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Observation of spontaneous polarization of tourmaline*

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Since Tetsujiro Kubo indirectly found the spontaneous polarization of tourmaline through absorbing copper ions in copper sulfate aqueous solutions in 1980s, there is no other evidence to demonstrate the existence of the spontaneous polarization in tourmaline. It was found that after a tourmaline particle was bombarded by electron beams, a spot appeared on the surface of the sample, and that one half of the spot was brighter than the other half under scanning electron microscope. After tourmaline was treated for 2 h at 1223K and then bombarded by electron beams, the bombardment spot did not appear because the crystal structure of tourmaline is destroyed. The existence of the bombardment spot accounts for the spontaneous polarization. The shape and brightness of the bombardment spot not only shows the existence of a surface electric field induced by spontaneous polarization, but also the relation with the direction of the crystal plane of tourmaline.

Keywords: spontaneous polarization, tourmaline, electron beam bombardment
PACC: 9160P, 0779, 6116P

1. Introduction

Tourmaline is a kind of complex borosilicate mineral with a general chemical formula[1,2] of $XY_3Z_6Si_6O_{18}(BO_3)_3W_4$. The X site is commonly occupied by Na, but it can also be replaced by K, Ca and vacancies. Tourmaline contains two main types of octahedral sites as Z and Y. The Z site is occupied by Al, but Fe^{2+}, Fe^{3+}, Ti, Mg, Cr, and V^{3+} may frequently replace it, whereas the Y site can be occupied by a variety of cations such as Fe, Mg, Mn, Al, Li, and Ti. The W site is occupied by OH, but is also replaced by F and O. It was found early[3] that tourmaline had the properties of pyroelectricity and piezoelectricity. But it is not ferroelectric.[4] The pyroelectricity of tourmaline has been used in thermal imaging sensor and the net-flux radiometer contained in the Galileo probe, which was released into the atmosphere of Jupiter on 1995 July 13.[5] The fundamental study on tourmaline has become less since the World War II, because no new property was found. However, in 1980s the Japanese environmental expert, Tetsujiro Kubo,[6,7] found that tourmaline could purify water, and demonstrated that the antilogous pole could absorb copper ions in copper sulfate aqueous solution. Therefore, he suggested that tourmaline should have "permanent electrode". The permanent electrode should be attributed to its spontaneous polarization. But to date, there has been no other evidence to support this viewpoint. Electron micrographic technique has been widely used in the study of surface property of materials.[8,9] Ji and co-workers[10] found that absorption and repellence existed between the particles of tourmaline by scanning electron microscope (SEM) measurements. The dipolar nature of tourmaline was observed in this study through electron probe in SEM (Philips XL30-TMP), indicating that spontaneous polarization existed in tourmaline.

2. Experiment

A mono-energetic electron beam has been employed, whose cross section and driving voltage are respectively 3nm and 25kV. The current density of the incident electron beam was 33μA. The experimental powdered sample was the schorl-dravite crystal ($R3m$, $a = b$=1.59782nm, c=0.715569nm). The samples were treated at 573, 973, 1153, and 1223K for 1 h separately, and one of the sample was treated at 1225K for 2 h.

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3. Results and discussion

Figures 1(a) and 1(b) show the scanning electron microscope (SEM) images of the samples before and after electron beam bombardment, respectively. In Fig. 1(b), a new phenomenon was found that an electron beam hitting spot appears on the particle, and one half of the spot was brighter than the other half. This phenomenon was found by chance[10] when we used electron probe to analyse the elements in tourmaline.

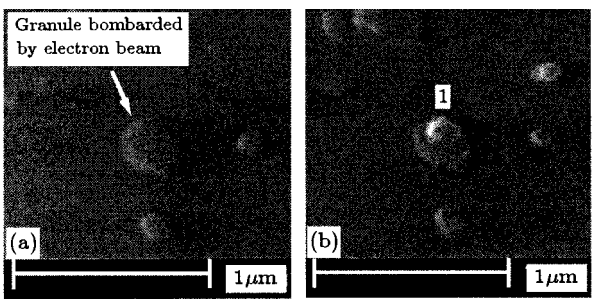


Fig.1. Images of tourmaline granules by SEM, 20000× (a) Image of the tourmaline granule before the bombardment by electron beams; (b) image of the tourmaline granule after the bombardment by electron beams.

The existence of bombardment spot reflects the difference of electron density between the spot and other part on the surface of tourmaline. If spontaneous polarization exists, its direction should be along the reverse direction of the c-axis of a tourmaline crystal, because copper ions are absorbed on the antilogous end of tourmaline.[6] Therefore, the directions of the electrostatic fields should be different at the two ends of the vertical c-axis of a tourmaline crystal. An electrostatic field can exist on the specimen surface, but its direction may be different depending upon different conditions. The different direction of the field may have different influence on the beams of the electron probe. The brighter part implies that more electrons from the probe beam accumulate on the surface of a tourmaline particle, or more secondary electrons are hit out, and the dark part implies that less electrons accumulate on the surface, or less secondary electrons are hit out. Therefore, the shape and brightness contrast between the two parts of a bombardment spot not only reflect the intensity of the electrostatic field and its direction, but also show a relation with the crystal index.

Figure 2 presents an image of the sample heat-treated at 573K for 1 h. There is one bombardment spot by electron beams on the surface of the sample. It clearly shows that one half of the spot is brighter than the other half, and the brighter half is almost equal to the darker half. Therefore, the direction of the crystal plane bombarded by electron beams should be vertical to the c-axis of the tourmaline crystal (see the arrow in Fig.2).

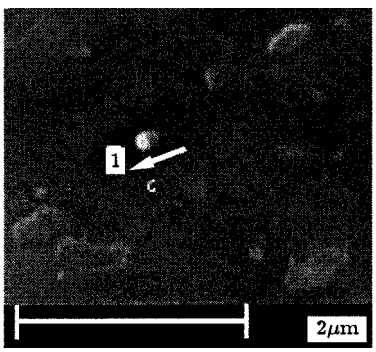


Fig.2. SEM image of tourmaline heat-treated at 573K for 1 h, 10000×.

Figure 3 illustrates the image of the sample heat-treated at 973K for 1 h. There are two bombardment spots which are almost round. This shows that the direction of the crystal plane bombarded by electron beams is different from that in Fig.2, it is almost parallel to the direction of the c-axis. The tourmaline granule does not melt at this temperature, and the spontaneous polarization does not disappear.

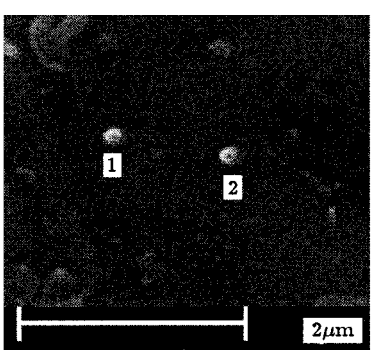


Fig.3. SEM image of a sample heat-treated at 973K for 1 h, 10000×.

Figure 4 is the SEM image of a sample heat-treated at 1153K for 1 h. Four sites on different surfaces of three tourmaline granules are selected, which have been bombarded by electron beams. There are four spots produced. From these four spots, it can be found that spot 1 has a brighter and bigger area than spot 2, and the shapes of the two spots are almost similar. The directions of the crystal planes at the two locations are slightly different. But the spots 3 and 4

are located on other two smaller particles, which melt and stick to a big particle. They are completely different from spots 1 and 2. Therefore, the directions of the crystal planes of sites 3 and 4 (corresponding to spots 3 and 4) are completely different from those of sites 1 and 2. Figure 4 also shows that the granule of tourmaline begins to melt, and the smaller granules have been sintered together with the bigger granule at 1153K for 1 h. But the spontaneous polarization does not disappear.

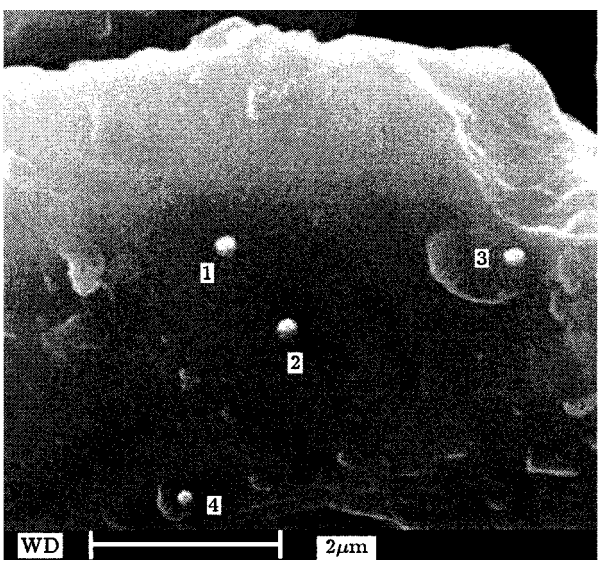


Fig.4. SEM image from a sample heat-treated at 1153K for 1 h, 10000×.

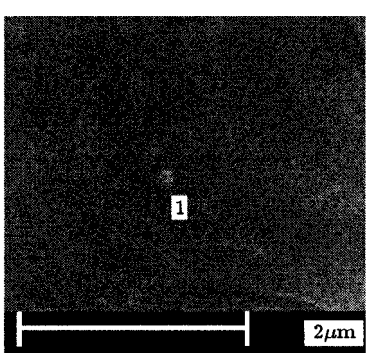


Fig.5. SEM image from the sample heat-treated at 1223K for 1 h, 10000×.

Figure 5 shows the SEM image of the sample heat-treated at 1223K for 1 h. From Fig.5, it can be seen that the spot is not clear, and the spontaneous polarization should almost disappear at this temperature. When the sample is heat-treated for 2 h, the spot completely disappears (the SEM image has not been given here). Complete disappearance of the spontaneous polarization is due to the fact that the crystal structure has been destroyed.

The spontaneous polarization of a tourmaline crystal would produce an electric dipole, especially in a small granule with a diameter of several microns or less. Therefore, a strong electrostatic field exists on the surface of a tourmaline granule. Because a single-crystal tourmaline has no fixed dissociated planes, the small granule shivered from a single tourmaline crystal is in a very irregular way. Thus, the crystal plane index of the granule is very complicated, and so is the direction of the electrostatic field. The spot bombarded by an electron beam has a given nature that relates to the crystal plane index. Yamaguchi[11] studied the surface electric fields of tourmaline, and found that gases absorbed on the surface influence the intensity of the electrostatic field induced from the pyroelectric effect. Heat-treatment and electron-beam bombardment may influence the absorption of gases, which may have a certain effect on the surface electrostatic field. But from the experimental result in this paper there is no evidence showing any effect on it.

Kubo[6] found that the permanent "electrostatic electrode" (spontaneous polarization) disappeared at a temperature range of 1000–1050°C. Similar results have been found in the present experimental results, indicating that the spontaneous polarization began to disappear at 1223K, and the crystal began to melt at 1153K, which is consistent with that in Ref.[12].

4. Conclusion

Spots can be formed after the electron-beam bombardments on the surface of tourmaline granules. The spot reflects the existence of spontaneous polarization in tourmaline. The shape and brightness of the spot formed by electron-beam bombardment are related to the direction of the crystal plane. The spontaneous polarization of the tourmaline disappears when heated to 1223K.

References

[1] Yavuz F 1997 *Computers & Geosicence* **23** 947

[2] Selway J B, Milan N, Hawthorne F C *et al* 1998 *Am. Mineralogist* **83** 896

[3] Dietrich R V 1985 *The Tourmaline Group* (New York: Van Nostrand Reinhold) p 173

[4] Wang Y X, Zhong W L, Wang C L and Zhang P L 2002 *Acta Phys. Sin.* **51** 171 (in Chinese)

[5] Lang S B 1999 *Ferroelectrics* **230** 99

[6] Nakamura T and Kubo T 1992 *Ferroelectrics* **137** 13

[7] Kubo T 1996 *United States Patent* 5569388

[8] Zhang J and Sun R G 2002 *Chin. Phys.* **11** 776

[9] Shen D H 2001 *Chin. Phys.* **10** 163

[10] Ji Z J, Liang J S, Jin Z Z and Wang J 2002 *J. Synthetic Crystal.* **31** 507 (in Chinese)

[11] Yamaguchi S 1983 *Appl. Phys.* A **31** 183

[12] Ji Z J, Liang J S, Jin Z Z and Wang J 2002 *Acta Mineralogy.* **22** 280 (in Chinese)