



## Synthesis and characterization of Cr<sup>4+</sup>-doped Ca<sub>2</sub>GeO<sub>4</sub> tunable crystal



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### ARTICLE INFO

#### Article history:

Received 4 November 2014  
Received in revised form 13 February 2015  
Accepted 16 February 2015  
Available online 23 February 2015

#### Keywords:

Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal  
Structure characterization  
Spectral analysis

### ABSTRACT

The growth, structure and spectral properties of a Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> single crystal have been reported in this paper. XPS analysis demonstrated that the chromium in the single crystal is tetravalent; this is further confirmed by fluorescence spectroscopy. The near-infrared, visible absorption and near-infrared luminescence spectrum of the Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal are presented in this paper. In the absorption spectra, the transitions from the <sup>3</sup>A<sub>2</sub> ground state to the three orbital components of the <sup>3</sup>T<sub>1</sub> and <sup>3</sup>T<sub>2</sub> excited state are observed. The range of the fluorescence spectroscopy band of the Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal at room temperature is from 1000 nm to 1600 nm. The single band with a maximum peak at 1317 nm at room temperature is attributed to the <sup>3</sup>T<sub>2</sub> → <sup>3</sup>A<sub>2</sub> transition of the Cr<sup>4+</sup> ions. The FWHM of the fluorescence spectrum is 201.19 nm, and the fluorescence lifetime and emission cross section are up to 12 μs and 4.61 × 10<sup>-19</sup> cm<sup>2</sup>, respectively.

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## 1. Introduction

Diode pumped passively Q-switched laser produces high peak power and high repetition rate laser light in the nanosecond and sub-nanosecond range, which is characterized by compact structure, economy, and solidification [1,2]. This laser can be widely used in radar, ranging, remote sensing, nonlinear optical processing, and material processing [3–6]. Cr<sup>4+</sup> ions in a crystal show great potential for use in a tunable solid-state laser in the spectral range of 1.1–2 μm at room temperature [7]. Cr<sup>4+</sup> ion laser crystal mainly includes Cr<sup>4+</sup>:YAG [8,9]. The main absorption bands of the crystals include 0.48 μm, 0.65 μm, and 1 μm. The absorption transition that is excited from ground state <sup>3</sup>A<sub>2</sub> to state <sup>3</sup>T<sub>1</sub> results in 0.65 μm absorption band, whereas 1 μm infrared absorption band is the result of absorption transition that is excited from ground state <sup>3</sup>A<sub>2</sub> to state <sup>3</sup>T<sub>2</sub>. Cr<sup>4+</sup>:YAG crystal growth, spectroscopic properties, and laser properties were studied [10,11]. Moreover, the research indicated that not only 1.06 μm Nd:YAG is the ideal pump source of Cr<sup>4+</sup>:YAG, but also InGaAs high-power diode is the preferred pump source of Cr<sup>4+</sup>:YAG lasers, which are toward all-solid state and miniaturization. Cr<sup>4+</sup>:YAG crystal have large amounts of

Cr<sup>3+</sup> ions as impurities, leading to low Cr<sup>4+</sup> concentrations and reducing the figure of merit in the crystal [12,13]. Cr<sup>4+</sup>:YAG crystal requires a charge-compensating codopant during crystal growth process. In addition, the nonradiative relaxation of the laser level is significant in Cr<sup>4+</sup>:YAG crystals. Moreover, the fluorescence-quenching effect of Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> is significantly less than that of Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> at room temperature. Therefore, Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal is a promising near-infrared laser material. Researchers state that these crystals are ideal optical communication tunable laser crystals. Several wide practical applications, such as in medicine, telecommunication fiber sensing, and semiconductor diodes, have been recently demonstrated for Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal [14–18]. In this paper, we present the flux growth and properties of the Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal.

## 2. Experimental details

In this experiment, Cr<sub>2</sub>O<sub>3</sub>(5N), GeO<sub>2</sub>(5N), CaCO<sub>3</sub> (analytical grade) and CaCl<sub>2</sub> (analytical grade) were used as reagents. The Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystal was grown by the flux growth method from the flux of CaCl<sub>2</sub> with a Ca<sub>2</sub>GeO<sub>4</sub> concentration of 65 wt.% and a Cr<sub>2</sub>O<sub>3</sub> concentration of 0.5 wt.%. The crystallization parameters were as follows: growth direction is [100]; the platinum wire seeding temperature range was 700–1000 °C; the pulling rate was 0.1–0.2 mm/h; the seed rotation speed was 20–60 rpm; the growth atmosphere was oxygen. Finally, the fully transparent, dark-green Cr<sup>4+</sup>:Ca<sub>2</sub>GeO<sub>4</sub> crystals with more than Ø15 mm × 60 mm were been grown under the growth conditions. In this experiment, the GeO<sub>2</sub> content was in excess by 5–8% to account for the volatility of GeO<sub>2</sub> at the high temperatures used. The crystal image is shown in Fig. 1.

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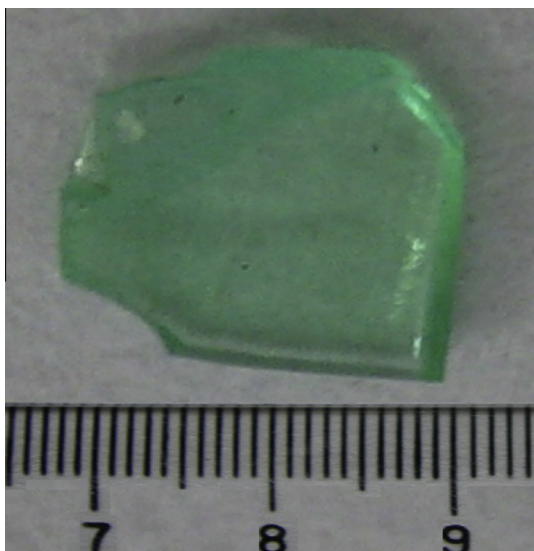
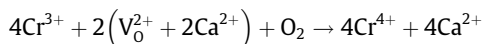


Fig. 1. Image of  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal.

### 3. Results and discussion

#### 3.1. The formation mechanism of the $\text{Cr}^{4+}$ ion

In the case of a  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal grown by the flux method, the  $\text{Cr}^{4+}$  ion was obtained by oxidizing of  $\text{Cr}^{3+}$  from  $\text{Cr}_2\text{O}_3$  in the oxygen atmosphere with the Ca element added to the melt as a charge compensator. The roles of Ca and  $\text{O}_2$  are explained using the following chemical reaction [19]:



where  $\text{V}_0^{2+}$  indicates the oxygen vacancy in the crystal.

The powder X-ray diffraction results for the 0.5 wt.%  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  single crystal are shown in Fig. 2. A single phase of the  $\text{Ca}_2\text{GeO}_4$  with no additional peaks indicates that  $\text{Cr}^{4+}$  has been successfully incorporated in the crystal by the flux method. The result is in accordance with the standard JCPDS card (No. 26-0304). According to the JCPDS26-0304 card, the crystal structure can be indexed as an olivine-type structure. According to the diffraction formula:

$$2d \sin(\theta) = n\lambda \quad (1)$$

When  $n = 1$ , this formula can be written as follows:  $d = \lambda/2 \sin(\theta)$ .

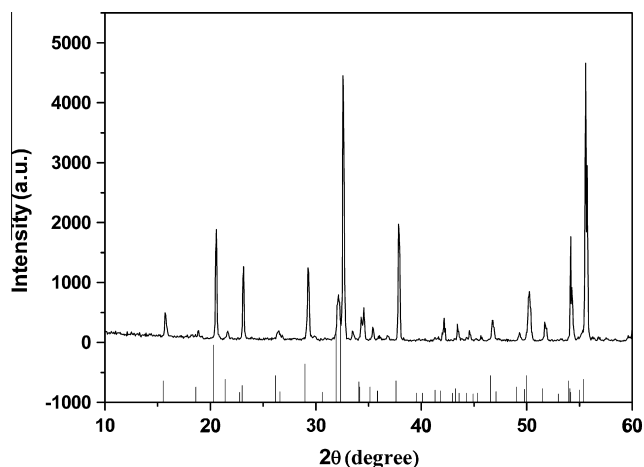


Fig. 2. XRD curve of the 0.5 wt.%  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal.

The lattice constants of the  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal can be obtained by the following calculation formula of the tetragonal system.

$$d = \frac{abc}{\sqrt{h^2a^2b^2 + h^2b^2c^2 + k^2a^2c^2}} \dots \quad (2)$$

$d$  values can be obtained with Formula (1). We selected four different crystal plane ( $hkl$ ) values, such as (111), (121), (200) and (002), and then we placed the corresponding  $d$  values into Formula (2) to produce four equations. The lattice constant has been obtained by solving equations with  $a = 5.3209 \text{ \AA}$ ,  $b = 6.6648 \text{ \AA}$ , and  $c = 11.2606 \text{ \AA}$ . The results are very similar to those of the pure  $\text{Ca}_2\text{GeO}_4$  phase. The lattice distortion caused by  $\text{Cr}^{4+}$  ions is quite small because the radii of the  $\text{Cr}^{4+}$  and  $\text{Ge}^{4+}$  are very similar.

#### 3.2. Raman spectra

The Raman spectra of the  $\text{Ca}_2\text{GeO}_4$  single crystal are shown in Fig. 3. The two strongest lines at  $736$  and  $760 \text{ cm}^{-1}$  in the  $\text{Ca}_2\text{GeO}_4$  crystal are attributed to the  $(\text{GeO}_4)^{4-}$  tetrahedral  $\nu_3$  and  $\nu_1$  stretching modes. The weak Raman peaks at  $428$  and  $680 \text{ cm}^{-1}$  are similar to those peaks that were reported in literature [20].

#### 3.3. XPS analysis of the $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$ crystal

Fig. 4 shows the XPS survey spectra of the 0.5 wt.%  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal. Fig. 4 demonstrates that the  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal has Cr, Ca, Ge, O and C elements, where the C element is not an inherent component in the crystal. Information about the hydrogen element cannot be obtained from photoelectron spectroscopy, Thus,  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  crystal may have an H-element.

The atomic concentrations of major elements and the peak banding energy of the elements in the crystal are shown in Table 1. The table does not present the content of Cr element because the  $\text{Cr}^{4+}$  ion content in this crystal is less than the lowest measured value limits (0.1 mol%) used in the photoelectron spectroscopy, the content of the Cr element cannot be detected because of two main reasons. the sensitivity of the apparatus is low, the segregation coefficient of Cr element is small, which results in the low actual concentration of  $\text{Cr}^{4+}$  ions in this crystal.

In addition, the ratio of the main elements Ca:Ge:O is 1.98:1:4.15 in the crystal sample, but the ratio is 2:1:4 in  $\text{Ca}_2\text{GeO}_4$  crystal. This difference is caused by impurities in the Ca, Ge, and O

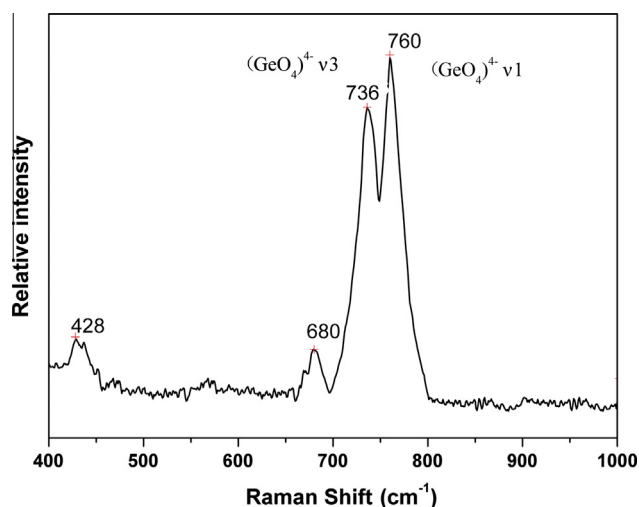


Fig. 3. Raman spectra of the  $\text{Cr}^{4+}:\text{Ca}_2\text{GeO}_4$  polycrystallines.

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