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The nature of Mn^{4+} luminescence in the orthorhombic perovskite, $GdAlO_3$

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In this paper we report on the spectroscopic properties of Mn^{4+} ($3d^3$) ion in the orthorhombic perovskite, $GdAlO_3$ and calculate the energy levels using the exchange charge model of crystal-field theory. The calculated Mn^{4+} energy levels are in good agreement with the experimental data. The results of our calculations yield the crystal-field splitting and Racah parameters of $Dq = 2083$ cm^{-1}, $B = 780$ cm^{-1} and $C = 2864$ cm^{-1}, with $C/B = 3.67$. The emission spectrum is composed of the zero phonon line ($^2E_g \rightarrow {}^4A_{2g}$ transition) with dominating intensity and its vibrational sidebands. We have also calculated Mulliken atomic charges and bond populations for three isostructural perovskites ($GdAlO_3$, $LaGaO_3$ and $CaZrO_3$) to seek correlation between the energy position of the Mn^{4+} ^2E level and the covalence of Mn^{4+}–O^{2-} chemical bonding.

1. Introduction

Professor Georges Boulon has contributed to the fundamental understanding of the optical properties of transition metals ions such as Mn^{4+} and Cr^{3+} in solids [1–6]. In the spirit of his contributions we wish to report on the spectroscopic properties of the Mn^{4+} ion in the orthorhombic perovskite $GdAlO_3$. This investigation is a part of our effort to provide an understanding of the factors which govern two properties of interest: (1) the variations in the crystal-field splitting (10Dq), and (2) the electron-electron (Racah) parameters, B and C [7–19]. The Racah parameters are responsible for the energy of the Mn^{4+} emission transition ($^2E_g \rightarrow {}^4A_{2g}$). Cataloging these properties and conducting a cross-cutting comparative study sheds light on "structure-property" relationships that can guide the search for new commercially important phosphors.

In this work we examine the room temperature luminescence of Mn^{4+} in the perovskite $GdAlO_3$, calculate the Mn^{4+} energy level structure by the exchange charge model of crystal-field theory and compare the obtained theoretical results with the experimental data. A comparative study of the optical properties of Mn^{4+} in the orthorhombic perovskites $LaGaO_3$, $CaZrO_3$, $YAlO_3$ and the rhombohedral perovskite $LaAlO_3$ is also presented.

2. Experimental

The syntheses were carried out by the conventional solid-state reaction technique. The materials were formulated as $Gd_{1-x}Ca_xAl_{1-x}Mn_xO_3$. The substitution of Ca^{2+} for Gd^{3+} assists in stabilizing the Mn^{4+} on the Al^{3+} sites of the $GdAlO_3$ lattice (due to need for charge compensation). The required amounts of high purity starting materials Gd_2O_3, $CaCO_3$, Al_2O_3 and Mn_2O_3 are blended and heated twice at 1300 °C for a period of 10 h in a covered alumina crucible. The samples were homogenized between the two heating steps.

The X-ray diffraction pattern indicates the formation of $GdAlO_3$ phase (Fig. 1). Luminescence measurements were performed as previously described [7]. The spectra were corrected for the wavelength dependent variations in the Xe-lamp intensity and the photomultiplier response.

3. Results and discussions

3.1. Crystal structure of $GdAlO_3$

In the cubic ABO_3 perovskites, the A cations are present in a

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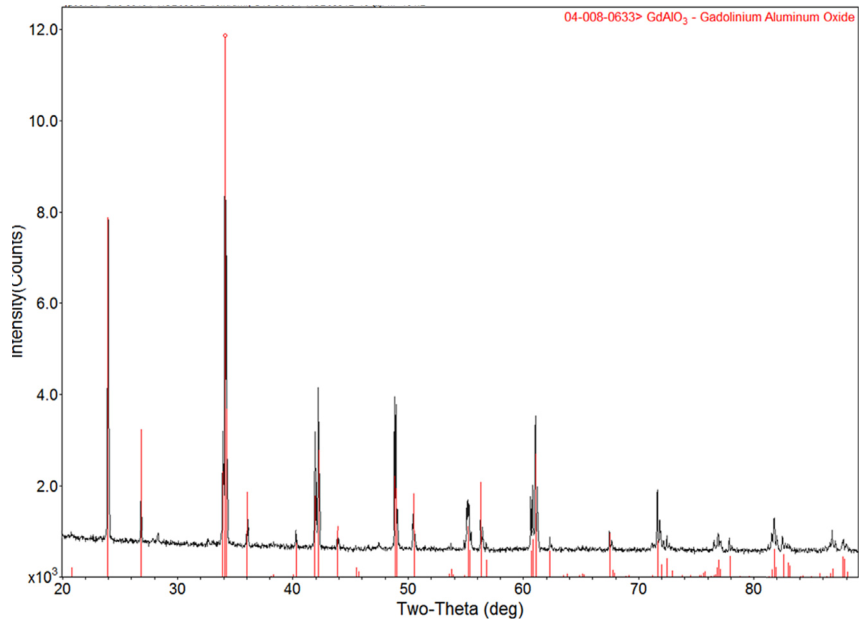

Fig. 1. The powder X-ray diffraction pattern of $Gd_{0.999}Ca_{0.001}Al_{0.999}Mn_{0.001}O_3$.

twelve fold coordination and the B cations are in an octahedral (six fold) coordination. In the $GdAlO_3$ perovskite, a cooperative rotation of the octahedral groups along the cubic [110] axis yields the orthorhombic $GdFeO_3$ (space group Pbnm) structural type in which the Gd^{3+} ions are coordinated to eight O^{2-} ions [20]. The perovskite $GdAlO_3$ crystallizes with space group Pbnm (#62) and lattice constants $a = 5.3049$ Å, $b = 7.4485$ Å and $c = 5.2537$ Å [21]. Fig. 2 illustrates one unit cell of $GdAlO_3$. The Gd^{3+} cations are in eight-fold oxygen coordination. The Al^{3+} cations are in six-fold oxygen coordination with average Al^{3+}–O^{2-} bond distance of 1.906 Å (Fig. 3); the AlO_6 octahedral clusters are aligned along the *c* crystallographic axis.

3.2. Method of calculations

Although the details of calculation are available elsewhere we think it benefits the readers to summarize the computational method in this section. The energy levels of impurity ions with an unfilled d-shell in a crystal field of arbitrary symmetry are calculated by diagonalizing the following CF Hamiltonian [22]:

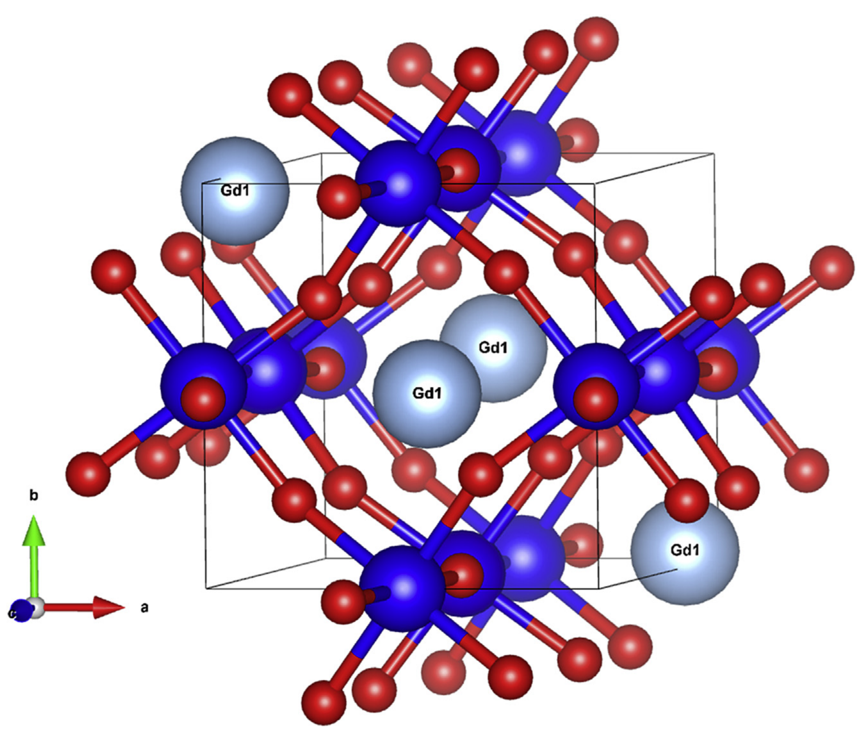

Fig. 2. One unit cell of $GdAlO_3$. The Al^{3+} ions are located inside the octahedra formed by the oxygen ions. Drawn with VESTA [17].

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