

Influence of Chemical Environment on the Optical Properties in Transition Metal Ions Doped Materials

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The sensibility of luminescent properties in transition metal doped materials to the matrices' chemical environment is explained in this paper, this is because of their strong phonon-electron coupling which are caused by the 3d electrons exposed nature. The influence of the chemical environments on the Mn²⁺-doped materials' optical properties, including the structure type of coordinate polyhedron, the polyhedral bridge linking manner and the lattice parameter, was illustrated in detail in this work. The impact of crystal field strength parameter (10 Dq) on the maximum energy differentiae in spontaneous emission band of Cr³⁺: ${}^4T_{2g} \rightarrow {}^4A_{2g}$ and in excited state absorption band ${}^4T_{2g} \rightarrow {}^4T_{1g}$ (4F), and covalent bond intension's impact on the optical properties of Os⁴⁺ were also analyzed. This work's purpose is to discover the principle of the sensibility character, then we can use it to optimal the design of materials in order to find the excellent luminescent materials for practical utilization.

KEY WORDS: Transition metal ions; optical properties; chemical environment.

INTRODUCTION

The luminescent materials are widely [1–4] used in modern industry, agriculture, military, optical storage and burning, medical, and optical communication. The demand for the luminescent materials with excellent optical properties will keep on increasing with years as the process of modernization and progress of science and technology. So the study of luminescent materials and its optical properties are becoming more and more important and necessary, this subject is involved with the metal, optics, material physical chemistry, and optoelectronics.

It is well known that lanthanide ions or transition metal ions always act as the activation center in luminescent materials. The lanthanide ions doped materials have attracted much attention for many years [5–9], due to their excellent and stable optical properties because

of the weak phonon–electron coupling which are caused by the shielded nature of 5f electrons. But as a distinct comparison, the transition metal ions have much stronger phonon–electron coupling because the 3d electrons are always exposed to the outside environment, and they usually have only one meta-stable excite state with a lifetime long enough to show luminescence. So the optical properties of transition metal ions are very sensitive to the chemical environment of the matrices [10]. However, it is a useful tool for the design and synthesis of materials, and we can use it to change the chemical environment in purpose to look for desirable luminescent materials with excellent optical properties.

THE STRUCTURE TYPE OF COORDINATE POLYHEDRON, THE POLYHEDRAL BRIDGE LINKING MANNER, AND THE LATTICE PARAMETER INFLUENCE ON THE OPTICAL PROPERTIES OF MN²⁺-DOPED MATERIALS

The Mn²⁺/Yb³⁺ co-doped materials have proved to be new and efficient upconversion materials [11]. In the research [12,13] on Yb³⁺-doped Rb₂MnCl₄ and

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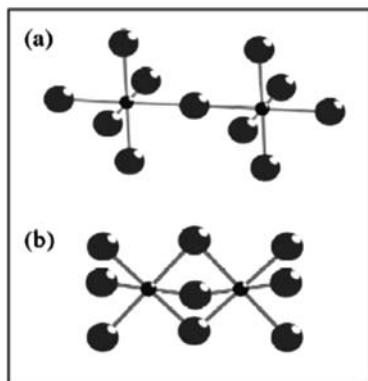


Fig. 1. Bridging of $[\text{YbX}_6]^{3-}$ and $[\text{MnX}_6]^{4-}$ octahedral units in (a) corner-sharing manner as in $\text{Yb}^{3+}:\text{Rb}_2\text{MnCl}_4$ and (b) face-sharing manner as in $\text{Yb}^{3+}:\text{CsMnBr}_3$.

CsMnBr_3 , it was found that the polyhedral bridge linking manner could greatly influence the Mn^{2+} optical properties. Yb^{3+} and Mn^{2+} are octahedral coordinate in the form as $[\text{YbX}_6]^{3-}$ and $[\text{MnX}_6]^{4-}$ respectively. In $\text{Yb}^{3+}:\text{Rb}_2\text{MnCl}_4$, $[\text{YbCl}_6]^{3-}$ and $[\text{MnCl}_6]^{4-}$ octahedral units are bridged in a corner-sharing manner by sharing a common Cl^- ion as shown in Fig. 1a. In $\text{Yb}^{3+}:\text{CsMnBr}_3$, on the other hand, $[\text{YbBr}_6]^{3-}$ and $[\text{MnBr}_6]^{4-}$ octahedral units are linked in a face-sharing manner (see Fig. 1b). And the upconversion efficiency of $\text{Yb}^{3+}:\text{Rb}_2\text{MnCl}_4$ is nearly three times large than that of $\text{Yb}^{3+}:\text{CsMnBr}_3$.

It is interesting to discover that $\text{Yb}^{3+}/\text{Mn}^{2+}$ energy exchange is strongest in perovskite-type (ABO_3) lattice among all the structure types, so the upconversion efficiency of $\text{Yb}^{3+}:\text{CsMnCl}_3$ with perovskite-type is five times larger than that of $\text{Yb}^{3+}:\text{Rb}_2\text{MnCl}_4$ without perovskite-type. The structure of perovskite-type in CsMnCl_3 and CsMnBr_3 are shown in Fig. 2.

In the work of Diaz *et al.* [14] on the optical properties in Mn^{2+} -doped solid solution $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ and $\text{Sr}_{1-x}\text{Ba}_x\text{F}_2$, the luminescence of $\text{Mn}^{2+}:^4\text{T}_{1g} (^4\text{G}) \rightarrow ^6\text{A}_{1g} (^6\text{S})$ is closely connected with the lattice parameters. It is

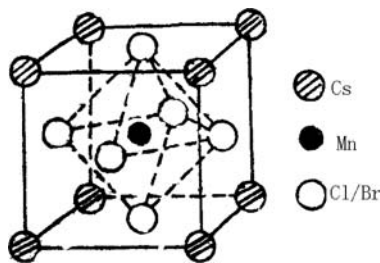


Fig. 2. The structure of perovskite-type (ABO_3) in CsMnCl_3 and CsMnBr_3 .

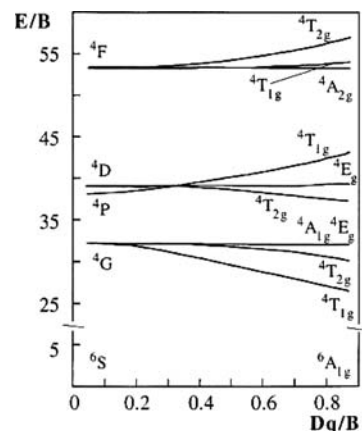


Fig. 3. Tanabe-Sugano diagram of Mn^{2+} in Oh symmetry for a ratio of the Racah parameters, $C/B = 4.48$.

well known that Ca^{2+} , Sr^{2+} , and Ba^{2+} are alkaline-earth metal ions, and the radius relation is $\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$, so the $\text{R}^{2+}-\text{F}^-$ lattice distance will increase when Sr^{2+} substitutes for Ca^{2+} and Ba^{2+} for Sr^{2+} , therefore the lattice distance of $\text{R}^{2+}-\text{F}^-$ keeps on increasing when x is increased. Then the energy of $^4\text{T}_{1g} (^4\text{G}) \rightarrow ^6\text{A}_{1g} (^6\text{S})$ transition is decreased with increasing lattice distance. These changes can be explained well using the configurational coordinate model based on the Tanabe-Sugano energy level diagrams: As for Mn^{2+} ion with d^5 electron in a cubical environment, there is an increase in the electron-lattice interaction in the mixed crystals $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ and $\text{Sr}_{1-x}\text{Ba}_x\text{F}_2$ when x is increased, so the energy level $^4\text{T}_{1g} (^4\text{G})$ curve is bent downward to the ground state $^6\text{A}_{1g} (^6\text{S})$ as shown in Fig. 3. Thus the energy difference between $^4\text{T}_{1g} (^4\text{G})$ and $^6\text{A}_{1g} (^6\text{S})$ should decrease with increasing lattice distance. In the same way, the configurational coordinate model can also explain why the quench temperature decreases with increasing lattice distance.

INFLUENCE OF CRYSTAL FIELD STRENGTH PARAMETERS (10Dq) ON THE MAXIMUM ENERGY IN SPONTANEOUS EMISSION BAND $\text{Cr}^{3+}:^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$ AND EXCITED STATE ABSORPTION (ESA) BAND $\text{Cr}^{3+}:^4\text{T}_{2g} \rightarrow ^4\text{T}_{1g} (^4\text{F})$

Cr^{3+} is one of the most thoroughly studied transition metal ions in the field of optical spectroscopy because of the tunable laser output in the broad emission band 830–1100 nm [15]. It is Cr^{3+} acting as the active ion in the first laser [16]. The spontaneous emission transition $^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$ and excited state absorption $^4\text{T}_{2g} \rightarrow ^4\text{T}_{1g} (^4\text{F})$ are two main character of Cr^{3+} -doped materials. Compare

Table I. Crystal Field Strength Parameters (10 Dq) Impact on the Maximum Energy in Spontaneous Emission Band $\text{Cr}^{3+}:^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$ and Excited State Absorption (ESA) Band $\text{Cr}^{3+}:^4\text{T}_{2g} \rightarrow ^4\text{T}_{1g}$ (^4F)

Matrix	10 Dq	$E: ^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$	$E: ^4\text{T}_{2g} \rightarrow ^4\text{T}_{1g}$ (^4F)
$\text{Cr}^{3+}:\text{Cs}_2\text{NaScCl}_6$ [17]	12,800	10,550	9,000
$\text{Cr}^{3+}:\text{LiNaAlF}_6$ [18]	16,000	13,000	10,000
$\text{Cr}^{3+}:\text{Gd}_2\text{ScGa}_3\text{O}_{12}$ [19]	16,100	13,100	9,000

Note. All numbers are given in units of cm^{-1} .

the works of Wenger and Gudel [17] and Lee *et al.* [18] with Moncorge and Benyalton [19] study, the datum of their corresponding results are shown in Table I. It is easy to find out that the energy difference of $^4\text{T}_{2g} \rightarrow ^4\text{A}_{2g}$ transition is always increasing with the crystal field strength parameters (10 Dq), but the energy difference of $^4\text{T}_{2g} \rightarrow ^4\text{T}_{1g}$ (^4F) transition is independent of the crystal field strength. From the knowledge of chemical kinetics, the probability of a spontaneous emission increase with decreasing transition energy, thus it is more difficult to achieve the particle reversal for laser emission. So the principle can be used to pick out those materials with weak crystal field strength parameters from the candidates for Cr^{3+} -doped luminescent materials.

The quench temperature (75 K) of $\text{Cr}^{3+}:^2\text{E} \rightarrow ^2\text{A}_2$ in $\text{Cr}^{3+}/\text{Yb}^{3+}$ co-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ [20] is increased compared to that of $\text{Y}_3\text{Ga}_5\text{O}_{12}$ [21]. As the crystal field strength of $\text{Y}_3\text{Al}_5\text{O}_{12}$ is larger than that of $\text{Y}_3\text{Ga}_5\text{O}_{12}$, so it was assumed that the energetic separation of ^2E is increased when crystal field strength is increased, thus leading to the increase in the quench temperature of Cr^{3+} luminescence. Therefore, by further increasing the crystal field strength, more efficient room temperature

upconversion can be obtained in $\text{Cr}^{3+}/\text{Yb}^{3+}$ co-doped systems.

INFLUENCE OF COVALENT BOND STRENGTH ON THE OPTICAL PROPERTIES OF Os^{4+} -DOPED MATERIALS

In the studies on the optical properties of $\text{Cs}_2\text{ZrCl}_6:\text{Os}^{4+}$, $\text{Cs}_2\text{ZrBr}_6:\text{Os}^{4+}$, and $\text{CsGeF}_6:\text{Os}^{4+}$ [22–24], because the order of covalent band strength is $[\text{OsF}_6]^{2-} > [\text{OsCl}_6]^{2-} > [\text{OsBr}_6]^{2-}$, so the maximum vibration energy of the $[\text{OsX}_6]^{2-}$ ($X = \text{F}^-$, Cl^- and Br^-) octahedral units decrease in the sequence of $\text{F} \rightarrow \text{Cl} \rightarrow \text{Br}$. The maximum vibration energy of $[\text{OsCl}_6]^{2-}$ is roughly 350 cm^{-1} , and the corresponding energy of $[\text{OsBr}_6]^{2-}$ is smaller than 230 cm^{-1} . As shown in Fig. 4, the energy differential between the level Γ_1 ($^1\text{A}_{1g}$) and its neighboring level with lower energy is decreased with decreasing $[\text{OsX}_6]^{2-}$ vibration energy. The luminescence of Os^{4+} mainly corresponds to the transition from Γ_1 ($^1\text{A}_{1g}$) into the lower energy levels Γ_5 ($^1\text{T}_{2g}$) or Γ_3 ($^1\text{E}_g$). As for CsGeF_6 , no Γ_1 ($^1\text{A}_{1g}$) luminescence can be observed so far because the energy gap about 9000 cm^{-1} is too large for efficient multi-phonon relaxation. It can be concluded that low-lying triplet excited state leads to efficient multi-phonon relaxation as a result of its stronger electron-phonon coupling. Through comparison of the luminescence spectrum of $\text{Cs}_2\text{ZrCl}_6:\text{Os}^{4+}$ and $\text{Cs}_2\text{ZrBr}_6:\text{Os}^{4+}$ (Fig. 5), it is easy to find out that the corresponding upconversion band situations of Γ_1 ($^1\text{A}_{1g}$) \rightarrow Γ_4 ($^3\text{T}_{2g}$) and Γ_1 ($^1\text{A}_{1g}$) \rightarrow Γ_1 ($^3\text{T}_{1g}$) are different between Cs_2ZrCl_6 and Cs_2ZrBr_6 . This is because the mechanism and luminescent paths always change with the energy levels situation

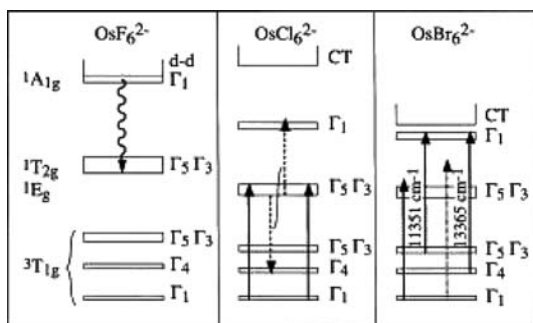


Fig. 4. Schematic energy level diagrams of $[\text{OsX}_6]^{2-}$ ($X = \text{F}^-$, Cl^- , and Br^-). The solid arrows correspond to excited and upconversion transfer, the curly and dashed arrows represent multi-phonon relaxation.

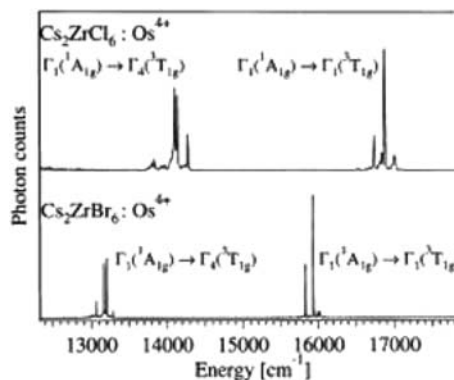


Fig. 5. Upconversion luminescence spectrum of $\text{Cs}_2\text{ZrCl}_6:\text{Os}^{4+}$ and $\text{Cs}_2\text{ZrBr}_6:\text{Os}^{4+}$ excited at $11,226$ and $11,351 \text{ cm}^{-1}$, respectively.

(Fig. 4); in the meanwhile, the energy levels situation strongly depends on the chemical environment.

CONCLUSIONS

The optical properties of transition metal ions doped materials are very sensitive to the chemical environments of the matrices, due to their strong phonon–electron coupling because their 3d electrons are always exposed to the outside environment. And it is a useful tool for the synthesis and design of materials to change the chemical environment in purpose to find out the desirable materials with excellent luminescent properties.

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