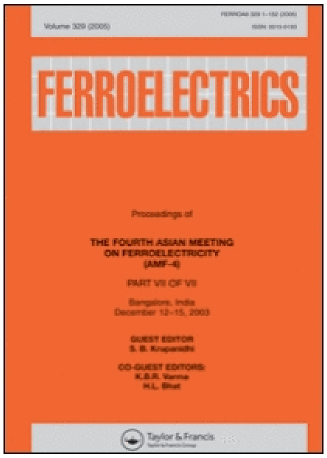

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Vibrational Spectroscopy of $Ba_{1-x}R_xF_{2+x}$ (R = La, Nd) Superionic Conductors

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Vibrational properties of superionic crystals with fluorite structure $Ba_{1-x}R_xF_{2+x}$ (R = La, Nd) were studied using infrared spectroscopy, Raman scattering and inelastic neutron scattering. Selected spectra were measured on heating as a function of temperature. Their main features are: (a) peaks due to translational symmetry breaking, (b) low-frequency modes assigned to localized vibrations of clusters of defects, (c) peaks connected to the presence of small regions with tysonite-like structure (RF_3) at higher doping rates.

Keywords: Infrared reflectivity; Raman scattering; inelastic neutron scattering; localized modes; ionic conductivity

1 INTRODUCTION

Mixed rare-earth doped fluorine conductors with the fluorite structure have been attracting the interest of researchers as a model system with partial disorder and superionic conductivity due to F^- anions. Their general formula is $(MF_2)_{1-x}(RF_3)_x$ where M = Ca, Sr, Ba or Pb; R is a rare-earth element or Y and x is the doping rate. The overall cubic crystal symmetry (sp. gr. Fm3m) is conserved within $0 \leq x \leq x_{\max}$ where $x_{\max} \approx 0.4$–0.5 depending on M, R [1]. Around

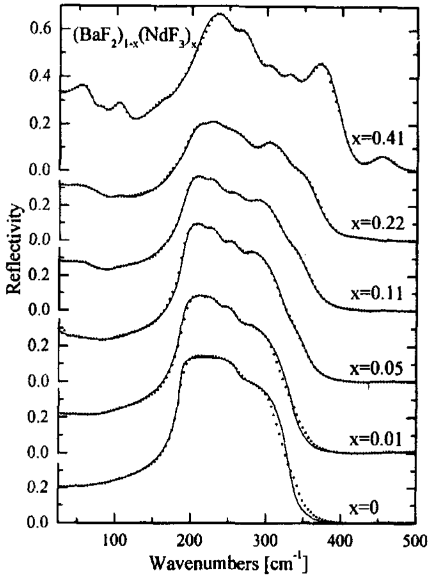

FIGURE 1: IR reflectivity spectra of $(BaF_2)_{1-x}(NdF_3)_x$ crystals: experimental data (symbols) and fits (solid lines).

the R^{3+} cations, clusters of defects are formed. Their structure depends, in general, on M and R [2, 3]. The lattice around the clusters is distorted, forming so-called defect regions [4] in the fluorite matrix. The Enhanced Ionic Motion model [5] assumes that at the interface between the clusters and matrix, these distortions decrease locally the activation enthalpy for hops of F^- anions. Consequently, the conductivity increases by several orders of magnitude with doping.

The present paper reports new infrared reflectivity (IR) and inelastic neutron scattering (INS) results on $Ba_{1-x}R_xF_{2+x}$ single crystals (R = La, Nd). These results are discussed in the light of our recent articles on La-doped fluorites [6, 7], which are briefly reviewed here.

2 INFRARED SPECTRA

Room temperature IR reflectivity spectra of $Ba_{1-x}Nd_xF_{2+x}$ single crystals with $x \leq 0 \leq 0.41$ are shown in Figure 1. The solid lines represent calculated spectra obtained by fitting, using the factorized form of the dielectric function [8].

In pure BaF_2, the only IR-active mode predicted by the theoretical group analysis is observed, together with a small supplementary feature of two-phonon origin. At $x = 0.01$, differences induced by doping appear. A new peak can be seen near $240\,cm^{-1}$, probably due to a perturbation of the symmetry-allowed mode. Another one appears near $30\,cm^{-1}$. We assign the latter to a localized vibrational mode related to small displacements of defects. At this doping rate, there is almost no difference between the spectra of neodymium and lanthanum doped samples, as the dopants form point defects only.

For $x > 0.01$, other new modes appear. The spectra differ clearly from those of La doped samples [7], probably due to different structures of clusters. In Nd doped crystals, the main band splits into five modes. Below its transverse optical frequency ($\omega_{TO} \approx 200\,cm^{-1}$) up to four peaks are present. The frequencies of new peaks between 65 and $270\,cm^{-1}$ correspond to the values of energy where the phonon dispersion curves of BaF_2 are flat and off the centre of the Brillouin zone [9]. Thus it is evident that these modes become IR active as a consequence of relaxing of selection rules, since the translation symmetry is broken. We can also see an increase of most mode frequencies as a function of x; the best visible example is the longitudinal optical (LO) mode of the main band. Such a hardening was also observed in La doped samples [7]. We presume that it is mainly due to the decrease of the lattice parameter with increasing x [1].

The highest-frequency mode caused by doping at $x = 0.22$ comes up near $420\,cm^{-1}$. In the $x = 0.41$ sample, it lies by ca. $30\,cm^{-1}$ higher and it becomes more distinct. The same feature has been observed in the La-doped samples [7], where such a mode was detected starting from $x = 0.25$. It is possible to find a semi-quantitative explanation for this effect using the percolation model with two critical points [10]. The crystals are considered as a low-conducting matrix (BaF_2) containing insulating particles (the clusters), the interfaces being highly conductive. The last assumption is in accordance with the Enhanced Ionic Motion model [5]. Based on these assumptions it is expected that at the first percolation threshold, the interfaces start to join throughout the volume and an increase in conductivity occurs (this occurs at $x \approx 0.05$, [11]). At the second percolation threshold on, the volume occupied by clusters ceases to be discontinuous, which causes a qualitative change in force constants. This manifests itself

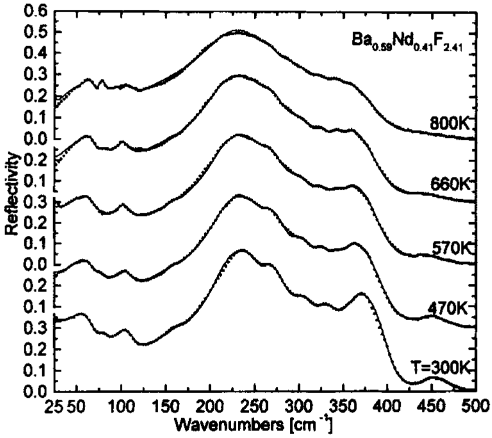

FIGURE 2: Temperature dependence of the IR reflectivity spectra of $Ba_{0.59}Nd_{0.41}F_{2.41}$. The symbols are the same as in Figure 1.

in the appearance of the new mode, which is predicted approximately above $x = 0.2$ [7]. Its presence supports also strongly the formerly proposed idea [12] that when the clusters gather, fragments similar to the tysonite structure (that of LaF_3 and NdF_3) develop. Note that the highest LO frequencies ω_{LO} of IR active modes in NdF_3 are near $470\,cm^{-1}$ [13], which can be considered as an extrapolation of ω_{LO} of this supplementary mode as a function of x (see Figure 1).

Figure 2 shows the temperature dependence of the reflectivity spectra of $Ba_{0.59}Nd_{0.41}F_{2.41}$. On heating, as expected, most peaks broaden and become smeared. An unusual behaviour can be seen in the low-frequency region: below $50\,cm^{-1}$, the reflectivity drops clearly. The marked slope in this region suggests the presence of another mode beyond our achievable spectral range. The fits we have performed included such a mode with $\omega_{TO} \approx 20\,cm^{-1}$, $\omega_{LO} \approx 25\,cm^{-1}$. The increase of the slope with T manifests itself in a decrease of the damping constants Γ_{TO}, Γ_{LO}: whereas their values at $T = 300\,K$ are about $46\,cm^{-1}$, at 800 K it is only $15\,cm^{-1}$ and $12\,cm^{-1}$, respectively. To explain this effect, we suggest that these modes are due to localized vibrations of clusters. According to the model [5], the mobile ions move mainly at the interfaces between clusters and the matrix and their mobility increases with T. We suppose that at low temperatures, where the F^- ions are less mobile, they interact by Coulomb forces with the clusters and thereby hinder

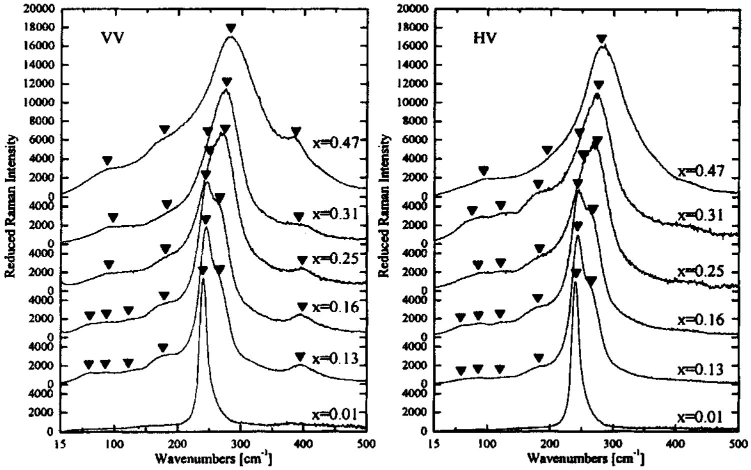

FIGURE 3: Raman spectra of $Ba_{1-x}La_xF_{2+x}$ crystals: (a) VV polarization, (b) HV polarization. The triangles mark positions of Lorentz-shaped peaks obtained by fitting.

their motion. With increasing T, the mobile ions' time of residence decreases. Therefore, they adapt more easily their positions to the motions of clusters; in other words, the 'molten sublattice' becomes 'less viscous' and the damping of the related modes decreases. We have to stress that this is a qualitative model only. In particular, it does not explain why no analogous effect was observed in La doped samples.

3 RAMAN SPECTRA

The room temperature Raman spectra (Figure 3) present similar features as the IR spectra. In the weakly doped sample ($x = 0.01$), the T_{2g} peak has the same frequency as in pure BaF_2 ($240\,cm^{-1}$); the weak doping makes it asymmetric. With increasing x, several peaks develop in the spectra. Below $200\,cm^{-1}$, four of them can be observed; some of them disappear with doping. As they are located close to frequencies obtained by fits of IR spectra, we attribute them also to modes off the Brillouin zone centre, activated by the breaking of the translational symmetry. Another strong peak develops at $260\,cm^{-1}$, near the main sharp line. With increasing x, it be-

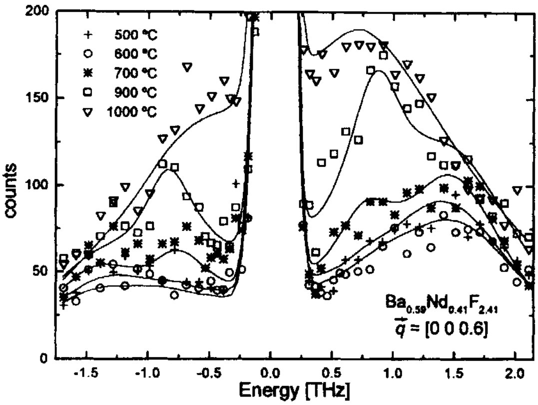

FIGURE 4: The INS spectra of $Ba_{0.59}Nd_{0.41}F_{2.41}$ at $\vec{q} = [0\ 0\ 0.6]$ as a function of T. Symbols: experimental data, solid lines: fits.

comes stronger than the 240 cm^{-1} peak which eventually disappears for $x = 0.47$.

The last peak due to doping is present in the VV Raman spectra near 400 cm^{-1} but it is missing in the HV spectra (the weak features in Figure 3b are most probably due to polarization leakage). This observation, too, is analogous to the Raman spectra of LaF_3 [14] which contain a very strong mode just below 400 cm^{-1} in the $x(zz)y$ scattering geometry, while it is much weaker in the $z(yx)y$ geometry and missing in $z(xz)y$. We suppose that this Raman peak is equally due to the local crystal structure within clusters similar to that of LaF_3. Note that the peak is present for $x \geq 0.13$; i.e., the doping rate where it appears is lower than the one where the 420 cm^{-1} IR active peak does. This is in accordance with the general fact that Raman scattering is more sensitive to the short-range structure whereas IR spectroscopy is rather sensitive to long-range Coulomb forces.

4 INELASTIC NEUTRON SCATTERING

INS experiments were performed in the Laboratoire Léon Brillouin, Saclay on the triple-axis spectrometers 1T, (4F1, 4F2) installed at a thermal (cold) neutron source. Pyrolytic graphite crystals were used as monochromators and analysers. The samples were mounted in high-vacuum aluminium furnaces using niobium sample holders and heated up to 1000°C. The scans were performed at a fixed scattered wave vector of $|\vec{k}_F| = 2.662$ Å^{-1}. The scattering geometry was chosen in order to analyse mainly vibrations which are transverse with respect to $\vec{q}$.

Temperature dependent measurements of INS spectra were performed on different crystals of $Ba_{0.84}La_{0.16}F_{2.16}$, $Ba_{0.69}La_{0.31}F_{2.31}$ and $Ba_{0.59}Nd_{0.41}F_{2.41}$. The main doping-induced effects present in various directions of the Brillouin zone are (a) supplementary peaks, and (b) quasielastic components observed in certain cases. In a 16% La-doped sample, both kinds of modes were observed in the $[0\ 0\ \zeta]$ direction of the Brillouin zone for different values of ζ [6]. This was explained as due to a partial short-range ordering of the clusters. It appears that these features depend partly on the thermal history of the samples. Up to now, no systematic explanation of these effects is available.

One of the most interesting properties of the samples under study is the presence of inelastic peaks which cannot be attributed to acoustic branches. Their energy is typically about 1 THz and they have been observed in samples of all three compositions.

As an example, Figure 4 shows the temperature dependence of the INS spectra of the Nd-doped sample at $\vec{q} = [2\ 2\ 0.6]$ measured on the 1T spectrometer. The fits are results of a comparison of the measured data with the convolution of the scattering function $S(\vec{q}, \omega)$ and the resolution function of the spectrometer. The model of a damped harmonic oscillator was used for the inelastic contributions to $S(\vec{q}, \omega)$.

One can see that between room temperature and 500°C, there is only one weak maximum near 1.5 THz corresponding to the TA branch of BaF_2 [9]. This peak increases with T due to the Bose-Einstein factor. At 700°C, a second one appears at $E = 0.8\,\mathrm{THz} \approx 27\,\mathrm{cm}^{-1}$; on further heating, it becomes much stronger and at 1000° C, it dominates the TA phonon. As its frequency is close to that used for fitting of IR spectra of this sample, we interpret this effect in the same way as described in Section 2.

The quasielastic peaks were observed in some of the spectra of La doped samples. Their presence is apparently related to hops of mobile ions; however, a deeper understanding of this phenomenon is still lacking.

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References

[1] B. P. Sobolev, *Butll. Soc. Cat. Ciėn.*, **XII**, 275 (1991).
[2] J. M. Réau and P. Hagenmuller, *Appl. Phys. A*, **49**, 3 (1989).
[3] P. P. Fedorov. *Butll. Soc. Cat. Ciėn.*, **12**, 349 (1991).
[4] A. K. Ivanov-Shits, N. I. Sorokin, P. P. Fedorov and B. P. Sobolev, *Solid State Ionics*, **31**, 253 (1989).
[5] K. E. D. Wapenaar and J. Schoonman. *J. Electrochem. Soc.*, **126**, 667 (1979).
[6] F. Kadlec, F. Moussa, P. Simon and B. P. Sobolev, *Solid State Ionics*, **119**, 131 (1999).
[7] F. Kadlec, P. Simon and N. Raimboux, *J. Phys. Chem. Solids*, **60**, 861 (1999).
[8] F. Gervais, *Infrared and Millimeter Waves*, volume 8, pp. 279–339, Academic Press, New York (1983).
[9] J. P. Hurrell and V. J. Minkiewicz, *Solid State Commun.*, **8**, 463 (1970).
[10] H. E. Roman. A. Bunde and W. Dieterich, *Phys. Rev. B*, **34**, 3439 (1986).
[11] A. K. Ivanov-Shits, N. I. Sorokin, P. P. Fedorov and B. P. Sobolev, *Solid State Ionics*, **31**, 269 (1989).
[12] S. V. Chernov, W. Gunßer and I. V. Murin, *Solid State Ionics*, **47**, 67 (1991).
[13] R. P. Lowndes. J. F. Parrish and C. H. Perry, *Phvs. Rev.*, **182**, 913 (1969).
[14] R. P. Bauman and S. P. S. Porto, *Phys. Rev.*, **161**, 842 (1967).