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INTERNATIONAL MULTIDISCIPLINARY SCIENTIFIC GEOCONFERENCE SGEM
Secretariat Bureau

Phone: +359 2 4051 841
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INSOLUBLE ANHYDRITE AS PRODUCT GYPSUM DEHYDRATION ACCORDING TO ELECTRON PARAMAGNETIC RESONANCE SPECTRA

Khasanov R.A.^{1,2}
Khasanova N.M.¹,
Nizamutdinov N.M.¹
Izotov V.G.¹

¹ Kazan federal university, IG&NGT, Kazan, **Russia**

² Central Research Institute for Geology of Industrial Minerals, Kazan, **Russia**

ABSTRACT

Electron paramagnetic resonance studies were carried out with two main aims. Firstly, to detect the appearance of an insoluble phase anhydrite formed due to the dehydration of gypsum. Secondly, to study the dynamics of development of insoluble phases in the dehydration sequence in natural gypsum.

Annealing gypsum products ("Marino steklo") are mineral polyphase system, in which there are co-crystallization and recrystallization processes to form a system of point defects in each of the phase components of the mixture. Found that in the range 25-450 °C temperature annealing products may include gypsum, α and β bassanite, α and β soluble anhydrite, insoluble anhydrite (Crystallography. Reports, vol.59(3), pp.399, 2014). In this paper, we continue the detailed study of the formation of the crystalline structure of the insoluble anhydrite during dehydration. It was found that the lines of the EPR spectra of radical ions that are typical of structure of natural anhydrite, begin to appear with 225 °C. In the temperature range 275-350 °C dehydration formation of an insoluble anhydrite becomes the dominant process.

In the temperature range from 225 to 450 °C during the dehydration of gypsum was recorded the birth and formation of the EPR lines, structurally different radical ions SO_2^\cdot , SO_3^\cdot and atomic ion-radical O^\cdot .

Keywords: gypsum, electron paramagnetic resonance, anhydrite, radiation, dehydration, annealing/

INTRODUCTION

The insoluble anhydrite is a common rock-forming mineral. He has long attracted the attention of specialists in physics of minerals occupies a special structure, composition and properties of minerals depending on their genesis, the distribution by age and genetic complexes, types of deposits. EPR is the main method of solid state spectroscopy for solving these problems, because only with its help is possible to identify fine features of the crystal structure of minerals, which are determined by the presence of radical ions and electron-hole centers.

In the crystal structure of anhydrite found wide variety of point defects. The genetically different specimens of anhydrite was established about 50 ion-radicals and paramagnetic centers (PC) from the EPR spectra [1-7]. This is primarily associated with PC tetrahedral complexes SO_4^{2-} having oxygen vacancies. These include the ion-radicals SO_2^\cdot and SO_3^\cdot . Another group of centers is related to the isomorphic substitution of calcium on Y, Gd and sulfur to P, B, Na, K to form stable centers YO,

YO₂, PO₃³⁻, BO₂, and oxygen centers O₂³⁻-Y³⁺, O₂³⁻-B³⁺, (H)O₂³⁻-Na⁺ or K⁺, and et al. A particular group PC is represented by atomic and molecular ion radicals O[•], O₂[•], S₂[•], O₃[•]. Several of the observed PC in single anhydrite and parameters of their spectra are given in Table 1 below.

Table 1. The parameters of the EPR spectra of PC in anhydrite

№	PC	g-tensor			CTC (mT)			K _M	TK	reference
		g _{xx}	g _{yy}	g _{zz}	A _{xx}	A _{yy}	A _{zz}			
1	SO ₂ [•]	2.0012	2.0104	2.0055				1	77	1
2	SO ₂ [•] (I)	2.0022	2.0092	2.0058					290	2
3	SO ₂ [•] (II)	2.0020	2.0098	2.0058					290	2
4	SO ₂ [•] M	2.0026	2.0114	2.0040					290	2
5	SO ₂ [•]	2.003	2.008	2.005				4	290	4,5
6	SO ₃ [•] (I)	2.0045	2.0032	2.0025				2	300	3
7	SO ₃ [•] (I)	2.0042	2.0036	2.0020				2	290	2
8	SO ₃ [•] (I) int	2.0042	2.0038	2.0024					290	2
9	SO ₃ [•] (I)	2.0031	2.0041	2.0025	10,7	9,6	12,1			7
10	SO ₃ [•] (II)	2.0040	2.0038	2.0019				2	300	3
11	SO ₃ [•] (II) int	2.0064	2.0052	2.0014					77	2
12	SO ₃ [•] (II)	2.0040	2.0025	2.0013				2	77	2
13	SO ₃ [•] (II)	2.0039	2.0041	2.0022	9,3	9,4	13,1			7
14	SO ₃ [•] (III)	2.0040	2.0027	2.0013				2	300	6
15	-SO ₃ [•] M int	2.0094	2.0064	1.9994					77	2
16	SSO ₃ [•]	2.028	2.023	2.003				4	290	4,5
17	SSO ₃ [•]	2.027	2.0218	2.0114				1	77	2
18	PO ₃ ³⁻	2.0026	2.0017	2.0017	43,07	57,5	2	300	6	
19	PO ₃ ³⁻	2.0036	2.0012	2.0012	56,6	49,9	2	290	4	
20	PO ₄ ³⁻	2.0095	2.0126	2.016		A _{iso} =2,85	1	77	6	
21	PO ₄ ³⁻	2.018	2.014	2.014	2,8	2,9	2			4
22	O ₂ [•] (I)	1.9940	1.9950	2.0238					290	2
23	O ₂ [•] (II)	1.9940	1.9950	2.0176					290	2
24	O ₂ [•] int	1.9946	1.9958	2.0250			1	77	2	
25	(H) O ₂ [•] int	1.9915	1.9910	2.0631			2	77	2	
26	O ₂ [•]	1.9946	1.9950	2.0245			4	300	1	
27	S ₂ [•]		2.74					290	4,5	
28	O [•] (I)	2.0118	2.0105				1	300	6	
29	O [•] (II)	2.0317	2.0075	2.0023	0,5	0,59	0,54	4	300	1
30	SSO [•]	2.003	2.0016	2.009			4		4,5	
31	O [•]	2.019	2.011				2		4,5	
32	O ₃ [•] (I)	2.0140	2.0144	2.056			2	290	2	
33	O ₃ [•] (II)	2.0108	2.0146	2.0052			2	77	2	
34	O ₃ [•] -M	2.0056	2.0158	2.0134			1	77	2	
35	O ₂ ³⁻ -B ³⁺	2.0089	2.0122	2.0120	1,17	0,9	0,92	2	290	2
36	O ₂ ³⁻ -Y ³⁺	2.0029	2.0262	2.0122	0,63	0,49	0,49	2	290	2
37	O ₂ ³⁻ -Y ³⁺	2.0078	2.0300	2.0168	0,42	0,42	0,47	2	290	2

Researchers evaluated controversial temperature range of formation of insoluble anhydrite in determining the phase composition of the dehydration of gypsum products. Example in [8] the temperature range estimated within the range of 400-900 °C, in [9] - within the range 300-750 °C and [10] - within the range 200-600 °C. Therefore, the aim of this work was to determine the beginning of the formation of insoluble anhydrite in the product dehydration of gypsum in the temperature range (25-425 °C). For this purpose registration of the ESR spectra were in the gypsum and the products of its isothermal annealing, identification and comparison of their spectroscopic parameters

with already known EPR spectra detected in natural minerals - anhydrite.

EXPERIMENTAL RESULTS

Recording EPR spectra was carried out at 25 °C on a spectrometer X-band PC_100X (ADANI, Belarus). The intensity of the ESR spectra was compared using a reference spectrum of an Al₂O₃:Cr³⁺, sample inserted into the cavity through a lateral hole.

Preparation of the samples to the study, as well as the recording conditions of the EPR spectra are described in detail in the [11]. The initial non-irradiated single crystals of gypsum EPR spectra are not registered. The X-ray irradiation of samples at 25 °C for 3 hours to induce PC with the EPR spectrum in the field of g = 2.0023. They are identified as ion-radicals SO₃[•] и SO₂[•] [11, 12].

The insoluble anhydrite - a product of dehydration of gypsum

EPR spectra characteristic of natural anhydrite, are securely fixed in the dehydration of gypsum products starting from 275 °C. However, the first signs of the formation of anhydrite are detected at lower temperatures the dehydration of gypsum - 225 °C. At this temperature, the ESR spectrum of the line begins to take shape clearly from the g-factor of the corresponding g = 2.0039, and the width of the central narrow intense line (g = 2.0028) is marked with the point g = 2.0027 (Fig. 1), which quite reliably be attributed to the ion-radical SO₃[•] (III) in a single crystal having a value g_{xx} = 2.0040 and g_{yy} = 2.0027 (Table. 1). Line with g-factor corresponding g_{zz} = 2.0013 for the ion-radical in the gypsum product of annealing at 225 °C in the EPR spectrum is not observed.

Also found the line with g = 2.0033, which, together with the point g = 2.0025 located on the lower ridge of the center line, may belong to the ion-radical SO₃[•] (I), with parameters g_{xx} = 2.0045; g_{yy} = 2.0032; and g_{zz} = 2.0025 in a single crystal of anhydrite [3]. The line with g = 2.0045 not detected in the spectrum. In the same range there are two weak lines with g-factor: - g = 2.0085 g = 2.0065 and related, apparently, to the ion-radical SO₂[•] (I) with the parameters g_{xx} = 2.0022; g_{yy} = 2.0092; g_{zz} = 2.0058 in the single crystal [2].

After dehydration of gypsum at 250 °C and its subsequent X-ray exposure in the EPR spectrum are observed the same line, owe the appearance of radical ions SO₃[•] (I), SO₃[•] (III), SO₂[•] (I), as well as an additional line width of 2.6 gauss in the range of g-factor of 2.0091 to 2.0108, which may be present lines belonging ion radicals and O[•] and SO₂[•] (I) [2, 6]. Additional broad line despite the absence of clear-cut shapes, lines characteristic of the spectra of the powders can be attributed to a range of axially symmetric g-tensor with parameters, g_{||} = 2.0108 and g_⊥ = 2.0091, which close values of the principal components of the tensor g-ion-radical O[•] (I) in a single crystal (Table. 1).

The EPR spectrum of the product of dehydration of gypsum at 275 °C after X-ray irradiation there are new lines belonging to PC insoluble anhydrite (Fig. 1). This spectrum is fixed lines belonging to radical ions: SO₃[•] (I) - g_{yy} = 2.0033; g_{zz} = 2.0025; SO₃[•] (III) - g_{xx} = 2.0039; g_{yy} = 2.0027 in the width of the central line of intense; g_{zz} = 2.0013; SO₂[•] (I) - g_{xx} = 2.0022; g_{yy} = 2.0084; g_{zz} = 2.0068; O[•] (I) - g_{||} = 2.0107; g_⊥ = 2.0091. There were lines belonging to the ion-radical SO₂[•] [1]. The main value of its g - tensor - g_{xx} = 2,0012; g_{zz} = 2.0053; g_{yy} - hidden in the width of the lines belonging to the ion-radical O[•] (I), similar values of the g-tensor in a single crystal of this radical - g_{xx} = 2.0012; g_{yy} = 2.0104; g_{zz} = 2.0055 (Table. 1).

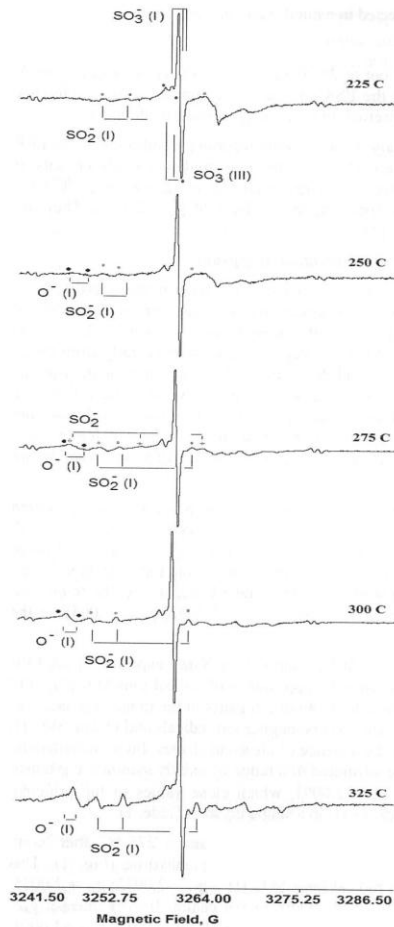


Fig.1. The EPR spectra of radical ions $\text{SO}_2\cdot^-$, $\text{SO}_3\cdot^-$, $\text{O}\cdot^-$ in the products of dehydration of gypsum in the temperature range 225-325 °C. Parameters PC resulted in Table 2.

It should be noted that with increasing temperature dehydration of gypsum intensity of most of the observed spectral lines of the EPR after a subsequent X-ray exposure is growing.

That is naturally associated with an increase in the proportion of the phase component formed insoluble anhydrite in the total mass of the material subjected to heat treatment

There appear new lines in the spectra relating to certain ion-radicals, which are absent in the low-temperature dehydration.

Table 2. Parameters of the EPR spectra of ion-radicals formed during X-ray irradiation products of dehydration of gypsum

Temperature, °C	Ion-radicals	g - tensor			
		g_{xx}	g_{yy}	g_{zz}	g_{\perp}
225	$\text{SO}_3\cdot^-$ (I)	-	2.0033(2)	2.0025(2)	-
	$\text{SO}_3\cdot^-$ (III)	2.0039(4)	2.0027(1)	-	-
	$\text{SO}_2\cdot^-$ (I)	-	2.0085	2.0065(2)	-
250	$\text{SO}_3\cdot^-$ (I)	-	2.0033(2)	2.0025(2)	-
	$\text{SO}_3\cdot^-$ (III)	2.0039(4)	2.0027(1)	-	-
	$\text{SO}_2\cdot^-$ (I)	-	2.0084(3)	2.0065(2)	-
	$\text{O}\cdot^-$ (I)	-	2.0108(5)	2.0091(1)	-
275	$\text{SO}_3\cdot^-$ (I)	-	2.0033(1)	2.0025(2)	-
	$\text{SO}_3\cdot^-$ (III)	2.0039(9)	2.0027(0)	2.0013(5)	-
	$\text{SO}_2\cdot^-$	2.0012(3)	2.0104(1)	2.0053(4)	-
	$\text{SO}_2\cdot^-$ (I)	2.0022(1)	2.0084(9)	2.0068(9)	-
	$\text{O}\cdot^-$ (I)	-	2.0107(8)	2.0091(1)	-
300	$\text{SO}_3\cdot^-$ (I)	-	2.0033(1)	2.0025(1)	-
	$\text{SO}_3\cdot^-$ (III)	2.0039(3)	2.0027(0)	2.0013(5)	-
	$\text{SO}_2\cdot^-$	2.0012(3)	2.0104(1)	-	-
	$\text{SO}_2\cdot^-$ (I)	2.0021(5)	2.0089(2)	2.0068(8)	-
	$\text{O}\cdot^-$ (I)	-	2.0107(2)	2.0099(1)	-
325	$\text{SO}_3\cdot^-$ (I)	-	2.0033(21)	2.0025(2)	-
	$\text{SO}_3\cdot^-$ (III)	2.0038(7)	2.0027(0)	2.0013(5)	-
	$\text{SO}_2\cdot^-$	2.0012(3)	2.0104(7)	-	-
	$\text{SO}_2\cdot^-$ (I)	2.0020(9)	2.0090(5)	2.0068(9)	-
	$\text{SO}_2\cdot^-$ (c)	2.0030(1)	2.0070(7)	-	-
350	$\text{O}\cdot^-$ (I)	-	2.0114(0)	2.0105(3)	-
	$\text{SO}_3\cdot^-$ (I)	2.0043(6)	2.0031(9)	2.0025(2)	-
	$\text{SO}_3\cdot^-$ (III)	2.0039(3)	2.0027(0)	2.0012(9)	-
	$\text{SO}_2\cdot^-$	2.0012(3)	2.0104(1)	2.0048(5)	-
	$\text{SO}_2\cdot^-$ (I)	2.0022(1)	2.0090(4)	2.0068(8)	-
	$\text{SO}_2\cdot^-$ (c)	2.0030(7)	2.0071(9)	2.0049(1)	-
375	$\text{O}\cdot^-$ (I)	-	2.0111(5)	2.0104(7)	-
	$\text{SO}_3\cdot^-$ (I)	2.0045(4)	2.0031(9)	2.0024(5)	-
	$\text{SO}_3\cdot^-$ (III)	2.0037(4)	2.0027(0)	2.0012(9)	-
	$\text{SO}_2\cdot^-$	2.0012(3)	2.0104(7)	2.0054(1)	-
	$\text{SO}_2\cdot^-$ (I)	2.0021(5)	2.0089(8)	2.0059(0)	-
	$\text{SO}_2\cdot^-$ (c)	2.0030(1)	2.0070(7)	2.0052(2)	-
400	$\text{O}\cdot^-$ (I)	-	2.0114(6)	2.0105(3)	-
	$\text{SO}_3\cdot^-$ (I)	2.0046(0)	2.0031(9)	2.0025(0)	-
	$\text{SO}_3\cdot^-$ (III)	2.0038(7)	2.0027(0)	2.0012(9)	-
	$\text{SO}_2\cdot^-$	2.0012(2)	2.0104(1)	2.0054(0)	-
	$\text{SO}_2\cdot^-$ (I)	2.0022(1)	2.0091(1)	2.0059(0)	-
	$\text{SO}_2\cdot^-$ (c)	2.0030(0)	2.0071(3)	2.0050(3)	-
425	$\text{O}\cdot^-$ (I)	-	2.0113(0)	2.0105(3)	-
	$\text{SO}_3\cdot^-$ (I)	2.0045(4)	2.0031(9)	2.0025(1)	-
	$\text{SO}_3\cdot^-$ (III)	2.0038(7)	2.0028(8)	2.0012(9)	-
	$\text{SO}_2\cdot^-$	2.0012(3)	2.0104(7)	2.0054(0)	-
	$\text{SO}_2\cdot^-$ (I)	2.0021(5)	2.0091(1)	2.0058(4)	-
	$\text{SO}_2\cdot^-$ (c)	2.0030(1)	2.0070(7)	2.0050(3)	-

There were lines belonging to the ion-radical SO_2^- [1]. The main value of its g -tensor - $g_{xx} = 2.0012$; $g_{zz} = 2.0053$; g_{yy} - hidden in the width of the lines belonging to the ion-radical $\text{O}^-(\text{I})$, similar values of the g -tensor in a single crystal of this radical - $g_{xx} = 2.0012$; $g_{yy} = 2.0104$; $g_{zz} = 2.0055$ (Table 1).

The EPR spectrum arising in the product dehydration of gypsum at 300 °C, almost similar to the spectrum observed after the dehydration of gypsum at 275 °C. There is a new line with $g = 2.0053$ owned SO_2^- radical ions. Still are observed spectral lines belonging to the ion-radicals $\text{O}^-(\text{I})$, SO_2^- , $\text{SO}_2^-(\text{I})$, $\text{SO}_3^-(\text{I})$, $\text{SO}_3^-(\text{III})$. Their main components g -tensor are represented in Table 2.

Beginning with temperature of 325 °C the dehydration lines observed EPR spectrum become clearer shape, approaching the ideal characteristic and undirected systems. Previously identified in the single crystals of insoluble anhydrite paramagnetic centers are present ion-radicals $\text{O}^-(\text{I})$, SO_2^- , $\text{SO}_2^-(\text{I})$, $\text{SO}_3^-(\text{I})$, $\text{SO}_3^-(\text{III})$ (Table 2). In this spectrum started to be shown clearly another radical ion SO_2^- with principal values g -tensor - $g_{xx} = 2.0030$ and $g_{yy} = 2.007$, which are close to their values of the principal values of g -tensor ion-radical SO_2^- single crystal [4, 5] (Table 1).

View of the EPR spectrum of irradiated product is almost identical in the temperature range from 350 °C dehydration of gypsum up to 425 °C inclusive. Only the intensity of the observed lines changes in the direction of increasing (Figure 2). Part minor lines then occur, and then disappear.

Thus, in this temperature range as a result of dehydration of X-radiation occurs EPR spectrum lines which characterize the same set of PC. It should be noted that the shape of the lines observed in this temperature range, more precise and closer to the idealized shape of the lines of the first derivative.

DISCUSSION AND CONCLUSIONS

Presented in Table 2 confirms the results previously published data by dehydration of gypsum and hemihydrate [10, 13], where it was noted that the insoluble anhydrite is formed in significant quantities at temperatures above 200 °C.

It should be noted that after the X-ray irradiation product of dehydration of gypsum at 225 °C, the ESR spectrum lines appear radical ions SO_3^- ; $\text{SO}_3^-(\text{I})$ и $\text{SO}_3^-(\text{III})$ in the new phase of insoluble anhydrite. In this case, the total ESR spectrum stored lines SO_3^- radical ions belonging to gypsum, bassanite and gamma-anhydrite.

This fact indicates the participation of SO_3 molecular groups in the process of crystallization, that is, SO_3 group is a structural unit of the sediment material in the phase transition of the first kind [12]. Ion-radicals from the structure of gypsum SO_3^- transformed into the structure bassanite, gamma - anhydrite and natural anhydrite without changing the electronic configuration.

The broad lines observed even in the EPR spectrum of the product of dehydration of gypsum at 250 °C (Figure 1), attributed the ion-radical type SO_3^- , which were formed in the structures of gypsum and bassanite not recorded above this temperature, which is a consequence of the lack of data mineral formations in products annealing. Above 250 °C reliably recorded EPR spectra of radical ions characteristic of the structure of natural anhydrite.

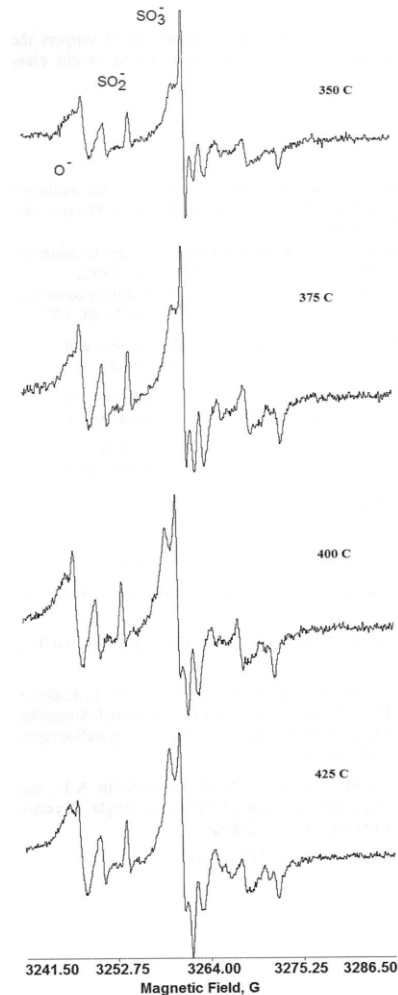


Fig.2. The EPR spectra of ion-radicals SO_2^- , SO_3^- , O^- in the temperature range 350-425 °C. Parameters PC resulted in Table 2.

To observe a set of PC are the same radical ions that previously found at a lower temperature dehydration –two ion-radicals SO_3^- , three – SO_2^- and single O^- .

The values of principal components g -tensor aforementioned radical ions observed in the products of dehydration of gypsum carried out at various temperatures shown in Table 2.

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