission of undoped Ba_2MgteO_6 material. Generally tellurates without any activator ions doesn't show any kind of luminescence. But here we have got an excellent cyan emission for undoped Ba_2MgTeO_6 material. The as fabricated cyan LED emit light in the 350 – 750 nm region with the maximum emission at 484 nm region. Now, we plan to file a patent application regarding the invention of cyan emitting LED based on the unusual emission property of undoped tellurate material.

Published Paper

1. Nithin Jayan Suraja, Ambazhathil Mahesh, Kaithakkal Solaman Sibi, Subodh Ganesanpotti. Insights into the crystal structure and multifunctional optical properties of A_2CdTeO_6 [A= Ba, Sr, Ca] double perovskites. Journal of Alloys and Compounds 865 [2021] 158902.