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ARTICLE

Effect of Europium Ion on Pseudoboehmite Phase Transition and Microstructure

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Abstract: After doping $Eu(NO_3)_3$ into pseudoboehmite sol suspension, europium-doped pseudoboehmite xerogel was prepared by a spray-drying process. Effects of Eu^{3+} ions on pseudoboehmite phase transition and microstructure were investigated by differential thermal gravimetric analysis, X-ray powder diffraction and field emission transmission electron microscopy. Results show that upon doping of Eu^{3+} ions into pseudoboehmite, the phase transition temperatures of γ-Al_2O_3→θ-Al_2O_3 and θ-Al_2O_3→α-Al_2O_3 increase by 172 °C and 13 °C, respectively. It is found that Eu^{3+} ions entirely enter γ-Al_2O_3 or θ-Al_2O_3 crystal lattices, and the crystallinity of γ-Al_2O_3 is improved, resulting in increasing of the phase transition temperature of γ-Al_2O_3→θ-Al_2O_3. When α-Al_2O_3 is generated in the phase transition process, all of Eu^{3+} ions exist among α-Al_2O_3 grain boundaries in the form of compound $EuA1_{12}O_{19}$, which will hinder the bulk diffusion of Al^{3+} resulting in an increase of phase transformation temperature of θ-Al_2O_3→α-Al_2O_3 process.

Key words: pseudoboehmite; phase transition; Eu^{3+} doped; microstructure

Pseudoboehmite (AlOOH) is a crystal imperfect boehmite. When pseudoboehmite is calcined at 400~700 ℃, product γ-Al_2O_3 is widely used as a catalyst carrier, catalyst and adsorbent. Nano α-Al_2O_3, obtained by sintering pseudoboehmite at 1200 ℃, is extensively employed as a paint additive, top-grade ceramic, petrochemical efficient catalyst, sub-micron/nano abrasive and polishing materials, cosmetic filling materials and inorganic membrane materials. The study of pseudoboehmite phase transition on its application has received extensive attentions [1,2].

Phase transition temperatures of γ-Al_2O_3→θ-Al_2O_3 and θ-Al_2O_3→α-Al_2O_3 can be changed by adding metal ionic salts or metal oxides, which are reported in the literatures [3-25]. According to the literature survey, additions of B_2O_3, La_2O_3, Y_2O_3, CaO and salts of Ba, Sr and Ca can elevate phase transition temperature of θ-Al_2O_3→α-Al_2O_3. Additions of Fe_2O_3, CuO/Cu_2O, TiO_2, V_2O_5, $MgAl_2O_4$, γ-Al_2O_3 and α-Al_2O_3 can reduce phase transition temperature of θ-Al_2O_3→α-Al_2O_3. Additions of Ta_2O_5, Li_2O and MgO have no apparent effect on phase transition temperature of θ-Al_2O_3→α-Al_2O_3. Effects of Cr_2O_3, SiO_2 and ZrO_2 on phase transition temperature of θ-Al_2O_3→ α-Al_2O_3 are under way to be further studied.

Effects of Eu^{3+} ions on phase transition temperature of pseudoboehmite have not been reported yet in literature. Therefore, we would like to conduct the above mentioned investigation so as to provide technical evidence for pseudoboehmite applications in various fields.

1 Experiment

Pseudoboehmite powder supplied by the Aluminum Corporation of China Limited was prepared by a HNO_3 peptization method. The reagents were HNO_3 (analytical purity reagent) and $Eu(NO_3)_3$ (analytical purity reagent). AlOOH powder and redistilled water were mixed according to their stoichiometry and agitated to produce a suspension of solid content of 5% AlOOH. The suspension was continuously stirred and 5 mol/L nitric acid solution was

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added simultaneously to produce AlOOH colloid under the conditions of pH = 2 and stirring time for 3 h. AlOOH gel was obtained through drying and spraying by SD-06 spray dryer (Labplant, UK). And the sample obtained was labeled as Sp. $Eu(NO_3)_3$ with a molar ratio of $Eu(NO_3)_3$:AlOOH = 0.02:1 was proposed to AlOOH colloidal suspension. $Eu(NO_3)_3$ was fully dispersed into AlOOH sol via stirring for 1 h. Eu^{3+} doped AlOOH sample (labeled as Sp-E) was dried and sprayed by the spray dryer as mentioned above. Spray dying conditions were determined as follows: the colloidial suspension flow of 15 mL/min, air temperature of 150 ℃ and the sample outlet temperature of 62 ℃. Samples of Sp and Sp-E were sintered at 600, 900 ℃, 1100 and 1300 ℃, under ambient condition for 3 h with heating rate of 10 ℃/min GSL1600X tube furnace.

XRD analysis of the samples was conducted by a D/max-2500/PC type XRD diffractometry (Rigaku, Japan). Differential thermal gravimetric analysis (TG/DSC) of the sample was carried out using a STA 449C type thermal analyser (Netcsch, Germany). The sample (about 15 mg) was placed into the platinum crucible under N_2 atmosphere with a flow rate of 15 mL/min, heating rate of 10 ℃/min and the detection temperature range of 40 ℃ to 1500 ℃. Morphologies of samples were analyzed by Tecnai G2 F20 field emission transmission electron microscope (FETEM) (Philip. Netherlands).

2 Results and Discussions

Fig.1 shows the TG/DSC curves of AlOOH sample (Sp) under optimum conditions from the ambient temperature to 1500 ℃ in nitrogen atmosphere. The first endothermic peak of Sp sample is formed at 392 ℃. Both TG and DSC curves indicate that 23% mass loss between 220~450 ℃ is resulting from the loss of hydrate of AlOOH nH_2O. The second exothermic peak appearing at 882 ℃ is cuased by phase transition of γ-Al_2O_3→θAl_2O_3. Therefore, phase transition temperature of γ-Al_2O_3→θAl_2O_3 is estimated to be about 882 ℃. The third exothermic peak appearing at 1224 ℃ is caused by phase transition of θ-Al_2O_3→α-Al_2O_3, which corresponds to the phase transition temperature of θ-Al_2O_3→α-Al_2O_3. The last exothermic peak appears at 1396 ℃, which is caused by the reduction of surface energy, and thought to be the crystal growth of α-Al_2O_3.

Fig.2 shows TG/DSC curves of Eu^{3+} doped AlOOH sample (Sp-E). From the curves it can be seen that an endothermic peak at 122 ℃ results from the desorption of physical adsorbed water. The endothermic peak at 390 ℃ is the loss of crystal water in Sp-E sample. Above 535 ℃, AlOOH→γ-Al_2O_3 phase transition happens and Eu^{3+} ions replace Al^{3+} ions and enter the crystal lattice of γ-Al_2O_3 in the process of AlOOH→γ-Al_2O_3 phase transition. The endothermic reaction exists when Eu^{3+} ions substitute Al^{3+} ions in the lattice of γ-Al_2O_3. Endothermic effect starts at

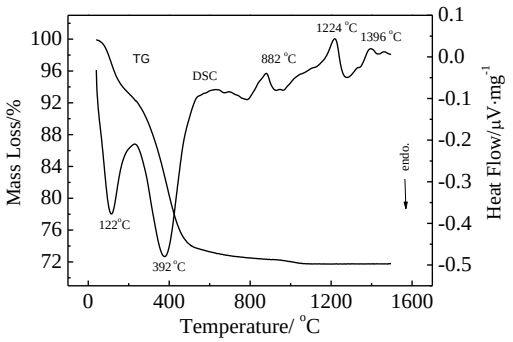

Fig.1 TG/DSC curves of AlOOH samples (Sp)

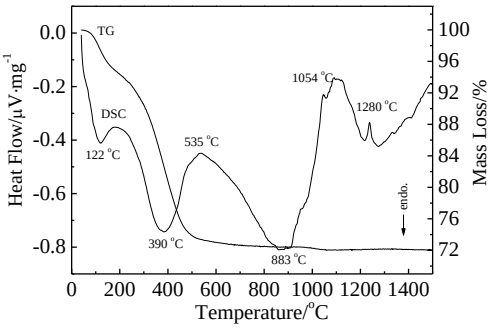

Fig.2 TG/DSC curves of Eu^{3+} doped AlOOH samples (Sp-E)

535 ℃ and is finished at 883 ℃. There is no significant phase transition endothermic peak of AlOOH→γ-Al_2O_3 in the temperature range of 500~900 ℃. Therefore, AlOOH→γ-Al_2O_3 phase transition temperature of Sp-E sample can't be inferred according to DSC curve. Exothermic peaks appearing at 1054 and 1237 ℃ are corresponding to the γ-Al_2O_3→θ-Al_2O_3 and θ-Al_2O_3→α-Al_2O_3 phase transitions, respectively. Due to addition of europium ions, phase transition temperatures of γ-Al_2O_3 →θ-Al_2O_3 and θ-Al_2O_3→α-Al_2O_3 are apparently elevated by 172 and 13 ℃, respectively.

XRD patterns of AlOOH samples Sp are shown in Fig.3. It can be summarized that the main phases are γ-Al_2O_3 with cubic structure at the sintering temperature of 600 ℃, γ-Al_2O_3 and a small amount of θ-Al_2O_3 with monoclinic structure at 900 ℃, θ-Al_2O_3 and a few α-Al_2O_3 rhombohedral structure at 1100 ℃, and single θ-Al_2O_3 phase at 1300 ℃. It further indicates that 882 ℃ and 1224 ℃ are the phase transition temperatures of γ-Al_2O_3→θ-Al_2O_3 and θ-Al_2O_3→α-Al_2O_3, respectively. Simultaneously, diffraction peaks of γ-Al_2O_3 and θ-Al_2O_3 are broadened obviously and diffraction peaks of α-Al_2O_3 sharpen, suggesting that γ-Al_2O_3 and θ-Al_2O_3 are composed of nano grains with the lower crystallinity and α-Al_2O_3 has a higher crystallinity.

XRD patterns of Eu^{3+} doped AlOOH samples Sp-E are shown in Fig.4. From the figure it is obvious, after

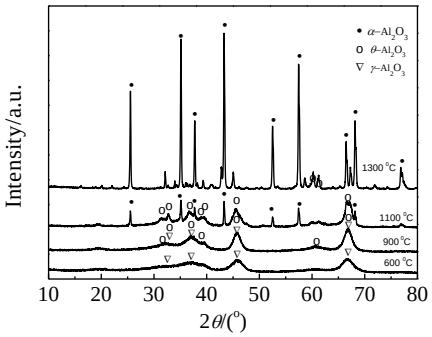

Fig.3 XRD patterns of AlOOH samples (Sp) sintered at different temperatures

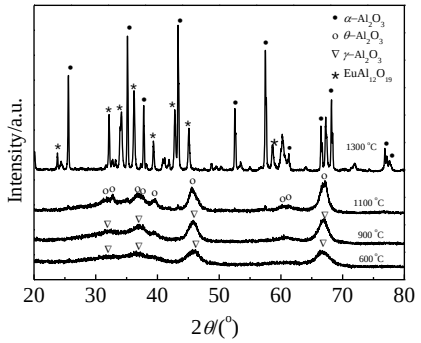

Fig.4 XRD patterns of Eu^{3+} doped AlOOH samples (Sp-E) sintered at different temperatures

calcination at 600 and 900 ℃, the Sp-E samples display a cubic structure of γ-Al_2O_3. Monoclinic structure of θ-Al_2O_3 is obtained at 1100 ℃, while the phase transition from γ-Al_2O_3 to θ-Al_2O_3 happens at 1054 ℃ as shown in Fig.2. The principal phase is α-Al_2O_3 with rhombohedral structure at 1300 ℃, suggesting that the phase transition of θ-Al_2O_3→α-Al_2O_3 occurs at 1237 ℃ according to Fig.2.

According to γ-Al_2O_3 and α-Al_2O_3 crystal parameters in Fig.3 and Fig.4, lattice constants (*a*, *b*, and *c*) and cell volume (*V*) of γ-Al_2O_3 and α-Al_2O_3 generated in the process of Sp and Sp-E phase transitions were calculated and are listed in Table 1. Crystal face (311) of γ-Al_2O_3 was taken to calculate the lattice constant *a* and cell volume ($V = a^3$) of γ-Al_2O_3. For orthorhombic crystals of α-Al_2O_3, (012), (110) and (113) crystal faces were chosen to calculate the lattice constants *a*, *b*, *c* and cell volumes ($V=abc$) of α-Al_2O_3.

It can be concluded from Table 1 that cell volume of γ-Al_2O_3 obtained from Sp-E sample is greater than the corresponding cell volume gained from Sp sample sintered at 600 ℃ and 900 ℃. The main reason is that Eu^{3+} ions substitute Al^{3+} ions and enter crystal lattice of γ-Al_2O_3, resulting in an increase of γ-Al_2O_3 cell volume. According to XRD patterns in Fig.4, Eu-containing compounds are not found at 1100 ℃, 900 ℃ and 600 ℃. Eu^{3+} ions, which are in the presence of substitution doping, entirely enter γ-Al_2O_3 and θ-Al_2O_3 lattices. Cell volumes of α-Al_2O_3 generated by Sp-E and Sp sample phase transitions are similar, suggesting that the Eu^{3+} ions do not enter α-Al_2O_3 lattice, but exist wholly in the form of $EuA1_{12}O_{19}$.

Table 1 Lattice constants of AlOOH (Sp) and Eu^{3+} doped AlOOH (Sp-E) sintered at different temperatures

Sample	Sintering temp./℃	Phase	*a*/nm	*b*/nm	*c*/nm	V/nm^3	$B_{1/2(400)}$*	$D_{(400)}$**
Xerogel	600	γ-Al_2O_3	0.795 08	0.795 08	0.795 08	0.502 61	2.69	3.167 7
	900	γ-Al_2O_3	0.799 08	0.799 08	0.799 08	0.510 24	1.76	4.841 5
	1300	α-Al_2O_3	0.291 66	0.412 64	1.301 52	0.156 6	-	-
Eu doped xerogel	600	γ-Al_2O_3	0.797 56	0.797 56	0.797 56	0.507 33	2.79	3.055 7
	900	γ-Al_2O_3	0.803 12	0.803 12	0.803 12	0.518 01	1.90	4.487 0
	1300	α-Al_2O_3	0.291 51	0.411 86	1.300 91	0.156 2	-	-

Note: $B_{1/2(400)}$*-full width at half maximum, $D_{(400)}$**-grain size

FETEM images of Eu^{3+} doped and undoped AlOOH samples Sp and Sp-E sintered at 1300 ℃ are shown in Fig.5. Comparing Fig.5a and Fig.5b, it is clear to see that crystallinity degree of α-Al_2O_3 is increased by Eu^{3+} doping. Additionally, it is found that the $EuA1_{12}O_{19}$ is formed along α-Al_2O_3 grain boundaries, which prevent the bulk diffusion of Al^{3+} ions, as shown in Fig.5b. Hence the phase transition temperature of θ-Al_2O_3→α-Al_2O_3 is raised accordingly. This observation was also evidenced by the Ref. [26] that the $EuAlO_3$ compound existed between α-Al_2O_3 grain boundaries, resulting in an increase in the crystallization temperature of α-Al_2O_3 when Eu^{3+} ion was doped.

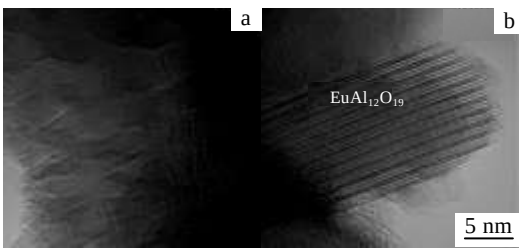

Fig.5 FETEM images of AlOOH samples (Sp) (a) and Eu^{3+} doped AlOOH samples (Sp-E) (b) sintered at 1300 °C

3 Conclusions

1) Phase transition temperatures of γ-Al_2O_3→θ-Al_2O_3 and θ-Al_2O_3→α-Al_2O_3 in the phase transition process of Eu^{3+} doped AlOOH sample are raised by 172 and 13 ℃, respectively. Eu^{3+} ions in the form of substitution doping replaces Al^{3+} ions and enter lattices of γ-Al_2O_3 and θ-Al_2O_3. Crystallinity degree of γ-Al_2O_3 can be improved by doping Eu^{3+} ion, which may be the main reason for the elevation of γ-Al_2O_3→θ-Al_2O_3 phase transition temperature.

2) Cell volume of α-Al_2O_3 formed in the phase transition process of Eu^{3+} doped AlOOH sample is found to be essentially constant, suggesting that Eu^{3+} ions do not enter the α-Al_2O_3 lattice, while exist in the form of $EuA1_{12}O_{19}$ compound. $EuA1_{12}O_{19}$ compound exists along α-Al_2O_3 grains boundaries, which hinder the bulk diffusion of Al^{3+} ions. Therefore, phase transition temperature of θ-Al_2O_3→α-Al_2O_3 is increased.

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铕离子对拟薄水铝石相变和微结构的影响机理研究

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摘 要：拟薄水铝石溶胶中加入 $Eu(NO_3)_3$ 后，采用喷雾干燥拟薄水铝石干凝胶。通过 TG-DSC、XRD 和 FETEM 等方法，对比分析了 Eu 离子对拟薄水铝石相变和微结构的影响机理。结果表明，掺杂 Eu 离子使拟薄水铝石相变过程中 γ-Al_2O_3→θ-Al_2O_3 和 θ-Al_2O_3→α-Al_2O_3 的相变温度分别提高了 172 ºC 和 13 ºC。Eu^{3+}离子全部进入 γ-Al_2O_3 和 θ-Al_2O_3 晶格，并提高了 γ-Al_2O_3 结晶度，因此提高 γ-Al_2O_3→θ-Al_2O_3 相变温度。相变生成 α-Al_2O_3 时，Eu 离子全部以 $EuA1_{12}O_{19}$ 存在于 α-Al_2O_3 晶界间阻止了 Al^{3+}体相扩散，因此导致 θ-Al_2O_3→α-Al_2O_3 相变温度升高。

关键词：拟薄水铝石；相变；微结构；铕离子掺杂

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