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DTA AND X-RAY DIFFRACTION STUDY OF THE PHASE TRANSFORMATION OF SILICA MINERALS

Leszek Stoch, Maria Łączka, Irena Wacławska
University of Mining and Metallurgy, Cracow, Poland

ABSTRACT

Results of the investigations of the quartz polymorphous transformation by means of the DTA and X-Ray method have been presented. The influence of quantity and a type of isomorphous substitutions on temperature and kinetics of transformation into high temperature cristobalite was determined. Usefulness of DTA and X-Ray as a method of quantitative determination of quartz and cristobalite is discussed.

INTRODUCTION

The transformation of quartz into cristobalite occurs through an amorphous, transition phase which nature is not throughly recognized. The degree of the transformation of quartz into cristobalite preceding melting, influences the melting rate and the quality of obtained silica glass /1/. The investigations of the transformation of quartz into cristobalite and its melting have been carried out so far on rock crystal of a very high chemical purity. However, quartz usually contains some quantity of impurities as isomorphous substitutions/Al^{3+}, Na^{+}, K^{+}, Li^{+}, Ca^{2+}/. The impurities influence on the rate of the transformation into cristobalite, the amorphous transition phase formation and melting of quartz/2,3/. This fact became a cause of undertaking the investigations of high-temperature transformations of quartz showing varying degrees of chemical purity.

EXPERIMENTAL

As minerals for investigations rock crystals and vein quartzes were choosen. These were four varietes of rock crystal of the trade names: Anjole, Watanabe, Telequartz green and red varietes and Polish quartzes taken from the 11 locations in Lower Silesia. The samples were broken up by the method of thermal shocks, heating them to the temperature of 700°C and cooling rapidly in water and then they were grinded in a mostar. The 0,1-0,5 mm fraction,

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as the one used in the technology of silica glass, was taken to investigations. All samples were analysed for trace impurities using AAS method. The studies of transformation of quartz into cristobalite were carried out at 1500°C. The samples were heated in a superkhantal electric furnace during different periods of time, from 0,5 to 12 hours. To estimate the content of quartz and cristobalite by DTA, method of calibration curves was used. The height of DTA peaks of $\beta \rightarrow \alpha$ quartz transformation at 573°C and $\beta \rightarrow \alpha$ cristobalite transformation at 230-240°C was the measure of a given modification content. Standard mixtures were made from the given quartz and standard cristobalite which was obtained through crystallization of silica glass. To estimate the content of quartz by the X-Ray method, the intensity of 0,335 nm reflection in the tested sample and in sample of quartz which was not heated was measured. For the estimation of the content of cristobalite 0,404 nm reflection was used. The X-Ray crystallinity index /4/ was determined. The activation energy of the $\beta \rightarrow \alpha$ quartz and $\beta \rightarrow \alpha$ cristobalite transformation was determined from the DTA curves by the Piłojan-Novikova method /5/.

RESULTS AND DISCUSSION

The X-Ray and the DTA methods show that the samples of quartz heated at 1500°C contain quartz and cristobalite. The sum of these phases determined by both the X-Ray and the DTA method was smaller than 100%. It was assumed that rentgenographically amorphous phase or the phase which does not give the DTA peak, defined as the transition phase, makes the complement to 100%. The contents of quartz and cristobalite determined by the DTA method differ considerably from the one determined by the X-Ray method. The character of relation degree of transformation of quartz into cristobalite vs. heating time, determined by both methods, is the same, however.

On the basis of the rate of the cristobalite formation expressed by its content after 12 h heating at 1500°C, the quartzes can be divided into two groups.

The first group contains quartzes having a very weak tendency to change into cristobalite / all samples of rock crystal, vein quartz from Podgórzyn and Rozdroże Izerskie /.

The second group includes the remaining vein quartzes. They are showing a strong tendency to change into cristobalite. Comparing the

differences of the transformation rate of quartz into cristobalite with the impurities content, it can be noticed, that impurities accelerate or inhibit the cristobalite formation. Alkaline ions and alkaline earths promote the formation of the transition phase and subsequently its crystallization into cristobalite. Ions Al^{3+} substituting for Si^{4+} in the structure of quartz, stabilize the transition phase, inhibiting the crystallization of cristobalite. It has been stated that the contents of quartz in the samples heated at the temperature 1500°C measured by the DTA were, as a rule, lower than determined by X-Ray analysis. These differences were increasing according to extending the time of heating. Prolonged heating of samples causes a decrease in temperature of the beginning of the DTA peak of quartz $\beta \rightarrow \alpha$ transformation. and its widening. The value of the activation energy of the transformation decreases according to the time of heating. The change of quartz into an amorphous-transition phase occurs through a gradual increase of disorder of its structure. In the consequence as the time of heating of quartz extends, the X-Ray crystallinity index decreases. and the half-breadth of 0,335 nm reflection increases. This indicates the reduction in the size of crystallites. The DTA peak of disordered quartz in the state preceding the transformation into an amorphous phase becomes broad and unmeasurable. This is the cause of differences in determining the contents of quartz by the DTA and X-Ray methods. The disorder of structure effects the DTA peak of the polymorphous transformation of cristobalite. The content of cristobalite determined by the DTA method was also smaller than the one measured by the X-Ray method. Heating causes ordering of cristobalite structure and increasing of crystallites sizes.

As it results from the obtained data, the disorder of the quartz structure, due to its transition into an amorphous phase, preceding the formation of cristobalite appears in the change of kinetics of the $\beta \rightarrow \alpha$ transformation. The size and the shape of the DTA peak connected with the intensity of the X-Ray lines let estimate the degree of amorphization of quartz structure.

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