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Abstract

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THE EFFECT OF THE RADIOACTIVE RADIATION OF $Na_2\overset{\times}{W}O_4$ AND $Na_2\overset{\times}{S}O_4$ ON THE PHASE TRANSFORMATIONS OF THESE COMPOUNDS

Phase transformations are structure-sensitive properties. The appearance of defects and the emergence of additional electric fields in the crystalline structure of a solid after its radiation treatment can evidently lead to a change in the composition of the phases and in the temperature of their transformations. The existence of regions of local heating (thermal wedges), as one type of radiation damage under the action of neutrons, protons, and α-particles ([1,2]), may be confirmed by the appearance of a high-temperature phase of a substance as a result of irradiation, as was found for alloys of uranium with molybdenum and niobium ([3–6]), and for certain metals and nonmetals ([7–9]). The action of electrons on the white modification of tin ([10]) did not lead to a change in the crystalline structure.

Very little data exist on the influence of radiation on the phase transformations of chemical compounds. After irradiation of monoclinic zirconium dioxide ([11]) with fast or thermal neutrons, it was established by X-ray diffraction that a cubic modification of ZrO_2, usually stable at temperatures above 1900°, arises in the sample. Heating the irradiated sample above 800° makes it possible to convert the high-temperature phase back into the low-temperature modification. Upon irradiation of barium titanate with fast neutrons, an analogous phenomenon was observed, as well as a lowering of the phase-transition temperature, which the authors ([12,13]) explained by the presence of nuclei of a new crystalline structure.

We investigated the effect of irradiation with slow neutrons and γ-rays on the phase states of two salts—Na_2WO_4 and Na_2SO_4, whose transformations have been well covered in the literature ([14–16]). Both of these salts become radioactive after neutron treatment. Therefore it was of particular interest to study the effect of the radioactive radiation of these objects on the temperature of their phase transitions. For carrying out the experiments, the thermographic method was chosen. Chemically pure sodium tungstate and sulfate were twice recrystallized from water, calcined at temperatures of 100 or 800°, respectively, and then subjected to thermographic recording. The measured temperatures of the polymorphic transformations and the melting points of the initial sam-

ples did not differ from the most recent reliable data. Preparations of Na_2WO_4 and Na_2SO_4 were subjected in a nuclear reactor to a flux of slow neutrons of $8 \cdot 10^{12}$ n/cm$^2 \cdot$ s and to γ-radiation of intensity $4 \cdot 10^7$ r/h. In this process, in Na_2WO_4 the radioactive isotopes Na^{24}, W^{181}, W^{185}, and W^{187} were formed, and in Na_2SO_4–Na^{24} and S^{35}. Identification of the resulting isotopes was carried out by recording β- and γ-spectra on a 100-channel amplitude analyzer. Since Na^{24} and W^{187} are short-lived isotopes and the fraction of W^{181} is insignificant, after some aging of the irradiated preparations the emitters during the study of the phase transitions were, in Na_2WO_4–W^{185}, $E(\beta)_{max} = 0.4$ MeV, $T_{1/2} = 73.2$ days, and in Na_2SO_4–S^{35}, $E(\beta)_{max} = 0.167$ MeV, $T_{1/2} = 87.1$ days. Measurements of the absolute activity were carried out on a 4π counter. Thermograms were taken on a Kurnakov pyrometer, FPK-59,

with a Pt–PtIr thermocouple. The sample weights were 0.5 g. The average heating rate was 14°/min, and the cold-junction temperature was 0°. Aluminum oxide was used as the standard. Thermograms for irradiated and unirradiated specimens were recorded under strictly identical conditions. The temperature readings for phase transitions of one and the same specimen in our investigation, in parallel experiments, sometimes differed from one another by ±2°, which corresponds to a difference of 0.5 mm on the thermograms. To improve the accuracy of determining the temperature difference between transformations of nonradioactive and radioactive specimens, a compensation circuit was used, consisting in the application to the thermocouple-pyrometer circuit of an opposing emf from a dc potentiometer up to the required temperature, which served as the zero point in such a recording. Thus, the temperature intervals of interest to us were recorded with an accuracy of ±0.25°.

Table 1

Comparison of thermograms from the first and second recordings of irradiated Na_2WO_4 samples

Experiment No.	Time, days: irradiation in the reactor	Time, days: holding	Specific radioactivity (mCi/g): after irradiation	Specific radioactivity (mCi/g): on the day of operation	Thermogram recording No.	Temperature of phase transitions, °C: I	Temperature of phase transitions, °C: II	Temperature of phase transitions, °C: melting
1	10	115	12.4	0.30	1	–	595	696
1	10	115	12.4	0.30	2	–	595	696
2	75	121	80.3	25.70	1	–	591	692
2	75	121	80.3	25.70	2	–	591	692
3	15	6	25.4	24.20	1	125	593	697

Experiment No.	Time, days: irradiation in the reactor	Time, days: holding	Specific radioactivity (mCi/g): after irradiation	Specific radioactivity (mCi/g): on the day of operation	Thermographic recording No.	Temperature of phase transitions, °C: I	Temperature of phase transitions, °C: II	Temperature of phase transitions, °C: melting
3	15	6	25.4	24.20	2	—	593	697

All the data given below were obtained using heating curves, which give more reliable results than cooling curves. The temperatures of phase transformations on the cooling curves lie somewhat lower owing to supercooling phenomena. The experiments were carried out as follows. In the first run the irradiated powder was heated; in the second and third runs, the melts that had solidified after the preceding measurement were heated. Defects of the crystal lattice, which may arise during bombardment of the specimen by neutrons or as a consequence of prolonged radioactive decay during irradiation and holding of the salt taken, should have been detected during the first heating of the sample. Repeated operations of thermal recording, which were carried out after short intervals of time (the entire series of measurements took 1-2 days), characterized already the influence of the intensity of the radioactive radiation occurring in the compound under study on its phase transitions. Table 1 compares the results of the first and second thermal recordings for $Na_2\overset{\times}{W}O_4$ specimens subjected to irradiation and subsequent holding for various periods of time.

As we see, the melting points and the temperature of the phase transformation do not change if one compares the thermograms of the powdered irradiated specimen and of the product obtained after its melting. Thus, treatment of sodium tungstate in a nuclear reactor does not create stable transformations of the crystal structure that could be detected thermographically. It is possible that changes in the phase composition or defects of the crystal lattice nevertheless arise, but are rapidly annealed even at ordinary temperature. In this respect, experiment No. 3 (Table 1) is of interest; it shows that after short-term holding (6 days) of sodium tungstate irradiated for 15 days with neutrons, a phase transition at 125° is detected in the specimen, accomp—

released by the evolution of heat. Obviously, the new phase is formed with absorption of energy due to the action of radiation. It disappears both when the sample is melted and when it is kept for a long time under ordinary-temperature conditions.

Radioactive radiation of the substances studied has a more substantial effect on the phase transitions. As is seen from the data in Table 2,

Table 2

Effect of radioactive radiation on phase transitions

Preparation No.	Time, days: irradiation in the reactor	Time, days: holding	Specific radioactivity, mCi/g: after irradiation	Specific radioactivity, mCi/g: on the day of operation	Temperature of phase transitions, °C: polymorphic transformation	Temperature of phase transitions, °C: melting
					Na_2WO_4	
1	0	–	–	–	595	700
2′		107		0.36	595	696
2″	2	303	4.0	0.02	595	700
3′		115		0.30	595	695
3″	10	169	12.4	0.17	595	698
3‴		308		0.04	595	700
4′		121		25.70	591	692
4″	75	372	80.3	2.40	595	694
4‴		424		1.60	595	698
5′	15	6	25.4	24.20	593	697
					Na_2SO_4	
1	0	–	–	–	248	884
2′		105		0.35	244	878
2″	10	142	0.8	0.25	246	880
3′		8		0.70	246	882
3″	15	77	0.8	0.40	248	884

for both compounds studied the melting points and the temperatures of the polymorphic transformations are lowered in comparison with nonradioactive preparations. The figures given are averages from the results of 2–3 heating experiments on samples that had first been melted.

As W^{185} or, respectively, S^{35} decays, the melting temperature of $Na_2\overset{\times}{W}O_4$ and $Na_2\overset{\times}{S}O_4$ gradually increases and, with a corresponding decrease in their activity, reaches the value corresponding to the nonradioactive preparation. Thus, the phenomenon described cannot be explained by the formation of any radiochemical impurities during radiation treatment of the initial salts or as a result of the decay of the radioactive isotopes formed.

It should be noted that the magnitude of the lowering of the melting point itself depends not only on the specific radioactivity of the substances studied, but also on the period for which they are kept after irradiation: the longer the

holding period at the same residual radioactivity, the greater the lowering of the melting temperature. In addition, the duration of treatment of the salts studied in the nuclear reactor also plays a role. Figure 1 shows how, depending on the indicated conditions, return to the normal tem-

Fig. 1. Dependence of the decrease in the melting temperature of Na_2WO_4 samples on the duration of irradiation, the holding time, and the specific radioactivity. Duration of irradiation in the reactor: 2—2 days, 3—10 days, 4—75 days (holding before the start of measurements 100-120 days); 5—15 days (holding 6 days)

melting temperature for different samples of radioactive sodium tungstate.

For radioactive samples of $Na_2\overset{\times}{W}O_4$, a decrease in the temperature of the polymorphic transformation is observed only at a comparatively high specific radioactivity, $\sim$ 25 mCu/g (Table 2). This is explained by the greater heat of phase transition II compared with the heat of melting, which we observed in the state diagrams $\Delta t^\circ - \tau$ (time). For sodium sulfate, a noticeable decrease in the temperature of the polymorphic transformation is observed already at low specific radioactivity (0.2-0.4 mCu/g) and after comparatively short-term irradiation of the preparation in a nuclear reactor. The dependence of the effect on the duration of irradiation and on the period of storage of the samples also occurs here.

The decrease in the temperature of the phase transitions for the radioactive substances studied apparently depends on the increased free energy that they possess as a result of the continuously occurring radioactive radiation. The emission of β-particles creates additional electric fields in the preparations and leads to excitation of electrons in the atoms. Preliminary experiments carried out by us have shown that radioactive sodium tungstate, in accordance with the assumptions stated, is characterized by a more complex EPR spectrum than nonradioactive samples of this compound. The reasons for the influence of the duration of irradiation and of the storage time on the temperature of the phase transitions of the salts investigated are being studied by us.

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REFERENCES CITED

1. V. V. Pen' kovskii, *Effect of Irradiation on Metals and Certain Refractory Materials*, 1962, p. 48.

2. D. Dienes, D. Vineyard, *Radiation Effects in Solids*, IIL, 1960.

3. Ch. Tucker, R. Senio, J. Appl. Phys., **27**, 207 (1956).

4. S. T. Konobeevskii, N. F. Pravdyuk, V. I. Kutaidzev, Materials of the International Conference on the Peaceful Uses of Atomic Energy in Geneva, **7**, Publishing House of the Academy of Sciences of the USSR, 1956, p. 263.

5. M. L. Bleiberg, L. J. Jones, B. Lustman, J. Appl. Phys., **27**, 1270 (1956).

6. S. T. Konobeevskii, N. F. Pravdyuk et al., *Atomic Energy*, **4**, 31 (1958).

7. J. Teodorescu, A. Glodeany, Phys. Rev. Lett., **4**, 231 (1960).

8. D. L. Chipman, B. E. Warren, G. J. Dienes, J. Appl. Phys., **24**, 1251 (1953).

9. J. Fleeman, G. J. Dienes, J. Appl. Phys., **26**, 652 (1955).

10. A. Sosin, Bull. Am. Phys. Soc., **1**, Ser. 2, 129 (1956).

11. M. C. Wittels, F. A. Cherill, J. Appl. Phys., **27**, 643 (1956); **28**, 606 (1957).

12. M. C. Wittels, F. A. Cherill, Phys. Rev. Lett., **3**, 176 (1959).

13. J. M. Warde, J. R. Johnson, J. Am. Franklin Inst., **260**, 455 (1955).

14. F. Hoermann, Zs. anorg. Chem., **177**, 152 (1929).

15. Yu. P. Simanov, L. F. Kiryukina, ZhNKh, **2**, 699 (1957).

16. N. E. Shmidt, V. A. Sokolov, ZhNKh, **6**, 2613 (1961).

Note: Figure translations are in progress. See original paper for figures.