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Abstract

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ON THE STRUCTURAL IMPURITY OF TUNGSTEN AND GALLIUM IN CRYSTALS OF SYNTHETIC QUARTZ

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In natural quartz crystals of various genesis, about 20 impurity elements have been detected by methods of spectrochemical analysis: Cu, Al, B, Fe, Mg, Ca, Ti, W, Ga, Mn, Ba, Ge, Li, Na, K, Cs, H (1-4). The isomorphous character of the impurities Ge, Al, Ti, Fe, which substitute for silicon in tetrahedra, has been demonstrated directly by the method of electron paramagnetic resonance (e.p.r.). The localization of the impurities Na, Li, K, H in structural channels of quartz has also been established with sufficient accuracy by the e.p.r. method and infrared spectroscopy (5-10). As a rule, these investigations were carried out either on crystals of natural quartz or on crystals of artificial quartz synthesized in aqueous solutions of Na_2CO_3 (NaOH), K_2CO_3 (KOH), i.e., in alkaline systems. Attempts to introduce into quartz, in the indicated media, other impurities suitable on crystallochemical grounds (including the impurities Ga, W) were unsuccessful.

We carried out experiments on growing quartz crystals with Ga and W impurities from aqueous weakly acidic fluorine-containing solutions. As is known, such solutions (along with alkaline ones) are good solvents for quartz. The growth of quartz using such solutions was carried out in small autoclaves (with a volume of 150-350 cm^3) by the temperature-gradient method at relatively low temperatures and pressures. To prevent corrosion of the autoclave walls and the entry of other impurities into the solution, fluoroplastic liners were used.

Table 1

Distribution of W and Ga in quartz crystals grown in weakly acidic fluorine-containing solutions

Amount of introduced impurity, mg/l	Amount of introduced impurity, mg/l	Content in crystals, wt. %	Content in crystals, wt. %	Growth rate, mm/day
WO_3	Ga_2O_3	W	Ga	
80		$4 \cdot 10^{-4}$		0.38
160		$4 \cdot 10^{-3}$		0.32
	80		$3 \cdot 10^{-2}$	0.08
	160		$3.6 \cdot 10^{-2}$	0.07
	80		$1.2 \cdot 10^{-4}$	0.02 (NaOH)

Tungsten or gallium oxide was placed in the lower, higher-temperature zone of the autoclave together with quartz chips, in the amounts indicated in Table 1. The same table gives data from spectrochemical analyses for W and Ga in the crystals obtained. It is interesting to note that the content of the Ga impurity in quartz grown in an alkaline medium is approximately two orders of magnitude lower than in the case of fluorine-containing solutions.

The grown quartz crystals had no visible coloration and were sufficiently transparent for optical measurements. Plates measuring 5 × 10 × 12 mm for optical measurements and rods (2 × 2 × 10) mm for investigations by the EPR method were prepared from the crystals. These samples were subjected to γ-irradiation (Co^{60} source, dose 10^6–10^7 roentgens), which caused them to acquire an amethyst-like color of low intensity (quartz with a W impurity) and a yellow-brown color (quartz with a Ga impurity). Optical absorption spectra were studied on SF-4 and SF-8 spectrophotometers (in the range 2200–11000 Å), and the EPR spectra on an RE-13-01 radiospectrometer (frequency $\sim$ 9.30 GHz) at room temperature and at the temperature of liquid nitrogen (77° K). We note that the optical absorption and EPR spectra described below are observed only in irradiated quartz crystals, so that it is precisely the action of ionizing radiation that leads to the formation of the corresponding color centers.

In quartz samples grown with W additions, an EPR spectrum was observed that is described by a spin Hamiltonian of the form:

$$H = (g_z H_z S_z + g_x H_x S_x + g_y H_y S_y)\beta$$

with the following constants ($s = 1/2$)

$$g_z = 2.0023 \pm 0.0005, \qquad g_x = 2.011 \pm 0.001, \qquad g_y = 2.074 \pm 0.002.$$

A hyperfine structure (h.f.s.) was observed consisting of two satellites with $I = 1/2$, and with a ratio of the intensities of the main line and the h.f.s. line of approximately $1 : 0.08$. The constants of the h.f.s. tensor are as follows:

$$A_z = 18 \pm 1 \text{ Oe}, \qquad A_x = 9 \pm 1 \text{ Oe}, \qquad A_y = 1.5 \pm 1 \text{ Oe}.$$

The unit cell contains 6 equivalent paramagnetic centers of this type, differing in the orientation of the axes of the g-tensor (the direction of the g_z axis is approximately parallel to the Si–Si direction in quartz). The magnitudes of the principal values of the g-tensor and the presence of h.f.s. from an isotope with $I = 1/2$ indicate that this center is a strongly perturbed paramagnetic ion-radical O^- ([13,14]) in a tetrahedron in which a tungsten ion (W^{4+}) replaces a silicon ion (Si^{4+}). Indeed, tungsten has the isotope W^{183} ($I = 1/2$, abundance 14.4%), and the calculated value of the ratio of the intensity of the h.f.s. line to the main one should be 1 : 0.084, which is close to that observed. The following argues in favor of the assumption that tungsten enters quartz in the form W^{4+}: if complexes $(WO_4)^{2-}$ were formed (i.e., tungsten in the form W^{6+}), then the formation of a hole center O^- would lead to a lowering of the charge of such a complex. But since in the structure the complex $[SiO_4]^{4-}$ is replaced, one should rather expect the formation of an electron center (ion radical) $[WO_4]^{3-}$, which has been well studied ([5],[6]). Therefore we believe that what occurs is the formation of an O^- center in the complex $[WO_4]^{4-}$.

The optical absorption spectrum of quartz crystals with an impurity after radiation exposure contains weak absorption bands in the regions 2800; 3500; 4500; 5200; 6300 Å. It should be noted that the EPR spectrum described at room temperature is not observed because of the short spin-lattice relaxation time. Both the coloration and the EPR lines in such crystals are not observed after annealing at $T \sim 200°$. The absorption bands in the regions 4500 and 6300 Å are probably associated with a small number of Al centers, which are practically always present in quartz crystals. The 3500 and 5200 Å bands are close in position in the spectrum to analogous absorption bands in amethysts, whose coloration, as is known, is due to an unpaired electron localized on a defective tetrahedron in which a silicon ion is replaced by an iron ion. Thus, the centers in quartz

with W and Fe impurities have a similar structure (a strongly perturbed O^- center), which is also manifested in the similarity of the colors of these crystals. It may be assumed (11) that the 2800 Å band is due to electron-trapping centers.

We also investigated quartz crystals with a gallium impurity. Gallium has the electronic structure $[A]3d^{10}4s^2 4p$, and, consequently, the Ga^{3+} ion has the electron shell $[A]3d^{10}$. As is known, such systems are capable of forming *spd*-hybrid tetrahedral bonds.

Irradiation of quartz crystals grown with Ga additions leads to their coloration in a weakly intense brown color and to the appearance of a characteristic e.p.r. spectrum. At room temperature the e.p.r. spectrum consists of two isotropic lines ($g_1 = 2.011 \pm 0.001$, $g_2 = 2.028$). No hyperfine structure is observed for a line half-width (measured between inflection points) of ~ 4.5 Oe. At liquid-nitrogen temperature the e.p.r. spectrum in such crystals consists of a large number of lines with an anisotropic g-factor; the anisotropy range extends from $g_{\min} = 2.00 \pm 0.01$ to $g_{\max} = 2.072 \pm 0.001$. Two types of paramagnetic centers are observed, each of which has three possible orientations of the axes of the g-tensor. Hyperfine structure is observed from the isotopes Ga^{71} ($I = {}^3/_2$, abundance 40%) and Ga^{73} ($I = {}^3/_2$, 60%).

It may be assumed that the e.p.r. spectrum is due to Ga^{4+}, formed under γ-irradiation. Indeed, Ga^{4+} has the electronic configuration $[A]$, $3d^9$, i.e., is isoelectronic with the Cu^{2+} ion. The electronic structure of tetrahedral Cu^{2+} complexes should be the same as the structure of octahedral complexes, but with the order of levels reversed. In the case of a distorted tetrahedron the ground state is the state transforming according to the representation B_1, while the excited states are those transforming according to the representations B_2, A_2, A_1 (in order of increasing energy) (17). The value of the spin-orbit constant is large, and this leads for Ga^{4+} to strong Jahn-Teller coupling and, consequently, to the occurrence of distortions of tetrahedral complexes (as a result of the Jahn-Teller effect) in addition to those already present in the structure (18,19). In this case one can explain the isotropy of the g-factor at room temperature and the anisotropy of the g-factor at low temperatures for Ga^{4+}, just as was done for Cu^{2+} in a number of crystals (20–22). The optical absorption spectrum of such irradiated crystals contains bands in the regions 6400 Å (15400 cm^{-1}) and 3400 Å (29400 cm^{-1}). Intense absorption begins at 2650 Å (38000 cm^{-1}), and it should probably be attributed to a charge-transfer band. The data presented show that Ga^{3+} isomorphously replaces Si^{4+}; moreover, in contrast to Al^{3+} (for which the role of donors of additional electrons necessary for the formation of tetrahedral bonds and charge compensation in quartz is usually played by Na^{1+}, Li^{1+} ions), for the Ga^{3+} ion the charge compensation is nonlocal and is probably effected in the form of OH groups, whose presence is recorded in Ga-containing quartzes by infrared absorption bands in the region 3300–3600 cm^{-1}.

It is interesting to note that in natural quartz crystals tungsten and gallium are detected extremely rarely, despite the fact that in ore veins tungsten is often found in close intergrowths with wolframite or hübnerite, while gallium, as a rule, is constantly noted in many sulfides and aluminosilicate minerals associated with quartz. The experimental data set forth above indicate the possibility of isomorphic incorporation of tungsten and gallium into natural quartz, especially if crystallization occurred in weakly acidic fluorine-containing solutions.

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References Cited

1. N. I. Vasil’ kova, S. G. Solomkina, *Typomorphic features of fluorite and quartz*, 1965.
2. *Minerals*, 2, issue 2, “Nauka,” 1965.
3. J. D. Dana, E. S. Dana, K. Frondel, *System of Mineralogy*, 3, Minerals of Silica, Moscow, 1966.
4. J. M. Stanly, S. Theekritoff, *Am. Mineralogist*, **41** (1956).
5. I. H. E. Griffiths, J. Owen, L. M. Word, *Nature*, **173**, 439 (1954).
6. M. C. M. O’ Brien, *Proc. Roy. Soc. A*, **239**, 404 (1955).
7. J. H. Anderson, I. A. Weil, *J. Chem. Phys.*, **31**, 427 (1959).
8. J. H. Mackey, *J. Chem. Phys.*, **33**, 63 (1963).
9. P. M. Writh, J. A. Weil et al., *Nature*, **197**, 304 (1963).
10. T. I. Barry, P. McNamara, W. J. Moore, *J. Chem. Phys.*, **42**, 2599 (1965).
11. L. I. Lipober, M. I. Samoilovich, L. A. Gordienko, *Crystallography*, **10**, 879 (1965).
12. L. G. Chentsova, L. I. Tsinober, M. I. Samoilovich, *Crystallography*, **11**, 236 (1966).
13. M. J. Blandomer, L. Shields, M. C. Symons, *J. Chem. Soc.*, **1964**, 4352.
14. A. I. Novozhilov, M. I. Samoilovich, A. A. Sergeev-Bobr, *Vestn. LGU*, **6**, 24 (1967).
15. G. H. Azarbaejani, *Bull. Am. Phys. Soc.*, **7**, 1131 (1965).
16. V. Low, *Paramagnetic Resonance in Solids*, Foreign Literature Publishing House, Moscow, 1964.
17. K. Balkhausen, *Introduction to Ligand Field Theory*, Moscow, 1964.
18. C. A. Bates, W. S. Moore et al., *Proc. Phys. Soc.*, **79**, 73 (1962).
19. R. I. Arnot, A. Wold, D. B. Rogers, *J. Phys. Chem. Solids*, **25**, 161 (1964).

20. M. de Wite, A. R. Reinberg, *Phys. Rev.*, **163**, 264 (1967).

21. R. F. Ticker, *Phys. Rev.*, **112**, 725 (1958).

22. A. Abragam, M. H. L. Pryce, *Proc. Phys. Soc.*, **163**, 409 (1950).

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