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Storage of oxygen in the interconversion $R_2O_2S/R_2O_2SO_4$ obtained by thermal decomposition of sulfonate rare earth

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Abstract

In this study, two compounds presenting characteristics different from each other were produced from the reaction between hydrated Eu+3 sulfate and Ba+2 diphenylamine-4-sulfonate using, respectively, aqueous solution for producing the Eu+3(C12H10NSO3)3.7H2O (A) compound and water/ethyl alcohol (7:1) solution for the Eu+3(C12H10NSO3)3.5H2O (B) production. The presence of alcohol molecules in the solution will interfere in the structural arrangement of anionic surfactant DAS- (diphenylamine-4-sulfonate) around the metal ions Eu3 allowing differentiation in the stoichiometric formulas, morphology, and thermal properties of these compounds and their derivatives. Thus, when treating both compounds under oxidizing atmosphere, we found different temperatures of the water loss and conversion of the intermediate pair oxydisulfate [Eu2O(SO4)2]/dioxysulfate [(Eu2O2SO4)]. However, the effect of water/surfactant/alcohol interactions in the metal ion structural arrangement becomes still more evident under reducing atmosphere. After this thermal treatment, significant changes were observed in the morphological characteristics and physical properties of the (Eu2O2S oxysulfide) in compound B with respect to compound A.

Keywords (Palavras chaves): Rare earth, Storage oxygen, Thermal analisys.

1. Introdução

Metal sulfonates participate in a wide range of applications in the field of ionic exchange, electrochemistry, catalysis activity in organic reactions, in the construction of polymers building blocks, and the pillared/layered structures [1–4]. The decomposition of metal ''d'' sulfonates generally gives oxides as final products while the decomposition of the lanthanide sulfonates (less of Ce^{3+}) sulfides and oxysulfates derives from their thermal and chemical stabilities. Due to these characteristics, they were very widely used in areas such as semiconductors, doping of phosphorescent materials, radiation detectors, X-ray-computed tomography, and in the oxygen storage [1, 5–12]. The versatile range of applications shown by these compounds originates from the intrinsic capacity of the sulfonate anion to occupy various coordination positions around the Eu^{3+} ion in particular ways. This is why, depending on the type of metal ion, the surfactant molecule can act as mono, bi, or tridentate ligand,

allowing the three oxygen atoms bonded to the central sulfur atom to interact with up to six metal cores [1, 4, 13, 14]. Apparently, this set of interaction opportunities appears due to the different degrees of negative charge polarization near oxygen atoms of the sulfonate group strongly induced by the ion charge of metal [1, 4, 14, 15]. Combining the metal ion-induced polarization, the electronic displacement, and the steric hindrance of organic groups, the actuation of a sulfonate group can vary from an electron sharing ligand to a site with redox characteristics [13, 15–17]. The final result of this interaction will confer specific properties to each molecule containing different types of sulfonates. The thermal decomposition of these compounds can appear in the form of oxides, sulfates, sulfides, oxysulfides, and oxysulfates [1, 5, 9, 13–15].

In this work, the storage of oxygen in the conversion of $R_2O_2S/R_2O_2SO_4$ obtained by thermal decomposition of sulfonate rare earth in air dynamic

atmosphere and reduce of $H_2/Ar:N_2$ is showed with the intention of verification in what temperature of thermal decomposition in that both samples are formed.

2 - Experimental procedure

The sulfonate materials were obtained by reaction of sulfonate of Barium $Ba(DAS)_2 \cdot H_2O$ with hydrates sulfate of europium $Eu_2(SO_4)_3 \cdot 8H_2O$, in the aqueous solution and ethanol/aqueous solution (1:7), this materials were characterization by elementar analysis, TG/DTG curves of the obtained and interconversion and XRD powder patterns.

3 Results and discussion

The elementar analysis reveals the stoichiometry for both samples obtained by aqueous solution rote (compound A, $Eu(DAS)_3 \cdot 7H_2O$) and ethanol/aqueous solution (compound B, $Eu(DAS)_3 \cdot 5H_2O$) can be represented by, compound A $[Eu(C_{12}H_{10}NSO_3)_3 \cdot 7H_2O]$ (MM = 1022.88 g/mol) (%C_{exp} = 42.27, %C_{calcd} = 42.62; %H_{exp} = 4.30, %H_{calcd} = 4.25; %N_{exp} = 4.11, %N_{calcd} = 4.15, and %Eu_{exp} = 14.87, %Eu_{calcd} = 14.61) and compound B $[Eu(C_{12}H_{10}NSO_3)_3 \cdot 5H_2O]$ (MM = 985. 96 g mol^{-1}) (%C_{exp} = 43.81, %C_{calcd} = 43.02; %H_{exp} = 4.06, %H_{calcd} = 4.03; %N_{exp} = 4.26, %N_{calcd} = 4.45, and %Eu_{exp} = 15.41, %Eu_{calcd} = 15.61) was defined by combining elemental analysis data and TG/DTG (A and B) curves under dynamic air atmosphere and a reduce mixture of (H_2 10%; Ar 90% /N_2 100%) (both at 10° C·min^{-1}) (Fig. 1a, b).

Thermal decomposition of compound A (diphenyl-4-aminesulfonate of Eu^{3+} heptahydrated) (Fig. 1a) has a total of five stages. In the simulation shown in Table 1, dehydration (Dm = 12.06 %) at temperature interval of 30–170° C is suggested as the first step. The anhydrous compound will decompose in the following four stages (170–1000° C). A more significant loss (Δm = 34.94 %) is attributed to interval 515–650° C, which also indicates the formation of an intermediate nonstoichiometry within $Eu_2O_{1.5}(SO_4)_{1.5}$ [18–20]. Curve stabilization occurs at 800° C. The last loss (Δm = 1.93 %) occurs in the 800 and 1000° C intervals and leaves the residue (dioxysulfate) $Eu_2O_2SO_4$, the XRD of which, is shown in Fig. 2a [20]. Decomposition of compound B (Fig. 1b) is also simulated in five consecutive stages (Table 2). The first of these losses (Dm = 5.13 %) was attributed to the dehydration of the compound at the 30–170° C interval. However, different from the previous process (A), water loss still persists at the interval between 170 and 350° C. After significant mass losses (Δm = 23.99 % and Dm = 29.61 %, respectively) in the third (350–504° C) and fourth (504–732° C) stages, the intermediate Eu^{3+} oxydisulfate $[Eu_2O(SO_4)_2]$ will be produced, which is finally converted in the fifth stage (732–1000° C) into dioxysulfate $(Eu_2O_2SO_4)$ with Δm = 4.06 % as it is shown by the XRD of the final product that is presented in Fig. 2b [20].

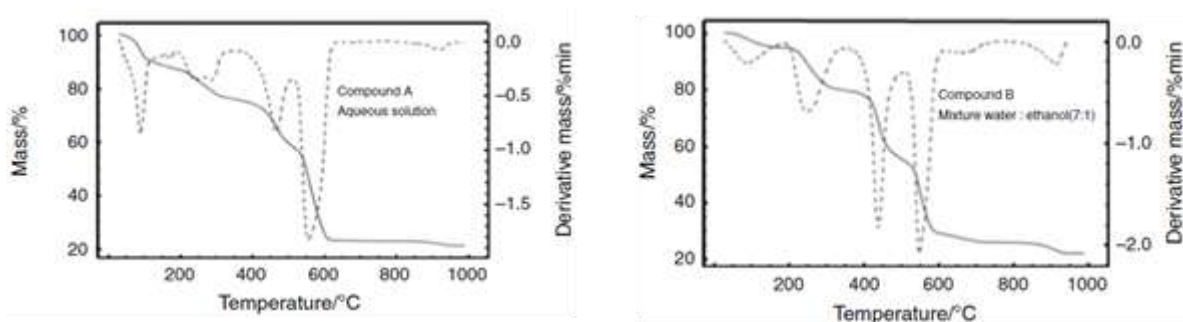Figure 1 - TG/DTG curves of $Eu(DAS)_3 \cdot 7H_2O$ (a) and $Eu(DAS)_3 \cdot 5H_2O$ (b) obtained about air atmosphere dynamic with rate 10° C·min^{-1} to 1000° C and flow 50 mL·min^{-1}.

Both compounds $Eu_2O_2SO_4$ obtained after thermal decomposition of compound A and B, were submitted at reduce atmosphere of (H_2 10%:Ar 90%/N_2 100%) about heating, and from this were obtained the dioxisulfide of Eu^{3+} Eu_2O_2S.

After at obtain of dioxisulfide, both compounds A and B dioxisulfide were submitted at the heating and were obtained the dioxisulfate $Eu_2O_2SO_4$ in different temperature showed in the figure 2.
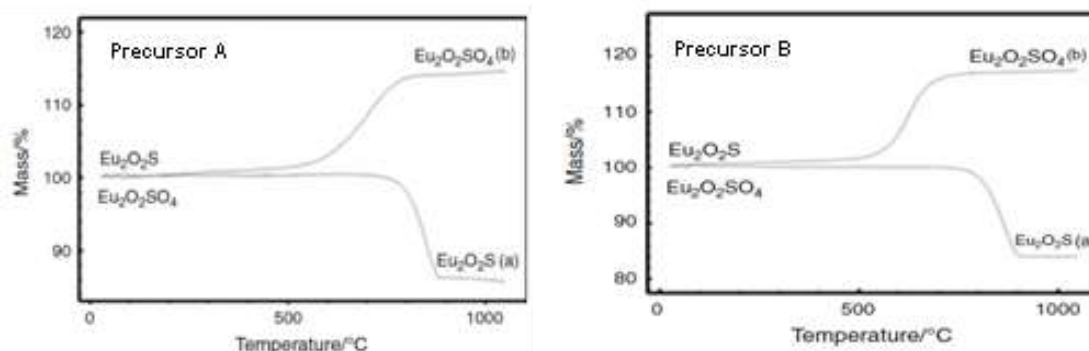

Figure 2 - Storage and loss of oxygen in the conversion and interconversion of $Eu_2O_2S/Eu_2O_2SO_4$ under dynamic air atmosphere and $R_2O_2SO_4/R_2O_2S$ in reduce atmosphere of (H_2:Ar/N_2).

The $Eu_2O_2SO_4$ (A) reduction carried out now at 950° C produces a product of 84.42 % (MM = 364.63 g mol^{-1}) (15.58 % loss). This value can be considered closest to that expected for Eu_2O_2S (85.18 % and MM = 367.92 g mol^{-1}). XRD (Fig. 3a) indicates Eu_2O_2S as a predominant phase, still occurring with low intensity peaks referring to oxide. This can indicate that below this temperature (Fig. 3a at 950° C), the Eu_2O_2S (A) can be constituted as single phase [21]. The previous procedure was adopted for the $Eu_2O_2SO_4/Eu_2O_2S$ (B) reduction under a reducing atmosphere (Fig. 2b). XRD (Fig. 3b) of the residue at 1050° C also indicated the presence of Eu_2O_2S [22]. We also observed peaks referring to Eu_2O_3. To delimit the ranges that are typical of Eu_2O_2S phase, other experiments were carried out at 920 and 1150° C. The loss in reduction up to 920° C (8.92 %) produced a 91.08 % residue, and the XRD diffraction pattern (Fig. 3b) indicated $Eu_2O_2SO_4$, Eu_2O_2S, and Eu_2O_3 [20, 22]. Finally, in the reduction at 1150° C, mass loss of 14.92 % of $Eu_2O_2SO_4$ left an 85.08 % residue (MM = 367.5 g mol^{-1}). In this case, XRD (Fig. 3b at 1050° C) can be attributed to compound Eu_2O_2S (14.82 and 85.18 % product (MM = 367.9 g mol^{-1}) as single phase [21, 22]. The oxysulfides

(Eu_2O_2S) obtained from A and B were weakly susceptible to storage oxygen to $Eu_2O_2SO_4$ under air at intervals 600–825° C (A) and 595–780° C (B) [21]. However, some details attracted our attention. Both $Eu_2O_2SO_4$ (A and B) were initially reduced at intervals of 770 and 880° C and 765 and 905° C, respectively. XRD of these residues at several temperatures (Fig. 3a, b) clearly indicate that the Eu_2O_2S (B) phase predominates at 1150° C (Fig. 3b), whereas Eu_2O_2S (A) can exist below 950° C (Fig. 3a). Then, the reason why reoxidation under air of the A residue is more probable is identified. The 880–950° C interval would be characterized by predominance of the reduced species Eu_2O_2S (A). Accordingly, Eu_2O_2S (B) product was in the temperature range (765–905° C) also containing oxidized species such as $Eu_2O_2SO_4$ and Eu_2O_3 (Fig. 3b at 920° C). Thus, as indicated by Figs. 2b and 3b, at 780° C, part of Eu_2O_2S (B) is already stored oxygen. The (B) spectrum is well defined because it was obtained at a temperature (1150° C) in which Eu_2O_2S is constituted as a single phase (Fig. 3b). The band broadening of Eu_2O_2S (A) XRD peaks at 1150° C can be explained by the presence of Eu_2O_3 and Eu_2O_2S (Fig. 3a).
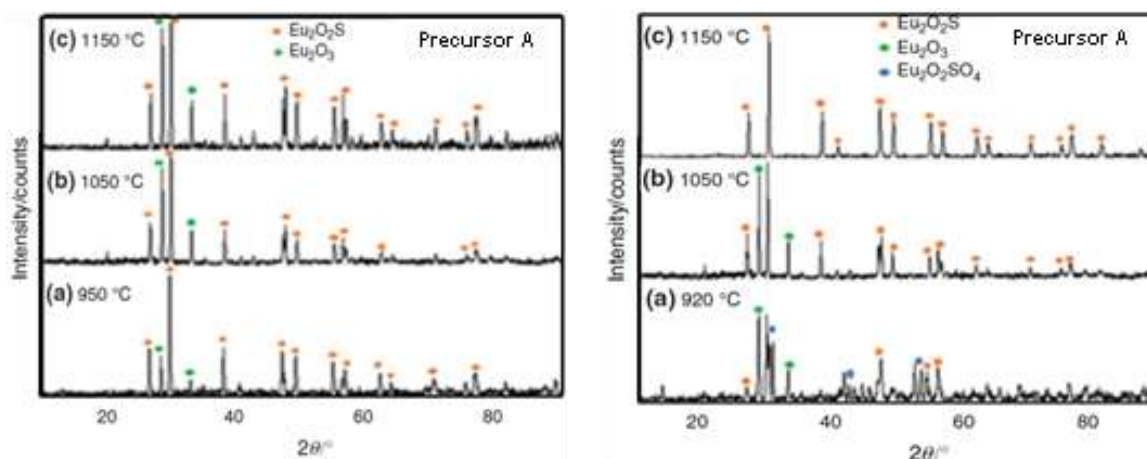
Figure 3 - XRD of $Eu_2O_2SO_4/Eu_2O_2S$ (Precursor A) conversion: (a) 950, (b) 1050 and (c) 1150° C and $Eu_2O_2SO_4/Eu_2O_2S$ (Precursor B) conversion: (a) 920, (b) 1050 and (c) 1150° C.

4 Conclusion

In the presence of ethyl alcohol is remarkable not only in stoichiometric, but also on the temperature of conversion and interconversion. The ethyl alcohol present of precursor B and absent the precursor A showed different degree hydration, the precursor A have 7 H2O [Eu(DAS)3▫7H2O)] and the precursor B have 5 H2O [Eu(DAS)3▫5H2O)] and their products Eu2O2S, Eu2O2SO4 are obtained in different temperatures. The reduction of Eu2O2S from precursor A start at 800° C whereas what the precursor B start at 680° C, however at conversion in EuO2SO4 from the precursor B start at 820 °C whereas what the conversion this compound from the precursor A start in 780° C.

5 References

1. Zhang H, Jiang H, Gong H, Sun Z-L. Characteristics of thermal decomposition products of rare earth, alkali earth metal and transition metal p-toluenesulfonates. J. Therm. Anal. Calorim. 2005;79:731–5. doi:10.1007/s10973-005-0604-y.

2. Wang M, Jiang H, Wang Z-C. Dehydration studies of Co(II), Cu(II) and Zn(II) methanesulfonates. J. Therm. Anal. Calorim. 2006;8:751–4. doi:10.1007/s10973-005-7064-2.

3. Delgado S, Molina-Ontoria A, Medina M-E, Pastor C-J, Jimenez-Aparicio R, Priego JL. An unexpected sulfinate–sulfonate mixed coordination polymer of copper(II). Inorg. Chem. Commun. 2006;9:1289–92. doi:10.1016/j.inoche.2006.06.026.

4. Yang J, Li L, Ma J-F, Liu Y-Y, Ma J-C. Two new barium sulfonates with pillared layered structures. J. Mol. Struct. 2006;788:43–8. doi:10.1016/j.molstruc.2005.11.016.

5. Selvan R-K, Gedanken A. Synthesis and characterization of hierarchically structured La2O2M@C:Eu3+. Eur. J. Inorg. Chem. 2010;0: 5685–91. doi: 10.1002/ejic.201000632.

6. Llanos J, Sanchez V, Mujica C, Buljan A. Synthesis, physical properties, and electronic structure of rare earths oxysulfides Ln2O2S (Ln=Sm, Eu). Mater. Res. Bull. 2002;379:2285–91. doi:10.1016/S0025-5408(02)00936-4.

7. Bang J, Abboudi M, Abrams B, Hooloway P. Combustion synthesis of Eu, Tb and Tm doped Ln2O2S(Ln=Y,La,Gd) phosphors. J. Lumin. 2004;106:177–85. doi:10.1016/j.jlumin.2003.09.005.

8. Zhao F, Yuan M, Zhang W, Gao S. Monodisperse lanthanide oxysulfide nanocrystals. J. Am. Chem. Soc.

2006;128:11758–9. doi:10.1021/ja0638410.

9. Ikeue K, Kawano T, Eto M, Zhang D, Machida M. X-ray structural study on the different redox behaviors of La and Pr oxysulfates/oxysulfides. J. Alloys and Compd. 2008;451:338–40. doi:10.1016/j.jallcom.2007.04.145.

10. Zhang D, Yoshioka F, Ikeue K, Machida M. Synthesis and oxygen release/storage properties of Ce-substituted La-oxysulfates, (La1-XCeX)O2SO4. Chem. Mater. 2008;20:6697–703. doi:10.1021/cm801629b.

11. Machida M, Kawamura K, Ito K, Ikeue K. Large capacity oxygen storage by lanthanide oxysulfate/oxysulfide systems. Chem. Mater. 2005;17:1487–92. doi:10.1021/cm0479640.

12. Machida M, Kawano T, Eto M, Zhang D, Ikeue K. Ln dependence of the large-capacity oxygen storage/release property of Ln oxysulfate/oxysulfide systems. Chem. Mater. 2007;19:954–60. doi:10.1021/cm062625n.

13. Machado L-C, Marins A-A-L, Muri E-J-B, Biondo A, Matos J-R, Mazali I-O. Complexation of the Fe(III) and Fe(II) sulphates with diphenyl-4-amine barium sulphonate (DAS): synthesis, thermogravimetric and spectroscopic studies. J. Therm. Anal. Calorim. 2009;97:289–96. doi:10.1007/s10973-009-0259-1.

14. Yang J, Ma J-F, Wu D-M, Guto L-P, Liu J-F. Syntheses, crystal structures and characterization of divalent transition metal sulfonate complexes with o-phenanthroline. J. Mol. Struct. 2003;657:333–41. doi:10.1016/S0022-2860(03)00428-9.

15. Charbonner F. Thermal behavior of some compounds of methanesulfonic acid with transition metals. Thermochim. Acta. 1979;33:31–9. doi:10.1016/0040-6031(79)87027-6.

16. de Maria M-F-V, Matos J-R, de Farias R-F. Synthesis, characterization and a thermal (TG-DSC) study of gadolinium and lutetium methanesulfonate coordination compounds with pyridine-N-oxide and 2-, 3- and 4- picoline-N-oxides. J. Serbian Chem. Soc. 2005;70:1041–8. doi:10.2298/JSC0509041d.

17. de Moura M-F-V, Matos J-R, de Farias R-F. Thermal degradation study of gadolinium and lutetium methanesulfonates. Thermochim. Acta. 2004;414:159–66. doi:10.1016/j.tca.2003.12.020.

18. dos Santos A-V, Matos J-R. Dehydration studies of rare earth p-toluenesulfonate hydrates by TG/DTG and DSC. J. Alloys and Compd. 2002;344:195–8. doi:10.1016/S0925-8388(02)00339-0.

19. dos Santos A-V. p-Toluene sulfonates of earth rare hydrated:synthesis, characterization and study thermoanalytic in different atmospheres. Ph.D. Thesis, Chemistry Institute of São Paulo, 1998.

20. Karsruhe FIZ, ICSD Collection code 95819.

21. Machado L-C, D'azeredo M-T-O, Corrêa H-P-S, Matos J-R, Mazali I-O. Formation of oxysulfide Ln2O2S and oxysulfate Ln2O2SO4 phases in the thermal decomposition process of lanthanide sulfonates (Ln = La, Sm). J. Therm. Anal. Calorim. 2012; 107:305–11. doi:10.1007/s10973-011-1451-7.

22. JCPDS—International Centre for Diffraction Data, 1996;26:1418.