

THE VARIOUS METHODS OF PREPARATION OF THE PEROVSKITE COMPOUND SrCeO₃ BY LIQUID METHODS

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Abstract

The research of authors is focused on the possibility of preparation SrCeO₃ by liquid methods. Sr(NO₃)₂ and Ce(SO₄)₂·4H₂O were selected as starting materials for three basic methods of preparation – the precipitation method, citrate method (sol-gel) and oxalic acid method. It was studied which technique and reaction conditions will be the most appropriate for preparation of SrCeO₃ as a basic lattice for doping by lanthanides. The emphasis was placed especially on the change of phase composition of samples with increasing temperature. Doped SrCeO₃ could be used as an inorganic pigment depending on its chemical and physical properties.

Introduction

Perovskite group is derived from mineral calcium titanium oxide CaTiO₃ which was discovered by German mineralogist Gustav Rose in 1820 (1839) in the Akhmatovskaya Pit, Namyamskiye Mountains, Zlatoust district, Urals^{1,2}. The name perovskite obtained from Russian mineralogist Lev. A. Perovski, because he characterized the structure of this mineral². The typical formula of perovskite group is ABX₃ where A is large cation with different valence, B is transition metal and X represents oxide or halide³ (most frequently referred to as formula ABO₃). The crystals include octahedral units BO₆ with large A atoms occupying the interstitial positions⁴. Perovskites are generally mixtures of binary oxides types AO:BO₂ and A₂O₃:B₂O₃, i.e. ABO₃⁵. Compounds of this group received great interest in material science due to many diverse electric, magnetic, piezoelectric, optical, catalytic or magnetoresistive properties³.

Compounds in Sr-Ce-O system depending on the oxidation states of cerium, Ce⁴⁺: SrCeO₃ and Sr₂CeO₄ in SrO-CeO₂ system or Ce³⁺: SrCe₄O₇ and Sr₂Ce₂O₅ in SrO-Ce₂O₃ system⁶. SrCeO₃ has orthorhombic space group *Pmcn*. It is mostly used as the high-temperature proton conducting electrolyte in hydrogen pumps, solid oxide fuel cell, in hydrogen sensors etc.^{6,7}.

Compounds with SrCeO₃ structure (with or without dopants) can be prepared by many ways. The basic method was solid state reaction - the mixing of oxides, firing (one temperature⁸, sequential firing⁹ or change atmosphere e.g. oxygen¹⁰), compounds can be milled¹¹ and at the end pressed into pellets and subsequently fired¹². The next were wet methods: from solutions - citrate method (from nitrates with citric acid) and oxalic acid method (from nitrates with oxalic acid)¹³ were called sol-gel methods. Another option was preparation via chelated water-soluble complex method (from nitrates with citric acid and EDTA¹⁴) or synthesis by ethylene glycol (from nitrates with nitric acid and chelating agent EG¹⁵). Preparation by glycine-nitrate gel combustion method was next - starting materials were dissolved in nitric acid, mixed, glycine and ammonia were added, subsequently evaporated to form a gel and combustion by flame¹⁶. Perovskites can be performed by direct inductive melting in cold crucible¹⁷.

Experiment

The samples were prepared by three methods - the precipitation method with or without using polyvinyl alcohol (PVA) as a surface-active substance, oxalic acid method and citrate method. The precipitation method: Sr(NO₃)₂ (Sigma-Aldrich, ≥ 99,0 %) and Ce(SO₄)₂·4H₂O (ML-chemica, 97+ %) were mixed and dissolved in distilled water to create 0.2 M solutions of total metal ions. Prepared solutions were mixed together and 2 ml of 10 % solution of PVA were added. The 4 M NaOH solution (amount of Na⁺ was 2 times bigger than the amount of total metal ions) was added to the mixture slowly and formed light yellow precipitate was filtered and washed with the distilled water to remove redundant OH⁻. The resulting precipitate was dried at 80 °C to obtain the precursor powder. The next sample was prepared using the same procedure except the PVA solution was

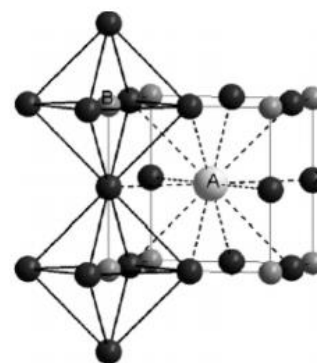


Figure 1. Ideal cubic perovskite structure³.

not added and NaOH solution was added to the mixture rapidly. The precipitate was also filtered and dried at 80 °C. For the oxalic acid method, there were also used 0.2 M solutions of metal ions from Sr(NO₃)₂ and Ce(SO₄)₂·4H₂O which were mixed together and the pH was adjusted to 3.5 using aqueous ammonia solution. The 0.8 M aqueous solution of oxalic acid was added to the mixture in amount 1.2 times larger than the amount of metal ions (in moles). Stirring was continued for another 20 minutes and the precipitate was filtered and dried at 110 °C for 24 hours. For the citrate method Ce(SO₄)₂·4H₂O and Sr(NO₃)₂ were dissolved in distilled water to create 0.2 M solutions and pH was adjusted to 3.5 using 1 M NaOH solution. The solution of citric acid was added in 1.5 larger amount than there was the total amount of metal ions. The mixture was stirred and heated to 95 °C for polymerization reaction for 4 hours. After formation of a porous mass, the sample was dried at 120 °C for 24 hours. Both acid based samples were treated at 400 °C for 20 minutes to remove the organic compounds and subsequently ground. The oxalic acid and precipitation based samples were fired in the temperature range from 900 to 1400 °C for 5 hours. For the sample prepared by citric acid method, 700 °C has been chosen as a starting firing temperature because of presumed lower thermal stability. The phase composition was verified by using X-ray diffractometer MiniFlex 600 (Rigaku; Japan) with a vertical goniometer (step size 0.02°), scanning speed 10 °C/min and 2 Θ geometry (10 – 80°). The copper cathode is used as a source of X-ray radiation and high-speed silicon strip detector is required for registration of X-ray signal. The device is equipped with extensive PDXL database for the evaluation of measured data.

Discussion and result

Coprecipitation without surface-active substance

The sample prepared by using the precipitation method without the use of PVA as a surfactant provides at the all temperatures the three-phase composition - SrCeO₃, CeO₂ and SrSO₄ (Table I). The rising temperature caused the slow decomposition of SrSO₄ and gradual increase in the amount of product SrCeO₃. However, even at the maximum firing temperature, there was still present residual amount of SrSO₄ in the system. The quantity of CeO₂ remained constant with the increasing temperature. Nevertheless, this method has provided the highest percentage of product SrCeO₃ (PDF No. 01-074-8250)¹⁸ of all the methods. The diffractogram of the sample fired at the temperature 1400 °C is shown at the figure 2-1b.

Table I

Phase composition of samples prepared by coprecipitation method without PVA depending on the firing temperature

temperature (°C)	PDF No.	formula	crystal system
900	01-075-7750	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-074-2035	SrSO ₄	orthorhombic
1000	01-075-8371	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1100	03-065-5923	CeO ₂	cubic
	01-082-2427	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1200	03-065-5923	CeO ₂	cubic
	01-074-8250	SrCeO ₃	orthorhombic
	01-089-0953	SrSO ₄	orthorhombic
1300	01-075-8371	CeO ₂	cubic
	01-074-8250	SrCeO ₃	orthorhombic
	01-089-0953	SrSO ₄	orthorhombic
1400	01-075-8371	CeO ₂	cubic
	01-074-8250	SrCeO ₃	orthorhombic
	01-089-0953	SrSO ₄	orthorhombic

Coprecipitation with PVA as a surface-active substance

It was examined if the use of PVA as surfactant will have the positive impact on the formation of product SrCeO₃ in the second sample. The results are shown in Table II. The reactions were very similar to the previous method. At the lowest temperature of 900 °C, there was recorded a small amount of Sr₂CeO₄ phase (PDF No. 00-

050-0115), but after the increase of the firing temperature, this compound has not been detected again. At the temperature higher than 1000 °C the three-phase system was recorded as same as for the previous method - CeO₂, SrCeO₃ and SrSO₄. Their amount was constant with increasing temperature. The only exception is the sample fired at 1400 °C. The almost complete decomposition of SrSO₄ caused an increase in the amount of the product SrCeO₃ (PDF No. 01-082-2427). The diffraction pattern of this sample is shown in Figure 2-1a. Using PVA had not a positive influence on the formation of the product.

Table II

Phase composition of samples prepared by coprecipitation method with PVA (as a surface-active substance) depending on the firing temperature

temperature (°C)	PDF No.	formula	crystal system
900	01-080-4828	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
	00-050-0115	Sr ₂ CeO ₄	orthorhombic
1000	00-034-0394	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1100	00-034-0394	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1200	00-034-0394	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1300	01-075-8371	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1400	01-075-8371	CeO ₂	cubic
	01-082-2427	SrCeO ₃	orthorhombic
	01-089-0954	SrSO ₄	orthorhombic

Oxalic acid method

As a third way of synthesis, the oxalic acid method was chosen. In all evaluated temperatures, the three-phase system was detected (Table 3). At 900 °C the very broad peaks were measured, indicating that the system is not fully reacted and crystallinity of the sample is low. As the temperature increases, there is a gradual improvement in these parameters but it has no significant influence on the phase composition. For this sample, the highest amount of SrSO₄ phase was measured and it does not disintegrate even at the highest temperature. This fact is clearly shown in the diffraction pattern in Figure 2-2.

Table III

Phase composition of samples prepared by oxalic acid method depending on the firing temperature

temperature (°C)	PDF No.	formula	crystal system
900	01-075-7750	CeO ₂	cubic
	00-047-1689	SrCeO ₃	orthorhombic
	00-005-0593	SrSO ₄	orthorhombic
1000	00-034-0394	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1100	00-034-0394	CeO ₂	cubic
	01-082-2370	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic
1200	00-034-0394	CeO ₂	cubic
	01-074-8250	SrCeO ₃	orthorhombic
	01-075-6773	SrSO ₄	orthorhombic

temperature (°C)	PDF No.	formula	crystal system
1300	01-080-6915	CeO ₂	cubic
	01-074-8250	SrCeO ₃	orthorhombic
	01-074-2035	SrSO ₄	orthorhombic
1400	01-080-6915	CeO ₂	cubic
	01-074-8250	SrCeO ₃	orthorhombic
	01-074-2035	SrSO ₄	orthorhombic

Citrate method

The samples prepared by the citrate method were also investigated. The results are shown in Table IV. Due to the presumed lower thermal stability, the 700 °C was chosen as the lowest firing temperature. It was obtained the three-phase system – CeO₂, SrCO₃ and Na₂SO₄. When the temperature rises, there has been no change in phase composition and thus it was approached to firing at 900 °C. It caused formation of the multi-phase system and the entire sample was sintered. Given that the product SrCeO₃ was not created and the powder form of the sample has not been preserved, this method of synthesis is entirely unsuitable for our purposes.

Table IV

Phase composition of samples prepared by citrate method depending on the firing temperature

temperature (°C)	PDF No.	formula	crystal system
700	01-081-9325	CeO ₂	cubic
	01-084-1778	SrCO ₃	orthorhombic
	01-078-1883	Na ₂ SO ₄	hexagonal
800	01-081-9325	CeO ₂	cubic
	01-084-1778	SrCO ₃	orthorhombic
	01-078-1883	Na ₂ SO ₄	hexagonal
900	01-071-4807	CeO ₂	cubic
	00-024-1139	2Na ₂ SO ₄ +Na ₂ CO ₃	hexagonal
	01-080-0523	SrSO ₄	orthorhombic
	01-074-1624	SrCO ₃	trigonal
	01-089-8433	Ce ₇ O ₁₂	trigonal

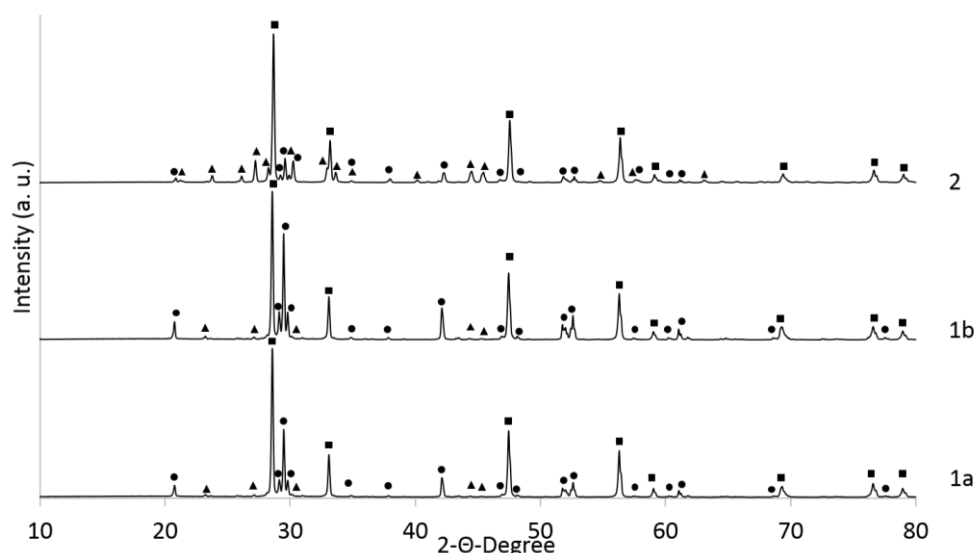


Figure 2. Diffractograms of the samples prepared by coprecipitation with PVA (1a), coprecipitation without PVA (1b) and oxalic acid method (2) at the temperature 1400 °C (● SrCeO₃; ■ CeO₂; ▲ SrSO₄).

Conclusions

The aim of the research was to verify the possibility of preparation SrCeO₃, which could serve as a potential basic matrix for doping metal ions and could find use as a thermally stable inorganic pigment. The three possible methods for the synthesis were tested - precipitation (with and without use PVA as a surfactant), oxalic acid method and citrate method. The precipitation proved to be the most effective method used because it gives the highest amount of the product SrCeO₃. However, the main phase of the samples represents CeO₂. The single-phase product was also not obtained using the oxalic acid method, and moreover, the quantity of required product SrCeO₃ was lower than in the case of precipitation. Citrate method has proven to be totally unsuitable for the synthesis of pigment lattice due to the product was not prepared and the sample was sintered at 900 °C. Neither method thus provides an appropriate single-phase product SrCeO₃, which could serve as a lattice for doping metal ions. The methods of preparation and firing processes will have to be adjusted to obtain a better-quality product which can be used for pigment preparation and application purposes.

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