Crystal structure of mixed fluorites $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$ and luminescence of $Eu^{2+}$ in this crystals.

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Abstract. Within the framework of the virtual crystal method implemented in the shell model and pair potential approximation the crystal structure of mixed fluorites $Ca_{1-x}Sr_xF_2$ and $Sr_{1-x}Ba_xF_2$ has been calculated. The structure of impurity center $Eu^{2+}$ and the distance $Eu^{2+} - F^-$ in this crystals have been also calculated. The low level position of excited $4f^{6}5d$ configuration of the $Eu^{2+}$ ion has been expressed using phenomenological dependence on distance $Eu^{2+} - F^-$. The dependences of Stokes shift and Huang-Rhys factor on $x$ have been received for yellow luminescence in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$. The value $x$, for which the $e_g$-level of $Eu^{2+}$ ion will be in conduction band in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ has been calculated.

1 Introduction

Fluorites $CaF_2$, $SrF_2$, $BaF_2$ and mixed crystals on their base attract attention of researchers more than four decades [1] [2] [3] [4] [5]. The crystals, doped by rare-earth ions, are good luminophors and are a basis for solid state lasers. The properties of luminescence and absorption depend on electronic structure of matrix crystal. The blue luminescence with zero phonon line (ZPL) is observed in $Ca_{1-x}Sr_xF_2 : Eu^{2+}$. The yellow luminescence without ZPL is observed in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ at $x > 0.2$. 


2 Calculation of the crystal structure 
\(Ca_{1-x}Sr_xF_2\) and \(Sr_{1-x}Ba_{x}F_2\).

The method of virtual crystal have been implemented within the framework of the pair potential approximation and shell model. The method used has been described in previous work [6]. We have calculated the crystal structure of mixed fluorites \(Ca_{1-x}Sr_xF_2\) and \(Sr_{1-x}Ba_{x}F_2\) and of impurity center \(Eu^{2+}\) in this crystals. Dependence of a lattice constant of \(Sr_{1-x}Ba_{x}F_2\) from \(x\) is given on fig.1.

The calculated dependence is in agreement with Wegard rule, though at medial concentrations is appreciable some difference from results of calculation. Similar dependence has been calculated for \(Ca_{1-x}Sr_xF_2\).

3 Impurity ion \(Eu^{2+}\) in crystals \(Ca_{1-x}Sr_xF_2\) and \(Sr_{1-x}Ba_{x}F_2\)

The luminescence and adsorption spectra of \(Eu^{2+}\) in \(Ca_{1-x}Sr_xF_2\), \(Sr_{1-x}Ba_{x}F_2\) deals with interconfigurational transitions between low excited levels of \(4f^65d\) configuration and by \(^8S(4f^7)\) ground state [5]. The ion \(Eu^{2+}\) is in center of cube formed by eight fluorines \(F^-\). The splitting of \(^8S(4f^7)\) ground state is small in cubic crystal field and does not exceed 0.2\(cm^{-1}\) [7]. Level 5\(d\) is enough feebly bound by with \(4f^6\) orbitals in excited configuration \(4f^65d\). The level splits to \(e_g\) and \(t_{2g}\) levels 12 – 16 \(×\) 10\(^3\)\(cm^{-1}\) [8]. The split considerably exceeds \(LS\) interaction in \(t_{2g}\) state and multiplet split of \(4f^6\) levels [8]. Spectrum of the impurity ion is substantially defined by distance impurity ion–ligand. We have calculated the distance \(Eu^{2+}–F^-\) in the crystals and then have calculated a phenomenological dependence of standing \(e_g\) and \(t_{2g}\) levels from the distance. Standing of \(e_g\) level in \(Ca_{1-x}Sr_xF_2 : Eu^{2+}\), is expressed by dependence:

\[
\nu(r) = C + \frac{A}{r^n} - \frac{B}{r^k} \tag{1}
\]

where \(n = 12, k = 5\). The first term determines standing of 5\(d\) level in free ion \(Eu^{2+}\), the second term determines shift of the level at placing \(Eu^{2+}\) in a crystal and third term deals with influence of crystal field on \(t_{2g}–e_g\) splitting. Parameters \(A,B,C\) have been received by fitting the dependence to standing
Figure 1: The lattice constant of $Sr_{1-x}Ba_xF_2$ from $x$. Square symbol refer to experiment [1].
Figure 2: $t_{2g}$ and $e_g$ levels of $Eu^{2+}$. Square symbol refer to experiment[2].
ZPL in CaF$_2$ and SrF$_2$ crystals \[3\] and $t_{2g} - e_g$ splitting in MeF$_2$ (Me = Ca, Sr, Ba) \[3, 4\]. The parameters are: $A = 439.7 \times 10^6 cm^{-1} \times A^{12}$, $B = 280 \times 10^5 cm^{-1} \times A^5$, $C = 36940 cm^{-1}$. The dependence of ZPL position from $x$ we can receive using calculated distance $Eu^{2+} - F^-$ in $Ca_{1-x}Sr_xF_2 : Eu^{2+}$ at various $x$. It is possible to calculate the $t_{2g}$-level position by means of \[7\] taking into account that third term in \[7\] is equal to $6Dq$ (fig.2). The difference of the calculated $t_{2g}$-level position with short-wave adsorption peak can be explained by Stokes shift in adsorption.

The blue and yellow luminescence is observed in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ for $x \in [0.2, 0.5]$ in intervals 430 – 450 and 500 – 580 nm accordingly. The yellow luminescence at $x > 0.5$ is only observed \[3\]. Yellow luminescence due to interconfigurational transitions between levels of impurity exciton (which is formed by transition of electron to twelve nearby cations) and the ground state $^8S(4f^7)$ \[3, 4\] (fig.3). Position of $e_g$-level can be calculated in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ using the expression \[4\]. The top of valence band is formed by $2p$-states of fluorine in $SrF_2$ and $BaF_2$. The bottom of conduction band is formed by $s$-states of cation. Forbidden zone varies practically linearly in row $CaF_2$, $SrF_2$, $BaF_2$ \[4\]. The distance from $e_g$ level to bottom of conduction band in $SrF_2 : Eu^{2+}$ was taken from McClure work \[10\]. Assuming the position of $2p$-states of fluorine does not change at replacing cations $Sr^{2+}$ by $Ba^{2+}$, it is possible to calculate the changing of conduction zone bottom as a function from $x$. According to ours calculation, $e_g$-level will be in a conduction band for $x = 0.2$ in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$. The yellow luminescence will begin at this $x$ in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ \[3\]. We have calculated configuration curves connected with $A_{1g}$ -coordinate knowing how the energy of the crystal $E$ depends on compression or expansion of a fluorine cube which surrounds $Eu^{2+}$. The deduced dependences $E(Q)$ (where $Q$ is the symmetrical coordinate) for $Sr_{1-x}Ba_xF_2 : Eu^{2+}$ are close to parabolic form $kQ^2/2$. Similar calculations was carried out for exciton state. The coefficient $k$ dependences of the configurational curves on $x$ are received: $k_{ES} = 33.95 - 5.26 \times x$, $k_{GS} = 21.18 - 4.61 \times x$, where $x \in [0, 1]$, ( in $eV \times A^{-2}$). The coefficients $k_{ES}$ and $k_{GS}$ are decreasing at increasing the barium concentration. It compounded with the fact that the elastic modules $BaF_2$ are less than $SrF_2$. The fluorine cube is exposed to compression at formation of the exciton, the compression depends linearly on the concentration $x$ in $Sr_{1-x}Ba_xF_2 : Eu^{2+}$: $\Delta R = 0.143 + 0.036 \times x$ (in $\AA$). We can receive the Stoks shift for yellow luminescence as we know $k_{GS}$ and change of distance $Eu^{2+} - F^-$ at transition from exciton to the ground state:
Figure 3: Configuration coordinate diagrams for describing the blue and yellow luminescence in CaF$_2$: Eu$^{2+}$ and SrF$_2$: Eu$^{2+}$ [10]
\[ E_s = 1090 \times x + 5011 \text{ (in cm}^{-1}\text{).} \]
The yellow luminescence have been observed in \( Sr_{1-x}Ba_xF_2 : Eu^{2+} \) at \( x \in [0.2, 1] \), and with increasing \( x \) its peak is shifting to the long-wave part of the spectrum \cite{3}. According to our calculation the Stoks shift is increased on \( 800\text{cm}^{-1} \). We can estimate \( A_{1g} \) frequency of a cube from eight ions \( F^- \):

\[
\nu_{A_{1g}} = \sqrt{\frac{k_{GS}}{m_F}} \tag{2}
\]

where \( m_F \) - a mass of the fluorine. According to our calculations \( n = 547 - 63\times x \), \( (n \text{ in cm}^{-1}) \). We can calculate Huang-Rhys factor for yellow luminescence as we know \( E_s \) and \( n \). The factor is increasing from 9 to 12 at increasing \( x \) from 0 to 1 in \( Sr_{1-x}Ba_xF_2 : Eu^{2+} \).

4 Conclusion

The method of virtual crystal implemented in shell model and framework of pair potential approximation allows us to calculate the crystal structure and lattice constant for mixed fluorites \( Ca_{1-x}Sr_xF_2 \) and \( Sr_{1-x}Ba_xF_2 \). This method allows us to calculate the distance \( Eu^{2+} - F^- \) in doped crystals \( Ca_{1-x}Sr_xF_2 : Eu^{2+} \) and \( Sr_{1-x}Ba_xF_2 : Eu^{2+} \). The low level position of excited \( 4f^65d \) configuration of an ion \( Eu^{2+} \) is expressed by phenomenological dependence on \( Eu^{2+} - F^- \) distance. The dependences of Stokes shift and Huang-Rhys factor on \( x \) have been calculated for yellow luminescence in \( Sr_{1-x}Ba_xF_2 : Eu^{2+} \). According to our calculation the Stokes shift is increasing by \( 1000\text{cm}^{-1} \), the Huang-Rhys factor is increasing from 9 to 12 while \( x \) changes from 0 to 1. According to calculation the \( e_g \) level of \( Eu^{2+} \) ion will be within the conduction band for \( x \geq 0.2 \) in \( Sr_{1-x}Ba_xF_2 : Eu^{2+} \).

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