Synthesis and Optical Properties of $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$: Cr^{3+} Powders*

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The $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ powders with dopant contents ranging from $x = 0.005$ to 0.35 have been prepared by sol-gel method. The powders were prepared from aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, chrome nitrate $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and citric acid and heat-treated at $650\text{--}1300^\circ\text{C}$ for 5 h. The effect of dopant concentration and heat-treating temperature on the structural and optical properties of the synthesized samples has been studied. The results showed that the structure, the size and optical properties of $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ crystallites strongly depended on the mole fraction x and heating temperature. At low heating temperatures, the samples with the low mole fraction x exhibit $\gamma\text{-Al}_2\text{O}_3$ phase and the emission spectra consist of a broad asymmetric peak with the maximum at 691 nm. With the high mole fraction x , the samples consist of $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_3 phases. By increasing the mole fraction x , the emission bands are broadened and shifted towards the long-wavelength side. At high heating temperatures, all the synthesized samples are $\alpha\text{-Al}_2\text{O}_3$ single phase and the emission spectra mainly consist of lines at 691.6 and 693.2 nm. [DOI: 10.1380/ejsnt.2011.531]

Keywords: Cr^{3+} -doped Al_2O_3 powders; Sol-gel method; Structural properties; Optical properties

I. INTRODUCTION

Aluminium oxide materials play a key role in many technologies due to its remarkable physical properties, such as a high melting point, hydrophobicity, high elastic modulus, high optical transparency, high refractive index (about 1.76 at 632.8 nm wavelength), thermal and chemical stability, low surface acidity, and dielectric characteristics. The Al_2O_3 materials exhibit more than 15 distinct crystallographic phases, and it can undergo a variety of transitions until the most-stable $\alpha\text{-Al}_2\text{O}_3$ phase, in which all the cations are in a six-coordinate environment, forms at high temperature [1]. It is well-known that $\gamma\text{-Al}_2\text{O}_3$ is an extremely important form of the known alumina crystalline phases, widely applied as a catalyst and catalyst support of transition element clusters in the automotive and petroleum industries. $\alpha\text{-Al}_2\text{O}_3$ doped with transition metal Cr^{3+} and Ti^{3+} ions is the most important phase for laser hosts, possessing excellent emitting properties [2]. The $\text{Al}_2\text{O}_3\text{:Cr}^{3+}$ crystal has no absorption band in the near infrared range and has ever acted as a landmark in development of laser history [3], and will still play an important role in future. There are many methods to prepare $\text{Al}_2\text{O}_3\text{:Cr}^{3+}$ materials, such as the sol-gel method, solid-state reaction, pulsed laser deposition, hydrothermal method and so on. Because of the existence of many various crystallographic phases, in order to obtain the alumina materials with desired phase, in this work we studied the effect of dopant concentration and heat-treating temperature on the structural and optical properties of the $\text{Al}_2\text{O}_3\text{:Cr}^{3+}$ samples synthesized by sol-gel method.

II. EXPERIMENTAL

The $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ powders with dopant contents ranging from $x = 0.005$ to 0.3 have been prepared

by sol-gel method. The powders were prepared from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and citric acid. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solutions were mixed with the Al^{3+} -to- Cr^{3+} mole ratios of $(2-x) : x$. Citric acid aqueous solution was added to the above solution and the mixed solution temperature was kept constant at 70°C until a highly viscous gel was formed. After drying in air at 120°C for 24 h, the gel is converted to a xerogel more opaque and dense. The xerogel was annealed in the temperature range of $650\text{--}1300^\circ\text{C}$ in air for 5 h. The crystal structure of the samples was characterized by a Siemens D5005 X-ray diffraction (XRD) diffractometer. Photoluminescence (PL) spectra and photoluminescence excitation (PLE) spectra were measured at room temperature using a Fluorolog FL3-22 spectrofluorometer with a xenon lamp of 450 W being used as an excitation source.

III. RESULTS AND DISCUSSION

The XRD patterns of the of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$ and heat-treated at $650\text{--}900^\circ\text{C}$ are shown in Fig. 1. The samples heat-treated at 650 and 750°C are amorphous. The $\gamma\text{-Al}_2\text{O}_3$ phase with very broad diffraction peaks are clearly seen in the samples calcined at $800\text{--}900^\circ\text{C}$. In the XRD patterns no any peak of impurity phase has been observed. In the heat-treating temperature range from 800 to 900°C , the position and the full width at half maximum of the diffraction peaks are similar.

Figure 2 shows the XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.1$ and heat-treated at $650\text{--}900^\circ\text{C}$. Unlike the samples with $x = 0.005$, for the samples with $x = 0.1$, the characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ phase can be clearly seen already in the samples calcined at 750°C .

The XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.2$ and heat-treated at $650\text{--}900^\circ\text{C}$ are shown in Fig. 3. Contrary to the case of the samples with $x = 0.005$ and 0.1 , in the XRD pattern of the sample with $x = 0.2$ undergone a heat-treatment at the temperature of 650°C , the peaks corresponding to Cr_2O_3 phase appeared. No additional peaks due to $\gamma\text{-Al}_2\text{O}_3$ phase are observed. With increasing heat-treatment temperature, the intensity of

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FIG. 1: XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, heat-treated at different temperatures. (a) $T = 650$, (b) 750 , (c) 800 , (d) 850 , and (e) 900°C .

FIG. 3: XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.2$, heat-treated at different temperatures. (a) $T = 650$, (b) 750 , (c) 800 , (d) 850 , and (e) 900°C .

FIG. 2: XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.1$, heat-treated at different temperatures. (a) $T = 650$, (b) 750 , (c) 800 , (d) 850 , and (e) 900°C .

FIG. 4: XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.35$, heat-treated at different temperatures. (a) $T = 650$, (b) 750 , (c) 800 , (d) 850 , and (e) 900°C .

the diffraction peaks of Cr_2O_3 phase decreases, but that of the diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ phase increases. Besides, some weak diffraction peaks of $\alpha\text{-Al}_2\text{O}_3$ phase are also observed.

The lattice constants and the average crystalline sizes of all the mentioned samples calculated from the XRD patterns are shown in Table I. It can be seen from the table, for each value of x , the lattice constants almost keep constant in the calcined temperature range of $750\text{--}900^\circ\text{C}$. It is also interested to notice that the grains of the $\gamma\text{-Al}_2\text{O}_3$ phase in the samples calcined at the temperatures in the range of $750\text{--}900^\circ\text{C}$ have very small average sizes of $6\text{--}7\text{ nm}$.

For studying the effect of high dopant concentration on the structure of the synthesized samples, the XRD patterns of the samples with $x = 0.35$, heat-treated at different temperatures were examined. The results presented in Fig. 4 show that at heat-treating temperature 650°C , in addition to the diffraction peaks of the Cr_2O_3 phase, the $\alpha\text{-Al}_2\text{O}_3$ phase narrow peaks are observed, although it is well-known that the $\alpha\text{-Al}_2\text{O}_3$ phase only exists at the high temperature. For higher heat-treating temperature, the $\gamma\text{-Al}_2\text{O}_3$ phase weak peaks are observed. With in-

creasing heat-treatment temperature, the intensity of the diffraction peaks of the Cr_2O_3 phase decreases, but that of the diffraction peaks of the $\alpha\text{-Al}_2\text{O}_3$ phase increases. Different from the samples with $x = 0.2$, for the samples with $x = 0.35$, the intensity of the $\alpha\text{-Al}_2\text{O}_3$ phase peaks stronger than that of the $\gamma\text{-Al}_2\text{O}_3$ phase peaks.

For examining the effect of dopant concentration on the structural properties of the synthesized samples at high heat-treating temperature, the XRD patterns of samples with different mole fractions x and undergone a heat-treatment at 1000°C and 1300°C were investigated and the results are presented in Figs. 5 and 6, respectively. At 1000°C , for $x = 0.005$, the XRD patterns present the cubic $\gamma\text{-Al}_2\text{O}_3$ phase with additional weak peaks that correspond to the presence of the hexagonal $\alpha\text{-Al}_2\text{O}_3$ phase. With increasing the mole fraction x , the intensity of the diffraction peaks of the $\gamma\text{-Al}_2\text{O}_3$ phase decreases, but that of the diffraction peaks of the $\alpha\text{-Al}_2\text{O}_3$ phase increases and for $x = 0.35$, no diffraction peaks of the $\gamma\text{-Al}_2\text{O}_3$ are observed. Besides, for $x = 0.25$, characteristic peaks of the Cr_2O_3 phase are observed. At 1300°C , all the synthesized samples with different mole fractions x are pure $\alpha\text{-Al}_2\text{O}_3$ phase. It can be noticed that at high heat-treating

TABLE I: The dependence of the lattice constants and the average crystalline sizes on the amount of Cr in $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ with different heat-treatment temperatures.

x	T (°C)	a (Å)	D (nm)
0.005	800-900	7.92 ± 0.02	7
0.1	750-900	7.94 ± 0.02	6 - 7
0.2	750-900	7.96 ± 0.02	6

FIG. 5: XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with different mole fractions x , heat-treated at 1000°C . (a) $x = 0.005$, (b) 0.1 (c) 0.25, (d) 0.3, and (e) 0.35.

FIG. 6: XRD patterns of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with different mole fractions x , heat-treated at 1300°C . (a) $x = 0.005$, (b) 0.1 (c) 0.25, (d) 0.3, and (e) 0.35.

temperature, with increasing the mole fraction x , the position of the diffraction peaks shifted towards the high-theta side, which is associated with a increase in the d_{hkl} and the lattice constants. The values of d_{hkl} and the lattice constants of the samples calculated from the XRD patterns are shown in Table II.

The PL spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, heat-treated at $650\text{--}900^\circ\text{C}$, excited by 556 nm wavelength are shown in Fig. 7. The results showed that the PL spectra of the $\gamma\text{-Al}_2\text{O}_3$ nanocrystalline samples with size $6\text{--}7\text{ nm}$ consist of a broad asymmetric peak with the maximum at 691 nm (noted by R-line). The position of the peak at 691 nm indicates that the broad band belong to the non-uniformly broadened $^2\text{E}(^2\text{G}) \rightarrow$

FIG. 7: PL spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, heat-treated at different temperatures, excited by 556 nm wavelength. (a) $T = 650$, (b) 750 , (c) 800 , (d) 850 , and (e) 900°C .

FIG. 8: PL spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with different mole fractions x , heat-treated at 900°C , excited by 556 nm wavelength. (a) $x = 0.005$, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.15, and (f) 0.2.

$^4\text{A}_2(^4\text{F})$ transitions in the Cr^{3+} ions. The extended long-wavelength structure of the non-uniformly broadened R-line is assigned to a vibronic tail of the pure electronic $^2\text{E}(^2\text{G}) \rightarrow ^4\text{A}_2(^4\text{F})$ transitions [4].

Figure 8 shows the PL spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with different mole fractions x and undergone a heat-treatment at 900°C , excited by 556 nm wavelength. It is seen from Fig. 8, with increasing the mole fraction x , the emission bands are broadened and shifted towards the long-wavelength side. As can be seen from table 1, with increasing the mole fraction x , the lattice constants of the $\gamma\text{-Al}_2\text{O}_3$ nanocrystals slightly increase, which is associated with a decrease in the ligand field located of the

TABLE II: The dependence of the d_{hkl} and lattice constants on the mole fraction x with different heat-treatment temperatures.

x	$T = 1000\text{ }^{\circ}\text{C}$				$T = 1300\text{ }^{\circ}\text{C}$			
	d_{012} (Å)	d_{104} (Å)	$a = b$ (Å)	c (Å)	d_{012} (Å)	d_{104} (Å)	$a = b$ (Å)	c (Å)
0.005	-	-	-	-	3.488	2.554	4.13	12.99
0.1	3.500	2.563	4.15	13.04	3.492	2.558	4.14	13.03
0.25	3.504	2.566	4.15	13.05	3.499	2.565	4.14	13.06
0.3	3.506	2.566	4.16	13.05	3.505	2.566	4.16	13.05
0.35	3.509	2.569	4.16	13.06	3.512	2.572	4.16	13.09

FIG. 9: PL spectrum of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, heat-treated at 1300°C , excited by 556 nm wavelength. FIG. 10: PLE spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, heat-treated at 1300°C , recorded at all the emission peaks shown in Fig. 9

Cr^{3+} ions. Therefore, the broad emission bands may be due to the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions. In addition, a large quantity of hanging bonds and defects also exist in these nanosized imperfect crystals, in particular, for the samples with high dopant contents, which further leads to the broadening towards the long-wavelength side of the emission band related to the Cr^{3+} ions.

The PL spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, undergone a heat-treatment at 1300°C , and excited by 556 nm wavelength are shown in Fig. 9. Unlike the samples with $x = 0.005$, heat-treated at $650\text{--}900^{\circ}\text{C}$, the PL spectrum of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$,

heat-treated at 1300°C consists of two strong lines at 691.6 and 693.2 nm and weakly lines at 659 , 699 , 674 , 678 , 700 , 706 , 712 , and 725 nm . Two lines at 691.6 (noted by R_1 -line) and 693.2 nm (R_2 -line) are well-known due to the $\bar{\text{E}}({}^2\text{E}({}^2\text{G})) \rightarrow {}^4\text{A}_2({}^4\text{F})$ and $2\bar{\text{A}}({}^2\text{E}({}^2\text{G})) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions within the Cr^{3+} ions in the $\alpha\text{-Al}_2\text{O}_3$ octahedral crystal field, respectively [4–6]. Figure 10 shows the PLE spectra of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ samples with $x = 0.005$, heat-treated at 1300°C , recorded at all the emission peaks shown in Fig. 9. As seen from the Fig. 10, the PLE spectra of sample did not depend on the recorded wavelengths. This result shows that the lines at 659 , 699 , 674 , 678 , 700 , 706 , 712 , and 725 nm are phonon-sidebands of the lines R_1 and R_2 . The PLE spectra consist of two strong broad absorption bands with peak positions at around 399 and 556 nm , corresponding to spin-allowed ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ and ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_2({}^4\text{F})$ transitions of the Cr^{3+} ions on the octahedral sites of $\alpha\text{-Al}_2\text{O}_3$ [5, 6]. Beside, a weak sharp peak at 692 nm corresponding to the transitions from the basic level ${}^4\text{A}_2({}^4\text{F})$ to the lowest excited level ${}^2\text{E}({}^2\text{G})$, is also observed.

IV. CONCLUSION

The effect of dopant concentration and heat-treating temperature on the structural and optical properties of the synthesized samples has been studied. The results showed that the structure, the size and the optical properties of the $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$ crystallites strongly depended on the mole fraction x and the heating temperature. At low heating temperatures, the samples with the low mole fraction x exhibit the $\gamma\text{-Al}_2\text{O}_3$ phase and the emission spectra consist of a broad asymmetric peak with the maximum at 691 nm corresponding to the ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions within the Cr^{3+} ions in the octahedral sites of the $\gamma\text{-Al}_2\text{O}_3$ and a vibronic tail of the pure electronic ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions. With the high mole fraction x , the synthesized samples consist of the $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_3 phases. By increasing the mole fraction x , the emission bands, which originate from the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions within the Cr^{3+} ions in the octahedral sites of the $\gamma\text{-Al}_2\text{O}_3$ phase, are broadened and shifted towards the long-wavelength side. At high heating temperatures, all the synthesized samples are $\alpha\text{-Al}_2\text{O}_3$ single phase and the emission spectra consist of mainly lines at 691.6 and 693.2 nm corresponding to the $\bar{\text{E}}({}^2\text{E}({}^2\text{G})) \rightarrow {}^4\text{A}_2({}^4\text{F})$ and $2\bar{\text{A}}({}^2\text{E}({}^2\text{G})) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transitions of the Cr^{3+} ions in the $\alpha\text{-Al}_2\text{O}_3$ octahedral crystal field.

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