

Tellurites of Some *s–f* Elements: Synthesis, X-Ray Diffraction, and Electrophysical Properties

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Abstract—A possibility of solid-phase synthesis of new cerium double tellurites with *s*-elements from the oxides of cerium(IV), tellurium(IV) and magnesium (calcium, strontium) carbonates was demonstrated. It was determined by the X-ray diffraction method that the magnesium–cerium tellurite crystallizes in a cubic system, while calcium–cerium and strontium–cerium tellurites crystallize in the tetragonal crystal system. The temperature dependence of the electrical resistance of these compounds in the range of 300–600 K was measured. The plots include sharp anomalous jumps due probably to the phase transitions of type II.

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Producing new materials is an important task that forms the basis of scientific and technological progress in various branches of science-intensive production. New discoveries in medicine, electronics, photonics, spintronics, nano- and biotechnology in the last decade have led to intensive development of a new scientific field, the chemical materials. Owing to the features of the electronic structure of lanthanides, the compounds based on the rare-earth metals possess a unique combination of electrical, magnetic, thermal, optical and other properties that can be widely used in modern microelectronics and many fields of modern technology to create multifunctional systems [1]. The variety of these properties depend on the composition, structure and method of producing a particular oxide.

From this viewpoint the comprehensive and systematic study of compounds based on selenium and tellurium possessing such physical and chemical properties as semiconductor, segnetoelectric, and piezo-electric, are of great interest. The recent studies in this area of chemistry have shown that polyinorganic compounds synthesized on the basis both of typical and transition metals and nonmetals are more likely to exhibit a variety of physical and chemical properties. Polyselenites (selenates), polytellurites, and double selenates and tellurites of *s–d*- and *s–f*-elements are the compounds poorly studied in this respect. Based on the foregoing, it is possible to claim that a systematic study of synthesis methods,

revealing the structure and X-ray study of thermodynamic and physical properties of polyselenites (selenates), polytellurites, and double selenate–tellurites of *s–d*- and *s–f*-elements are of considerable practical and theoretical interest for inorganic material science and present a relevant problem to the modern inorganic chemistry. In this connection, we perform a systematic research and development of the scientific base for the targeted synthesis of new selenium and tellurium oxo-compounds with unique physical properties [2, 3].

The aim of this work was the synthesis and study of radiographic and electrical properties of cerium double tellurites $\text{Me}^{\text{II}}\text{CeTe}_3\text{O}_9$ ($\text{Me}^{\text{II}} = \text{Mg, Ca, Sr}$).

The initial components for synthesis were cerium(IV) and tellurium(IV) oxides and magnesium (calcium, strontium) carbonates (pure grade) in a stoichiometric ratio. The synthesis of compounds was performed by solid-phase annealing in three stages at different temperatures. The reagent mixtures were thoroughly triturated in an agate mortar, then it was charged quantitatively into alundum crucible with a lid for the annealing in a silite furnace. The synthesis was carried out as follows: stage I, 10 h at 400°C, stage II, 10 h at 800°C with periodical grinding in a mortar, then at 1300°C for 10 h.

The formation of the equilibrium composition of the compounds was monitored by X-ray analysis on a DRON-2.0 instrument using CuK_α -radiation filtered by

Table 1. X-ray indexing of double cerium tellurites

$I/I_0, \%$	$d, \text{Å}$	$10^4/d_{\text{exp}}^2$	hkl	$10^4/d_{\text{calc}}^2$	$I/I_0, \%$	$d, \text{Å}$	$10^4/d_{\text{exp}}^2$	hkl	$10^4/d_{\text{calc}}^2$
MgCeTe₃O₉									
39	4.4509	505	111	511	52	1.6308	3760	233	3750
42	4.3992	517	111	511	15	1.5605	4106	224	4091
100	3.1179	1029	112	1023	15	1.3523	5468	044	5455
27	2.7029	1369	022	1364	33	1.2424	6478	116	6478
64	1.9114	2737	004	2728					
CaCeTe₃O₉									
8	3.2943	921	204	921	2	1.9491	2632	0.0.10	2633
23	3.2482	948	006	948	2	1.7886	3126	500	3122
14	3.1262	1023	214	1045	3	1.7504	3264	2.1.10	3257
100	2.9783	1127	300	1127	4	1.6973	3471	513	3484
3	2.8876	1199	116	1198	7	1.6323	3753	3.1.10	3757
4	2.8116	1265	311	1275	4	1.6262	3781	0.0.12	3792
3	2.7029	1369	303	1361	2	1.5629	4094	442	4101
1	2.5259	1567	216	1572	11	1.4915	4495	600	4496
1	2.4004	1736	322	1729	3	1.2420	6483	713	6481
7	1.9886	2529	317	2539					
SrCeTe₃O₉									
6	3.4512	840	213	844	13	1.9142	2729	415	2725
31	3.2573	943	006	937	11	1.8128	3043	500	3050
14	3.1510	1007	221	1002	6	1.6845	3524	520	3538
25	3.1229	1025	214	1027	12	1.6329	3750	0.0.12	3750
100	3.0212	1096	300	1098	12	1.5107	4382	600	4392
6	2.9090	1182	116	1181	2	1.4915	4495	602	4496
10	2.8254	1253	311	1246	2	1.4407	4818	527	4814
2	2.5153	1581	320	1586	4	1.3534	5459	616	5452
2	2.4292	1695	322	1690	4	1.2953	5960	700	5978
9	1.9980	2505	317	2496					

Ni-filter (U 30 kV, J 10 mA, rotation rate 1.000 pulses per second, time constant τ 5 s, angular range 2θ from 10 to 90°). The intensity of the diffraction maxima was evaluated using a 100-unit scale. The indexing of powder X-ray of the compounds was performed by homology method [4].

The indexing reliability was monitored by the comparison for satisfactory coincidence of experimental and calculated $10^4/d^2$ values, as well as by the consistency of values of X-ray and pycnometric densities of these compounds. As an indifferent fluid

in determining the pycnometric density of the investigated phase tetrabromethane of analytical grade was used in the pycnometer of 1.00 ml capacity.

Table 1 shows the results of indexing the X-ray diffractograms [2] of the powder of the compounds under study. The satisfactory agreement between experimental and calculated $10^4/d^2$ values listed in Table 1, as well as the consistency of X-ray and pycnometric density values of the compounds (Table 2) confirm the validity of the indexing.

Table 2. Types of crystal system and unit cell parameters of tellurites

Compound	Crystal system	Lattice parameters, Å		$V_{\text{el. cell.}}^0$ Å ³	V^0 Å ³	Z	Density, g cm ⁻³	
		<i>a</i>	<i>c</i>				XRD	pycnometric
MgCeTe ₃ O ₉	Cubic	7.66	–	112.36	449.46	4	10.10	9.95±0.15
CaCeTe ₃ O ₉	Tetragonal	8.95	19.49	195.15	1561.20	8	6.01	6.01±0.00
SrCeTe ₃ O ₉	Tetragonal	9.05	19.60	200.84	1606.71	8	6.24	6.21±0.05

As seen, the experimental and calculated $10^4/d^2$ values (Table 1), X-ray and pycnometric densities (Table 2) are in satisfactory agreement, which confirms the validity of indexing. It also suggests that the combined magnesium–cerium tellurite (MgCeTe₃O₉) crystallizes in a cubic crystal system, while calcium–cerium (CaCeTe₃O₉) and strontium–cerium (SrCeTe₃O₉) tellurites crystallize in the tetragonal system. Table 2 lists their unit cell parameters.

As a rule, electrical properties of ceramic segnetoelectrics depend on temperature. We studied the temperature dependence of the resistivity (*R*) of CaCeTe₃O₉ and SrCeTe₃O₉ tellurites in the range 300–600 K. For this purpose the samples were placed in a special temperature-controlled furnace. Since ceramic materials have a certain inertia, changes in the electrical properties and the data on integral electric

capacity were determined only after pre-exposure for about 0.5 h at a fixed temperature. The measurements were carried out continuously by a bridge circuit method at 1 kHz in dry air in the thermostatic mode with exposure at each fixed temperature. This is especially important for the measurements in the region of abnormal changes of the above characteristics. The temperature was measured with a chromel–alumel thermocouple with a differential voltmeter B2-34. The rate of temperature change was approximately 5 K per minute. The exposure duration at the each measurement was 10 min.

For the measurements flat-parallel samples as discs of 10 mm diameter with a binding agent (~1.5%) were prepared. The samples of the compounds were pressed at a pressure of 20 kg cm⁻². Then they were kept for 8 h at 100°C in order to give them sufficient strength

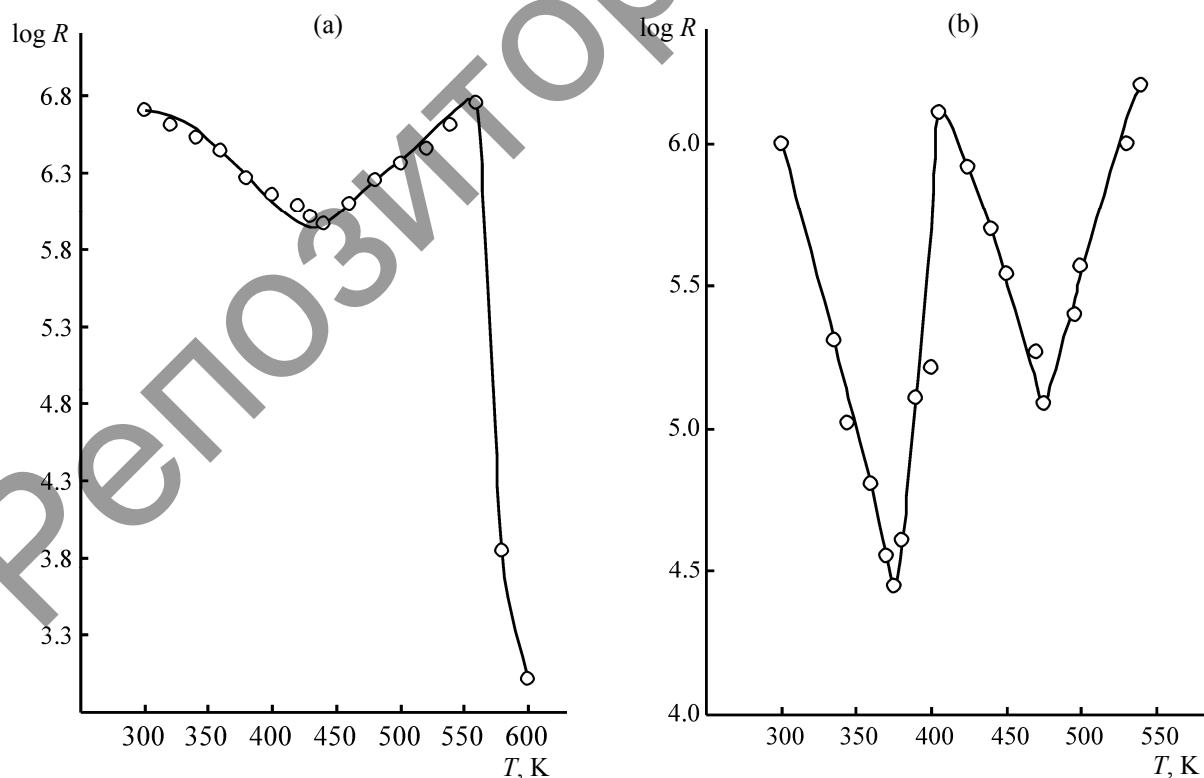
**Fig. 1.** Temperature dependence of electroresistance of tellurites in the range 300–600 K: (a) CaCeTe₃O₉, (b) SrCeTe₃O₉.

Table 3. Temperature dependence of electroresistance of double cerium tellurites

<i>T</i> , K	<i>R</i> , Ω	log <i>R</i>	<i>T</i> , K	<i>R</i> , Ω	log <i>R</i>
CaCeTe ₃ O ₉					
300	5011000	6.70	460	1260000	6.10
320	4074000	6.61	480	1778000	6.25
340	3311000	6.52	500	2238000	6.35
360	2754000	6.44	520	2818000	6.45
380	1820000	6.26	540	4074000	6.61
400	1412000	6.15	560	5623000	6.75
420	1202000	6.08	580	7079	3.85
430	1023000	6.01	600	1023	3.01
440	912000	5.96			
SrCeTe ₃ O ₉					
300	1000000	6.00	425	831000	5.92
335	204000	5.31	440	501000	5.70
345	104000	5.02	450	346000	5.54
360	64000	4.81	470	186000	5.27
370	36000	4.56	475	123000	5.09
375	28000	4.45	495	251000	5.40
380	40000	4.61	500	371000	5.57
390	128000	5.11	530	1000000	6.00
400	165000	5.22	540	1585000	6.20
405	1288000	6.11			

to perform the experiment. The resulting samples were rigorously double-sided polished. Two-electrode system was applied, the silver electrodes were deposited by heating paste [3]. Results are listed in Table 3.

Considering the data in Table 3 we conclude that the synthesized compounds have a sufficiently high electrical resistance (*R*). As the temperature increases, a significant change occurs in this characteristics in a certain temperature range, as is typical of ceramic materials. For example, electrical resistance of CaCeTe₃O₉ in the range 300–440 K falls with a minimum at 440 K and then abruptly increases in the region of 440–560 K (Fig. 1a). The forbidden band gap is 0.72 eV. In the case of SrCeTe₃O₉ in the range of 300–375 K the electrical resistance decreases, and then in the temperature range of 380–405 K a monotonic increase in the resistance occurs. Then, at a temperature of 405–475 K there is an abrupt jump where the electrical resistance decreases to the minimum at

475 K (Fig. 1b), then at 475–540 K, the change is reverse, that is, electroresistance increases. The band gap is 0.81 eV and 1.32 eV. The thermal coefficients of electroresistance are as follows: for CaCeTe₃O₉ $\alpha_T = 0.067 \text{ K}^{-1}$ and for SrCeTe₃O₉ $\alpha_{T1} = 1.49$, $\alpha_{T2} = 0.18 \text{ K}^{-1}$.

It should be noted that the negative thermal coefficient of resistance at 300–440 K for CaCeTe₃O₉ and at 300–375 K and 405–475 K for SrCeTe₃O₉ is typical for semiconductors. Trivial reasons for this pattern may be changing the type, quality and nature of the charge carriers. We found that the final treatment regime (temperature and duration) of the annealing carried out in air can significantly change the electrophysical properties. However, the positive temperature coefficient of resistance at 440–560 K for CaCeTe₃O₉ and at 380–405 K and 475–540 K for SrCeTe₃O₉ suggests probably the presence of a phase transition of II type in these areas. The probability of coexistence of two phases in this temperature range indicates a possibility of structural changes.

Based on the foregoing, we can say that we have synthesized new double cerium tellurites by the solid-phase method. By the X-ray analysis the types of symmetry and unit cell parameters were determined. These X-ray studies showed that all the synthesized compounds crystallize as a distorted perovskite structure of *Pm3m* type. The X-ray features of the new tellurites can be included into fundamental handbooks and data banks as the information arrays and are of interest for chemical informatics.

The observed anomalous jumps in the curves of the temperature dependence of electroresistance of the synthesized compounds indicate the phase transitions of II type due to valuable electrophysical properties of new double cerium tellurites. The results can be used to predict the synthesis and study of new compounds of tellurium and rare earth elements with important electrophysical properties.

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