Mn$^{2+}$ doped CdAl$_2$O$_4$ phosphors with new structure and special fluorescence properties: experimental and theoretical analysis†

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Mn$^{2+}$-activated CdAl$_2$O$_4$ phosphors with the new structure of space group $R\overline{3}$ (no. 148) have been prepared by a high-temperature solid-state reaction and their luminescence properties have been investigated in detail. The reduction of Mn$^{4+}$ to Mn$^{2+}$ in air atmosphere has been observed in CdAl$_2$O$_4$ powders for the first time. The structural properties including the phase purity and structural parameters were analyzed through Rietveld analysis. The typical transitions of Mn$^{2+}$ ions in emission and excitation spectra were observed both in MnCO$_3$ and MnO$_2$ prepared CdAl$_2$O$_4$:0.01Mn$^{2+}$ phosphors, which means that the luminescent centers of Mn$^{2+}$ ions were from the Mn$^{4+}$ ions which were reduced. Meanwhile, the energy band structures of CdAl$_2$O$_4$ and CdAl$_2$O$_4$:Mn$^{2+}$ were measured with an ultraviolet-visible diffuse reflection spectroscopy (UV-vis DRS), the electronic structures were calculated using the plane-wave density functional theory (DFT). The Mn$^{2+}$-activated CdAl$_2$O$_4$:Mn$^{2+}$ phosphor prepared in air atmosphere is a potential blue-green emitting phosphor.

1. Introduction

Phosphors prepared by the high-temperature solid-state reaction method have a high luminous intensity and good thermal stability. Therefore, the high-temperature solid-state reaction is the most used method for the preparation of phosphors. When the luminescence centers need to be prepared at a lower valence state, people usually add reducing atmosphere such as H$_2$ into the reaction process. However, the introduction of reducing atmosphere not only improved the technological requirements and costs but also restricted the scope of applications. For example, when there exist some transition metal elements such as W, Mo, V, Cd, etc. which were easy to be reduced by reducing atmosphere in the host, there is no way to get low-valence luminescence centers. Therefore, reducing emitting ions to provide low-valence luminescence centers in an air atmosphere in the high-temperature solid-state reaction is still a research difficulty. At present, according to the reported literature, Eu$^{3+}$ ions can be reduced to Eu$^{2+}$ in an air atmosphere in some special crystal structure. Peng believe that it is closely related to the crystal structure and charge compensation.

Mn$^{2+}$ ions as a common non-rare earth luminescence centers have been widely used. The energy levels of Mn$^{2+}$ ions are strongly affected by the lattice environment. The luminescence properties have a great difference in different host lattices which made Mn$^{2+}$ be an ideal non-rare earth luminescent center. However, people usually use the high-temperature solid-state reaction method in a reducing atmosphere to obtain Mn$^{2+}$ ions activated phosphors. It greatly limits the scope of application of Mn$^{2+}$ ions.

In this paper, we firstly synthesized CdAl$_2$O$_4$:Mn$^{2+}$ phosphors by standard high-temperature solid-state reaction in an air atmosphere. The phosphors were characterized by X-ray diffraction (XRD), photoluminescence (PL) studies and Fourier transform infrared spectroscopy (FTIR). And the crystallographic parameters were refined through Rietveld analysis. The reduction activity of CdAl$_2$O$_4$ host was carefully studied by changing the manganese source. The geometry optimization and electronic structure calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) code. After analyzing the band structure and density of states, the emitting and energy transfer mechanism were detailed investigated. And the crystal field splitting parameter $10D_q$ was been calculated.

2. Synthesis and characterization

2.1 Sample synthesis

Samples of CdAl$_2$O$_4$ and CdAl$_2$O$_4$:Mn$^{2+}$ were synthesized by the solid-state reaction method in an air atmosphere. The raw
materials were CdO (99.99%), Al₂O₃ (99.99%), MnCO₃ (99.99%) and MnO₂ (99.99%). The starting materials were weighed according to the stoichiometric ratio and mixed with ethanol in an agate container and ball milled with agate balls for 12 h. After milling, the mixed materials were dried in an oven at 60 °C for 24 h. The dried materials were put into the alumina crucible and calcined in a muffle furnace at 1200 °C for 3 h, and then the white powder phosphor was obtained. All samples were ground into a powder with an agate mortar and pestle for further analysis.

2.2 Experimental methods

The powder diffraction data of CdAl₂O₄ and CdAl₂O₄:0.03Mn²⁺ for Rietveld analysis were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu Kα radiation, λ = 0.15406 nm) and linear VANTEC detector. The step size of 2θ was 0.02°, and the counting time was 1 s per step. The Rietveld refinement was performed using the General Structure Analysis System (GSAS) program. Room-temperature photoluminescence emission (PL) and excitation (PLE) spectra were recorded using a Hitachi F-4600 spectrophotometer equipped with a 150 W xenon lamp as an excitation source. The luminescence decay curves were obtained from a FluoroLog-3-TCSPC. And the temperature-dependent luminescence properties were measured by a FluoroLog-3 spectrophotometer, which was combined with TAP-02 high-temperature fluorescence controller (Orient KQJ, Tianjin). With the crystal structure data, which were obtained by Rietveld refinement, DFT calculations on the trigonal CdAl₂O₄ host and the Mn²⁺ doped samples were carried out by using the CASTEP code.¹¹

3. Results and discussion

3.1 Phase identification and morphology

The space group of CdAl₂O₄ in this paper is R₃, which is different from the reported CdAl₂O₄ spinel structure with space group Fd3m.¹² The structure of CdAl₂O₄ in this paper has the same structure with Zn₂SiO₄, both of them have the similar crystal structure with β-Si₃N₄.¹³ Therefore, the structure model of CdAl₂O₄ in this paper is selected on Zn₂SiO₄. As shown in Fig. 1, compared with Zn₂SiO₄ (R₃ PDF# 37-1485), the prepared CdAl₂O₄ powder with space group R₃ (PDF# 34-0071) has the similar position and intensity of diffraction peaks. The XRD pattern of the CdAl₂O₄ sample was defined by a Rietveld refinement implemented with the Zn₂SiO₄ (ICSD #67235) R₃ (148) structure model. The observed, calculated, background and the difference patterns of the XRD refinement of CdAl₂O₄ are shown in Fig. 2. The final refinement converged with weighted profiles of R_p = 6.03%, R_w = 8.41% and χ² = 2.624, which illustrates there is no detectable impurity phase observed in this obtained sample. As the crystallographic data of CdAl₂O₄ shown in Table 1, this compound exhibits a trigonal crystal system with the space group R₃ (no. 148), Z = 18, and the cell parameter is a = b = 14.2210 Å, c = 9.5733 Å, V = 1676.69 Å³. As shown in Fig. 2, the refinements were stable and gave low R-factors. And the refined structural parameters of CdAl₂O₄ are listed in Table 1. The optimized crystal structural parameters of CdAl₂O₄ after geometry optimization are listed in Table S1.† It can be seen that the results of Rietveld refinement are very similar to those of structure calculated after geometry

![Fig. 1 XRD patterns of (a) CdAl₂O₄ samples and standard card of (b) CdAl₂O₄ and (c) Zn₂SiO₄ powders.](image)

![Fig. 2 Rietveld analysis patterns of X-ray powder diffraction data of CdAl₂O₄ phosphors.](image)

| Table 1 Refined structural parameters of CdAl₂O₄ obtained from the Rietveld refinement⁹ |
|-----------------|-----------|---------|---------|----------|
| Element symbol | Mult. Wyck. | x/a     | y/b     | z/c      | U (Å³)   |
| Cd1             | 18f       | 0.2061  | 0.1835  | 0.2456   | 0.0261   |
| A1              | 18f       | 0.2072  | 0.1977  | 0.5818   | 0.0260   |
| A2              | 18f       | 0.2166  | 0.1970  | 0.9170   | 0.0229   |
| O1              | 18f       | 0.3425  | 0.3469  | 0.2456   | 0.0147   |
| O2              | 18f       | 0.2201  | 0.1110  | 0.0494   | 0.0221   |
| O3              | 18f       | 0.2172  | 0.1210  | 0.4467   | 0.027    |
| O4              | 18f       | 0.1935  | 0.1391  | 0.7514   | 0.0234   |

¹ a = b = 14.2210, ε = 9.5733, α = β = 90°, γ = 120°, V = 1676.69 Å³, space group R₃, R_p = 8.41%, R_w = 6.03%, χ² = 2.624.
optimization with CASTEP program. From the first principles calculation, to investigate the reasonableness of the CdAl2O4 structure, the phonon spectrum of CdAl2O4 was calculated after geometry optimization (see Fig. S1†). The absence of any imaginary frequency phonon modes proves the dynamical stability of the CdAl2O4 with R3 structure.

In the crystal structure of CdAl2O4 shown in Fig. 3, the Cd atoms occupy the 18f site coordinated by four O atoms to form CdO4 tetrahedron. Al atoms are occupied the 18f site in the center of AlO4 tetrahedron.

### 3.2 Luminescence properties and valence analysis of Mn

Fig. 4 shows the manganese source dependent PL and PLE spectra of Cd0.99Mn0.01Al2O4 phosphors. As seen from the PL and PLE spectra, their shape and intensity of fluorescence spectrum are very similar. The emission spectra just have one single emission peak at about 495 nm, which is consistent with the traditional Mn2+ emission.14-17 This indicates that whether using MnCO3 or MnO2, the phosphors prepared by high-temperature solid phase reaction method in air atmosphere have typical characteristic peaks of Mn2+ ions. CdAl2O4:0.01-Mn2+ fluorescent material has a strong characteristic emission of Mn2+ ions when MnCO3 was added as manganese source. This indicates that Mn2+ ions were not oxidized in an air atmosphere in high-temperature solid-state reaction. In addition, we further investigated the luminescent properties of CdAl2O4:0.01Mn2+ phosphor with MnO2 as manganese source. Although the manganese source has only Mn4+ ions, the CdAl2O4:0.01Mn2+ phosphor still exhibits a strong characteristic emission of Mn2+ ions. It means that the luminescent centers of Mn2+ ions come from the Mn4+ ions which were reduced at high temperatures. Compared with the emission intensity of Cd0.99Mn0.01Al2O4 phosphor prepared by MnCO3, the emission intensity prepared by MnO2 was only reduced 2.6%. This could be a result of experimental errors. And there is a very strong reduction activity in the CdAl2O4 host. The Mn4+ ions were reduced almost entirely to Mn2+ in air atmosphere by a high-temperature solid-state reaction.

The XPS test was employed to analyze the valence of Mn in CdAl2O4:Mn phosphors. The CdAl2O4:0.015Mn2+ phosphor which was prepared in air atmosphere by MnO2 was selected. Fig. S2(a)† displays the survey scan of CdAl2O4:Mn phosphors, where the principal peaks are corresponding to cadmium (Cd 3d), aluminum (Al 2s, Al 2p), carbon (C 1s) and oxygen (O 1s). The binding energy for the Mn 3s orbital of Mn2+ is not evident due to the low doping concentration. Therefore, we can’t use the gap of two peaks in Mn 3s orbital to determine the valence of Mn. The XPS spectrum of the phosphor in 2p3/2 and 2p1/2 region of Mn is shown in Fig. S2(b).† The binding energy of 641 and 653 eV indicates that the Mn ion has +2 oxidation state. However, a principal peak at about 651 eV which belong to the binding energies of Cd 3p3/2 affects the judgment of the oxidation state of Mn. Therefore, the valence of the Mn is not clear from XPS, and it should be considered from the viewpoint of the fluorescence properties. As can be seen from Fig. 5, since CdAl2O4:Mn2+ fluorescent material exists only broadband emission at about 495 nm, which is consistent with Mn2+ ions fluorescence characteristics.18-20 And there is no typical linear emission peak of Mn4+ in the red-light region. Therefore, the valence of Mn element in CdAl2O4:0.015Mn2+ sample prepared by using MnO2 in air atmosphere is Mn2+.

Fig. 5(a) shows the excitation spectrum of the pure CdAl2O4 sample monitored at about 395 nm. The asymmetric broadband at about 200–260 nm (40 000–38 460 cm−1) was decomposed into two components (220.8 nm and 236.9 nm) by Gaussian fitting. Fig. 5(b) shows the excitation spectrum of the CdAl2O4:0.01Mn2+ sample monitored at about 495 nm. Compared with Fig. 5(a), the excitation band at about 264.5 nm (37 810.51 cm−1) can be assigned to the O–Mn charge transfer band of CdAl2O4:0.01Mn2+ phosphor. The Fig. 5(c) shows an enlarged view in the 330–470 nm range. The excitation spectrum presents many narrow transitions, associated to 6A1(6S)−4E2g(4D) (354 nm), 6A1(6S)−4T2g(4G) (426 nm), 6A1(6S)−4T1g(4G) (436 nm), 6A1(6S)−4T1g(4G) (460 nm) electronic transitions. This indicates that although the Mn2+ were used as Mn source, it was eventually reduced to Mn2+ ions in CdAl2O4 phosphors via a high-temperature solid-state reaction method in an air atmosphere. Fig. 5(d) shows the emission spectrum of CdAl2O4:0.01Mn2+ phosphor. The maximum of the emission is at about 495 nm,
with an FWHM of only 1053 cm$^{-1}$ (26 nm). Moreover, the emission spectrum shows asymmetrical double sigmoidal (Asym2sig) fit (red) with $R^2 = 0.99986$. The Asym2sig function is distributed as follows:

$$y = y_0 + \frac{1}{1 + e^{-\frac{x-x_c}{w_1}}} - \frac{1}{1 + e^{-\frac{x-x_c}{w_2}}}$$

where $x_c$ is the peak position and $w_1$, $w_2$ and $w_3$ are related to the width and asymmetry of the peak distribution.\footnote{Mn$^{2+}$ doping Zn$_2$SiO$_4$ have been extensively studied in the reported literature.\cite{19,22–24} Excitation and emission spectra of as prepared Zn$_2$SiO$_4$:0.01Mn$^{2+}$ phosphor are shown in Fig. S3. It can be seen that the excitation and emission spectra of CdAl$_2$O$_4$:Mn$^{2+}$ are very similar to Zn$_2$SiO$_4$:Mn$^{2+}$ phosphor. The typical excitation and emission peaks of Mn$^{2+}$ were observed. There are three broad excitation bands and several sharp excitation peaks which positions are very close to CdAl$_2$O$_4$:Mn$^{2+}$ in the excitation spectra. And both of them have only one emission band which was explained by the asymmetrical double sigmoidal (Asym2sig) function.}

From Fig. 6, PL and PLE spectra of CdAl$_2$O$_4$, CdAl$_2$O$_4$:0.0001Mn$^{2+}$ and CdAl$_2$O$_4$:0.01Mn$^{2+}$ phosphors are presented in an immediate contrast. From Fig. 6(a), pure CdAl$_2$O$_4$ phosphor exhibits a strong blue-violet emission band with a maximum at about 395 nm. When monitoring at 395 nm, the excitation spectrum of CdAl$_2$O$_4$ exhibits a broad band in the range of 200–250 nm with the main peak at about 230 nm. As shown in Fig. 6(b), under the excitation of 230 nm, two broad emission bands centered at 395 nm and 495 nm were observed in CdAl$_2$O$_4$:0.0001Mn$^{2+}$ phosphor. The new emission band centered at 495 nm is attributed to the typical $^4T_{1g}(4G) \rightarrow ^6A_{1g}(6S)$ transition of the Mn$^{2+}$ ions. Fig. 6(c) shows the PL excitation and emission spectra of CdAl$_2$O$_4$:0.01Mn$^{2+}$ phosphor. As depicted in Fig. 6(c), the excitation spectrum monitored at 495 nm of CdAl$_2$O$_4$:0.01Mn$^{2+}$ sample primarily contains two broad bands centered at 230 nm and 260 nm. As for the emission spectrum, although the intensity of the blue emission is reduced compared to the pure CdAl$_2$O$_4$ phosphor, but the emission intensity of Mn$^{2+}$ ions increased as large as several hundred times. The emission spectrum of CdAl$_2$O$_4$ host and excitation spectrum of CdAl$_2$O$_4$:0.01Mn$^{2+}$ phosphor were shown in an immediate contrast in Fig. 6(d), the CdAl$_2$O$_4$ emission band centered at 495 nm showed a broad absorption at 230 nm, which is another emission band of Mn$^{2+}$ ions. Moreover, the emission intensity of Mn$^{2+}$ ions increased as large as several hundred times.\footnote{This journal is © The Royal Society of Chemistry 2017 RSC Adv., 2017, 7, 17612–17619 | 17615}
indicates that CdAl₂O₄:Mn²⁺ phosphors are more suitable for low-temperature environment application. From the emission spectra, it can be seen that Mn²⁺ ions emission intensity of the blue-green emission band increase until the maximum x at 0.015. When the concentration of Mn²⁺ is further increased above 0.015, the emission intensity begins to decrease which can be explained by the appearance of concentration quenching effect at high Mn²⁺ content. The PL excitation spectra of the samples with different concentrations of Mn²⁺ ions were monitored at the emission wavelength of 495 nm. However, the optimal doping concentration of 0.015 while 264 nm excitation band and d-d transition bands are 0.02. This indicates that the origins of excitation bands are different.

To further investigate the characteristics of CdAl₂O₄:Mn²⁺ phosphor, the thermal quenching behavior was measured. Fig. S4† depicts the temperature-dependent emission spectra. As can be seen from the picture, with the increase of environment temperature, the emission intensity gradually decreased. The emission intensity of CdAl₂O₄:Mn²⁺ phosphor has reduced by about 50% when the temperature exceeds 100 °C. This indicates that CdAl₂O₄:Mn²⁺ phosphors are more suitable for low-temperature environment application.

Furthermore, the decay curves of CdAl₂O₄:0.015Mn²⁺ phosphor (λex = 266 nm and λem = 495 nm) at room temperature was shown in Fig. S5.† The red curves are a fit of the experimental data to a first order exponential decay equation which indicates that there is one kind of luminescence center homogeneously distributed in the phosphor. This means that Mn²⁺ occupies the Cd²⁺ 18f sites. The decay curves were well fitted by a first-order exponential decay equation

\[ I(t) = I(0) \exp(-t/\tau) \]

where \( I(0) \) is the initial luminescence intensity, \( I(t) \) is the luminescence intensity at time \( t \), \( \tau \) is the decay constant for the exponential component. The fluorescence lifetime of the optimized blue-green emitting CdAl₂O₄:0.015-Mn²⁺ phosphor is 12.1 ms.

Fig. S6† exhibits the variation of the Commission Internationale de L’Eclairage (CIE) chromaticity coordinates of the CdAl₂O₄, CdAl₂O₄:0.0001Mn²⁺ and CdAl₂O₄:0.015Mn²⁺ phosphors under excitation at 230 nm. The pure CdAl₂O₄ host emits blue-violet light with CIE coordinates of (0.1674, 0.1053). When the concentration of Mn²⁺ is increased to 0.015, a blue-green light can be obtained with CIE coordinates of (0.0704, 0.4800). The results indicate that the emission light can be modulated from blue-violet to blue-green with the increasing doping content of Mn²⁺ ions.

3.3 Sites occupation and structural analysis

It is well known that Mn²⁺ ions with similar ionic radius and charge could enter into the lattice by substituting Cd²⁺ sites. In order to further investigate the phase formation depending on the Mn²⁺ substitution of CdAl₂O₄ phosphors, XRD patterns for the selected samples with 3% substitution amount of Cd for CdAl₂O₄ were shown in Fig. 8.

As shown in Fig. 8, all peaks were indexed by trigonal cell R3 (no. 148) with parameters close to CdAl₂O₄ crystal structures. The calculated and observed patterns fit fairly well, and no impurity phases were detected. The refined structural parameters of CdAl₂O₄:0.03Mn²⁺ are listed in Table S2.† With Mn²⁺ ions occupied Cd (18f) sites, the cell volume of compound is smaller than cell volume of CdAl₂O₄, which is in accordance with smaller value of ion radii (IR) of Mn²⁺ (CN 4, IR = 0.66 Å) in comparison with ion radii (IR) of Cd²⁺ (CN = 4, IR = 0.78 Å).

The Fourier transform infrared (FTIR) investigation was carried out to study the crystal structure. Fig. 9(a) and (b) shows the FTIR spectra of the as-prepared CdAl₂O₄ phosphor by high-temperature solid-state reaction method. The bands in the range 540–1000 cm⁻¹ can be attributed to the asymmetric stretching vibrations of [AlO₄]⁻ tetrahedral units as described in Fig. 9(a). And the bands in the range 540–400 cm⁻¹ was assigned

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**Fig. 7** Variation of excitation and emission spectra for CdAl₂O₄:xMn²⁺ samples.

**Fig. 8** Rietveld analysis patterns of X-ray powder diffraction data of CdAl₂O₄:0.03Mn²⁺ phosphors.
to asymmetric stretching vibrations of Cd–O bands of [CdO$_4^{6-}$] tetrahedral units as shown in Fig. 9(a).

3.4 Measurement of optical bandgap

Fig. 10 gives the UV-vis absorption spectra of CdAl$_2$O$_4$ and CdAl$_2$O$_4$:0.015Mn$^{2+}$ phosphors. It is observed that all of the samples have strong absorption of UV light. With the introduction of Mn$^{2+}$, the abstraction band edge of the CdAl$_2$O$_4$:0.01Mn$^{2+}$ phosphor redshifts obviously, which indicates that the introduced Mn$^{2+}$ ions provide a new absorption band. Simultaneously, the optical band gap of CdAl$_2$O$_4$ phosphor has been shrinking significantly. The correlation between the absorption coefficient of semiconductor oxides and optical band gap $E_{\text{gap}}$ can be determined by the following equation:\cite{25,26}

$$F(R_a)h\nu \propto (h\nu - E_{\text{gap}})^n$$

where $R_a$ is the reflectivity of the sample, $h$ is the Plank constant, $\nu$ is the photon energy, and $n$ is determined by the transition type ($n = 1/2, 2, 3/2$ or $3$ for allowed direct, allowed indirect, forbidden direct and forbidden indirect electronic transitions, respectively).

According to the calculation results of band structures from density functional theory (DFT) below (Fig. 11), CdAl$_2$O$_4$ and CdAl$_2$O$_4$:Mn$^{2+}$ has been confirmed to be allowed indirect band gap materials, therefore, $n = 2$:

$$hv - E_{\text{gap}} \propto (F(R_a)h\nu)^{1/2}$$

Based on the results, we can get the Tauc-plots of samples as shown in the inset of Fig. 10. As can be seen from the picture, with the introduction of Mn$^{2+}$ ions, the Mn$^{2+}$ doped band gap of CdAl$_2$O$_4$ was shrinking from 4.937 eV into 4.580 eV. The absorption boundary of Mn$^{2+}$ ions in CdAl$_2$O$_4$ host is 3.867 eV.

3.5 First principles calculation

We calculated the crystal structure optimization and electronic structure of the CdAl$_2$O$_4$ and CdAl$_2$O$_4$:Mn$^{2+}$ phosphors by the first-principles method. The optimized crystal structural parameters of CdAl$_2$O$_4$ after geometry optimization are listed in Table S1.\ddagger The optimized crystal structural parameters were very close to the results of Rietveld refinements. To further verify the reasonableness of the structure we calculate the phonon spectrum of CdAl$_2$O$_4$ after geometry optimization (see Fig. S1\ddagger). As can be seen from the Fig. S1,\ddagger the absence of any imaginary frequency phonon modes proves the dynamical stability of the CdAl$_2$O$_4$ with R3 structure.

The calculated band structures in Fig. 11 revealed that CdAl$_2$O$_4$:Mn$^{2+}$ is indirect band gap materials ($G$ point to $Q$ point). It is well known that the CASTEP simulation results tend to underestimate the band-gap energies of the semiconductor materials due to the limited dimension of the atomic cluster. Therefore, a scissors operator of 2.235 eV was introduced to widen the gap to consistent with the measured optical band gap value (4.937 eV) of CdAl$_2$O$_4$:Mn$^{2+}$ phosphors, which agrees well with the absorption edge (250 nm) of the CdAl$_2$O$_4$ without Mn$^{2+}$ doping.

According to the orbital population analysis of CdAl$_2$O$_4$ phosphor from Fig. 12 (left), the top of the valence band is...
dominated by the 2p orbitals of O atoms, the interband transition could be ascribed to the charge transfer from the O-2p to Cd-4d orbitals, which basically corresponds to the excitation energy of CdAl2O4 host in Fig. 5(a). From Fig. 12 (right) it can be seen that with the Mn2+ doping, the valence band is dominated by the 2p orbitals of O and 3d orbitals of Mn2+ ions, the interband transition could be ascribed to the charge transfer from the O-2p to Cd-4d orbitals and from the Mn-3d to Mn-3d orbitals, which basically corresponds to the excitation energy of CdAl2O4:0.015Mn2+ sample in Fig. 5(b).

Herein, by combining the excitation spectra of CdAl2O4:Mn2+ phosphors with the parity selection rules and Sugano–Tanabe energy diagram, a detailed spectral analysis and the fitting of crystal field parameters were performed. The sharp bands in the excitation spectra centered at 353 nm (2.83 x 10^4 cm⁻¹) and 426 nm (2.35 x 10^4 cm⁻¹) can be attributed to the parity forbidden transitions of 4E₇̃(4D) → 6A₁g(6S) and 4E₇̃(4G) → 5A₈g(6S) which are D₉q-independent, respectively. The vertical dashed line indicates the appropriate value of ΔB (4.98), and the horizontal ones are used to compare the peaks of the absorption of Mn2⁺ to the energy states in the Tanabe–Sugano diagram in Fig. 13. With the assignment of 17B + 5C = E(4E₉g(4D)) and 10B + 5C = E(4E₉g(4G)) the Racah parameters B and C for the tetrahedrally coordinated Mn2⁺ were calculated to be B = 692.8 cm⁻¹, C = 3307 cm⁻¹, and γ = C/B = 4.77. Δ/B = 4.98 and Δo = 3450 cm⁻¹. Since Mn2⁺ occupies the four-coordinated Cd2⁺ lattice in CdAl2O4, it is reported that ΔT for tetrahedral complexes is approximately 4/9 of Δo for an octahedral complex. Therefore, the crystal field splitting parameter 10D₉q = ΔT = 4/9Δo = 1533 cm⁻¹ of Mn2⁺ in CdAl2O4 were derived.

4. Conclusion

In conclusion, the structure of new CdAl2O4 material with space group R3 was determined. Mn2⁺ ions activated blue-green emitting phosphors CdAl2O4:xMn2⁺ have also been successfully obtained by a conventional high-temperature solid-state reaction method in an air atmosphere. The typical transitions of Mn2⁺ ions in emission and excitation spectra were observed both in MnCO3 and MnO2 prepared CdAl2O4:0.01Mn2⁺ phosphors. CdAl2O4:Mn2⁺ fluorescent materials have a strong characteristic emission of Mn2⁺ ions when MnCO3 was added as manganese source. That is to say in the CdAl2O4 host, Mn2⁺ ions were not oxidized in the air atmosphere in high-temperature solid-state reaction. For MnO2 as manganese source, the CdAl2O4:Mn2⁺ phosphors still exhibit a strong characteristic emission of Mn2⁺ ions. This indicates that the luminescent centers of Mn2⁺ ions come from the Mn4⁺ ions which were reduced at high temperatures. The crystal field splitting parameter 10D₉q was estimated to be 1533 cm⁻¹. Although the valence of manganese source was different, their shape and intensities of emission and excitation spectra were very similar. When excited by ultraviolet light, the Mn2⁺ ions occupied Cd sites emitting strong blue-green luminescence.

Acknowledgements

This work was supported by Science and Technology Development Plan of Shandong Province, China (2014GNC110013) and National Natural Science Foundation for Young (No. 2130696).
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