Journal of Solid State Chemistry 215 (2014) 265–270

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Phase transformation of $Ca_4[Al_6O_{12}]SO_4$ and its disordered crystal structure at 1073 K

Daisuke Kurokawa [a,b], Seiya Takeda [a], Maggy Colas [c], Toru Asaka [a], Philippe Thomas [c], Koichiro Fukuda [a,*]

[a] Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan
[b] R & D Center, Taiheiyo Cement Corporation, Chiba 285-8655, Japan
[c] Science des Procédés Céramiques et de Traitements de Surface (SPCTS), UMR 7315 CNRS, Université de Limoges, Centre Européen de la Céramique, 12 Rue Atlantis, 87068 Limoges Cedex, France

ARTICLE INFO

Article history:
Received 15 February 2014
Received in revised form
26 March 2014
Accepted 30 March 2014
Available online 8 April 2014

Keywords:
Yeelimite
X-ray powder diffraction
Rietveld method
Maximum entropy method
Electron density distributions
Disordered crystal structure

ABSTRACT

The phase transformation of $Ca_4[Al_6O_{12}]SO_4$ and the crystal structure of its high-temperature phase were investigated by differential thermal analysis, temperature-dependent Raman spectroscopy and high-temperature X-ray powder diffraction ($CuK\alpha_1$). We determined the starting temperature of the orthorhombic-to-cubic transformation during heating (=711 K) and that of the reverse transformation during cooling (=742 K). The thermal hysteresis was negative (=−31 K), suggesting the thermoelasticity of the transformation. The space group of the high temperature phase is $I\bar{4}3m$ with the unit-cell dimensions of $a=0.92426(2)$ nm and $V=0.78955(2)$ nm^3 ($Z=2$) at 1073 K. The initial structural model was derived by the direct methods and further refined by the Rietveld method. The final structural model showed the orientational disordering of SO_4 tetrahedra. The maximum-entropy method-based pattern fitting method was used to confirm the validity of the split-atom model, in which conventional structure bias caused by assuming intensity partitioning was minimized. At around the transformation temperature during heating, the vibrational spectra, corresponding to the Raman-active SO_4 internal stretching mode, showed the continuous and gradual change in the slope of full width at half maximum versus temperature curve. This strongly suggests that the orthorhombic-to-cubic phase transformation would be principally accompanied by the statistical disordering in orientation of the SO_4 tetrahedra, without distinct dynamical reorientation.

1. Introduction

Yeelimite, $Ca_4[Al_6O_{12}]SO_4$, belongs to a large family of sodalite (chemical formula $Na_4[Al_3Si_3O_{12}]Cl$, space group $P\bar{4}3m$, unit-cell dimension $a_c \approx 0.92$ nm and $Z=2$) with the general composition $M_4[T_6O_{12}]X$, where tetrahedral building blocks, TO_4 with T=Si, Al, Be or Fe^{3+}, are linked by oxygen apices to form a three-dimensional framework [1]. The open cages of the framework contain cations M (=Na^+, K^+, Ca^{2+} or Sr^{2+}) and anions X (=Cl^-, S^{2-} or SO_4^{2-}). Andac and Glasser (1994) have for the first time demonstrated the high-low phase transition in yeelimite, which occurred at 743 ± 5 K [2]. They have reported the X-ray powder diffraction (XRPD) data (d-spacings and corresponding intensities) of the high-temperature phase at 1073 K to determine the cubic unit-cell dimensions of $a_c \approx 0.91$ nm. Cuesta et al. (2013) have clarified the crystal structure of the low-temperature phase to be orthorhombic with space group $Pcc2$ ($Z=4$), showing a $\sqrt{2}a_c \times \sqrt{2}a_c \times a_c$ superstructure based on the cubic sodalite structure [3]. They have collected the high-temperature XRPD data at 743–1073 K to conclude that the high-symmetry phase is cubic or pseudocubic. However, their XRPD pattern taken at 1073 K, being characterized by the extra reflection at ~25.5° (2θ, $CuK\alpha_1$), was inconsistent with that reported by Andac and Glasser.

Recent advances in the field of crystal-structure analysis from XRPD data have enabled us to investigate unknown structures as well as complex structures, including positional disordering of atoms. To begin with initial structural models are required, which may be determined by, for example, the direct methods. The structural parameters are subsequently refined using the Rietveld method [4]. A combined use of the Rietveld method, the maximum-entropy method (MEM) [5] and the MEM-based pattern fitting (MPF) method [6] has enabled us to disclose new structural details. MEM is capable of estimating structure factors of unobserved reflections and improving those of overlapped reflections, which give MEM advantages over the classical Fourier method. However, the Rietveld method and MEM have a drawback in determining the electron-density distributions (EDDs) because the observed structure factors, F_o(Rietveld), are biased toward the

---

* Corresponding author.
E-mail address: fukuda.koichiro@nitech.ac.jp (K. Fukuda).

http://dx.doi.org/10.1016/j.jssc.2014.03.040
0022-4596/© 2014 Elsevier Inc. All rights reserved.

structural model assuming intensity partitioning. On the other hand, the MPF method can minimize the structural bias. Thus, the MEM and MPF analyses are alternately repeated (REMEDY cycle) until the reliability indices reach minima [7]. Crystal structures can be seen clearly from EDDs determined by MPF.

High-temperature X-ray diffraction is definitely one of the most powerful methods to clarify the mechanisms of phase transformations of crystals, although the EDDs deduced from this method correspond to the time- and space-averaged distributions of atoms around their mean positions in the crystal lattice. On the other hand, temperature-dependent Raman spectroscopy enables us to probe the dynamics and statistics of atomic groups (e.g., SO_4 tetrahedra) at high temperatures. With the bimetallic sulfates such as $Na_2Cd(SO_4)_2$, $K_2Cd_2(SO_4)_3$, $K_2Mn_2(SO_4)_3$ and $Tl_2Cd_2(SO_4)_3$ [1,8,9], the Raman band corresponding to the SO_4 internal stretching mode (ν_1), ranging between 985 and 1017 cm^{-1} [10], has been found to be sensitive to the dynamical reorientation of the SO_4 tetrahedra. For example with $Na_2Cd(SO_4)_2$, the abrupt jump in the line width of ν_1 mode observed at temperatures between 833 and 838 K has been attributed to an increase in the rotational degree of freedom of the SO_4 tetrahedra [8].

Intracrystalline microstructures in crystals are often induced by phase transformations, which involve changes in space group symmetry. When the low symmetry (LS) phase is a subgroup of the high symmetry (HS) phase, two fundamentally different types of microstructures result: twin domains and antiphase domains (APDs) [11]. The twin domains arise from the loss of a point symmetry element whereas the APDs arise from the loss of a translational symmetry element and/or a change in the size of the unit cell. If the HS and LS phases are of the different Bravais lattices, the twinning is by pseudo-merohedry. The number of domains (N) produced during the HS-to-LS phase transformation can be predicted by the relationship

$$N = (\text{change in cell size}) \times (P^{HS} \times L^{HS})/(P^{LS} \times L^{LS}),$$

where P and L represent the point group order and the number of lattice points, respectively [11]. Wang et al. (1991) have observed the multiple twinning of yeelimite using high-resolution electron microscopy, which could be induced by the high-low phase transformation on cooling [12].

In the present study, we have determined the crystal structure of yeelimite at 1073 K from the XRPD data. The initial structural model has been derived using direct methods and further modified into the split-atom model. The validity of the structural model has been confirmed by the three-dimensional EDDs determined by the MPF

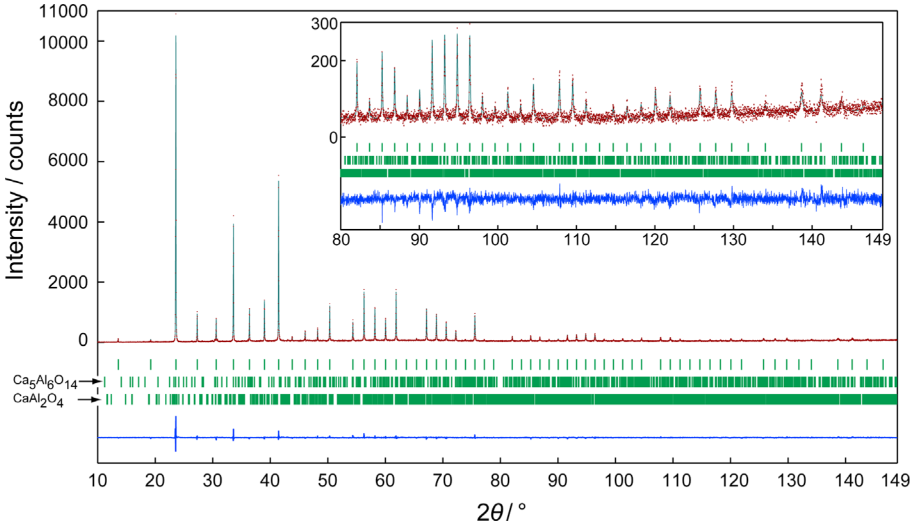

Fig. 1. Comparison of the observed diffraction patterns of $Ca_4[Al_6O_{12}]SO_4$, $Ca_5Al_6O_{14}$ and $CaAl_2O_4$ (symbol: +) with the corresponding calculated pattern (upper solid line). The difference curve is shown in the lower part of the diagram. Vertical bars indicate the positions of possible Bragg reflections.

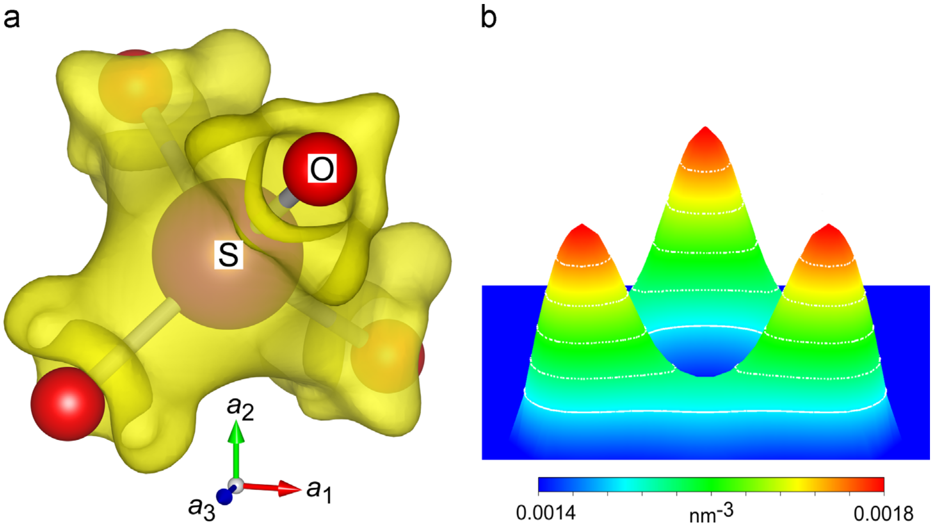

Fig. 2. (a) Three-dimensional electron-density distributions of the SO_4 tetrahedron determined by the MPF method with the initial model. Isosurface expressed in smooth shading style for an equidensity level of 0.0017 nm^{-3}; and (b) a bird's eye view of electron densities up to 2.56% of the maximum (0.0018 nm^{-3}) on the plane parallel to (111).