

16-Molecular Structure Determination by Methods other than Diffraction

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follow the changing environments of nucleating sites during the formation of glass ceramics. In this context, Small Angle X-ray Scattering (SAXS) can give additional information on the intermediate nm scale, revealing details on the microstructures underlying crystallite growth. It is clearly valuable wherever possible to monitor XAFS and/or WAXS/SAXS in conjunction with X-ray diffraction in order that the degree of long range order is ascertained at each stage. This paper will discuss the various non-crystallographic X-ray techniques for obtaining structural information from disordered materials, describing typical experimental configurations and describing the latest developments where these techniques are being combined to facilitate novel twin detector experiments in which the varying degrees of order in a material can be characterised *in-situ*.

MS-16.01.05 Monolayer dispersion model of oxides and salts on supports as well as its EXAFS evidences

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The dispersion phenomenon of salts and oxides on supports with large specific surface area has been investigated widely. Quite a number of models, such as, forming surface compound (SC), cluster (CR), microcrystalline (MC), multilayer dispersion (MUD), solid solution (SS), and so on have been proposed already. But unfortunately, up to date, many problems about structure can not be well explained yet.

Recently, on the basis of investigation upon great deal of these systems, we find a interesting and quite common phenomenon that salts and oxides can disperse spontaneously in monolayer on the surface of a support and it have been confirmed by XRD, XPS, ESR, AES, ISS, SIMS, TEM, LRS, IR, UV, and Mossbauer spectroscopy etc. The principle has been applied successfully in the preparation of some commercial absorbents and catalysts.

The monolayer dispersion model takes into consideration of the possible effect of dispersion condition, (such as, loadings, surface behavior of support and atmosphere) on the structure, but most other models assume that the ions dispersed have its definite and characteristic structure. If the dispersion structure is described by coordination polyhedra of interested ions and their connection or distribution ways. Their differences might be summarized as follows:

dispersion models	definiteness of polyhedra	connect. of polyhedra	effect on loading	coordination of surface behaviors
MOD	not so marked	not so marked	marked	marked
MUD	marked	marked	not marked	not so marked
SC	marked	marked	not marked	not so marked
CR	marked	marked	not marked	not so marked
MC	marked	marked	not marked	not marked
SS	marked	rather marked	not marked	not marked

For most spectroscopies, it is very difficult to recognize structurally the dispersion state as a monolayer among above models. But for the EXAFS, it becomes much easier, since EXAFS can give out plenty of information about chemical bonds and geometry distribution of atoms around interested ions. Much EXAFS structure information in this paper about NiO/ γ -Al₂O₃, CuBr₂/ γ -Al₂O₃, CuCl₂/ γ -Al₂O₃, NiSO₄/ γ -Al₂O₃, and etc. shows that monolayer dispersion is a spontaneous and chemical process and the monolayer dispersion state has particular coordination features. The coordination state of monolayer dispersion is close correlative and changeable with the dispersion condition. It is very different from MC, CR, MC and other dispersion models, but well agrees with the monolayer dispersion model.

Reference

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MS-16.01.06 EXAFS STUDY ON THE LOCAL STRUCTURE IN POTASSIUM TANTALATE. By Y. Nishihata*, O. Kamishima, A. Sawada and H. Maeda, Faculty of Science, Okayama University, Japan, and H. Kasatani and H. Terauchi, School of Science, Kwansei Gakuin University, Japan.

Many cubic perovskite crystals undergo phase transitions, where they transform to slightly distorted structures from the ideal perovskite structure. In KTaO₃, no phase transition occurs since long-range ordering of dipole moment is suppressed by the quantum fluctuation at very low temperatures. It was reported that the dielectric constant increases to a saturated value with decreasing temperature below 100 K (Samara & Morosin, 1973). An atomic vibrational analysis by the neutron diffraction implies that the mode of KTaO₃ at RT is of the Slater type (Harada, Axe & Shirane, 1970). A second-harmonic generation has been reported, although KTaO₃ is a centrosymmetric crystal (Vogt & Uwe, 1984). The purpose of the present work is to study a change of local structure from the ideal perovskite structure using the EXAFS technique.

EXAFS (Extended X-ray Absorption Fine Structure) measurements near the Ta-L_{III} edge of KTaO₃ at RT, 160, 80 and 32 K were carried out using the synchrotron radiation of the Photon Factory at the National Laboratory of High Energy Physics (KEK, Tsukuba). Figure 1 shows the x-ray absorption spectrum at 32 K. A well-defined EXAFS signal is found up to the Ta-L_{II} edge. The EXAFS function $\chi(k)$ was extracted from the spectrum in the usual way (Maeda, 1987). Figure 2 shows the radial structure function around the Ta atom at 32 K calculated by Fourier transform of $k\chi(k)$ in the range of $3.5 \leq k \leq 17.5 \text{ \AA}^{-1}$. The correction of phase shift is not taken into account. These three peaks can be assigned to O, K and Ta atoms, respectively from the crystallographic values obtained by the diffraction data. The broad distribution of the O atom is notable in comparison with that of the Ta atom. This broad distribution at very low temperature results from a large Debye-Waller type factor or a displacement of Ta atom from the center of oxygen octahedron. We use the Fourier filtering technique and a non-linear least-squares fitting method to determine the structural parameters. Preliminary result shows that the EXAFS signal $\chi(k)$ cannot be reproduced well by a 1-shell model because of the beat of $\chi(k)$. If we take the model that the Ta atom displaces from the center of oxygen octahedron along $\langle 001 \rangle$ directions; the peak of the O atom may consist of three shells and the peak of the K atom two shells. We will evaluate the direction of the atomic displacement and the distance from the center of the oxygen octahedron by the least-square calculations under restricted conditions.