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Short communication

Optical properties of Mn^{3+} ions in Cs_2NaAlF_6 and Cs_2NaGaF_6 single crystals

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ABSTRACT

The optical properties of Mn^{3+} ions in the elpasolites Cs_2NaGaF_6 and Cs_2NaAlF_6 have been investigated by absorption spectroscopy at 4.2 K. The absorption spectra are dominated by the spin-allowed $^5E \rightarrow {}^5T_2$ transition and the transition between the two Jahn-Teller components of the ^5E level. The crystal-field parameter Dq was determined and a low crystal-field situation was established for both Mn^{3+}-doped fluorides. The Jahn-Teller stabilization energies of the ^5E and $^5T_2$ levels were calculated and the obtained values shown a strong Jahn-Teller splitting in the ^5E ground state.

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1. Introduction

Recent advances in tunable solid-state lasers have generated a strong interest in the development and investigation of new light-emitting compounds in the visible and near-infrared spectral regions [1–5]. In common to all these materials is the use of 3*d* transition metal ions as active ions. The unfilled 3d electron shell of these ions has a number of low-lying energy levels, between among which optical transitions can occur generating luminescence emission. Since the 3d electrons are on the outside of the transition metal ion, their optical properties are directly affected by the static and dynamic properties of then, the associated optical spectra are characterized by broad and/or sharp bands. The broad bands are due to the electron-phonon coupling. Therefore, this coupling is interesting for the manufacture of tunable solid-state lasers at room temperature. However, the extent of the phonon spectrum of a crystal favors the nonradiative transitions that reduce strongly the laser efficiency. Consequently, it is interesting to choose materials that have a low cutoff frequency in comparison to the energy gap among the electronic levels of the metal transition ion. In this case, fluoride compounds are promising candidates because they present phonons cutoff frequency lower than 600 cm^{-1}. Moreover, many studies in the scientific literature have shown that the Jahn-Teller effect can have a strong influence in the Mn^{3+} ion optical spectra in octahedral coordination [6–8]. This effect distorts the ^5E ground state and increases the complexity of the observed structures in the optical spectra.

This work presents results of the optical absorption of Mn^{3+} ions in single crystals of Cs_2NaGaF_6 and Cs_2NaAlF_6. These hosts have the rhombohedral 12L-type crystal structure and belong to the $R-\bar{3}\,m$ space group with hexagonal lattice parameters a = 6.30 Å and c = 30.5 Å for Cs_2NaGaF_6 and a = 6.18 Å and c = 29.9 Å for Cs_2NaAlF_6 [9,10]. The Na^+ and Ga^{3+} (or Al^{3+}) cations are ordered and octahedrally surrounded by F^- anions. There are two not-equivalent sites for Ga^{3+} ions in Cs_2NaGaF_6 and Al^{3+} ions in Cs_2NaAlF_6, as shown in Fig. 1. One site is characterized by units of (GaF_6) or (AlF_6) linked to two octahedra of (NaF_6) by corners. The second site is similar to the first one but in this case the octahedra are linked by faces [11]. In the doped material Mn^{3+} ions (ionic radius r = 0.66 Å) replace Ga^{3+} ions (r = 0.62 Å) in Cs_2NaGaF_6 and Al^{3+} ions (r = 0.53 Å) in Cs_2NaAlF_6. The manganese centers in Cs_2NaGaF_6 and Cs_2NaAlF_6 were investigated through absorption measurements at low temperature. From the spectra the energy levels of the Mn^{3+} were assigned and the crystal-field parameters Dq, and the Jahn-Teller stabilization energy for both samples were calculated.

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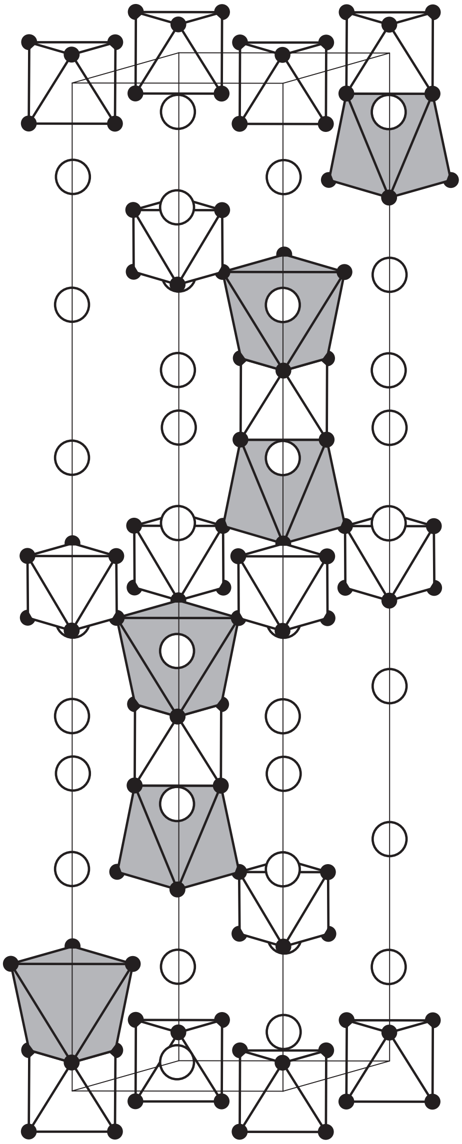

Fig. 1. A polyhedral representation showing the connectivity between the AlF_6 (or GaF_6) and NaF_6 octahedra. The white and gray polyhedra represent AlF_6 (or GaF_6) and NaF_6, respectively, while the white and black atoms correspond to cesium and fluorine. Some of the octahedra have been removed for clarity.

2. Experimental

The hydrothermal technique was used to produce single crystals of $Cs_2NaGa_{1-x}Mn_xF_6$ and $Cs_2NaAl_{1-x}Mn_xF_6$ doped with $x = 0.01$ (1.0%) of Mn^{3+} as described in Ref. [12]. An aqueous solution containing CsF (30–35 mol%) and NaF was prepared with the CsF/NaF varying from 4.8 to 5.2. The raw oxides Ga_2O_3 or Al_2O_3 were added with a desired Mn_2O_3 quantities. The synthesis was done by the direct temperature-gradient method, which consists of the transport of the precursors from a high temperature region to a region with lower temperature, in which the solution will be supersaturated and the crystal grows at a fixed temperature of 750 K, with a temperature gradient of 2K/cm and under pressures of 100–150 MPa. The hydrothermal conditions of high temperature and high pressure were achieved at autoclaves with copper liners with 40 cm^3 of volume. Single crystals up to 0.5 cm^3 in size were spontaneously nucleated in the upper region of the autoclave. The phase homogeneity and the crystal lattice parameters were tested by the X-ray diffraction method [11,12]. The most perfect single crystals were selected for optical measurements. In this work were studied samples with 1.0% of Mn^{3+} doping level. The samples were placed at a Janis ST-100 gas flow cryostat, for measurements at 4.2 K. The light source was a 50 W broadband tungsten lamp, with its intensity modulated by a variable speed chopper. The transmitted light was scanned with a 2061 MacPherson spectrometer equipped with a RCA C31034-128 photomultiplier for signal detection. The output signals were amplified by a phase-sensitive apparatus (lock-in) and stored in a personal computer. Absorption spectra were obtained with an average spectral resolution of 1 nm for the region between 350 and 1000 nm. The intensity of the transmitted light was corrected by the lamp emission intensity and the results were also corrected by the response of the detection system.

3. Results and discussion

The absorption spectra of Cs_2NaGaF_6 and Cs_2NaAlF_6 doped with 1.0% Mn^{3+} at liquid helium temperatures are shown in Figs. 2 and 3. These spectra are dominated by two strong absorption bands with maxima situated around 538 nm (band 1) and 732 nm (band 2) for $Cs_2NaGaF_6{:}Mn^{3+}$ and 556 nm (band 1) and 790 nm (band 2) for $Cs_2NaAlF_6{:}Mn^{3+}$. In the gallate, the bandwidths are of about 4250 and 2220 cm^{-1} for bands 1 and 2, respectively, while in the aluminate these values are 4650 and 1110 cm^{-1}. In addition to the broadbands, both spectra exhibit singularities (dips) on the long-wavelength side of the band 1.

The band 1 in each spectrum was assigned to the inter-configurational transition between the two quintet levels, i.e., the fundamental ^5E and the $^5T_2$ excited level. In fact, this is the only spin-allowed electronic transition for ions with d^4 electronic configuration. The large bandwidth at 4.2 K is caused mainly by the Jahn-Teller splitting of both energy levels which will be discussed below. From the energies of the $^5E \rightarrow {}^5T_2$ absorption band maxima the crystal-field parameter Dq were obtained: 1859 and 1799 cm^{-1}, for $Cs_2NaGaF_6{:}Mn^{3+}$ and $Cs_2NaAlF_6{:}Mn^{3+}$, respectively. The spin-forbidden quintet-triplet and quintet-singlet transitions (that is from the ^5E ground state to $^3T_1$, ^3E, $^1T_2$, ^1E and others) are characterized by narrow and weak lines and, thus, it is very difficult to observe them in the absorption spectra. The dips located at 588 and 585 nm in the $^5E \rightarrow {}^5T_2$ transition bands of the gallate and aluminate, respectively, are due to a Fano-antiresonance effect between the ^3E and $^5T_2$ levels [13]. In the Fano's model, the mixing between

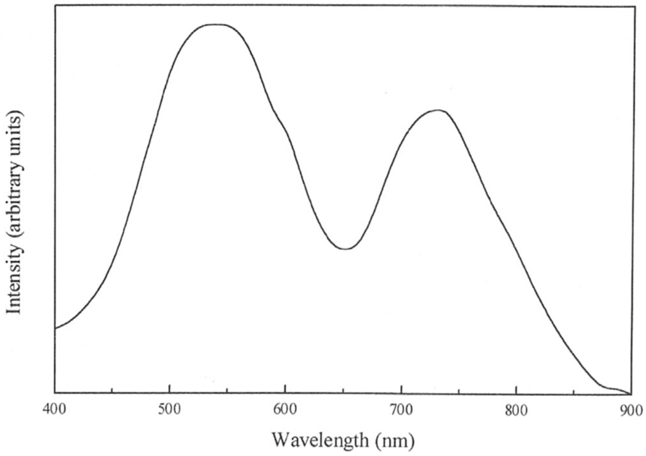

Fig. 2. Absorption spectrum of Cs_2NaGaF_6 with 1.0 at.% of Mn^{3+} at liquid helium temperature.

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