Synthesis and stability relations of zoisite $Ca_2Al_3Si_3O_{12}(OH)$ at 2-4 kbar
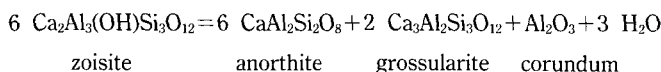
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ABSTRACT : The equilibrium pressure-temperature curve of the reaction :

$$6\ Ca_2Al_3(OH)Si_3O_{12} = 6\ CaAl_2Si_2O_8 + 2\ Ca_3Al_2Si_3O_{12} + Al_2O_3 + 3\ H_2O$$

zoisite   anorthite   grossularite   corundum

was experimentally determined using both externally and internally heated pressure vessels in the pressure range of 2-4 kbar. Synthetic zoisite, anorthite, grossularite and corundum were used as starting materials. Starting materials were synthesized at 13-16 kbar using the piston-cylinder apparatus. The dehydration temperature of zoisite at 2 kbar is $550 \pm 12°C$ and at 4 kbar is 575 ± 20 °C. Low thermal stability of synthetic zoisite relative to natural zoisite at 4 kbar is attributed to the structural disorder of synthetic anorthite.

Key Words : Synthetic minerals, reversal experiment, reaction direction, structural disorder
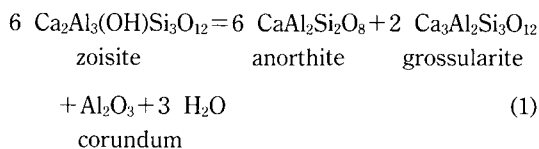
INTRODUCTION

Epidote group minerals having the chemical compositions close to the binary mixtures of $Ca_2Al_3Si_3O_{12}(OH)$ (zoisite) and $Ca_2Fe^{3+}_3Si_3O_{12}(OH)$ (pistacite) are important constituents of numerous metamorphosed calcareous and basaltic rocks. Although they occur typically as a product of regional metamorphism, they also form under thermal metamorphic conditions as well as during the crystallization of acid igneous rocks. The formation of zoisite is mainly restricted to medium grade regional metamorphic rocks typically of calcareous shales. Unlike members of the clinozoisite-epidote series, zoisite does not occur in assemblages developed under low-grade facies environments. It occurs, however, both as primary or secondary phase in eclogites and glauco-phanites (Deer *et al.*, 1986).

Early attempts to synthesize zoisite at low pressure have been summarized by Ehlers (1953) who found that within the temperature range 215-600°C, and water vapour pressures of 20-100 bar, zoisite does not crystallize from either glass or
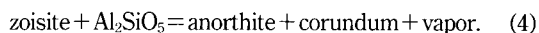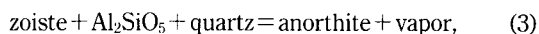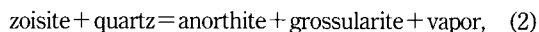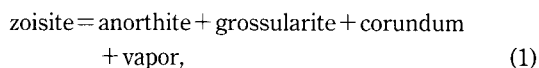
oxide mixtures of the zoisite composition. Anorthite and hydrogrossular were obtained above 400 °C, anorthite, hydrogrossular and hexagonal $CaAl_2Si_2O_8$ between 400 and 325°C, and sodium-free thomsonite at lower temperatures. Subsequently Merrin (1962) reported the synthesis of zoisite and gave details of its stability field in relation to pressure, temperature and composition. Merrin investigated compositions in the $Ca_2Al_3Si_3O_{12}(OH)$-$Ca_2Fe^{3+}Al_2Si_3O_{12}(OH)$ series at intervals differing by increments of 2.5 wt.% Fe_2O_3, and found that, with compositions containing 0.0 and 2.5 wt.% Fe_2O_3, zoisite crystallized at 7 kbar and higher water vapour pressure. In lower pressure experiments with gels of the zoisite composition, anorthite, corundum and grossular were produced.

Newton (1965) experimentally determined the equilibrium pressure-temperature curve for the reaction,

$$6\ Ca_2Al_3(OH)Si_3O_{12} = 6\ CaAl_2Si_2O_8 + 2\ Ca_3Al_2Si_3O_{12}$$

zoisite   anorthite   grossularite

$$+ Al_2O_3 + 3\ H_2O \qquad (1)$$

corundum

using hydrothermal "rod-bombs" and the piston-cylinder apparatus in the pressure range of 2-7 kbar. Newton used natural zoisite, anorthite and grossularite as starting material. At 2 kbar the dehydration of zoisite occurs at $574 \pm 7°C$ at which point the slope of the curve is $18.1 \, bar/°C$.

Reactions in which zoisite is involved in the system $CaO-Al_2O_3-SiO_2-H_2O$ have been investigated at pressures between 3 and 35 kbar and temperatures in the range 580°C to 1150°C (Boettcher, 1970). Sub-solidus reactions involving zoisite are

$$zoisite = anorthite + grossularite + corundum + vapor, \quad (1)$$

$$zoisite + quartz = anorthite + grossularite + vapor, \quad (2)$$

$$zoiste + Al_2SiO_5 + quartz = anorthite + vapor, \quad (3)$$

$$zoiste + Al_2SiO_5 = anorthite + corundum + vapor. \quad (4)$$

The equilibrium temperatures are $640 \pm 15°C$ at 3 kbar for reaction (1), and $595 \pm 15°C$ at 4 kbar for reaction (2).

The pressure-temperature relations of the above reactions (1), (2), and (3) were calculated by Perkins et al. (1977), and the slopes of the reactions later refined by Perkins et al. (1980) by incorporating their measurements of the low-temperature heat capacities of a number of the phases in the $CaO-Al_2O_3-SiO_2-H_2O$ system.

Since 1970, no experimental investigation of the reaction (1) has been carried out. Experiments using synthetic minerals as starting material have not been attempted yet. In this study, we experimentally determined the equilibrium pressure-temperature curve for reaction (1), using synthetic starting materials. Fig. 1 shows chemographic relations of zoisite, grossularite, anorthite and corundum in anhydrous ternary system $CaO-Al_2O_3-SiO_2$.

EXPERIMENTAL METHODS

Experimental Apparatus

Externally heated pressure vessels (at Korea

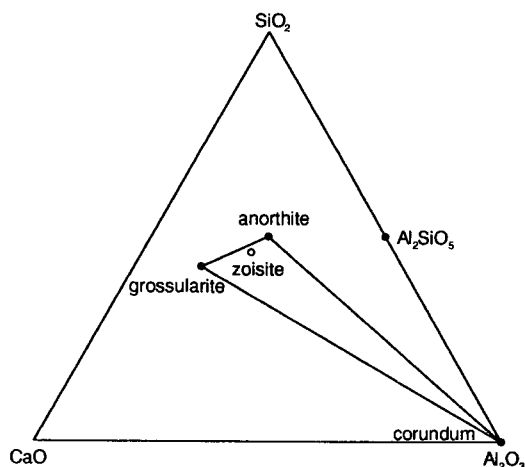**Fig. 1.** Compositions of zoisite $(Ca_2Al_3Si_3O_{12}(OH))$, anorthite $(CaAl_2Si_2O_8)$, grossularite $(Ca_3Al_2Si_3O_{12})$ and corundum (Al_2O_3) are plotted in the anhydrous $CaO-Al_2O_3-SiO_2$ system. Solid circles: anhydrous phases; open circle: hydrous phase.

Univ.) as well as internally heated pressure vessels and piston-cylinder pressure apparatus (both at Manchester Univ.) were used in this study. The externally heated pressure vessels were used for 2 kbar experiments. The pressure vessels were made of Rene 41 nickel based alloy. The vessels were pressurized using hydraulic pump with distilled water and argon gas. Pressures were measured directly with a Bourdon-type gauge (± 15 bar accuracy) which was built in the pressure line. Each pressure vessel was isolated from the pressure line by a valve. The pressure vessels were heated in TEMPRES molybdenum-wound furnaces. Temperatures of the experiments were monitored by Chromel-Alumel thermocouples placed in external thermocouple wells. The temperature difference from the thermocouple well to the charge area was checked by probing an empty pressure vessel in a hot furnace. Temperature control was accomplished with EUROTHERM digital controller which allowed a maximum variation of ± 2 °C. The maximum temperature uncertainty due to the day-to-day fluctuation in recording temperatures ($\pm 2°C$), calibration of the thermocouple ($\pm 2°C$) and the thermal gradient over the capsule length ($\pm 3°C$) was about $\pm 7°C$.

The internally heated pressure vessels were used for 4 kbar experiments. The pressure vessels were made of nickel-based alloy. The vessels were pressurized using an intensifier with argon gas. Pressures were directly measured with a Bourdon-type gauge ($\pm$ 15 bar accuracy). Temperatures were measured with Chromel-Alumel thermocouples ($\pm$ 2°C accuracy). For the runs in the pressure range of 13-16 kbar, a solid-presure piston-cylinder apparatus was used. A furnace assembly consisting of talc, graphite and alumina was used, and no pressure correction for friction was required. Capsules sealed with reactants and excess water were immersed in the talc solid-pressure medium. An internal graphite heater produced temperatures in the range 620°-750°C. Thermocouples of $Pt-Pt_{90}Rh_{10}$ were in contact with the sample capsule. Estimated uncertainties in P and T measurements are $\pm$ 10% of the reported P value and $\pm$ 5°C, respectively.

Starting Materials

Starting materials for the synthesis experiment were oxide glasses with the zoisite composition ($Ca_2Al_3Si_3O_{12}(OH)$). Table 1 shows experimental data for the synthesis. Starting mixtures were decarbonated by heating for 1-2 hours to approximately 1100°C and then completely melted by further heating for 20-30 minutes. Rapid quenching of the melt was achieved by

Table 1. Experimental conditions for synthesizing starting material

Experiment no.*	T (°C)	P (kbar)	Duration (hours)	Crystalline products**
K-43	620	14	24	zo
K-43-1	740	16	30	zo
K-42-1	750	14	48	an + gr + co
K-42-2	740	13	30	an + gr + co
K-42-3	700	13	30	an + gr + co

*All experiments were performed by H.S. Kim at Manchester University, U.K., using oxide glass of the zoisite composition.
**Experimental products were identified by powder X-ray diffraction. Abbreviations: zo, zoisite; an, anorthite; gr, grossularite; co, corundum.

immediately plunging the mixture into a shallow dish of water. The glass starting material was sealed in Pt capsules together with 15-20 wt.% H_2O. X-ray diffraction (XRD) results indicate that zoisite was synthesized at high pressure (K-43 and K-43-1) and grossularite + anorthite + corundum were synthesized at lower pressure (K-42-1, K-42-2 and K-42-3).

Experimental Procedures

Synthesis experiments commonly produce metastable phases due to the high reactivity of starting materials, and may produce erroneous result for determining the equilibrium P-T condition of a reaction. Newton (1966) demonstrated that, where the extent of reaction is not large, the direction of reaction cannot positively be recognized by comparison of XRD charts. Thus, reversal experiments are necessary to establish the equilibrium condition of a reaction. In the reversal runs, starting materials are prepared by mixing both reactant and product phases of a reaction in subequal proportion (Cho and Kim, 1986).

Starting mixtures for reversal experiments were made by mixing approximately equal proportions of synthetic zoisite and synthetic grossularite + anorthite + corundum. Eight experimental runs were carried out at 2 and 4 kbar. Each experiment was made by sealing 4-5 mg of starting material mixtures with 15-20 wt.% distilled H_2O in Ag, Ag-Pd or Au capsules. The welded capsules were weighed before and after the welding to ensure no loss of water, and tested for leakage by placing them for several hours in a drying oven at 110°C and then reweighing. At the termination of experiments, vessels removed from the furnace and then quenched using electric fan. Quenching time was about 10 minutes. After the quenching, each capsule was checked for leakage by weighing, puncturing and drying at 110°C.

Analyses of Experimental Products

The experimental products were examined

Table 2. Reversal experimental conditions and the results for the reaction, 6 zoisite=6 anorthite+2 grossularite+corundum+3H$_2$O at 2 and 4 kbar

Experiment no.	P (kbar)	T (°C)	Duration (days)	Experimental results
K-90	2	500±7	32	growth of zo
K-92	2	525±7	14	growth of zo
K-91	2	550±7	16	no definite reaction
K-103	2	575±7	49	growth of gr+co
K-60	4	450±7	12	strong growth of zo
K-70-2	4	490±7	15	growth of zo
K-70-1	4	550±7	15	growth of zo
K-70	4	602±7	15	growth of an+gr+co

Starting mixture consists of the subequal mixture of K-42-1 and K-43-1. Abbreviations are the same as in Table 1.

exclusively based on XRD method, owing to their extremely fine-grained nature. By comparing the major peak intensities of quenched experimental charges with those of starting mixtures, we determined the reaction direction. Experimental products were analyzed with a Rigaku X-ray diffractometer using Ni-filtered, CuKα radiation at Korea Mining Promotion Corporation. Scanning speed was 0.5° 2θ per minute.

EXPERIMENTAL RESULTS

The reversal experiments were performed to determine the reaction direction between 500°C and 575°C at 2 kbar and between 450°C and 602°C at 4 kbar. In the experiments at 2 kbar, zoisite grows at 500°C and 525°C (Table 2).

At 575°C, however, grossularite and corundum grow at the expense of zoisite. Because no reaction was detected at 550°C, the equilibrium point of the reaction at 2 kbar may be located near 550°C. Fig. 2 shows the diffractograms of the experimental products at 2 kbar.

In the experiments at 4 kbar, zoisite grows at 490°C and 550°C (Table 2). At 602°C, anorthite and grossularite grow at the expense of zoisite. Therefore, the equilibrium point at 4 kbar is located between 550°C and 602°C. All of three experiments showed strong reaction one way or the other (Fig. 3). Fig. 4 shows the results of experiment in a P-T diagram. The dehydration
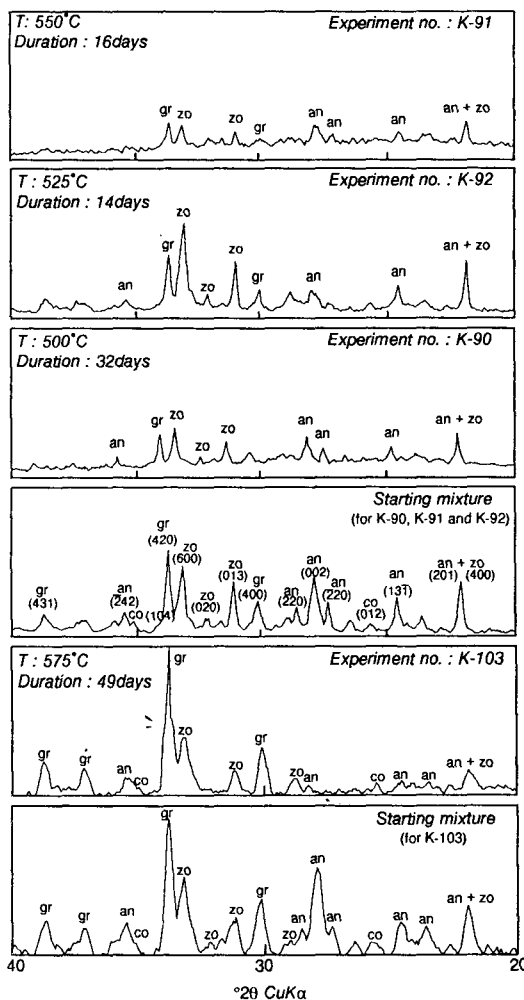

Fig. 2. X-ray diffractograms of the starting mixtures and experimental products at 2 kbar. ( ) indicates Miller index. Abbreviations are the same as in Table 1.

temperature at 2 kbar is 550± 12°C and at 4 kbar is 575± 20°C.

Molar volumes of zoisite, grossularite and anorthite were calculated from the unit cell parameters of X-ray data using the Appleman-Evans (1973) program. In Table 3, we have summarized the molar volume data of synthetic minerals in K-42-1. Molar volumes of synthetic zoisite and grossularite are consistent with those of JCPDS index but those of synthetic anorthite are not.
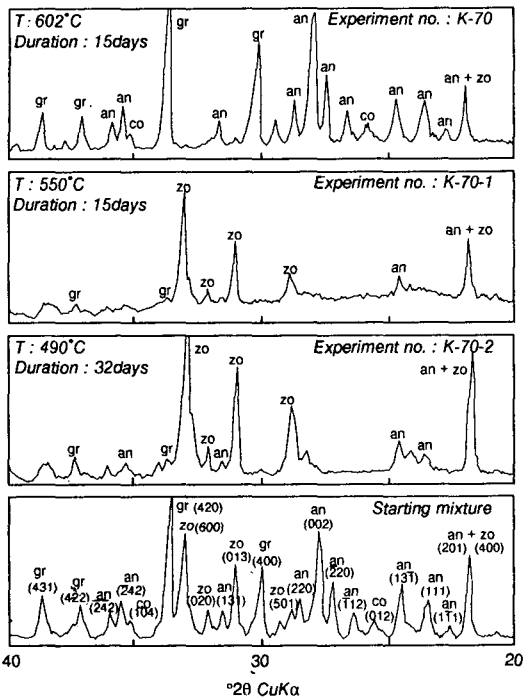
Fig. 3. X-ray diffractograms of the starting mixture and experimental products at 4 kbar. ( ) indicates Miller index. Abbreviations are the same as in Table 1.

DISCUSSION

Fig. 4 shows results of both previous and present experiments for reaction (1) which may result from structural disorder of anorthite. Newton (1965) determined the equilibrium pressure-temperature curve for the reaction (1). He used natural zoisite and grossularite containing significant impurities such as Fe_2O_3, MgO and MnO. His slope of the curve was $18.1\pm$ 0.5 bars/°C. Because small amoumt of Fe_2O_3 can significantly influence the equilibrium temperature of reaction (Kim, 1987), the difference in slopes between Newton (1965) and our experiment can be attributed to the impurity of starting materials.

Perkins et al. (1977, 1980) calculated the Clapeyron slopes for reactions (1), (2) and (3) in the CASH system, using both ordered and partially disorded $(S_{disorder}=0.7 \text{ cal} \cdot K^{-1} \cdot mol^{-1})$ anorthite. The slope for reaction (1) was slightly steeper if anorthite was disordered.

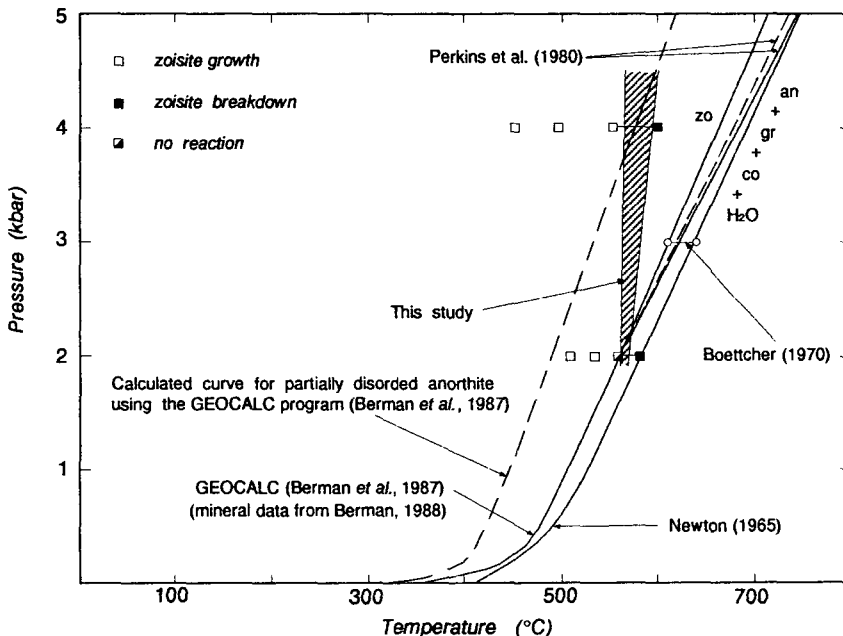X-ray data can supply some information regarding the structural state of plagioclase.

Fig. 4. Comparison of experimental results and calculated slopes for reaction (1), 6 zoisite = 6 anorthite + 2 grossularite + corundum + 3 H_2O. Solid and dashed curves are for ordered and partially disordered anorthite, respectively. Abbreviations are the same as in Table 1.
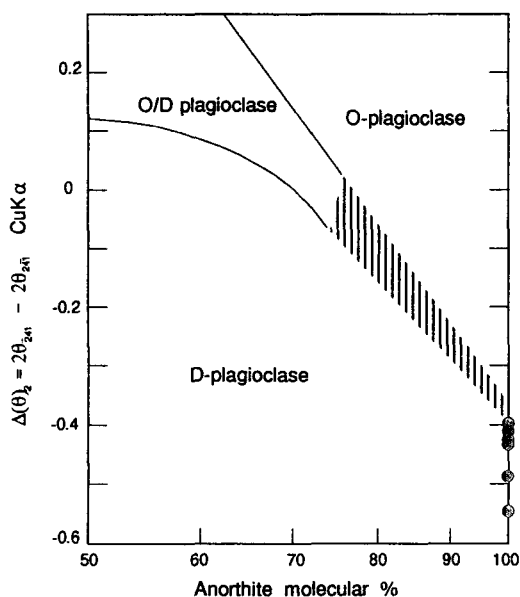
Fig. 5. Relationship between $\Delta(\theta)_2$ and plagioclase composition (Bambauer et al., 1967). All of the synthetic anorthites (closed circles) are plotted in D-plagioclase domain.

Bambauer et al. (1967) suggested the following convention: D-plagioclase = plagioclase with disorded Al, Si distribution (high plagioclase); O-plagioclase = plagioclase orded Al, Si distribution (low plagioclase); and O/D-plagioclase = plagioclase of intermediate structural state. Fig. 5 shows a plot of $\Delta(\theta)_2 = 2\theta_{241} - 2\theta_{2\bar{4}1}$ (CuKα) versus chemical composition of plagioclase. All of anorthite synthesized in this study belong to the D-plagioclase domain in Fig. 5. Thus, synthetic anorthitke is highly disordered.

Our results at 2 kbar experiment are consistent with those of Newton (1965) and Perkins et al. (1980). On the other hand, experimental results at 4 kbar are inconsistent with those by others (Fig. 4). We have calculated the curves of reaction (1) for both ordered and partially disordered ($S_{disorder} = 1.1$ cal·K^{-1}·mol^{-1}) anorthite, using the computer program GEOCALC (Berman et al., 1987). The experimental result of 4 kbar is consistent with the curve calculated by using partially disordered anorthite, whereas that of 2 kbar is not. Hence, our experimental brackets at 2 and 4 kbar are incompatible. Further studies are

Table 3. Molar volumes of synthetic zoisite, grossularite and anorthite.

Materials	zoisite cm³/mol	grossularite cm³/mol	anorthite cm³/mol
JCPDS	136.532	125.152	100.797
K-42-1	136.671± 0.865	125.334± 0.185	100.268± 0.203

required to solve this apparent discrepancy.

CONCLUSIONS

Reversal experiments of reaction, 6 zoisite = 6 anorthite + 2 grossularite + corundum + 3 H$_2$O, were performed at 2 and 4 kbar using starting minerals synthesized at 13-16 kbar. Results of 2 kbar are in good agreement with those of Newton (1965) and Perkins et al. (1980), whereas those of 4 kbar are inconsistent with each other. This discrepancy is partly attributed to structural disorder of synthetic anorthite. The effects of Al-Si disorder and other lattice defects in synthetic minerals, especially anorthite, will need to be addressed in future studies of synthesis and phase relations of zoisite.

ACKNOWLEDGEMENTS

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조이사이트 $Ca_2Al_3Si_3O_{12}(OH)$의 합성 및 2-4 kbar에서의 안정관계

김형식 · 박찬수

고려대학교 이과대학 지질학과

요   약 : 화학반응식 : 6 $Ca_2Al_3(OH)Si_3O_{12}$ = 6 $CaAl_2Si_2O_8$ + 2 $Ca_3Al_2Si_3O_{12}$ + Al_2O_3 + 3 H_2O

조이사이트   아놀사이트   그로슐라라이트 강옥

에 대한 평형 온도-압력 곡선이 외부 및 내부가열 압력용기(externally and internally heated pressure
vessels)를 이용하여 2-4 kbar의 압력범위에서 실험적으로 결정되었다. 인공합성된 조이사이트, 아놀
사이트, 그로슐라라이트 그리고 강옥이 시작물질(starting material)로 사용되었다. 시작물질은 13-16
kbar의 압력범위에서 피스톤-실린더 고압실험장치를 이용하여 합성되었다. 2 kbar와 4 kbar에서의
평형온도는 각각 550±12℃와 575±20℃이다. 4 kbar에서 자연산 조이사이트에 비해 합성 조이사
이트의 낮은 열적 안정성은 합성 아놀사이트의 구조적 무질서(structural disorder)에 기인한다.

핵심어 : 합성광물, 가역실험(reversal experiment), 반응방향, 구조적 무질서