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論 文 内 容 要 旨

Abstract

In the beginning of the 19th century, Brewster began to observe minerals using the polarized microscopy, and first found the sectors showing optically uniaxial and biaxial symmetries in a thin section of a morphologically tetragonal apophyllite in 1819. When the symmetry observed by polarized microscope was lower than a morphological or X-ray analytical symmetry, this optical property had been thought to be anomalous, and it has been termed an “optical anomaly” since the 19th century.

The objective of this study explains the origin of optical property termed an “optical anomaly” of some crystals, which is an interested problem since the 19th century. Based on the results from the optical observations and structural analyses, the origin of optical property was discussed from a structural viewpoint. In the first chapter, the significance of the mineralogical phenomenon termed an “optical anomaly” was discussed from the results of this and recent studies, and in the appendix, how to describe the crystal with growth sectors showing different symmetry was noted on the basis of the nomenclature proposed by International Mineralogical Association (IMA) and International Union of Crystallography (IUCr).

In the second chapter, the crystal structures of vesuvianite, which was from Bellecombe, Aosta, Italy, were studied by means of single crystal X-ray and P-FTIR analyses, and the origins of optical property and internal texture were discussed. The specimens showed triclinic property with optical observation, though the triclinicity was low, and therefore the crystal structure refinements were carried out in monoclinic symmetry. From P-FTIR analyses, OH dipole is randomly orientated in the sectors. The crystal structure refinement in monoclinic symmetry (space group *P2/n*) suggests that site occupancies are slightly different among the Al(2) series. A relationship between the surface and internal textures suggests that these sectored structures with different symmetry were produced during crystal growth, not by phase transition.

In the third chapter, the crystal structure of sectored mimetite, which was from Hay Yai, Thailand, was studied by single crystal X-ray methods, and the origin of the dilution of the symmetry from hexagonal to monoclinic was discussed. The {0001} sector consists of some fine domains between crossed nicols. From the observations of the crystal morphology and surface texture, these textures are considered to be produced during crystal growth with fine irregular domains on the (0001) surface. The $\{10\bar{1}0\}$ sector is optically monoclinic, and its X-ray diffraction pattern

suggests the possible space group $P2_1/m$. The results of refinement of site occupancy, thermal parameter, and bond length indicated the existence of a small degree of ordering of As and P at the As sites, which is considered to be the cause of the dilution of the symmetry from hexagonal to monoclinic.

Since the 19th century, the phenomenon termed an "optical anomaly" is explained, as the optical property does not correspond with the symmetry expected from the crystal form and X-ray diffraction. However this explanation is not suitable because the origin of the phenomenon termed an "optical anomaly" is atomic ordering, and this result is analyzed by X-ray methods. That is, optical property corresponds to X-ray analytical symmetry, and therefore this phenomenon termed an "optical anomaly" since the 19th century is not anomalous.

The primarily expected symmetry of vesuvianite is tetragonal, though the optical symmetry is monoclinic or triclinic in the second chapter, and therefore the true structure is also monoclinic or triclinic. The sectors with different crystal structures coexist in one crystal. In mineralogy, the substances, which have same chemical compositions and other structures, is regarded as other phases and given other mineral names. In thermal experiment of vesuvianite, the 2V value of the biaxial sector became small by heating, and the crystal structure changed toward tetragonal symmetry. It is suggested that the stable phase under ambient condition is triclinic, and tetragonal structure is stable under high temperature condition. Furthermore, the monoclinic and triclinic vesuvianite crystals have Al^{3+}-Fe^{3+} ordered structure. In general, ordered structure is regarded as low temperature phase than disordered structure, and therefore monoclinic and triclinic vesuvianite is considered low temperature phase than tetragonal vesuvianite, whereas it is considered that there is no significant difference of stability among the phases because the structures of these crystals are very similar. Since these phases are considered to have other crystal structures and other growth conditions, other mineral names can be mineralogically given to these phases. In the appendix, thus, how to describe the crystal with growth sectors showing other symmetry is noted, and it is proposed in the appendix that the crystal class is expressed by adjectival modifiers, and therefore, for example, the crystal in triclinic sector of vesuvianite is expressed as triclinic vesuvianite.

The phenomenon termed an "optical anomaly" since the 19th century is not anomalous, because it is shown in this study that the structural symmetry corresponds with the optical symmetry, and therefore the terms such "optical anomaly" is not suitable. Since the phenomenon is not mineralogically anomalous, this phenomenon need not made an exception.

論文審査の結果の要旨

田中利治提出の論文は，従来，鉱物の「光学異常」と呼ばれている現象の原因を，結晶構造の面から明らかにしたものである。

第一章では，光学異常の研究史が述べられている。先ず，結晶形態の対称性と一致しない光学的性質を示す結晶についての最初の報告について述べられている。　次に，結晶形態の対称性と光学的性質の対称性は，本来一致するべきものであるから，これが一致しないものを「光学異常」と呼ぶという定義が述べられ，「光学異常」の用語が最初に用いられた論文を引用している。

第二章では，ベスブ石の組織と結晶構造を解析し，セクター構造をもつベスブ石の対称性は{110}セクターが単斜晶系もしくは三斜晶系，{111}セクターが三斜晶系であることを明らかにし，その原因が結晶構造内のAl^{3+}と Fe^{3+}の秩序配列であることを明らかにした。また，このような秩序配列はセクターが成長する際のステップの進む方向と，それに伴うキンクサイトの大きさが異なることによると論じている。

第三章では黄鉛鉱の組織と結晶構造を解析し，セクター構造をもつ黄鉛鉱に六方晶系から単斜晶系へ対称性が低下しているものがあることを明らかにし，その原因が結晶構造内の微量のPと Asの秩序配列であることを明らかにした。

田中利治は，以上の結果に基づいて考察し，従来，鉱物の「光学異常」と呼ばれている現象は，特別なものではなく，各々のセクターの結晶系とそのセクターの光学的性質が示す結晶系は一致していることを示した。田中利治は，附録に光学異常を示す結晶の表記法に関する考察を述べ，光学的な対称性の異なるいくつかのセクターを有する結晶の記載には晶系を示す形容詞を鉱物名の前に付記することを提案している。

以上のように，田中利治は優れた業績を上げ，自立して研究活動を行うのに必要な高度の研究能力と学識を有していることを示している。したがって，田中利治提出の論文は博士（理学）の学位論文として合格と認める。